

# STAR REPORT

U.S. EPA Office of Research  
and Development's Science  
To Achieve Results (STAR)  
Research in Progress

# 9

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## EARLY RESULTS FROM TSE STAR RESEARCH GRANTS

While most Technology for a Sustainable Environment (TSE) STAR grants are still active, and final results are not yet complete, practical methodologies have already been successfully demonstrated and "scaled up" for commercial application in three important areas:

1. *Supercritical Fluids for cleaner, safer industrial processes*
2. *Green Cleaning and Related Processes*
3. *Biotechnology*

### **Supercritical Fluids for Cleaner, Safer Industrial Processes**

A type of industrial process called "alkylation reactions", used in gasoline formulation and other commercial applications, typically uses strong acids as catalysts. Alkylates are blending agents in gasoline formulation. Because they contain virtually no toxic components, alkylates are playing an increasingly important role in meeting the reduced



*Pollution prevention is the preferred strategy for reducing risks posed by the design, manufacture, and use of manufactured products and commercial chemicals. The long-range goal of this program is to develop safer commercial substances and environmentally friendly chemical syntheses to reduce risks posed by existing practices.*



the CO<sub>2</sub> solvents can be used, for example a potentially widespread application in polymer manufacturing that requires forming epoxides from allylic alcohols. A key scientific product of this work is a reliable computational technique generally applicable in high pressure phase behavior calculations across a range of reaction systems. In another study relevant to the petrochemical and plastics industries, EPA and NSF supported research by Drs. Alan Russell and Eric Beckman along with a team at the **University of Pittsburgh**, investigating the use of supercritical CO<sub>2</sub> to make polyester intermediates for urethane production. Their published findings provide a framework around which commercially viable processes can be developed.

emissions gasoline requirements established by the 1990 Clean Air Act. However, alkylation presents environmental and safety concerns because of two factors: 1) health, safety and environmental problems from liquid acid spillage, and 2) the need to dispose of toxic by-products. Developing “environmentally-friendlier” alkylation is thus especially needed and could have particularly widespread pollution prevention impacts. An alternative approach is to use solid rather than liquid catalysts, but these have the drawback of rapidly becoming inactive as coke deposits clog catalyst pores. Dr. Bala Subramaniam of the **University of Kansas**, working under a STAR grant, has demonstrated the effectiveness in this catalyzation of using a supercritical fluid (SCF). SCFs are neither liquids nor gases, having an optimum combination of liquid-like densities and gas-like transport properties. This application of the supercritical decoking concept to extend the life of solid alkylation catalysts may eliminate a major technological barrier to the use of solid acid catalysts in petroleum related and other alkylation processes.

A team of **University of Notre Dame** researchers led by Dr. Joan Brennecke is studying the behavior of supercritical CO<sub>2</sub> reaction systems. Their findings are directly applicable to the replacement of organic solvents in chemical reaction and purification processes. Their pioneering basic research on phase equilibria of CO<sub>2</sub>-based reaction systems lays a foundation for carrying out industrial chemical reactions without toxic solvents. Their published findings document specific conditions under which

## Green Cleaning and Related Processes Results

More than 30 billion pounds of toxic solvents are used world-wide each year as cleaning agents, dispersants and process agents. A team led by Dr. Joe DiSimone of the **University of North Carolina at Chapel Hill** has completed previous research with an environmentally benign, surfactant modified form of CO<sub>2</sub>, in processes that eliminate the use of toxic volatile organic compounds (VOCs). They received a STAR grant to build on this research, collecting the data needed to scale-up the use of compounds that act as soaps in CO<sub>2</sub>, potentially replacing VOCs in a wide range of cleaning and other applications. This research has led to successful commercialization of a new environmentally friendly dry cleaning process, using CO<sub>2</sub> rather than perchloroethylene. Other industrial cleaning and solvent applications are also being commercially explored.

## Biotechnology Results

This work involves engineering renewable organic materials to replace petrochemicals. Dr. Nancy Ho of **Purdue University** has made a significant breakthrough in producing ethanol from cellulose biomass rather than from petrochemical feedstocks, using yeasts to produce the necessary enzymes. Bioengineering of yeast rather than bacteria allows her to take advantage of existing, well-defined yeast-based processing methods.

*Their pioneering basic research on phase equilibria of CO<sub>2</sub>-based reaction systems lays a foundation for carrying out industrial chemical reactions without toxic solvents.*

## TSE RESEARCH SUPPORTED BY EPA'S STAR RESEARCH GRANTS PROGRAM

*These projects, begun in 1995 to 1998, will be completed from 1999 through 2002*

### Green Chemistry and Engineering Methods for Industrial Pollution Prevention

Under a 1998 grant following on their earlier STAR work described above, the **University of Kansas** is working to optimize the solid-acid alkylation process to increase yields. They are also moving it into new applications, including extending the life of catalysts for a chemical synthesis process called skeletal isomerization, and optimizing solid-catalyzed hydrogenation, a process widely used in the fine chemicals, pharmaceutical and food industries. **Texas A&M University** is also conducting research on solid acid catalysts for alkylate production. They are using nuclear magnetic resonance and computational chemistry to study in detail the performance of three types of catalysts.

The **University of Iowa** is developing an approach to reduce hazardous waste products from catalytic chemical syntheses that use zeolites. These aluminosilicate crystals are used in many processes, including oil cracking and detergent manufacture. Researchers are designing reactions to break down hydrocarbons in a gas phase so that hazardous organic solvents are not needed. Also, their process uses solar energy, and so is independent of fossil fuel energy sources.

Films that coat glass to provide solar shading are typically metal oxide coatings applied by spraying aerosol powders onto the hot glass. Standard methods for preparing these powders involve spray-drying chemicals dissolved in methylene chloride, a highly volatile and toxic organic solvent whose emission presents significant environmental and worker safety concerns. The **University of Colorado**, working in technical collaboration with Ford's Glass Division, has received a STAR grant to develop a process for depositing the films with water and supercritical CO<sub>2</sub>, using no organic solvents. The researchers will evaluate this method for full scale industrial use. Printed circuit board manufacturing is also a pollution intensive industry. **Colorado State University** is conducting basic research on properties of films of copper, nickel and gold made by

dry plasma deposition. Dry plasma deposition could eliminate the need for wet chemical processing and resulting treatment of toxic liquid wastes, and also reduce solid waste.

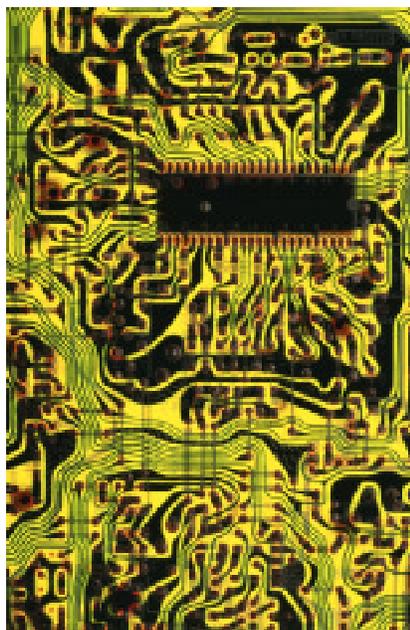
Nearcritical water (NCW) is an environmentally benign solvent with potential application in the chemical, pharmaceutical and plastics industries. EPA and NSF are supporting work by the **Georgia Institute of Technology** to expand available data on NCW interactions with numerous chemicals. NCW may replace solvents such as aromatic hydrocarbons and chlorinated compounds, avoid the use of strong acids and hazardous catalysts, and minimize byproducts. Under a second EPA grant, the **Georgia Institute of Technology** is studying miniemulsion polymerization, to help develop water-based polymer coatings to replace coatings made using organic solvents. Alkyd resins produced by this process have potential use in hard, long-lasting coatings with adjustable gloss.

Another **Georgia Institute of Technology** researcher is studying high yield membranes, which can be useful in producing olefins for gasoline, styrene for plastics production, and high purity aldehydes used to make flavors and

fragrances. These membranes offer technical advantages over ceramic or metallic membranes in addition to decreasing overall waste production and toxic byproducts.

In microelectronics manufacturing, wafers are cleaned between process steps using hydrofluoric acid (HF), other acids, bases and solvents. This is problematic in terms of environmental impact, material costs, produc-

tivity and disposal costs. The avoidance of aqueous baths that inherently risk worker exposure would increase safety, as well as reducing facility floor area needed for the cleaning process. The **Massachusetts Institute of Technology** is studying a novel HF-water vapor process for *in situ* dry cleaning of wafers, to develop it as a replacement for cur-



rent wet cleaning processes in microelectronics manufacturing. This "HF-H<sub>2</sub>O process" for removal of silicon oxides, other oxides and alkali metals greatly reduces the use of baths of liquid acids, bases and solvents with their associated risks. Additional potential process benefits include the following:

- 1) very rapid etching rates;
- 2) allowing the cleaning of layered oxides;
- 3) the surface after etching is not roughened; and
- 4) etching rate promotion by patterned wafer surfaces can be avoided.

**The Massachusetts Institute of Technology (MIT)** has also received joint EPA/NSF funding to develop a new class of solvents tailored for pollution reduction in the fine chemical and pharmaceutical industry. Typically, waste minimization involves either entirely new synthesis routes, or new mixtures of traditionally used solvents. The aim of the MIT research is to modify the solvents' needed chemical attributes and minimize their potential to enter the environment, while retaining their physical properties. As an example, the new techniques will be tested for producing chemicals used to make the HIV protease inhibitor

Crixivan. One approach is to immobilize solvent molecules by attaching them to other large molecules so that they do not enter the aqueous wastestream, yet the same critical chemical reactions can still take place. Research products will include guidelines for product recovery and solvent regeneration, including a complete life cycle analysis of the new solvents from synthesis through processing and regeneration. Under another grant, **Massachusetts Institute of Technology** scientists are analyzing solvation effects in SCF reaction media. They will attempt to develop Raman spectroscopy as an *in situ* diagnostic technique to assess solvation of reactants and the influence of solvent density on reaction pathways in SCFs. This will provide predictive modeling tools to enhance commercial applications of SCFs.

EPA and NSF are supporting a partnership project between **Oklahoma State University** and **Technology As-**

**essment & Transfer Inc.** to develop nanocoatings for cutting tools using "clean manufacturing" methods. One aspect of the approach involves creating nanocoats on cemented carbide tools through a process involving no chemicals and no harmful byproducts. The second aspect is to use the nanolayer coated tools in dry machining methods, which greatly reduce environmental releases. Tool life and wear studies will be conducted experimentally, and some prototype tools will be provided to users for evaluation.

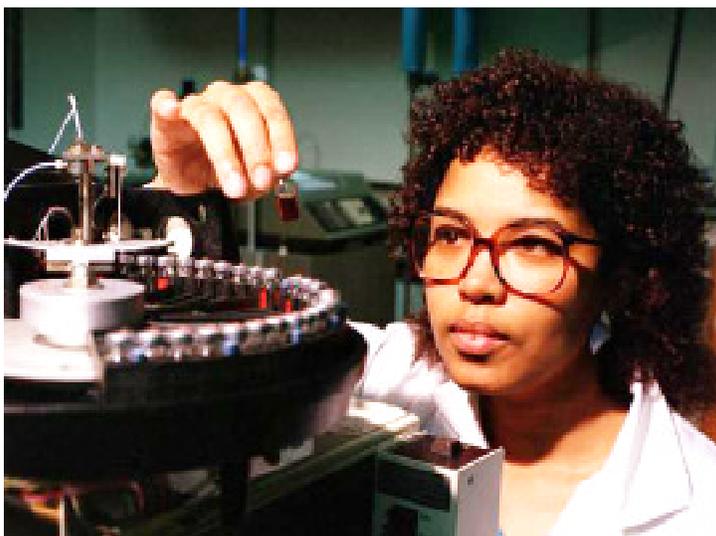
In research jointly funded by EPA and Eastman Kodak, the **Research Triangle Institute of North Carolina** is developing an acid-based catalyst for industrial condensation products. Over one billion pounds of two condensation products, methyl isobutyl ketone and 2-ethyl hexanol,

are produced in the U.S. every year, with a ratio of about 1:10 of spent catalyst generation per pound of product. Alternative catalysts produced in lower volumes will likely prove to be environmentally benign, resulting in processes that are cleaner as well as cheaper.

In a refrigeration study, EPA and NSF are jointly supporting research at **George Washing-**

**ton University** aimed at developing an experimental "pressure-exchange ejector" system that would use steam as the refrigerant instead of ozone-depleting chlorofluorocarbons (CFCs) or other harmful chemicals.

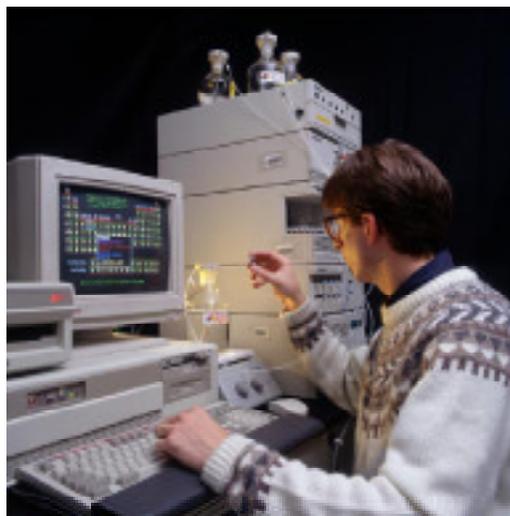
An important way of evaluating potential hazards of chemicals that are not yet commercially produced involves producing compounds in small amounts and subjecting them to toxicity and carcinogenicity tests. The **University of Massachusetts at Boston** is evaluating a way to make candidate compounds for such studies, replacing time-consuming, solvent-based chemical reactions and using simpler, inexpensive and readily available complexing reagents. The approach, called non-covalent derivation, involves forming molecular assemblies to manipulate bulk physical properties of compounds under study. As one example, one can form an association of the molecules with a simple, non-toxic water insoluble compound -- making the candi-



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date compound insoluble without using toxic intermediate compounds and producing toxic byproducts.

A number of fundamental "green chemistry" research studies are being supported that have potentially broad application across various industries. **Iowa State University** and **Virginia Polytechnical Institute** are collaborating to develop photochemical (light-induced) reactions which, if scaled up for commercial production, would reduce the need for toxic reagents and byproduct disposal. Industrial processes to be studied are acylation, alkylation and the addition of aldehydes to quinones, all using environmentally benign supercritical solvents. An **Ohio State University** researcher is investigating ways to better control the shapes of molecular structures formed in water solutions with an indium metal catalyst. A second grant to **Ohio State** supports work with transition metal catalysts and cheap, abundantly available carbohydrate-derived ligands to promote water-based syntheses of commercially important products ranging from amino acids to the widely used anti-inflammatory drugs called aryl propionic acids.



charge cycles. **University of Oklahoma** researchers are developing methods to design or retrofit closed circuit water cycles for chemical and petrochemical plants, based

on a "state space approach" originally developed to optimize heat and mass exchanges in other systems. The closed circuit design could allow better pollutant interception and eliminate pollutant discharge to surface waters. Another study applying the state space approach, jointly supported by EPA and NSF, is

being done at **Michigan Technological University**. The objective is to create a method by which manufacturers can construct an "environmentally conscious" state space model of a product or process system, to predict long term use and flow of materials and the transient effects of various system change options. The program will be developed based on data for representative large, medium and small facilities. The initial effort will be to collect data and build the input/output model for each company. Software will be created, and ultimately available on the World Wide Web.

Two groups are developing life cycle analysis (LCA) approaches for pollution prevention in a number of industries. North Carolina State University is developing an approach relevant to the power generation, waste management and related industries. As a test case, researchers will apply their analysis to the waste gasification process.

## Decision Support Tools and Process Design

Most precious metal manufacturing involves electroplating. There are over 3000 U.S. plants that electroplate parts with one or a combination of over 100 metallic coatings. This has given rise to waste streams containing a great variety of potentially toxic pollutants. While a number of waste minimization (WM) techniques have been developed, they are not fully in use throughout the industry. This is in part because methods have not been well classified and compared in terms of cost and efficiency. Selecting techniques by which particular plants can accomplish significant WM while maintaining productivity at affordable cost is not a trivial task. **Wayne State University** is developing a decision support system to help plating plants of any size make sense of the many WM options and select those optimum for them. Researchers hope that "deep" WM can be made attractive to more plant operators based on the ability of a sophisticated computerized knowledge base to help tailor processes to their needs. The system has been tested by selected plating plants over the project period, with an ultimate goal of introducing it throughout the plating industry.

One model pollution prevention approach for industrial plants is conversion to zero discharge processes, with closed circuits of water replacing standard wastewater dis-

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Factors considered include cost simulation, process performance, energy efficiency and emissions. An important component is a quantified approach for assessing and managing the risk involved in using new technologies. It is hoped that the resulting methodology will be used by



industry and environmental agencies in designing and reviewing new process proposals. Researchers at **Carnegie Mellon University** are working to streamline standard LCA methods,

which are typically very data intensive and thus expensive and time consuming. A simplified method, Environmental Input-Output Assessment, has been developed for the 500 economic sectors into which the Department of Commerce divides the USA economy. This research will develop the tool in more detail, so that specific products and processes within the major sectors can be assessed independently. The resulting method and an extended database using EPA discharge data will be provided on the Internet, together with an interactive user manual.

A potentially widely applicable decision support tool for industries interested in green chemistry approaches is being developed by Brandeis University. Scientists there are developing a computer program to predict the least environmentally hazardous synthetic routes for making specific organic compounds. The literature concerning all precedents for relevant reactions will be searched by the computer program. The fully operational version of the program, SYNGEN, will support choosing the synthesis approach with the least involvement of toxic or carcinogenic materials throughout the production cycle.

## Monitoring Methodology

The ability to conduct accurate, real time measurement of process emissions is important for the success of industrial pollution prevention. Measurement of gases at trace levels in a complex background mixture is of particular concern because many toxic pollutants are present at parts per trillion (ppt) to parts per million (ppm) levels in process emissions. The **University of Colorado at Boul-**

**der** is developing real time and ultrasensitive detection techniques to monitor a wide range of molecules in the gas phase, using resonance enhanced multiphoton ionization (REMPI) and time of flight (TOF) mass spectrometry. The new techniques are expected to be particularly useful for monitoring the products of fossil fuel combustion, including trace levels of aromatics, polycyclic aromatic hydrocarbons and dioxins and their derivatives, some of which are highly toxic.

## Biotechnology

Producing organic chemicals from resources other than petrochemical feedstocks can eliminate toxic precursor chemicals and byproducts and reduce dependence on non-renewable petrochemical supplies. Biotechnology methods involving bacteria offer many cost-effective and environmentally benign substitutions for petrochemical-based chemical production. The **University of Wisconsin at Madison** has received a STAR grant to investigate producing propylene glycol using natural sugar fermentation by the bacterium *Clostridium thermosaccharolyticum*. Propylene glycol is, among other uses, a less toxic replacement for ethylene glycol in antifreeze, with an annual production in the US of over one billion pounds, with a rapidly expanding market.

Researchers at **Michigan State University** are using genetically modified bacteria to make resorcinol from the natural sugar glucose. Resorcinol is a chemical building block with uses ranging from wood adhesives and tire manufacture to the synthesis of sunblocks and throat lozenges. It is currently made from benzene, which is carcinogenic. This basic research is assessing chemical pathways by which resorcinol can be most effectively and practically synthesized. The focus is on the pathways of polyketide biosynthesis and fatty acid biosynthesis, rather than on previously tried approaches involving aromatic amino acid biosynthesis.



**University of Florida** researchers are combining two environmentally safer approaches to making pharmaceuticals and other fine

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chemicals: 1) electrochemistry, by which oxidation and reduction reactions are mediated without organic solvents or harsh reaction conditions, and 2) biocatalysis, in which recombinant organisms and soil bacteria with certain genes blocked convert aromatic compounds to specific high quality biochemical reagents. Using these methods in tandem is expected to produce needed biochemical compounds with little creation of new toxic byproducts. In some cases, toxic chemicals can be used as feedstocks, resulting in a net decrease in toxics for which safe disposal methods must be found.

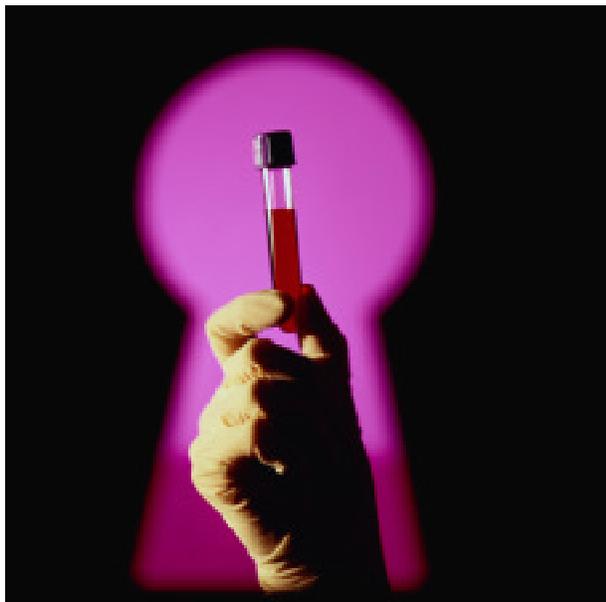
### Recycling and Reuse, and the Use of Biodegradable Materials

The films, coatings and foams used in huge quantities in packaging constitute a high percentage of the plastics in municipal waste. These typically are not biodegradable, and the packaging cannot be recycled without excessive cost and environmental burden. The **University of Massachusetts at Lowell** is doing research to develop substitutes from naturally abundant, renewable and biodegradable resource materials such as cellulose, starch, chitin and other materials. Although there has been some success with a first generation of such materials, they sometimes fail to meet needed performance standards. The current study will focus on product quality concerns, and emphasizes water-based technologies to reduce chemical pollution in the production process. **Wayne State University** is also investigating ways to replace petrochemical-derived products with biodegradable materials from agricultural byproducts. They are focusing on two lanthanide catalyst-based processes: 1) synthesizing cellulose ethers for a variety of industrial applications, and 2) grafting polyesters onto polysaccharides to produce novel copolymers that should combine water-soluble and insoluble properties and may be useful as new biodegradable materials. The **Colorado School of Mines** is de-

veloping a method for producing industrial scale quantities of polylactic acid (PLA) from agricultural feedstocks, also for use in packaging materials. PLA degrades to non-toxic lactic acid, can also be made into compostable packaging, and can be tailored through combination with other materials to meet a wide variety of packaging needs. The **University of Washington** is also developing bacteria that can use renewable feedstocks rather than petrochemicals to make needed products. They are trying to develop an optimized strain of the bacterium *Methylobacterium extorquens* AM1 to convert methanol into products such as the biodegradable plastic polybetahydroxy-butyrate, focusing on directing carbon flux into the most efficient metabolic pathways by manipulating the bacterial strain's pathways for formaldehyde production and consumption.

To examine cleaner processes based on biodegradable materials, **Michigan State University** has developed software called the Biodegradation Evaluation and Simulation System (BESS). This predicts the biodegradability of a compound based its structure and prevailing environmental conditions. The University has been awarded a STAR grant to refine BESS by organizing data on plausible enzyme transformations based on knowledge of microbial ecology and physiology. This reduces the potentially large number of transformations that might be relevant, making the information searching computationally feasible. BESS is intended to serve at least three functions: (a) to allow biodegradability to be considered early in product development; (b) for use by regulatory agencies in decisions regarding testing; and (c) as a tutorial to teach users what features of chemicals and the





environment restrict or promote biodegradation.

Although a number of processes have been developed or proposed for separation of waste plastics from manufacturing, none are completely satisfactory in terms of cost and performance. **Brown University** is conducting basic research to provide a technical basis for the development of a novel, liquid-fluidized bed classification (LFBC) technology for continuously separating complex waste plastic mixtures for in-process recycling and waste minimization. LFBC has a number of potential advantages: 1) It can be used to separate a number of particle types simultaneously, while other processes can only separate "lights" from "heavies"; 2) only unmodified water is required, eliminating the need for separation and recovery of water density modifying agents; and 3) unlike other density-based methods, processes to separate particles of different sizes but similar densities can be performed in conjunction with LFBC. LFBC is compatible with most other separation/identification methods, so it could be used in conjunction with other technology to improve overall cost efficiency. Data will be collected on dispersion and separation performance as related to factors such as particle size and engineering factors, particularly for irregularly shaped particles. These data and a model derived from them will be the basis for process design and an economic analysis of commercialization potential. A potential industrial partner has been identified, and USEPA's New England regional office has indicated an interest in the project.

Grants described in this report are part of EPA's Science to Achieve Results (STAR) program, a major research initiative designed to improve the quality of scientific information available to support environmental decision making. The STAR program is managed by EPA's National Center for Environmental Research and Quality Assurance in the Office of Research and Development (ORD). The program funds approximately 190 new grants every year, with the typical grant lasting three years. Funding levels vary from \$50,000 to over \$500,000 per year, with FY 1999 funding level at about \$95 million for grants to individual principal investigators or groups of investigators. Additional STAR funds are provided for a number of Research Centers specializing in scientific areas of particular concern to EPA, and for fellowship programs supporting graduate students conducting environmental research.

### **TSE Project Publications for Work Described in "Early Results" Section**

#### **University of Kansas (KS)**

B. Subramanian, "Applications of Supercritical Reaction Media in Fuels Production", seminar presented at Center for Applied Energy Research, University of Kentucky. January 27, 1998.

#### **University of North Carolina (NC)**

Dardin, A.; Cain, J. B.; DeSimone, J. M.; Johnson, Jr., C. S.; Samulski, E. T. "High-Pressure NMR of Polymers Dissolved in Supercritical Carbon Dioxide", *Macromolecules*, 1997, 30, 3593-3599.

Clark, M. R.; Kendall, J. L.; DeSimone, J. M., "Cationic Dispersion Polymerization in Liquid Carbon Dioxide", *Macromolecules*, 1997, 30, 6011-6014.

Canelas, D. A.; DeSimone, J. M., "Polymerizations in Liquid and Supercritical Carbon Dioxide", *Adv. Polym. Sci.*, 1997, 133, 103-140.

Cooper, A. I.; Londono, J. D.; Wignall, G.; McClain, J. B.; Samulski, E. T.; Lin, J. S.; Dobrynin, A.; Rubenstein, M.; Burke, A. L. C.; Frechet, J. M. J.; DeSimone, J. M., "Extraction of a Hydrophilic Compound From Water Into Liquid CO<sub>2</sub> Using Dendritic Surfactants", *Nature*, 1997, 389, 368-371.

Commercial website, Dr DiSimone's MiCELL Technology company: <http://www.micell.com>

#### **University of Notre Dame (IN)**

Benito A. Stradi, James P. Kohn, Mark A. Stadtherr and Joan F. Brennecke, "Phase Behavior of the Reactants, Products and Catalysts Involved in the Allylic Epoxidation of trans-2-Hexen-1-ol to (2R,3R)-(+)-3-

Propyloxiramehanol in High Pressure Carbon Dioxide," *J. Supercritical Fluids*, 12, 1998, p. 109-122.

James Z. Hua, Robert W. Maier, Steven R. Tessier, Joan F. Brennecke and Mark A. Stadtherr, "Interval Analysis for Thermodynamic Calculations in Process Design: A Novel and Completely Reliable Approach," *Fluid Phase Equilibria*, accepted for publication, 1998.

#### **University of Pittsburgh (PA)**

A. Chaudhary, J. Lopez, E.J. Beckman, A.J. Russell, "Biocatalytic Solvent-Free Polymerization to Produce High Molecular Weight Polyesters", *Biotech. Progr.* (1997), 13, 318

#### **Purdue University (IN)**

N. W. Y. Ho, Z. D. Chen, M. Sedlak, S. Mohammad, and A. Brainard. "Factors Crucial for Recombinant *Saccharomyces* Effective in Fermenting Xylose". Paper presented at Twentieth Symposium on Biotechnology for Fuels and Chemicals", May 3-7, 1998, Gatlinburg, Tennessee, USA. Abstract, 28-Aug-1998, at Oak Ridge National Laboratory website: [http://www.ornl.gov/divisions/ctd/Chem\\_Dev/Biochemical/Abstracts/PaperList.htm](http://www.ornl.gov/divisions/ctd/Chem_Dev/Biochemical/Abstracts/PaperList.htm) (Paper09).

*Biotechnology methods involving bacteria offer many cost-effective and environmentally benign substitutions for petrochemical-based chemical production.*

## Research Projects Described in This Report

### 1995 EPA Awards

**Ohio State University (OH)** Opportunities Offered by Indium-Promoted Carbon Bond Forming Reactions in Water

**University of Wisconsin (WI)** Fermentation of Sugars to 1,2 Propanediol by *Clostridium thermosaccharolyticum*

**Georgia Institute of Technology (GA)** High-Yield Membrane Reactors

**University of Colorado-Boulder (CO)** Replacement of Organic Solvents by Carbon Dioxide for Forming Aerosols in Coating Processes

**University of Kansas (KS)** Coking and Activity of Solid-Acid Alkylation in Supercritical Reaction Media

**University of Notre Dame (IN)** Phase Equilibria of CO<sub>2</sub>-Based Reaction Systems

**Wayne State University (MI)** Intelligent Decision Making and System Development for Comprehensive Waste Minimization in the Electroplating Industry

**University of Pittsburgh (PA)** Biocatalyst of Polymers in Carbon Dioxide

### 1996 EPA Awards

**University of Iowa (IA)** Environmentally Benign Photo-assisted Catalysis: Selective Oxidation Reactions in Zeolites

**Georgia Institute of Technology (GA)** Water-Based Coatings via Miniemulsion Polymerization

**Research Triangle Institute (NC)** Pollution Prevention in Industrial Condensation Reactions

**University of Massachusetts-Boston (MA)** Pollution Prevention with the Use of Molecular Assemblies

**Iowa State University (IA)** Photochemical Alternatives for Pollution Prevention

**University of Oklahoma (OK)** Chemical Plant Wastewater Reuse and Zero Discharge Cycles

**Brandeis University (MA)** Environmental Hazard Assessment for Computer Generated Alternative Syntheses

### 1996 Joint EPA/NSF Awards

**George Washington University (DC)** A Novel Pressure-Exchange Ejector Refrigeration System with Steam as the Refrigerant

**Georgia Institute of Technology (GA)** Near-Critical Water for Environmentally Benign Chemical Processing

**Michigan Technological University (MI)** Environmentally Conscious Design and Manufacturing with Input-Analysis and Markovian Decision Making

**Oklahoma State University (OK)** Novel Nanocoatings on Cutting Tools for Dry Machining

**University of Pittsburgh (PA)** Biocatalytic Polymer Synthesis in and from Carbon Dioxide for Pollution Prevention

### 1996 NSF Awards

**University of Massachusetts-Lowell (MA)** Bioengineering of Biosurfactants for Cleaning and Degreasing Applications

**Augustana College (SD)** Preparation of More-Biofriendly Quarternary Ammonium Compounds and their Decomposition to Useful Reagents

**Kansas State University (KS)** Two-Stage Fermentation of Whey Permeate for Biodegradable Deicer Production

**Washington State University (WA)** Coexisting Chemical-Biological Modifications of Chlorinated Solvents as a Basis for Waste Reduction in Pollution Prevention

**University of Massachusetts-Amherst (MA)** Reactive Distillation Systems for Waste Reduction and Productivity Improvement

**University of Dayton (OH)** Back-End Modifications of Portland Cement Plants to Reduce Emissions of Hazardous Air Pollutant

**University of Tennessee (TN)** Molecular-Based Study of Reversed Micelles in Supercritical in CO<sub>2</sub> for Solvents Substitution in the U.S. Chemical Industry

**Dartmouth College (NH)** Conversion of Paper Sludge to Ethanol and Potentially Recyclable Minerals

**Arizona State University (AZ)** Environmentally-Benign Processing of Low Dielectric Constant Polymers for Microelectronics Applications

**University of California (CA)** Hydrogen Formation and Transfer in Alkane Reactions Catalyzed by Cation-Modified Zeolites

**University of Maryland-Baltimore (MD)** Advanced Fluorescence-Based Environmental Sensors

**Carnegie Mellon University (PA)** Iron Catalysts for Bleach Activation Funded by NSF

### 1997 EPA Awards

**University of North Carolina at Chapel Hill (NC)** Non-ionic Surfactants for Dispersion Polymerization in Carbon Dioxide

**Michigan State University (MI)** Environmentally Benign Synthesis of Resorcinol from Glucose

**Engineering Purdue University (IN)** Development of Biotechnology to Sustain the Production of Environmentally Friendly Transportation Fuel Ethanol from Cellulosic Biomass

**University of Florida (FL)** Synthetic Methodology "Without Reagents" Tandem Enzymatic and Electrochemical Techniques for the Manufacturing of Fine Chemicals

**University of Massachusetts at Lowell (MA)** Aqueous Processing of Biodegradable Materials from Renewable Resources

**Michigan State University (MI)** BESS, A System for Predicting the Biodegradability of New Compounds

**Ohio State University (OH)** Catalysts for Environmentally Benign Organic Reactions in Water

**Colorado State University (CO)** Microstructural, Morphological and Electrical Studies of a Unique Dry Plasma Metal Deposition for Printed Circuit Boards (PCBs)

### 1997 Joint EPA/NSF Awards

**Massachusetts Institute of Technology (MA)** Tailored Solvents for Pollution Source Reduction in Pharmaceutical and Fine Chemical Processing

**Texas A & M University (TX)** Combined NMR and Theoretical Investigation of Alkylation Reactions on Solid Acids

**Wayne State University (MI)** Development of Green Chemistry for Syntheses of Polysaccharide-Based Materials

### 1997 NSF Awards

**Purdue University (IN)** An Integrated Approach to Environmentally Conscious Paper Mill Operations

"Green" chemistry and engineering – environmentally friendly, energy efficient approaches for use in industrial processes - are a major area of emphasis in the joint EPA/NSF research program on Technology for a Sustainable Environment (TSE) since its inception in 1995.

**University of Florida (FL)**  
Synthesis and Characterization of Solid Acids

**Cornell University (NY)** *In-Vivo* Synthesis of Lepidopteran Pheromone Precursors in *Saccharomyces cerevisiae*

**Purdue University (IN)**  
Cellulose Conversion Using Aqueous Pretreatment and Cellulose Enzyme Mimetic

**Tulane University (LA)**  
Water as Solvent for Metal-Mediated Carbon-Carbon Bond Formations

**University of Washington at Seattle (WA)** Ion Exchange without Chemical Regeneration: Raman Spectroscopy Studies of Hexacyanoferrate Derivatized Electrodes

#### 1998 EPA Awards

**University of Notre Dame (IN)**  
Multiphase Reactive Equilibria of CO<sub>2</sub>-based Systems

**Brown University (RI)**  
Continuous Micro-Sorting of Complex Waste Plastics Particle Mixtures Via Liquid-Fluidized Bed Classification for Waste Minimization and Recycling

**Colorado School of Mines (CO)**  
Environmentally Benign Polymeric Packaging from Renewal

**North Carolina State University (NC)**  
New Methods for Assessment of Pollution Prevention Technologies: Integration of Probabilistic Process Modeling and Design; Life-Cycle Analysis; and Regional Environmental Benefits Assessment

**Carnegie Mellon University (PA)**  
Economic Input-Output Life Cycle Assessment: A Tool to Improve Analysis of Environmental Quality and Sustainability

**University of Washington at Seattle (WA)** Metabolic Engineering of Methylophilic Bacteria for Conversion of Methanol to Higher Value Added Products

**Carnegie Mellon University (PA)**  
Elimination of VOC's in the Synthesis and Application of Polymeric Materials Using Atom

**University of Colorado - Boulder (CO)** Optimal Operation of Electric Arc

Furnaces to Minimize the Generation of Air Pollutants at the Source

**University of Alabama (AL)**  
Polymer-Based Aqueous Biphasic Extraction Technology for Reaction Engineering of the Alkaline Paper Pulping Process

**University of California at Los Angeles (CA)** Real-Time, Ultrasensitive Measurement of Process Emissions for Pollution Prevention

**Massachusetts Institute of Technology (MA)**  
*In Situ* Diagnostic Techniques for Probing Solvation Effects in Supercritical Fluid Reaction Media for Synthetic Organic Chemistry

**University of Kansas (KS)**  
Solid-Catalyzed Reactions in Supercritical Reaction Media

**University of Alabama (AL)**  
Solventless, Electron Beam-Cured Vinyl Ether Coating Formulations for Flexible Magnetic Media Manufacture

**Massachusetts Institute of Technology (MA)** Alternative Wafer Cleaning Using HF-H<sub>2</sub>O Processing

#### 1998 NSF Awards

**University of Kansas (KS)**  
Catalytic Oxidations in Supercritical Carbon Dioxide

**Massachusetts Institute of Technology (MA)** Colloidal Ferrofluids as Reactive Extractants for Sulfur Removal from Gasoline and Fuel Oils

**North Carolina State University (NC)** Towards a Greening of the Petroleum Industry: Minimizing Emulsion and Foam Formation

**Lehigh University (PA)**  
Dynamically Responsive Polymeric Additives for Process Improvements an Environmental Compability

**University of Akron (OH)**  
Environmentally Benign CO Insertion

**Wayne State University (MI)**  
Polymer Processing With Supercritical Fluid Solvents

**Brown University (RI)**  
Continuous Micro-Sorting of Complex Waste Plastics Mixtures via Liquid-Fluidized Bed Classification (LFBC) for Waste Minimization and Recycling



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