1999-2000

Academic Year
Highlights

The School of Chemical Engineering

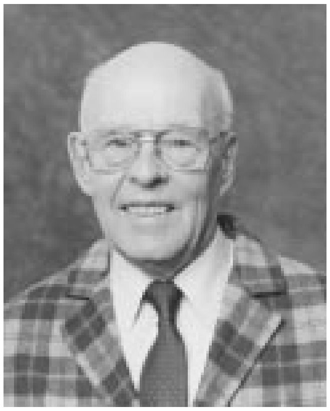
Faculty Summary

Table of Contents

Lyle F. Albright

***1955**

Professor Emeritus



Degrees

BS, University of Michigan, 1943

MS, University of Michigan, 1944

PhD, University of Michigan, 1950

Interests

Kinetics and processes of organic reactions (especially pyrolysis, alkylation of isobutane, nitration, and hydrogenation of vegetable oils)

High polymers and polymerization

Gasification and liquefaction of coal

Pulping of wood chips for paper production

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* *Year of joining the faculty.*

Ronald P. Andres

1981

Engineering Research Professor

Degrees

BS, Northwestern University, 1959

PhD, Princeton University, 1962

Interests

Ultrafine particles

Nanostructured materials

Nanoelectronic devices

Catalysis

Scanning Probe Microscopy

Research Areas

Molecular Electronics: The field of "molecular electronics" is in its infancy and demonstrations of sophisticated electronic functions by molecular based systems have been limited. However, an interdisciplinary team of researchers at Purdue has shown that metal nanocrystals can be "wired" to each other by means of conjugated organic molecules having appropriate end groups and these supramolecular systems show great promise in a wide range of ultra-high-density electronic and information storage applications. We are currently exploring applications of this technology in the fabrication of nanoelectronic devices and chemical sensors. Our ability to deposit uniform monolayers of chemically linked metal clusters is also an exciting enabling technology for semiconductor electronics. Among the potential applications that are being studied are: nanometer resolution etch masks, low resistance nanocontacts, and interconnect lines that are self-aligning, self-healing and conformal.

Synthesis of Ultrafine Metal Particles: Ultrafine metal particles or clusters with diameters in the nanometer size range have unique size-dependent electronic and physical properties. Nanostructured materials such as solids produced by consolidation of nanoscale powders or catalysts produced by dispersing nanoscale metal clusters on nonreactive supports also exhibit unique properties. The key to taking advantage of these enhanced properties are techniques for synthesizing the ultrafine particles of interest at high production rates and low cost. We have developed an aerosol reactor for nanoparticle synthesis that shows promise in this regard. Currently we are using this reactor to produce metal nanoparticles that contain more than one atomic species and are exploring applications of these particles as catalysts (Au / Ti / Si clusters) and as magnetic materials (Au / Fe clusters).

Self-Assembly of 2-D and 3-D Nanoparticle Structures: Many of the most exciting materials applications of ultrasmall clusters require that these particles be assembled into regular 2-D or 3-D superlattices. The only feasible way to accomplish this task appears to be via self-assembly, which can be defined as a process in which a supramolecular hierarchical organization is spontaneously established in a complex system of interlocking components. We have developed methods for the engineered self-assembly of cluster superlattices and are involved in improving these techniques and extending our understanding of the basic physics of the self-assembly process. The self- part of self-assembly refers to the fact that the process is driven by an overall free energy drop between the unassembled units and the final assembly. Thus, understanding the thermodynamics of nanoparticle systems is crucial. The speed and the scale-up of the self-assembly process are also important considerations.

Scanning Probe Microscopy: The Atomic Force Microscope (AFM) uses a sharp probe attached to a flexible cantilever to profile the morphology of a sample surface. Although a powerful technique for determining nanoscale structure, because of the finite size of the probe tip, an AFM has limited lateral resolution and tends to deform “soft” samples. We have largely overcome these problems by attaching a carbon nanotube to a flexible AFM cantilever. The carbon nanotube then serves as the effective probe tip. With this new probe we are able to resolve for the first time the nanoscale structure of “soft” surfaces. This capability opens up the possibility of using an AFM to image a wide range of biochemical and biomedical nanostructures.

Publications

P.J. de Pablo, E. Graugnard, B. Walsh, R.P. Andres, S. Datta, R. Reifenberger, “A simple, reliable technique for making electrical contact to multiwalled carbon nanotubes,” *Appl. Phys. Lett.*, 74, 323, 1999.

T. Lee, J. Liu, D.B. Janes, V.R. Kolagunta, J. Dicke, R.P. Andres, J. Lauterbach, M.R. Melloch, D. McInturff, J.M. Woodall, R. Reifenberger, “ An ohmic nanocontact to GaAs,” *Appl. Phys. Lett.*, 74, 2869, 1999.

K. Moloni, M.R. Buss, and R.P. Andres, “Tapping Mode Scanning Force Microscopy in Water Using a Carbon Nanotube Probe,” *Ultramicroscopy*, 80, 237, 1999.

D.B. Janes, V.R. Kolagunta, M. Batistuta, B.L. Walsh, R.P. Andres, J. Liu, J. Dicke, J. Lauterbach, T. Pletcher, E.H. Chen, M.R. Melloch, E.L. Peckham, H.J. Ueng, J.M. Woodall, T. Lee, R. Reifenberger, C.P. Kubiak, and B. Kasibhatla, “Nanoelectronic Device Applications of a Chemically Stable GaAs Structure,” *J. Vac. Sci. Technol. B*, 17, 1773, 1999.

K.B. Stavens, S.V. Pusztay, S. Zou, R.P. Andres, A. Wei, “Encapsulation of Neutral Gold Nanoclusters by Resorcinarenes,” *Langmuir*, 15, *8337*, 1999.

T. Lee, N.P. Chen, J. Liu, R.P. Andres, D.B. Janes, E.H. Chen, M.R. Melloch, J.M. Woodall, R. Reifenberger, “Ohmic nanocontacts to GaAs using undoped and p-doped layers of low-temperature grown GaAs,” *Appl. Phys. Lett.*, 76, 212, 2000.

E.E. Stangland, K.B. Stavens, R.P. Andres, W.N. Delgass, “Characterization of Gold-Titania Catalysts via Oxidation of Propylene to Propylene Oxide,” *J. of Catalysis*, 191, 332, 2000.

J. Liu, T. Lee, D.B. Janes, B.L. Walsh, M.R. Melloch, J.M. Woodall, R. Reifenberger, R.P. Andres, "Guided self-assembly of Au nanoclustrer arrays electrically coupled to semiconductor device layers," *Appl. Phys. Lett.*, 77, 373, 2000.

Meeting Presentations

"Self-Assembly of Patterned Films of Nanometer-Diameter Gold Clusters that are Linked by Organic Molecules," TMS Electronic Materials Conference, Santa Barbara, CA, July 1999.

"Directed Self-Assembly of Micro-patterned Monolayer and Bilayer Ribbons of Close-Packed Nano-Scale Metal Clusters," Materials Research Society Fall Meeting, Boston, *MA*, December 1999

Invited Lectures

"Aerosol Synthesis of Metal Nanocrystals and Their Self-Assembly into Electronic Nanostructures," Naval Research Laboratory, Washington, DC, July 1999.

"Aerosol Synthesis of Metal Nanocrystals and Their Self-Assembly into Electronic Nanostructures," Engineering Foundation Conference, Porvoo, Finland, July 1999.

"Aerosol Synthesis of Metal Nanocrystals and Their Self-Assembly into Electronic Nanostructures," Univ. of Texas, Chemical Engineering Seminar, Austin, TX, September 1999.

"Aerosol Synthesis of Metal Nanocrystals and Their Self-Assembly into Electronic Nanostructures," Plenary Session, American Association for Aerosol Research Conference, Tacoma, WA, October 1999.

"Aerosol Synthesis of Metal Nanocrystals and Their Self-Assembly into Electronic Nanostructures," Foresight Conference on Molecular Nanotechnology, Santa Clara, CA, October 1999.

"Aerosol Synthesis of Metal Nanocrystals and Their Self-Assembly into Electronic Nanostructures," UCLA, Chemical Engineering Seminar, November 1999.

"Aerosol Synthesis of Metal Nanocrystals and Their Self-Assembly into Electronic Nanostructures," Case Western Reserve University, Cleveland, OH, January 2000.

"Aerosol Synthesis of Metal Nanocrystals and Their Self-Assembly into Electronic Nanostructures," Penn State University, University Park, PA, February 2000.

"Aerosol Synthesis of Metal Nanocrystals and Their Self-Assembly into Electronic Nanostructures," Princeton University, Princton, NJ, February, 2000.

"Nanotechnology: A Revolution at the Limits of the Physically Possible," Purdue Research Foundation Spring Meeting, West Lafayette, IN, May 2000.

Osman Basaran

1995

Professor

Degrees

BS, Massachusetts Institute of Technology, 1978

PhD, University of Minnesota, 1984

Interests

Drop and bubble dynamics, fluid mechanics

Effects of electric, magnetic, and acoustic fields on fluids

Interfacial phenomena and measurement of dynamic surface tension

Non-Newtonian rheology and measurement of extensional viscosity

Computational analysis: finite element, boundary element and VOF methods

Experimental analysis: high speed visualization (0.1-1 ms); ultra-high speed visualization (down to 10 ns); velocity measurement and particle sizing by Phase Doppler Anemometry

Ink-jet printing

Atomization coating and painting

Crop spraying

Separations

Gary E. Blau

1998

Visiting Industrial Professor

Degrees

BASc, University of Waterloo, 1964
MSc, Stanford University, 1966
PhD, Stanford University, 1968

Interests

Mathematical Model Building of Engineering Systems
Operations Research
Optimization
Applied Statistics
Environmental Systems
Uncertainty / Risk Analysis

James M. Caruthers

1977

Professor

Degrees

SB (Chem), Massachusetts Institute of Technology, 1975

SM, Chemical Engineering, Massachusetts Institute of Technology, 1975

PhD, Chemical Engineering, Massachusetts Institute of Technology, 1977

Interests

Viscoelasticity of solids

Polymer rheology

Structure-property relationships in polymers

Composites

Awards and Major Appointments

National Research Council: Standing Committee on the Program and Technical Review of the U.S. Army Chemical and Biological Defense Command, 1995-present

David S. Corti

1998

Assistant Professor

Degrees

Ph.D., Princeton University, 1997
M.A., Princeton University, 1993
B.S.E., University of Pennsylvania, 1991

Interests

Statistical Thermodynamics
Metastable Liquids
Nucleation Phenomena
Colloidal Dispersions
Molecular Simulation Techniques

Research Areas

Entropic Control of Colloidal Stability, Phase Transition, and Particle Deposition: The ability to predict the behavior of colloidal dispersions rests upon our knowledge of the forces that arise between colloidal particles. An important class of interparticle forces is induced by the presence of other colloidal species and arises solely as a result of entropic considerations. These entropic forces, or depletion forces, are strong enough to affect the behavior, both equilibrium and dynamic, of various dispersions of interest. For example, depletion forces are able to promote order-disorder transitions in the dispersion microstructure and may be responsible for a disorder-disorder transition. Passive structures etched into the walls of container can create entropic force fields of sufficient range and magnitude so that the motion and position of large colloids can be controlled. An understanding of these entropic forces has impact in materials processing, offering new mechanisms in which particles self-assemble in pre-chosen patterns or are sorted or organized along geometric features etched into a substrate for microfabrication. We are currently developing theoretical and simulation methods to determine (1) the importance of entropic forces in affecting the stability, phase behavior, and particle deposition of dispersions and (2) the effectiveness of entropic forces as a mechanism for controlling the performance of dispersions. We are developing molecular theories that estimate entropic forces between particles and between particles and surfaces of various shapes. Such information provides the first step towards the prediction of the phase behavior and coagulation / deposition rates of dispersions. We are also investigating phase separations in colloidal dispersions using novel molecular simulation methods, determining both the compositions and structures of the equilibrium phases and the kinetics of the transitions. Simulation and analytical methods are also being employed to estimate the coagulation / deposition rates of particles confined within various entropic force fields. This research will provide insights into the complex forces and phase behavior exhibited by colloidal dispersions, particularly for systems that are difficult to study with current experimental techniques. We are also exploring the novel use of entropic forces as a mechanism for the manufacture of new materials (e.g., nanonmaterials and microelectronics).

Properties of Metastable Liquids; Molecular Theories of Nucleation: Metastable states arise, for example, when the temperature or pressure is changed from a value corresponding to a single, stable equilibrium phase to values corresponding to two phases in equilibrium. Instead of undergoing the equilibrium phase transition, the system remains in a one-phase metastable state. All phases of matter can exhibit metastability. Metastable liquids, in particular, are ubiquitous in nature, and have important technological applications. For example, superheated liquids (metastable with respect to the vapor phase) are important in maximizing yields during the rinsing and subsequent release of microelectromechanical devices after etching and in minimizing the erosion (via cavitation) of equipment in the chemical industry. The cyclic superheating of liquids with ultrasound is useful for cleaning surfaces, biological cell disruption, and the enhancement of chemical reaction and is important in the initial stages of sonoluminescence. In spite of their importance and widespread occurrence, fundamental questions persist about the properties of metastable liquids and their theoretical description.

We are studying both the equilibrium and kinetic properties of metastable systems using theoretical and molecular simulation methods. Molecular simulation studies of the thermophysical properties of superheated liquids are being performed in order to suggest ways in which van der Waals-like equations of state may be modified to provide a better description of the properties of superheated liquids. Molecular simulation methods will also be used to study stretched liquids confined between walls and to investigate how tensile strength changes under confinement. Another novel simulation approach focuses on local potential energy minima, called “inherent structures”, obtained by steepest-descent quenching of equilibrium configurations onto mechanically stable configurations in which the net force on each particle is zero. Simulations of the manner in which a system samples its potential energy surface or energy landscape have uncovered the importance of mechanically stable inherent structures in determining the properties of superheated liquids (including their tensile strengths). Inherent structures of superheated liquids are divided into a dense, amorphous phase and a void “phase” containing no atoms. Recent work analyzed the correlation between “weak spots” in the liquid (at high temperature) and the large voids formed in inherent structures (at absolute zero) demonstrating that atoms adjacent to large voids in the superheated liquid have a high probability of being found on the surface of the void “phase” in their corresponding inherent structures. This is a very important finding, as it establishes a direct correspondence between the appearance of large voids in superheated liquids and the sampling of suitable inherent structures. The analysis of inherent structures amounts to an entirely new way of looking at the kinetics of first-order phase transitions in liquids and should lead to an improved molecular-based understanding of bubble nucleation in superheated liquids. In addition, since the appearance of voids in inherent structures is solely due to the attractive part of the intermolecular potential, this work also promises to improve our understanding of the mechanical failure of liquids and amorphous materials in the bulk and at interfaces.

Publications

R. K. Bowles and D. S. Corti,, 2000, "Statistical Geometry of Hard Sphere Systems: Exact Relations for First-Order Phase Transitions in Multicomponent Systems, " *Mol. Phys.*, 429-438, 1998.

D. S. Corti, submitted,, 2000, "On the Correct Formulation of the Isothermal-Isobaric Ensemble," *J. Chem. Phys.*

Meeting Presentations

D. S. Corti* and R. K. Bowles, "Statistical Geometry of Hard Sphere Systems: Exact Relations for Additive and Nonadditive Mixtures," AIChE Annual Meeting, Dallas, TX, November 1999.

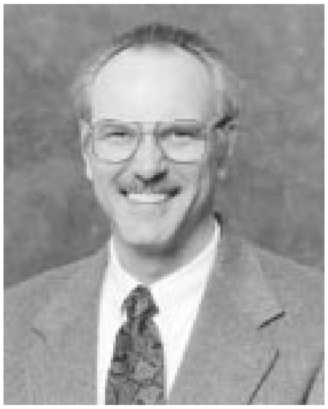
Invited Lectures

D. S. Corti, "Statistical Geometry of Hard Sphere Systems," Department of Chemistry, Purdue University, West Lafayette, IN, October 27, 1999.

W. Nicholas Delgass

1974

Professor and Associate Head of the School



Degrees

BSE, Chemical Engineering, University of Michigan, 1964
BSE, Mathematics, University of Michigan, 1964
MS, Stanford University, 1966
PhD, Stanford University, 1969

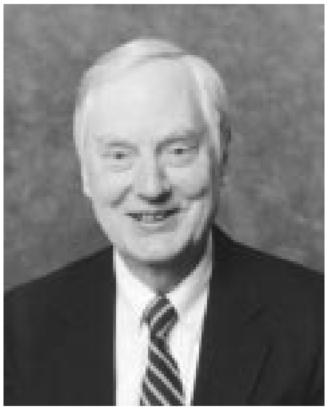
Interests

Heterogeneous catalysis
Selective hydrogenation over Raney nickel
Partial oxidation - epoxybutene
Nitric oxide reactions
Solid acid catalysts
NMR, XPS, FTIR

Roger E. Eckert

1964

Professor



Degrees

BS, Princeton University, 1948
MS, University of Illinois, 1949
PhD, University of Illinois, 1951

Interests

Statistical design of experiments
Flow properties of viscoelastic polymers
Mass transfer effect on reaction selectivity

Elias I. Franses

1979

Professor

Degrees

Dipl. Eng., National Technical University, Athens, 1974

PhD, University of Minnesota, 1979

Interests

Adsorption and tension equilibria and dynamics of surfactants and proteins at interfaces

Adsorption and transport of lung surfactants

Effects of processing on properties of thin organic coatings

Transport and ion exchange in thin organic Langmuir-Blodgett and spin-coated films

Infrared spectroscopy and ellipsometry of monolayers and multilayers of surfactants, lipids, proteins, and polymer films

Research Areas

Equilibrium Adsorption and Tension of Aqueous Surfactant and Lipids. Binary and multicomponent adsorption at air/water, oil/water, and liquid/solid interfaces and tension at fluid interfaces, are important factors in foam stability, emulsion stability, detergency, and coating flows, and lung surfactants function in the lung alveoli. Our main goals are to describe and predict competitive adsorption of nonionic or ionic surfactant mixtures from the surface behavior of the single surfactants and their mixing characteristics at the interface and in the bulk solution. We have been using the ideal or nonideal adsorbed solution models as our framework. For nonionic surfactant mixtures, we have developed such models and successfully tested them experimentally. We developed the first complete model to describe and predict tension and adsorption synergism, below and above the cmc (critical micellization concentration). The work is being extended to ionic surfactants, such as salts of fatty acids, where electrostatic effects are dominant (with A.J. Prosser). In addition, the equilibrium adsorption and spread monolayer isotherm of sparingly soluble higher alcohols is studied for determining the effect of their solubility and volatility on their surface tension behavior, and for their potential applications as ingredients of lung surfactant replacement drugs (with S.H. Myrick and E.M. Hernandez). Finally, with our Barcelona, Spain, collaborators (A. Pinazo, L. Perez, and M.R. Infante), we are studying the physical chemistry of new nonionic or gemini (two head groups, two tail groups) ionic surfactants they synthesized in Spain. Our goals are to probe directly the surface composition, stability, and microstructure of these monolayers using radiotracer, optical, and infrared spectroscopic probes.

Dynamic Adsorption and Tension of Aqueous Surfactants, Lipids, or Proteins. Fast processes such as foaming, cleaning, coating flows, and breathing are affected more by the dynamic than by the equilibrium behavior. We have been using primarily the bubble method for measuring dynamic surface tensions at constant area or at pulsating area. Our new models and data at constant area revealed cases of dynamic synergism, where the mixture of surfactants has superior performance than either of the individual components at the same total concentration. We have been seeking for new molecules or systems which can reduce the dynamic tension under pulsating area to below 10 or 5 mN/m, which are called "superlow tensions," and are major requirement for lung surfactant replacement drugs (there are, of course, many biophysical and other requirements as well). We and others have found that compressed monolayers of a very select group of lipids or lipid/protein mixtures can produce superlow tensions. We have discovered with (X. Wen) that dilauroylphosphatidylcholine and sodium myristate can also produce very low tensions. In our present and future research, we aim at understanding the key thermodynamic, dynamic (mass transfer and adsorption/desorption), colloidal, and molecular factors responsible for good (or poor) dynamic tension behavior. The dynamic adsorption and dynamic surface tension are molded for various surfactants, at constant or pulsating surface area, to help the description and the preduction of the efficiency of surfactants in generating low (< 10 mN/m) surface tensions (with Y.C. Liao). Direct optical and spectroscopic methods, primarily ellipsometry and infrared reflection, absorption spectroscopy (IRRAS), are also being used or further developed probing the interface and helping our model development and search for the most effective molecules.

With Professor G. Narsimhan, in the School of Agricultural and Biological Engineering, and Dr. D. Cho, we have studied the adsorption/tension behavior of Bovine Serum Albumin, as a model globular protein, alone with a lipid. The goal is to understand the factors affecting foam-based separation method and foam stability in food products. We have developed models for diffusion of the protein to and from the surface layer, and have used a radiotracer method to directly measure the surface concentrations and stability of protein and surfactant monolayers. Ellipsometry and IRRAS are used to study the competitive adsorption of proteins, surfactants, and lipids.

Production and Characterization of Ultrathin Organic Films. Ultrathin films are important in microlithography, membranes barrier materials, sensors, and nonlinear optical materials. We have studied the thickness, thickness uniformity, and transport properties (to water) of films (0.002 - 2 mm) produced with the spin coating or Langmuir-Blodgett methods (with C.B. Walsh). Spinning speed, polymer concentration, and surface wettability are some of the important factors affecting film quality. Ellipsometry, at multiple angles and wavelengths, and FTIR spectroscopy are the main methods used for characterizing such films and also adsorbed or spread monolayers at the air/liquid interface.

Publications

Myrick, S.H., and Franses, E.I., "Effect of Dispersed Tetradecanol Particles or Droplets on the Dynamic Surface Tension of Aqueous Tetradecanol Systems," *Langmuir*, 15, 1556-1561, 1999.

Pinazo, A., Wen, X., Pérez, L., Infante, M.-R., and Franses, E.I., "Aggregation Behavior in Water of Monomeric and Gemini Cationic Surfactants Derived from Arginine," *Langmuir,* 15, 3134-3142,1999.

Walsh, C.B., and Franses, E.I., "Thickness and Quality of Spin-Coated Polymer Films by Two-Angle Ellipsometry," *Thin Solid Films,* 347, 167-177, 1999.

Park, S.Y., Hannemann, R.E., and Franses, E.I., "Dynamic Tension and Adsorption Behavior of Aqueous Lung Surfactants," *Colloids Surfaces B,* 15, 325-338, 1999.

Park, S.-Y., Baatz, J.E., Hannemann, R.E., and Franses, E.I., "Dynamic Surface Tension of Aqueous Dispersions of SP-C and DPPC, and Their Monolayer Behavior," special volume in honor of Professor D.T. Wasan, *Emulsions, Foams, and Thin Films,* New York, pp. 329-348, 2000.

Wen, X., Lauterbach, J., and Franses, E.I., "Surface Densities of Adsorbed Layers of Aqueous Sodium Myristate Inferred from Surface Tension and Infrared Reflection Absorption Spectroscopy," *Langmuir,* 2000, in press.

Prosser, A.J., and Franses, E.I., "Adsorption and Surface Tension of Ionic Surfactants at the Air / Water Interface: Review and Evaluation of Equilibrium Models," *Colloids Surfaces A,* accepted June 2000.

Meeting Presentations

218th ACS National Meeting, New Orleans, LA, August 1999, "Unusually Low Dynamic Tensions and Direct Probing of Adsorbed Layers of Aqueous Sodium Myristate," with X. Wen; presented by X. Wen. (P)

AIChE Annual Meeting, Dallas, TX, November 1999, "Direct Probing of Adsorbed Aqueous Myristate Layers at the Air / Water Interface by Reflection Absorption Infrared Spectroscopy," with X. Wen; presented by X. Wen. (P)

Robert E. Hannemann

1969

Visiting Professor

Interests

Aerosols in medical practice

Surfactants in respiratory distress syndrome treatment

Non-invasive diagnostic techniques

Serum bilirubin determination by skin reflectance

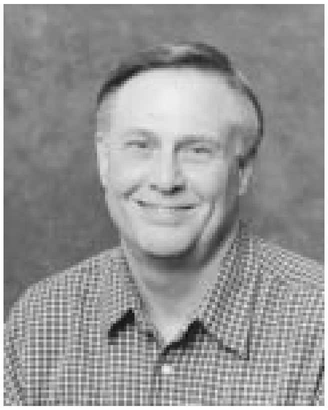
Awards and Major Appointments

Medical Technology Committee — Indiana Corporation for Science and Technology

R. Neal Houze

1969

Professor and Director of the Cooperative Education Program



Degrees

BS, Georgia Institute of Technology, 1960

MS, University of Houston, 1966

PhD, University of Houston, 1968

Interests

Interphase Mass Transfer

Free Boundary Turbulence

Awards and Major Appointments

Chairman of *Awards Committee*, Cooperative Education Division, American Society for Engineering Education

Member, *Clement J. Freund Award Committee*, American Society for Engineering Education

David P. Kessler

1964

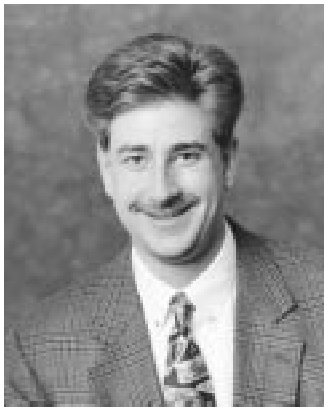
Professor and Head, Division of Interdisciplinary Engineering Studies

Degrees	BS, Purdue University, 1956 MS, University of Michigan, 1959 PhD, University of Michigan, 1962
Interests	Transport in disperse media Biomedical models

Jochen A. Lauterbach

1996

Assistant Professor



Degrees

Dipl. - Phys., University of Bayreuth, Germany, 1992

Dr. rer. nat., Free University of Berlin, Germany, 1994

Interests

Surface chemistry and heterogeneous catalysis

Laser light based microscopy

Time-resolved infrared vibrational spectroscopy

Hyperspectral imaging in the mid-infrared

Non-linear phenomena in catalysis

Low temperature oxidation catalysts

Polymer / metal interfaces

Combinatorial catalysis

Ultra-thin polymer films on metal and semiconductor surfaces

Hyperspectral imaging of bacteria, cells, and diffusion in biopolymers

Awards and Major Appointments

Faculty Early Career Development Award (CAREER) from National Science Foundation

Union Carbide Research Innovation Award

Research Areas

Professor Lauterbach's research focuses on the application of light-based techniques for the in situ characterization of processes on surfaces, in particular to study heterogeneously catalyzed reactions on the molecular level and on mesoscopic length-scales. Several key research areas are targeted:

A combinatorial approach to catalyst development leads to new avenues for materials discovery by accelerating the process of discovery, optimization, and understanding of heterogeneously catalyzed reactions. One of the key problems is high-throughput analysis of heterogeneous catalysts, which involves the unambiguous detection of specific molecules (i.e., products in the gas phase or reaction intermediates on the catalyst surface). Our group has developed the first parallel, chemically sensitive screening technique for combinatorial catalysis. This novel technology has also been applied to traditional solid bead based combinatorial chemistry.

It is well known that heterogeneously catalyzed reactions show spatio-temporal pattern formation under ultra high vacuum (UHV) conditions. We have established that spatio-temporal adsorbate patterns also form under reaction conditions at more realistic, higher pressures. This result confirmed that pattern formation is present at elevated pressures and has implications for the treatment of heterogeneously catalyzed reactions, showing that the traditional, spatially uniform Langmuir-Hinshelwood reaction mechanism may not be the correct way of describing certain chemical reactions. We also perform direct comparison studies of non-linear phenomena on supported catalysts and single crystal model systems in the same reactor under identical conditions, thereby bridging the gap between surface science and applied catalysis research. With these experiments we showed that the various explanations given for rate oscillations over supported catalysts may not be valid and other microscopic mechanisms play a crucial role in non-linear phenomena in catalysis.

The surface chemistry community has not studied the adsorption of larger molecules on metal surfaces extensively. We use time-resolved Fourier transform infrared (FTIR) spectroscopy, temperature programmed desorption, atomic force microscopy, ellipsometry, and electron microscopy to study adsorption of a variety of more complex molecules, such as methyl methacrylate and styrene, on metal surfaces. This allows us to gather valuable information about the structure of adsorbed monolayers and multilayers. We study the in situ photopolymerization of monomers preadsorbed on surfaces and have shown that it is possible to polymerize styrene in nm thick layers and to follow the kinetics of this reaction.

Non-linear phenomena in heterogeneous catalysis: Synergetic effects on very different length scales are among the most fascinating phenomena nature can create. During the past two decades, scientists and engineers from many disciplines have become increasingly interested in oscillations, multiple steady states, spatial structures, and wave propagation occurring in chemical, biochemical, and biological systems. Heterogeneously catalyzed reactions serve as model systems where pattern formation is restricted to two dimensions on the catalyst surface. Preparation of the catalyst under well-defined ultra-high vacuum (UHV) conditions provides a deeper understanding of the fundamental properties of the non-linear phenomena observed for many technologically and environmentally important reactions. Reactions are considered to be isothermal in the low-pressure regime. At higher pressures, however, the heat of exothermic reactions cannot be neglected, leading to a transition from reaction-diffusion control to additional thermokinetic control. Very little information about spatio-temporal pattern formation for heterogeneous reactions in this regime is available. This opens the fascinating possibility for both experimentalists and theorists working very closely together in the exploration of the expected new phenomena.

CO oxidation is the most fascinating reaction with respect to oscillatory behavior and spatio-temporal pattern formation. From the environmental point of view (automotive emission control), we also study the catalytic reduction of NO. Relatively few reaction studies involving NO at moderate pressures, encompassing NO concentrations more typical of those present in the three-way catalyst of automobiles, have been performed. It is known that both NO + CO and NO + NH_3 show rate oscillations and pattern formation. However, no information about oscillatory kinetics and pattern formation in this pressure range is presently available. Using EMSI, we can extend the investigation of non-linear phenomena above high vacuum pressures. We have extensively studied the parameter space for CO oxidation on Pt(100). Compared to low-pressure studies, several distinct differences were observed and the existence of spatio-temporal patterns was established. Front velocities on the catalysts are up to 20 times higher compared to lower pressure studies. This leads to very efficient spatial coupling of large areas of the catalyst. Successful modeling of the observed non-linear phenomena provides a more sophisticated reaction model for the CO oxidation on this particular surface and enables us to gain a deeper understanding into the interplay between reaction and diffusion on catalyst surfaces. We are currently developing a spatio-temporal reaction model for the Pt(100) surface using probability averaging in collaboration with Professor Ramkrishna. The model contains adsorption and desorption kinetics of the reactants. In addition, it also contains the adsorbate induced surface phase transition and adsorbate diffusion.

One major obstacle in the field of non-linear reaction dynamics is the fact that experimental results usually exist in two distinct pressure regimes - near atmospheric pressure for supported catalysts and in high vacuum for single crystal model catalysts. Due to experimental restrictions, this “pressure gap” and the associated “materials gap” have existed for over 20 years. Our light based techniques allow to bridge this gap and to perform experiments on supported catalysts. Our results show that the parameter space for self-sustained rate oscillations for both high- and low-pressure conditions is much wider with respect to temperature and CO/O_2 ratio compared to many other results reported in the literature. We have also been able to directly compare supported catalysts and single crystals in the same reactor under similar pressure and flow conditions, thereby allowing direct comparison for non-linear phenomena between single crystal model system and a supported catalyst.

Using time-resolved FTIR transmission spectroscopy, we study N_2O decomposition over Cu-ZSM5 catalysts. This decomposition reaction shows self-sustained rate oscillations, however, the exact reaction mechanism in unclear to date. Time-resolved FTIR spectroscopy allows us to follow adsorbates in situ and correlate them with the reaction rate. Results show that both adsorbed N_2O and N_2 are present on the catalyst surface and that their concentration changes during the rate oscillations. In collaboration with Professor Delgass, we take a similar approach to study propylene oxidation with hydrogen cofeed over Au/TiO_2 catalysts.

Combinatorial catalysis: Combinatorial technologies accelerate the speed of research, maximize the opportunity for breakthroughs, and expand the amount of available information by orders of magnitude compared with classical discovery methods. The underlying principle of the combinatorial approach is to synthesize small quantities of a large number of compounds and test these compounds quickly to determine which of them are potentially useful. To date, combinatorial chemistry has been applied almost exclusively as a method of drug discovery. There is, however, much potential for discovery in the broad range of materials science, where researchers are searching for better heterogeneous catalysts, electronic and magnetic devices, superconductors, or phosphors. Two main obstacles to the successful application of the combinatorial approach are the controlled synthesis of small amounts of materials and the high-throughput analysis of libraries of these materials. Inherent to the production of combinatorial libraries are therefore efforts to introduce and strengthen the analytical methodologies. Speed, through parallel experimentation, is currently the main bottleneck in the combinatorial discovery process and subsequent optimization of novel materials. We have developed a novel spectral imaging system, which allows us to simultaneously measure the IR spectra of many members of a combinatorial library, allowing the in situ parallel investigation of chemical reactions. This technique is applied to two different applications of high-throughput studies: (1) heterogeneous supported catalysts and (2) organic reactions on solid-phase bead materials.

(1) Catalyst design, which is most crucial for the development of novel catalytic processes, requires understanding of the molecular reaction mechanism and knowledge of the properties that determine the activity, selectivity, and lifetime of the catalyst. Studies of the interrelationship between structural and chemical properties of solid materials and their catalytic properties are at the origin of catalyst design. These studies are typically carried out using specially prepared model catalysts that are amenable to analysis with modern surface analytical methods, providing structural and chemical information on the molecular scale. Vibrational spectroscopy has always been an important in situ tool in catalysis and surface science research. The combination of FTIR imaging with reaction rate measurements provides us with in situ information about different adsorbate species and concentrations on multiple catalyst elements under the applied reaction conditions. By systematically varying the composition of the various catalyst pellets, we obtain fundamental structure/composition relationships for different catalyst formulations containing different levels of promoters. There are two obvious advantages to this approach. Firstly, a time advantage is gained by screening more than one catalyst at a time, and secondly, it is possible to study different catalyst formulations under exactly the same reaction conditions and with the same pretreatment for all samples.

(2) Combinatorial chemistry, the science of molecular diversity and "rational screening", has emerged over the past few years as one of the most powerful approaches to drug discovery. Highly effective synthetic schemes have been devised to generate millions of compounds immobilized on solid supports or as pooled mixtures in solution. Subsequently, these libraries are submitted to an assay method that allows for the selection of the chemical entities displaying the desired property. This step is usually followed by the structural elucidation of the selected species using direct methods. The screening and structural characterization phases have consistently been the bottleneck in the overall process and still constitute in most cases a very challenging task. Furthermore, none of these methods is capable of non-invasive, rapid, high throughput, and real-time spectroscopic monitoring of a binding or catalytic event within or around a resin-bound ligand or catalyst. Infrared-based techniques are useful for the analysis of combinatorial libraries because of the benefits of low cost, ease of use, and rapid data collection. We have established FTIR imaging as a powerful spectroscopic tool for the parallel identification of selected members of

resin-supported combinatorial libraries. This technique combines the chemical specificity and high sensitivity of mid-IR (4000-1000cm^{-1}) imaging with the ability to rapidly analyze multiple samples simultaneously. This includes both the identification of supported ligands and also the monitoring of reactions occurring on supported ligands. The chemical identity of a variety of ligands supported on resin beads can be determined in a single experiment without perturbing the system. The sampling geometry used is applicable to the identification of resin-bound compounds from a “split-and-pool” synthesis, where beads carrying different ligands are mixed together. It should be noted that this type of analysis is not limited to ligands that have well-separated spectral bands. An important benefit of combinatorial organic solid bead chemistry is its higher throughput compared to classical synthetic methods, as automated reactions are carried out on polymer resins. We employ FTIR imaging to the parallel, non-intrusive in situ analysis of compounds bound to resin beads. This approach has recently been pioneered using single bead spectroscopy or IR mapping using a scanning IR microscope. Our novel technology is up to several orders of magnitude faster that all previously used techniques, which provides us with the unique capability to perform in situ real time studies of reaction kinetics on polymer resins.

Surface Chemistry of metal interfaces: We study the adsorption on metals of monomers suitable for in situ photopolymerization. Our primary goal is to contribute to the understanding of the adsorption geometry and energetics of complex molecules on surfaces and how very thin, high quality polymer layers can be formed in situ on surfaces from these molecules. Such polymeric layers, particularly when possessing a high degree of two-dimensional order, are of importance from the point of view of both technological development and fundamental research, and for a variety of coating and device applications, such as corrosion resistance, and electrical insulation. One way to fabricate these layers on substrates is solvent-free, direct photopolymerization. We are studying elementary steps of monomer adsorption, desorption, and decomposition as a function of surface temperature, surface chemical composition, and electronic and geometric surface structure. The monomers include styrene, methyl methacrylate, and acrylic acid. The choice of the monomers allows us to investigate a series of systems of increasing complexity. Experiments are performed to characterize adsorption and photopolymerization kinetics on transition metal surfaces using a combination of time-resolved Fourier transform IR spectroscopy and other standard surface science techniques. Recently, we have also started to coadsorb monomer and photoinitiator on the surface in both layered and well-mixed structures to study the influence of the composition of the unpolymerized layer on polymerization kinetics and the properties of the final polymer film.

This project has recently been expanded to study organic compounds in monolayer form, which have demonstrated a great potential to serve in a wide variety of molecular technologies. Self-assembled monolayers (SAMs) are being studied both for their fundamental importance in understanding interfacial properties and for their potential applications in molecular technologies. An understanding of the detailed structure of SAMs provides a molecular level correlation of structure and surface properties, such as wetting, adhesion, lubrication, and catalysis. Understanding the parameters that control the structure formation is also the first step toward further fine-tuning of the structural features for specific applications, such as optoelectronics and molecular electronics. Our experimental set-up allows us to access information about the surface chemistry of these molecules. This information will contribute to a better fundamental understanding of the bonding mechanisms of SAMs to semiconductor and metal surfaces and can lead to the design of new SAMs fulfilling the requirements for nanoelectronic circuits.

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C.M. Snively, S. Katzenberger, G. Oskarsdottir, and J. Lauterbach, “Fast FTIR imaging utilizing a rapid scanning interferometer”, *Optics Letters,* 24; 1841-1843, 1999.

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J. Dicke, H.H. Rotermund, and J. Lauterbach, “Formation of surface oxides on Pt(100) during CO oxidation in the millibar pressure range”, *Surface Science, 454; 352-357, 2000.*

Invited Lectures

J. Lauterbach, “Combinatorial catalysis-a new approach to effective catalyst discovery”, presented at the BP-Amoco research center, Naperville, IL, November 1999.

J. Lauterbach, “Dynamic surface processes in catalysis”, presented at the Workshop for Complex Biological and Engineering Systems, Purdue University, December 1999.

J. Lauterbach, “Applications of FTIR spectroscopy and imaging to heterogeneous catalysis”, presented at the Lawrence Berkeley National Laboratory, CA, March 2000.

J. Lauterbach, “Applications of FTIR spectroscopy and imaging to heterogeneous catalysis”, presented at the Chemical Engineering Department, Princeton University, NJ, April 2000.

J. Lauterbach, “Combinatorial catalysis-a new approach to effective catalyst discovery”, presented at the BP-Amoco Catalysis Skills Symposium, London, U.K., May 2000.

J. Lauterbach, “Light-based spectroscopy and imaging tools in heterogeneous catalysis”, Union Carbide Research Innovation Award Lecture, Charleston, WV, May 2000.

Meeting Presentations

J. Lauterbach, “FTIR imaging - a novel tool for high throughput screening in combinatorial catalysis” presented at annual meeting of the American Chemical Society, New Orleans, LA, August 1999.

J. Dicke and J. Lauterbach, “The formation of surface oxides on Pt(100) during CO oxidation,” presented at the European Conference on Surface Science (ECOSS), Vienna, Austria, September 1999.

G. Oskarsdottir, C. Snively, and J. Lauterbach, “Novel imaging system for high-throughput screening of combinatorial libraries,” presented at the fall meeting of American Vacuum Society, Chicago, IL, October 1999.

J. Bai, C. Snively, and J. Lauterbach, “Adsorption and photopolymerization of styrene on polycrystalline platinum,” presented at the fall meeting of American Vacuum Society, Chicago, IL, October 1999.

P. Fanson, W.N. Delgass, and J. Lauterbach, “Time-resolved FTIR spectroscopy study of the N_2O decomposition over Cu-ZSM5,” presented at the fall meeting of American Vacuum Society, Chicago, IL, October 1999.

T. Lele, D. Ramkrishna, and J. Lauterbach, “Spatio-temporal pattern formation during CO oxidation on Pt(100): experimental and theoretical inquiry,” presented at the fall meeting of American Vacuum Society, Chicago, IL, October 1999.

C. Snively, G. Oskarsdottir, and J. Lauterbach, “Novel imaging system for screening of combinatorial catalyst libraries,” presented at the fall meeting of AIChE, Dallas, TX, November 1999.

J. Bai and J. Lauterbach, “Adsorption and photopolymerization of styrene on polycrystalline platinum,” presented at the fall meeting of AIChE, Dallas, TX, November 1999.

G. Oskarsdottir, C. Snively, and J. Lauterbach “High-throughput, chemically sensitive screening of combinatorial libraries,” presented at spring meeting of the American Chemical Society, San Francisco, CA, March 2000.

G. Oskarsdottir, C. Snively, and J. Lauterbach “ Rapid-scan FTIR imaging screening for combinatorial catalyst libraries,” presented at spring meeting of the American Chemical Society, San Francisco, CA, March 2000.

C. Snively, G. Oskarsdottir, and J. Lauterbach “Rapid-scan FTIR imaging - a novel high-throughput screening technique for combinatorial catalyst libraries,” presented at PittCon, New Orleans, CA, March 2000.

M. Horton, J. Bai, C.M. Snively, and J. Lauterbach, “Adsorption and photopolymerization of styrene on polycrystalline copper,” presented at the Materials Research Society meeting, San Francisco, CA, April 2000.

C. Snively, G. Oskarsdottir, and J. Lauterbach “Combinatorial catalysis,” presented at the spring meeting of the Prairie Chapter of the American Vacuum Society, West Lafayette, IN, May 2000.

G. Oskarsdottir, C. Snively, and J. Lauterbach "High-throughput, chemically sensitive screening of combinatorial libraries," presented at the spring meeting of the Prairie Chapter of the American Vacuum Society, West Lafayette, IN, May 2000 (won 1st prize in student poster competition).

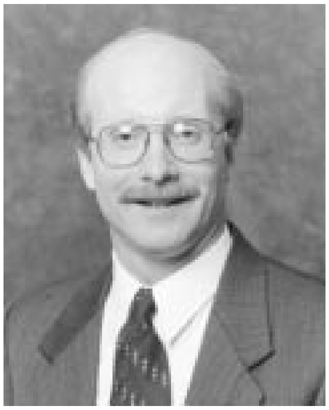
J. Bai, M. Horton, C.M. Snively, and J. Lauterbach, "Adsorption and photopolymerization of styrene on polycrystalline metal surfaces," presented at the spring meeting of the Prairie Chapter of the American Vacuum Society, West Lafayette, IN, May 2000.

P. Fanson, W.N. Delgass, and J. Lauterbach, "Time-resolved FTIR spectroscopy study of CO oxidation over supported platinum catalysts," presented at the spring meeting of the Prairie Chapter of the American Vacuum Society, West Lafayette, IN, May 2000 (won 3rd prize in student poster competition).

Joseph F. Pekny

1990

Associate Professor



Degrees

BS, Princeton University, 1985

PhD, Carnegie-Mellon University, 1989

Interests

Process scheduling, planning, & design

Parallel & distributed computing

Simulation

Combinatorial optimization

Nonlinear optimization

Software engineering methods

Nicholas A. Peppas

1976

Showalter Distinguished Professor of Biomedical Engineering

Degrees

DEng, National Technical University, Athens, 1971

ScD, Massachusetts Institute of Technology, 1973

Interests

Diffusion in polymers

Polymer / polymer adhesion

Polymerization reaction engineering

Controlled release

Biomedical engineering

Biomedical polymers

Bioadhesion

Awards and Major Appointments

General Electric, Senior Research Award, American Society for Engineering Education, 2000.

Herbert McCoy Award, Highest Research Achievement, Purdue University, 2000.

J. Heller Award, Best Research for 1999, Controlled Release Society, 2000.

APV Award, Best Ph.D. Thesis, International Pharmaceutical Association, 2000.

Best Paper Award, European Journal of Pharmaceutics and Biopharmaceutics, 2000.

Honorary Doctorate, University of Athens, Greece, 2000.

Fellow, American Association for the Advancement of Science,, 2000

Research Achievement Award in Pharmaceutical Technology, American Association of Pharmaceutical Scientists, 1999.

Honorary Doctorate, Doctor of Pharmacy, University of Parma, Italy, 1999.

Best Paper Award, Midwestern Meeting, American Association of Pharmaceutical Scientists, 1999.

Marion B. Scott Award, Purdue University, 1999.

Honorary Doctorate, University of Ghent, Belgium, 1999.

Research Areas

Diffusion in and Dissolution of Glassy Polymers: Penetrant transport in glassy polymers may be described by two coupled processes of penetrant diffusion and macromolecular relaxation. Dissolution of glassy polymers can be considered as a combination of solvent penetration featuring Case II transport and polymer dissolution controlled by polymer disentanglement. Anomalous transport models are developed for solvent penetration which is coupled with a disentanglement model for polymer dissolution. Solvent penetration is controlled by the relaxation or deformation of polymer and the diffusional Deborah number is shown to be a major model parameter. In the disentanglement model, dissolution of polymer molecules requires that solvent concentration be greater than a critical gel concentration and that a polymer molecule be allowed a certain time to complete the disentanglement or diffusion movement from the gel state to liquid state. This time is assumed to be equivalent to the reptation time, which is a function of molecular weight, solvent concentration and chain rigidity. A concept of disentanglement clock is introduced as the material time clock controlling the dissolution. The new model may explain many experimental observations, such as effects of type of solvent and polymer on dissolution rate and the thickness of the gel layer. Experimental studies are performed with well-characterized samples of polystyrene and poly(methyl methacrylate) in various solvents using laser interferometer and critical angle illumination microscopy. The solvent concentration profiles and dissolution rates are measured by ellipsometry. The necessary self-diffusion coefficient of the polymer is measured by pulsed gradient spin echo NMR spectroscopy. In addition, experimental studies are performed using poly(acrylic acid) and poly(vinyl alcohol) in water to study the influence of ionic conditions on dissolution.

Polymer/polymer Adhesion and Diffusion: The interdiffusion of compatible polymer / polymer pairs is studied using scanning electron microscopy, transmission electron microscopy and attenuated total reflectance. Fourier transform infrared spectroscopy. We examine the effect of molecular weight distribution of one component on the interdiffusion process and investigate the importance of branching and hydrogen bonding. Studies are performed with polystyrene / poly(vinyl methyl ether), polystyrene / polychlorostyrene, poly(vinyl chloride) / poly(ethyl methacrylate), and poly(vinyl chloride) / poly(methcrylate) systems. The results and associated molecular analysis have applications in healing and adhesion polymers.

Highly Crosslinked Poly(Meth)Acrylates for Information Storage Materials: The kinetics of polymerizations of multifunctional acrylate and methacrylate monomers as well as the crosslinked structure and properties of the ensuing polymers are studied by a variety of experimental techniques. Interferometric studies are used to calculate the relaxation of the polymer during the reaction, whereas shrinkage studies are related to conversion and the structure of the reacting monomers. The mesh size of the produced networks is analyzed using swelling studies. Differential scanning calorimetry and related thermal techniques provide information about this structure and mechanical properties of these networks. The results are used to verify and improve a kinetic model based on relaxation and to study relationships between monomer structure and applications in the information storage field.

Monte Carlo Simulations and Structural Analysis in UV Polymerizations: The project involves a detailed analysis of how the three-dimensional network structure forms in highly crosslinked polymers, coatings, resins, etc., that are produced by the polymerization of monomers in the presence of UV light. Various types of Monte Carlo simulations will be used to analyze the kinetics of polymerization and the gradual reaction of one or more double bonds in multifunctional methacrylates. This work has applications in the fields of information storage materials, biomaterials, membranes, coatings, and drug delivery systems.

Polymer Brushes and Poly(ethylene glycol) Structures: Simulations and Surface Properties: The primary goal of this research is to elucidate the effect of interdiffusion on adhesion. The selective control of the molecular weight of the polymer chains which can diffuse across an interface is essential. Thus, while good swelling behavior of the polymer base is required, the more heavily crosslinked surfaces have fewer and shorter dangling ends. The dilemma is circumvented by selectively grafting well characterized PEG chains onto crosslinked PAA surfaces. The molecular weight of the polymer chains at the surface may now be independently varied.

Self-Associating Hydrogels of Ethylene Glycol and Methacrylic Acid: The preparation, structure and properties of novel hydrogels of poly(ethylene glycol-g-methacrylic acid) copolymers are investigated. These hydrogels have been tailored so as to be sensitive to external environmental conditions, such as change of the pH, the temperature and the solvent composition. The swelling equilibrium characteristics and the diffusive properties of the gels are dependent on these external conditions and extremely sensitive to them. Such properties are of utmost importance in the development of novel separation systems. In aqueous swelling solutions at acidic pH, copolymer networks swell to a much lower extent than homopolymer networks. This behavior is attributed to complex formation between poly(ethylene glycol) and poly(methacrylic acid) segments. Nuclear Overhauser enhancement (NMR) measurements reveal that graft copolymers form complexes under a wider range of concentrations and poly(ethylene glycol) molecular weight than the two ungrafted homopolymers. This enhancement in complexation may be attributed to elimination of the unfavorable translational free energy change of complexation by covalent attachment of the complexing species.

Star and Dendritic Polymers for Functional Materials: Star and dendritric polymers are molecules of hyperbranched structures, often exhibiting fractal-like behavior, which start from one central core (nucleus) and consist of a large number of terminal groups with a definite geometrical growth. Polymers exhibiting this three-dimensional, hyperbranched structure are classified as star polymers and dendrimers. Star polymers are characterized by a central core which may be a slightly crosslinked polymer core from which a large number of branches of the same or different molecular structure propagate. Dendrimers and star-burst polymers, however, are a very specific class of polymers exhibiting symmetry in their three-dimensional structure. Unlike other polymers, dendritic polymers can have precisely defined architectures and surface groups, and may be prepared as non-interacting molecular ball bearings or as crosslinked networks. The size, shape, surface chemistry, flexibility, and topology can be precisely defined and controlled, and this allows for nanoscopic tailoring. The great density of surface groups may be functionally tailored for super- strong adhesives, chemical / biological molecule detection, catalysis of toxic molecules, and as interaction sites with linear polymers to modify bulk / solution properties. The interior of dendritic polymers can also be functionally tailored for a variety of uses including catalysis of toxic molecules and molecular recognition, which have been demonstrated at sites covalently bonded to the interior architecture (molecular imprinting).

From a pharmaceutical and a medical point of view, these polymeric system are particularly promising because they can serve as micro- or nanoparticulate carriers for drug delivery systems development. In addition, because of the very large number of free arms they can be used for immobilization of drugs, cells, enzymes or antibodies, whereby a very high density of biological agent is attained in a very small volume. We are synthesizing structurally intriguing dendrimers and star polymers. These have significant potential to serve as models for the investigation of supramolecular biological interactions, as well as for the study of highly ionic polymeric systems. Of particular importance in biomedical and pharmaceutical research is their ability to act as supports for immobilization of bioactive agents. The main components of a star- burst polymer are the core or foundation site from which the diverging branches of the dendritic structure start. One or more branching arms emanate from this core site, each one incorporating a further branch point. Finally, a terminal functionality is observed for each of the branches, usually having a reactivity which allows it to further react in the dendritic structure. Dendrimers are prepared using distinct stages of monomer addition, where a separate activation process is required before each new monomer generation is added. We are investigating the polymers’ structure, generation growth and functionality and are experimenting with the development of novel ionic star polymers.

Drug Targeting to Cancerous and Other Tissues by Mucin/Polymer Interactions: The goal of this work is the development of improved polymers that can be used for wound healing or as carriers for drug targeting to specific sites of the body. The effect of crosslinking, polymer hydrophilicity, and interdiffusion on the adhesion and cohesion of hydrogel with adhesive functional groups in contact with mucin will be investigated. Hydrogels will be prepared by free radical polymerization of acrylic acid, 2-hydroxy ethyl methacrylate and ethylene glycol dimethacrylate. The surface chemistry of selected polymers will be modified by grafting poly(ethylene glycol) of varying molecular weight. The surface and bulk properties will be characterized by contact angle measurements, gas chromatography, gel permeation chromatography, differential scanning calorimetry and Fourier-transform infrared (FTIR) spectroscopy. Near-field FTIR will be used to study the interdiffusion and adhesion process in contact with mucin and identify the molecular characteristics that will provide maximum mucoadhesion.

Temperature-Sensitive Block Copolymers for Controlled Release: Environmentally sensitive hydrogels have biomedical applications in drug delivery. Temperature- and pH-sensitive hydrogels were synthesized by polymerization of poly(ethylene glycol) (PEG), methacrylic acid (MAA), and N-isopropyl acrylamide (NIPAAm), with tetraethylene glycol dimethyacrylate added as a crosslinking agent. Because of an intercomplexation mechanism between the carboxylic acid of the MAA and the ether oxygens of the PEG, these gels exhibited pH-dependent swelling. Addition of oligo-NIPAAm chains resulted in temperature sensitivity due to the existence of a lower critical solubility temperature. Equilibrium swelling studies were done to examine the network structure as a function of temperature and pH. Studies were done using dimethyl glutaric acid buffered solutions ranging in pH from 3.4 to 7.4 at temperatures ranging from 25_C to 37_C. Equilibrium volume swelling ratios varied by an order of magnitude from the condition of low pH and high temperature to the case of high pH and low temperature. Modulated drug release studies were performed using proxyphylline to investigate the potential for pulsatile drug delivery.

Mucoadhesive/Bioadhesive Polymers for Protein Targetting: A promising method of directed delivery of peptides and proteins is by incorporation into H-bonding controlling polymers and injection / administration in the body. We are examining the polymer / biomedical conditions of improvement of the adhesive bond between free, branched or crosslinked polymer chains and the tissue, mucus or skin. The effect of crosslinking, polymer hydrophilicity, and interdiffusion on the adhesion and cohesion of bioadhesive hydrogels in contact with mucin will be investigated. Hydrogels will be prepared by free radical polymerization of a variety of monomers. The surface chemistry of selected polymers is modified by grafting poly(ethylene glycol) of varying molecular weight (PEG-tethered structures). The surface and bulk properties are characterized by contact angle measurements, GC, GPC, DSC, TGA and FTIR spectroscopy. Near-field FTIR is used to study the interdiffusion and adhesion of gels on gels or mucin. In collaboration with the Hoshi University, Tokyo, Japan we contact studies of nasal delivery of such systems.

New Biopolymers Based on Poly(acrylic acid) and Containing Poly(ethylene glycol) Chains as Mucoadhesive Drug Delivery System: The primary goal of bioadhesive controlled drug delivery is to localize a delivery device within the body to enhance the drug absorption process in a site-specific manner. Bioadhesion is affected by the synergistic action of the biological environment, the properties of the polymeric controlled release device, and the presence of the drug itself. The delivery site and the device designed are dictated by the drug’s molecular structure and its pharmacological behavior. Recent studies in our laboratory indicate that the mucoadhesive behavior of specific hydrophilic polymer structures used as carriers for drug delivery can be improved with the addition of poly(ethylene glycol) (PEG) as an adhesion promoter. PEG chains can be added to such structures by postreaction grafting leading to PEG-tethered hydrogels. An additional method is by loading PEG into an already swollen hydrogel structure. In the present work we develop, characterize and evaluate new drug delivery systems containing PEG. The fracture energy required to separate layers of hydrogel films in control with mucin is investigated to evaluate the impact of promoter chain diffusion on device / mucin adhesion and to obtain molecular information on the fracture energy in drug carrier mucoadhesion. PEG is incorporated in a hydrogel and used as an adhesion promoter. The influence of PEG molecular weight and contact time on PEG diffusion across the hydrogel / mucin interface is investigated by using tensiometry and near-field FTIR microscopy. Fracture analysis provides details about the mechanism of muco-adhesion and conditions of improved adhesion. In our work, we concentrate also on the practical development of such PEG-tethered or PEG-promoted systems for transmucosal, buccal and nasal delivery systems.

Books

N.A. Peppas, D.J. Mooney, A.G. Mikos and L. Brannon-Peppas, editors*: Biomaterials, Carriers for Drug Delivery, and Scaffolds for Tissue Engineering, AIChE,* New York, NY, 1997.

Publications

R.S. Parker, F.J. Doyle, III and N.A. Peppas, "A Model-based Algorithm for Blood Glucose Control in Type I Diabetic Patients," *IEEE Trans. Biomed. Eng.*, 46, 148-157, 1999.

J. Siepmann, K. Podual, M. Sriwongjanya, N.A. Peppas and R. Bodmeier, "A New Model Describing the Swelling and Drug Release Kinetics from HPMC Tablets," *J. Pharm. Sci.,* 88, 65-72, 1999.

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N.A. Peppas, "Poly(2-hydroxy ethyl methacrylate)," in J.E. Mark, ed., *Polymer Data Handbook*, 598-599, Oxford University Press, New York, 1999.

B. Narasimhan, J.E.M. Snaar, R.W. Bowtell, C.D. Melia, and N.A. Peppas, "NMR Imaging Analysis of Molecular Mobility During Dissolution of PVA in Water," *Macromolecules*, 32, 704-710, 1999.

C.S. Brazel and N.A. Peppas, "Mechanisms of Solute and Drug Transport in Relaxing, Swellable, Hydrophilic Glassy Polymers," *Polymer* , 40, 3383-3398, 1999.

W. Leobandung, G. McLennan, N. Patel, K.P. Moresco and N.A. Peppas, "The Characterization of P(PEGMA-co-PEGDMA) Gels for Use in Coating the Tract of a Transjugular Intrahepatic Porto-systemic Shunt," *Polym. Prepr.,* 40 (1), 337-338, 1999.

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H. Ichikawa and N.A. Peppas, "pH-Dependent Swelling of Nanosized Poly(methacrylic acid-g-ethylene glycol) Gels," *Polym. Prepr.,* 40 (1), 363-364, 1999.

L.M. Schwarte, K. Podual and N.A. Peppas, "Cationic Hydrogels for Controlled Release of Proteins and Other Macromolecules" in I. McCulloch and S.W. Shalaby, eds., Tailored Polymeric Materials for Controlled Delivery Systems, ACS Symposium Series, Vol. 709, 56-66, ACS, Washington, DC, 1999.

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A.M. Lowman, N.A. Peppas, M. Morishita and T. Nagai, "Novel Bioadhesive Complexation Networks for Oral Protein Drug Delivery," in I. McCulloch and S.W. Shalaby, eds., Tailored Polymeric Materials for Controlled Delivery Systems, ACS Symposium Series, Vol. 709, 156-164, ACS, Washington, DC, 1999.

C.S. Brazel and N.A. Peppas, "Dimensionless Analysis of Swelling of Hydrophilic Glassy Polymers with Subsequent Drug Release from Relaxing Structures," *Biomaterials,* 20, 721-732 ,1999.

C.M. Hassan and N.A. Peppas, "Novel Ethylene Glycol-Containing, pH-Sensitive Hydrogels for Drug Delivery Applications: "Molecular Gates" for Insulin Delivery," in S.M. Dinh, J.D. DeNuzzio, A.R. Comfort, eds., Intelligent Materials for Controlled Release, ACS Symposium Series, Vol.728, 54-69, ACS, Washington, DC, 1999.

A.M. Lowman and N.A. Peppas, "Pulsatile Drug Delivery Based on a Complexation / Decomplexation Mechanism," in S.M. Dinh, J.D. DeNuzzio, and A.R. Comfort, eds., Intelligent Materials for Controlled Release, ACS Symposium Series, Vol.728, 30-42, ACS, Washington, DC, 1999.

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A.M. Lowman and N.A. Peppas, "Hydrogels," in "Encyclopedia of Controlled Drug Delivery," E. Mathiowitz, ed., 397-418, Wiley, New York, NY, 1999.

B. Narasimhan, S.K. Mallapragada and N.A. Peppas, "Release Kinetics: Data Interpretation," in "Encyclopedia of Controlled Drug Delivery," E. Mathiowitz, ed., 921-935, Wiley, New York, NY, 1999.

J. Zhang and N.A. Peppas, "Interpenetrating Polymeric Networks with pH and Temperature Sensitivity," *Polym. Prepr., 40 (2), 201-202, 1999.*

J.H. Ward and N.A. Peppas, "Kinetic Gelation Modeling of Polymer Networks Formed by a Living Radical Polymerization," *Polym. Prepr.,* 40 (2), 364-365, 1999.

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Chaired Conferences/ Symposia

Advisory Board, 4th Jerusalem Conference on Pharmaceutical Sciences and Clinical Pharmacology, Jerusalem, Israel, October 1999

Organizing Committee, US-Israel NSF Chemical Engineering Workshop, Haifa, Israel, March 1999.

Organizing Committee, Symposium on Drug Delivery in the Third Millennium, Pisa, Italy, October 1999.

Chairman of Symposium on "Drug Delivery in the Third Mellenium," Pisa, Italy, October 1999.

Editorial Boards

Biomaterials (1980-82); Editor (1982-)

Advances in Chemical Engineering; Editor (1999-)

Journal of Applied Polymer Science (1976-)

Polymer Gels and Networks (1993-)

Journal of Biomaterials Science, Polymer Edition (1987-)

Journal of Controlled Release (1983-)

Encyclopedia of Controlled Drug Delivery (1997-)

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Advanced Drug Delivery Reviews (1992-)

Tissue Engineering (1994-)

S.T.P. Pharma Sciences (1987-)

AAPS PharmSci (1998-)

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European Journal of Pharmaceutics and Biopharmaceutics, U.S. Editor (1992-94); (1992-)

Tissue Engineering Books, Academic Press (1995-)

Biomedical Materials (1985-99)

Meeting Presentations

"Tailor-made Networks of Poly(ethylene glycol) for Controlled Drug Delivery," 26th International Symposium on Controlled Release of Bioactive Materials, Boston, MA, June 22, 1999, (P)*.

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"Recent Advances and Molecular Observations on the Controlled Drug and Protein Delivery," Third Central European Symposium on Pharmaceutical Technology, Portoroz, Slovenia, September 23, 1999 (P), Plenary Lecture.

"Long and Short Chains Tethered on Gel Surfaces," Annual AIChE Meeting, Dallas, TX, October 31, 1999 (A)*.

"Kinetic Simulation and Analysis of PEG-containing Networks synthesized by Free Radical Polymerizations," Annual AIChE Meeting, Dallas, TX, November 1, 1999 (A)*.

"Robust H_∞ Control of Type I Diabetic Patient Blood Glucose," Annual AIChE Meeting, Dallas, TX, November 2, 1999 (A)*.

"Analysis of Diffusional and Structural Characteristics of PVA Hydrogels Prepared by Freezing-Thawing Techniques," Annual American Association of Pharmaceutical Scientists Meeting, New Orleans, LA, November 16, 1999 (A).

"Poly(ethylene glycol) Tethered Chains and Their Roles in Gel Mucoadhesion," Annual American Association of Pharmaceutical Scientists Meeting, New Orleans, LA, November 16, 1999 (A).

"Molecular Structure and Diffusive Behavior of Poly(ethylene glycol)-Grafted Poly(acrylic acid) Hydrogels as Drug Carriers," Annual American Association of Pharmaceutical Scientists Meeting, New Orleans, LA, November 16, 1999 (A).

"Advances in Protein and Bioadhesive Delivery," US-Japan Drug Delivery Meeting, Maui, HI, December 14, 1999 (A).

"Development of Nano-sized pH-sensitive Complex Hydrogles for Oral Peptide Delivery," Annual Meeting of Society of Powder Technologies, Japan, Kobe, Japan, November 24, 1999.

"Gaseous and Solute Transport in Hydrogels," Symposium on Biomedical Polymers for the 21st *Century, Boston, MA, March 17,, 2000 (P),* Plenary Lecture.

"Novel Patterned Films for Free-Radical Polymerization Techniques," Annual American Physical Society Meeting, Minneapolis, MN, March 21,, 2000 (A)*.

"Kinetic Simulation of Networks Synthesized by Free Radical Polymerization," Annual American Physical Society Meeting, Minneapolis, MN, March 21,, 2000 (A)*.

"Morphology and Dynamics of Interpenetrating Polymeric Networks with Combined pH and Temperature Sensitivity," Annual American Physical Society Meeting, Minneapolis, MN, March 21,, 2000 (A)*.

"A New Mean-field Theory for Equilibrium Gel Swelling," Annual American Physical Society Meeting, Minneapolis, MN, March 21,, 2000 (A)*.

"Tethered Polymer Chains Contribute to Gel-Gel Adhesion," Annual American Physical Society Meeting, Minneapolis, MN, March 21,, 2000 (A)*.

“Fickian and non-Fickian Processes in Swellable Controlled Release Systems,” Annual American Chemical Society Meeting, San Francisco, CA, March 26,, 2000 (A), Invited Lecture.

“Cytotoxicity and Transport Enhancement of Proteins Through Cell Monolayers Using Novel pH-Sensitive Hydrogels,” Third World Meeting on Pharmaceutics, Biopharmaceutics and Pharmaceutical Technology, Berlin, Germany, April 6,, 2000 (P)*.

“Calculation of the Required Size and Shape of HPMC Matrices to Achieve Desired Drug Release Profiles,” Third World Meeting on Pharmaceutics, Biopharmaceutics and Pharmaceutical Technology, Berlin, Germany, April 6,, 2000 (P)*.

“Micropatterning and Molecular Imprinting for Medical Applications,” Sixth European Symposium on Controlled Drug Delivery, Noordwijk aan Zee, Netherlands, April 12,, 2000 (P), Invited Lecture.

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“Design of Advanced Biomaterials and Drug Delivery Carriers,” Sixth World Congress for Biomaterials, Kamuela, Hawaii, May 19,, 2000, (P), Plenary Lecture.

“Calcitonin Transport Through Poly(methacrylic acid)-PEG-Grafted Hydrogels Using a CaCo-2 Model,” Sixth World Congress for Biomaterials, Kamuela, Hawaii, May 16,, 2000 (P)*.

“Patterning and Molecular Imprinting with Polyfunctional Methacrylates,” Sixth World Congress for Biomaterials, Kamuela, Hawaii, May 16,, 2000 (P)*.

“Intelligent Biopolymers in Protein and Drug Delivery,” Eleventh North American Membrane Society Meeting, Boulder, Colorado, May 26,, 2000 (A), Plenary Lecture.

Doraiswami Ramkrishna

1976

Harry Creighton Peffer Distinguished Professor of Chemical Engineering

Degrees

BS, University of Bombay, 1960

PhD, University of Minnesota, 1965

Interests

Chemical reaction engineering

Dispersed phase systems

Biochemical engineering

Applied mathematics

Research Areas

Chemical Reaction Engineering: Research emphasis in reaction engineering is on orchestration of interfacial mixing and reaction to promote selectivity and conversion in heterogeneous, multiphase reactors.

In collaboration with Professor Delgass, spatial patterns of different catalysts have been investigated through the recent doctoral dissertation of Aaron Cote for a combination of reaction systems to improve selective conversion of a specific product. This improvement is effected by eliminating or minimizing unfavorable trends in which the reaction for the product of interest is hampered by equilibrium limitations, product inhibition, product instability and so on. Theoretical work has shown that substantial improvement in reactor performance can result through the use of such spatial patterns. Experimental work has pointed to problems with cross-contamination by reaction species so that it is felt that catalyst design must be integrated into the design of patterned reactors combining catalysts and reactions. Nonlinear analysis of patterned reactors has shown that in the presence of steady state multiplicity, improper coordination of steady state sequences along the reactor can seriously diminish the advantage from such spatial patterns. An interesting finding by Cote is that a recycle reactor incorporating a single sequential arrangement of catalysts, which represents a much simpler configuration from a practical standpoint, reproduces some of the features of the more complex spatially patterned reactors to produce significantly higher selective conversion than conventional (unpatterned) reactors.

In collaborative work with Professor Lauterbach we have developed a new mathematical framework for the analysis of reactions on catalytic surfaces in the presence of coverage-dependent phase transformation. Equations from the framework feature terms associated with dilution or augmentation of species coverage due to phase transformation that are missing in prior treatments in the literature. Since the presence of these terms affect the nonlinear behavior of the equations, the framework is important in the interpretation of experimental data. Applications to CO oxidation have been made by Tanmay Lele in his doctoral work currently in progress.

Through a grant from the Conoco Chemical Company, Fischer-Tropsch slurry reactors have been steady state multiplicity in order interpret pilot plant data at Conoco. New reactor configurations are under investigation by Dr. Hyun-Seob Song, a post-doctoral research associate in our group.

Dispersed Phase Systems: Precipitation systems have been investigated for the determination of nucleation and particle growth rates through the solution of inverse problems using dynamic particle size distributions. Alan Mahoney's doctoral dissertation shows that successful inversions can be obtained in the absence of aggregation. The effect of aggregation is under investigation. With Professor Doyle of the University of Delaware, the development of algorithms for control of particle size distributions in precipitation processes is in progress.

Joint work with Professor Basaran on the deformation and break-up of droplets in random pressure fields has been undertaken towards understanding of break-up in turbulent dispersions. In his doctoral work in progress, Pankaj Doshi is using boundary integral methods for investigating axisymmetric deformation of liquid bridges towards eventual application to deformation and break-up of liquid droplets in random flow fields.

In collaboration with Professor Sinclair, we have begun investigating the general dynamic equation for aggregation of aerosols in developing turbulent flows in tubes for surfactant delivery applications. Ron Hamilton, a PhD student is currently involved in the project.

Biochemical Engineering: In collaboration with Professor Hu and his group at the University of Minnesota, we have developed cybernetic models for the production of antibodies using Hybridoma cells. The models display experimentally observed multiple steady state behavior of continuous reactors. Abhijit Namjoshi has been investigating the nonlinear behavior of cybernetic models. Bifurcation methods show steady state multiplicity in continuous biological reactors when multiple substrate feeds are employed.

Collaborative work has just been initiated with support from the National Science Foundation with Professors Frank Doyle at the University of Delaware, Jeffrey Varner of Alan Konopka and Cindy Nakatsu at Purdue University on metabolic engineering of ethanol production guided by cybernetic modeling.

Stochastic analysis of biological systems focusing on cell death is in progress designed towards applications to radiation of cancerous tumors, sterilization processes and so on.

Applied Mathematics: Specific applications drive research effort in applied mathematics generally from the areas of linear operator theory, stochastic processes and the solution of inverse problems.

Publications

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Kumar, S., T. Pirog and D. Ramkrishna, “A New Method for Estimating Creaming/Settling Velocity of Particles in Poly-Dispersed Systems,” *Chem. Eng. Sci.*, 55, 1893-1904, 2000.

Guardia, M. J., A. Gambhir, A. Europa, D. Ramkrishna and Wei-Shou Hu, “Cybernetic Modeling and Regulation of Metabolic Pathways in Multiple Steady States of Hybridoma Cells, *Chem. Eng. Sci.*., in press.

Cote, A., W. N. Delgass and D. Ramkrishna, “Spatially Patterned Catalytic Reactors. Feasibility Issues,” *Chem. Eng. Sci. (ISCRE issue),* in press.

Ramkrishna, D., “A Second Course in Graduate Transport Phenomena,” *Chem. Eng. Educ.*, submitted.

Ramkrishna, D. “Population Balance. Theory and Applications to Particulate Systems in Engineering”, *Academic Press,* June 2000.

Invited Lectures

Department of Chemical & Bioresource Engineering, Colorado State University, Fort Collins, Colorado, April 16, 1999. Lecture on “Modeling of Metabolic Regulation. The Cybernetic Approach.”

Department of Civil Engineering, Purdue University, West Lafayette, Indiana, April 27, 1999. Lecture on “Modeling of Metabolic Regulation. The Cybernetic Approach.”

Chemical Engineering Division, Bombay University Department of Chemical Technology, July 8-22, 1999. Gave six lectures on Population Balances as Dow-Professor Sharma Distinguished Fellow. Also presented a popular lecture on “Modern Trends in Chemical Reaction Engineering,” on August 2, 1999.

Department of Chemical Engineering, Indian Institute of Technology, Bombay, July 30, 1999. Lecture on “Destabilization of Stored Emulsions.”

“Modeling, Simulation and Design in Process Engineering,” Sonderforschungsbereich (SFB) 412 ‘Computer Aided Modeling and Simulation for Analysis, Synthesis and Operation in Process Engineering’ of the University of Stuttgart, Germany, October 11-12, 1999. Lead Lecture on “Population Balance Modeling of Dispersed Phase Systems,” Tuesday, October 12, 1999.

McKnight Seminar Series sponsored by the Departments of Mathematics, Chemical Engineering and Bioprocess Techn-ological Institute of the University of Minnesota. Lecture on “Stochastic Modeling of Populations & Applications,” April 4, 2000.

Meeting Presentations

Cote, A., W. N. Delgass, “Enhancement of Selective Conversion in Spatially Patterned Reactors,” International Symposium on Reaction Kinetics and the Development of Catalytic Processes. Belgium, April 19-21, 1999.

Cote, A., W. N. Delgass, and D. Ramkrishna, “Enhancement of Selective Conversion in Spatially Patterned Reactors,” International Symposium on Reaction Kinetics and the Development of Catalytic Processes. Belgium, April 19-21, 1999.

Mahoney, A. W., D. Ramkrishna and F. J. Doyle, “Data-Driven Modeling of Particulate Growth and Nucleation,” Paper No. 83g, A.I.Ch.E., Annual Meeting 1999, October 31-November 5, 2000.

Cote, A. S., W. N. Delgass and D. Ramkrishna, “Spatially Patterned Catalytic Reactors,” Paper No. 288a, A.I.Ch.E., Annual Meeting 1999, October 31-November 5, 2000.

Mahoney, A. W., D. Ramkrishna and F. J. Doyle, “An Efficient Finite Element Technique for Precipitation Dynamics,” Paper No. 144f, A.I.Ch.E., Annual Meeting 1999, October 31-November 5, 2000.

Ramkrishna, D., “Solution of Inverse Problems in Population Balances,” Engineering Foundation Conference on “Population Balance Modeling of Particulate Systems,” in Kona, Hawaii, January 23-28, 2000.

Mahoney, A. W., D. Ramkrishna and F. J. Doyle, “An Inverse Problem Strategy for Identification of Nucleation and Growth,” Engineering Foundation Conference on “Population Balance Modeling of Particulate Systems,” in Kona, Hawaii, January 23-28, 2000.

Gintaras V. Reklaitis

1970

Professor and Head of the School

Degrees

BS, Illinois Institute of Technology, 1965

MS, Stanford University, 1969

PhD, Stanford University, 1969

Interests

Process systems engineering

Computer aided process operations

Batch process design, scheduling and analysis

Awards and Major Appointments

Computers & Chemical Engineering, Pergamon Press / Elsevier Science, Editor in Chief

Computer Applications in Engineering Education, Editorial Board

Council for Chemical Research, Governing Board, 1994- , Executive Committee, 1997, Chair, International Committee, 1993- , Vision 2020 Steering Committee, 1997-

American Institute of Chemical Engineers, Director, 1997-

Kirkpatrick Chemical Engineering Achievement Award, Board of Judges, 1991- , Chair, 1997

Advisory Committee, Department of Chemical Engineering, Carnegie-Mellon University, 1991-

Advisory Committee, Chemical & Environmental Engineering Department, Illinois Institute of Technology, 1997-

Jennifer Lynn Sinclair

1997

Associate Professor

Degrees

BS, Purdue University, 1983

MA, Princeton University, 1985

PhD, Princeton University, 1989

Interests

Gas-solid flow

LDV measurements in fluid-solid systems

CFD multiphase code development

Transport issues in microparticle drug delivery

Awards and Major Appointments

Editorial Advisory Board, Powder Technology, 1997 - Present

Teaching for Tomorrow Award, Purdue University

Trustee, CACHE Corporation, 1999 - Present

Council for Chemical Research Representative at Council for National Science Funding Presentations at Capital Hill, May 1999

Newsletter Editor, Particle Technology Forum, AIChE

National Science Foundation Review Panel, Career Awards, November 1998

National Science Foundation Review Panel, Engineering Research Centers, March 1999

George T. Tsao

1974

Professor and Director of the Laboratory of Renewable Resources Engineering (LORRE)

Degrees

BS, National Taiwan University, 1953
MS, University of Florida, 1956
PhD, University of Michigan, 1960

Interests

Biochemical Engineering
Renewable resource utilization

Venkat Venkatasubramanian

1988

Professor

Degrees

BTech, Chemical Engineering, University of Madras, India, 1977

MS, Physics, Vanderbilt University, 1979

PhD, Chemical Engineering, Cornell University, 1984

Interests

Process fault diagnosis and supervisory control

Process hazards analysis

Computer-aided molecular design and product formulation

Synthesis of operating procedures for batch process plants

Behavior of complex adaptive systems

Intelligent systems, neural networks, and genetic algorithms

Major Appointments

Editorial Board, *Process Safety Progress*

Member of the New Technology Task Force, American Institute of Chemical Engineers, 1996-98

Trustee, CACHE Corporation, 1996-99

Member, International Program Committee, *Seventh European Symposium on Computer-Aided Process Engineering*, ESCAPE 7, Trondheim, Norway, May 1997

Nien-Hwa Linda Wang

1980

Professor

Degrees

BS, National Taiwan University, 1971

MS, University of Wyoming, 1973

PhD, University of Minnesota, 1978

Interests

Biochemical Separation and Purification

Environmental Applications of Separation Techniques

Adsorption of Chemicals and Biochemicals

Mass Transfer in Chemical and Biological Systems

Multicomponent Batch Chromatography and Simulated Moving Bed Chromatography

Research Areas

Multicomponent Adsorption and Chromatography: Dr. Wang's group has made significant contributions in the area of multicomponent adsorption and chromatography. Their fundamental studies on the intrinsic adsorption kinetics of macromolecules show that the well-known Langmuir kinetics equation, which does not take into account steric hindrance at high surface coverage, can not explain break-through curves of proteins at high loading. Computer simulations that consider steric hindrance are used to develop modified kinetic equations to fully explain the observed adsorption kinetics that are much slower than predicted by the Langmuir kinetics (Jin et al. 1993). This study has also been extended to mixtures of solutes of different sizes (Talbot et al. 1993). The theoretical analysis predicts that multicomponent mixtures of molecules of different sizes show many unusual chromatographic phenomena because surface accessibility to a given solute is highly sensitive to the sizes of competing solutes, surface coverage, and local composition.

Their recent studies on asymmetric solutes show that the competition between energetic factors and steric hindrance factors leads to a gradual transition from side-on orientation at low coverage to end-on orientation at high coverage. As a result, the adsorption equilibria of asymmetric solutes can not be correlated by the well known Langmuir isotherm equation. They have proposed a new isotherm equation for asymmetric solutes (Jin et al. 1999). Since most solutes are asymmetric, this correlation should be of wide interest to the adsorption field.

Their studies on mass action effects and parallel pore and surface diffusion in multicomponent chromatography are also important contributions. Exchange of multivalent ions with monovalent ions can not be described by the equilibrium form of the Langmuir equation. Mass action effects are demonstrated using examples in which highly concentrated solutions of monovalent ions act as effective displacers to concentrate and displace multivalent ions. The model predictions agree closely with the breakthrough curves and displacement effluent histories for multicomponent ion exchange of two, three, and five component systems (Ernest et al. 1997). A related study shows that at low concentrations, both pore diffusion and surface diffusion give symmetric breakthrough curves, which can be explained by either a pore diffusion model, a surface diffusion model, or a linear driving force (lumped) model. At high loading, however, surface diffusion gives highly asymmetric breakthrough curves, which can not be explained by pore diffusion or the lumped model. A parallel pore and surface diffusion model has been developed for multicomponent adsorption in fixed beds and expanded beds; the model gives close predictions of multicomponent breakthrough curves of organics, amino acids, and ions (Ma et al. 1996; Koh et al. 1997); (Ernest et al. 1997).

VErsatile Reaction SEparation (VERSE) - A Dynamic Simulation Package for Batch and Simulated Moving Bed (SMB) Chromatography. VERSE simulation is based on a detailed rate model, which takes into account (1). competitive adsorption (or ion exchange) in a multicomponet mixture, (2). detailed mass transfer mechanisms (including extracolumn dispersion, intracolumn dispersion, film mass transfer, pore diffusion, and surface diffusion), (3). slow intrinsic adsorption or desorption (compared to convection or mass transfer rates), and (4). reactions among solutes in the solution phase or among adsorbed solutes. Different modes of chromatography or adsorption processes can be simulated, including (1). frontal chromatography (saturation), (2). isocratic or gradient elution chromatography, (3). displacement chromatography, or (4). any cyclic processes involving multiple step changes in inlet feed composition, temperature, pH, ionic strength, or flow rate.

Recently, VERSE has been expanded to consider more than just the traditional single column operations. This expansion is mainly in response to the growing interest in continuous chromatography/adsorption processes. The latest features are recycle chromatography, carousel processes, and simulated moving bed processes.

VERSE has been validated with many sets of batch and continuous chromatography /adsorption data for many different feed mixtures, including ions, sugars, acids, amino acids, peptides, and proteins. A list of publications related to VERSE is available in a web-based manual, which is updated from time to time.

VERSE is written in FORTRAN 90 and is available on various platforms. Most widely used are Windows 95 or 98. A comprehensive on-line manual is available and it provides users with a list of available choices of isotherm functions, intrinsic kinetic rate equations, and correlations for axial dispersion coefficient and film mass transfer coefficient. Dynamic memory allocation is used in the program to perform the simulations efficiently. A minimum of 64 MB of memory (RAM) is recommended for running simulations of multicomponent systems with sharp fronts for single column operations. Carousel and SMB simulations usually require more than 64 MB RAM. Actual memory required will vary with the complexity and the accuracy required for a specific system.

VERSE simulations can be compared with experimental data to gain fundamental understanding of complex dynamic chromatography phenomena. The simulations can also provide significant cost savings in process design and development by substantially reducing the number of experiments that are normally required to study the effects of all possible operating parameters in a separation. In many applications, a pilot scale chromatography test can cost $100,000 or more. It is not practical to search for optimal designs by experimental trials. If the isotherm and mass transfer pasameters are validated with pilot scale data, VERSE simulations can be used to find the optimal design according to a given objective function. VERSE can be licensed from the Purdue Research Foundation. Several chemical and pharmaceutical companies in the US and Europe are currently using VERSE for research, process design, and process optimization.

Ion Exchange Processes for Removing Cesium from Nuclear Waste Solutions: Over the last fifty years, more than 100 million gallons of radioactive wastes generated mostly from the production of nuclear weapons have been stored in over 300 underground single-shell or double-shell tanks at Hanford, Savannah River, Oak Ridge, and other DOE facilities. It is estimated that about half of the single shell tanks are leaking, posing serious environmental threats to many states.

Efficient separation technologies are needed to treat the wastes and to allow safe long-term storage of the separated wastes. Remediation of the tank waste is estimated to cost over 100 billion dollars. This is considered by many experts one of the greatest technical and financial challenges facing the U.S. today.

Major contributors to the radioactivity in the wastes are cesium and strontium. The removal of cesium, from the supernatants is an important early step in the waste treatment process. Dr. Wang’s group has been collaborating with researchers from Westinghouse and Oak Ridge National Laboratories in developing an ion exchange process for the remediation. The challenge is to develop highly selective and efficient continuous processes for removing low (1-0.001mM) concentrations of radioactive Cs+ ions from concentrated aqueous solutions (1-14 M) of sodium hydroxide, sodium nitrite, and other electrolytes. They have also developed detailed dynamic models of fixed-bed ion exchange, accounting for competitive mass action ion exchange equilibria and mass transfer effects. Detailed process simulations are used to explore innovative designs of carousel processes (Ernest et al. 1997, Hritzko et al., 2000). A case study of a pilot carousel unit shows that full utilization of cesium capacity and maximum throughput can be achieved in an optimal carousel design. Reducing sorbent particle size from 400 to 290 microns, for example, increases throughput by 40% (Ernest et al. 1997). Their analysis shows that intraparticle diffusion controls wave spreading in low pressure ion exchange systems, and dimensionless mass transfer zone length is a simple linear function of particle Peclet number. To establish the linear constant of this correlation, only a few breakthrough experiments are needed for a given waste. Once the constant is found, the mass transfer zone length at a given linear velocity can be easily calculated. A robust three-segment carousel ion exchange process can be designed based on the mass transfer zone length. Dynamic simulations can be used to check switching time, transient period (time to reach steady state), column utilization, and effluent concentrations (Hritzko et al., 2000). This strategy can significantly reduce the number of expensive and time-consuming experiments in process development. Their designs are being tested experimentally for large scale waste processing.

Removal and Recovery of Organics from Water and Waste Waters: Contamination of water supplies by synthetic organics, pesticides, herbicides, and other industrial chemicals is a widespread problem in the U.S. and many other countries. Many of the chemicals are known to be carcinogenic and must be removed to safeguard drinking water supplies and the environment. Among many treatment techniques, adsorption using activated carbon beds has been the best available technology for removing dissolved organics from a dilute (ppm level) solution. Because of high selectivity, activated carbon beds can achieve virtually complete removal of many organics. This technique, however, is quite expensive. Cost of treatment ranges from $0.1 to $19.00 per 1000 gal. This high cost is due to (1) process inefficiency as a result of low throughput and low capacity utilization, (2) high capital and labor costs due to the nature of batch operation in conventional technologies, (3) sorbent attrition and incomplete, costly regeneration, and (4) loss of the organics during sorbent regeneration. Dr. Wang’s group has developed a novel continuous separation process to recover amino acid derivatives and sodium chloride from a process stream containing 3.6 M sodium chloride and 40 mM of the amino acids. Thermal regeneration, instead of chemical regeneration, was developed for the continuous process. Experimental and theoretical results indicate that this continuos process is a promising solution to an important industrial problem. High purity (>95%) amino acids can be recovered at high yield (>90%). The cost of separation and recovery is estimated to be about $0.01 per gallon. They are collaborating with an industrial sponsor to explore the potential of this technology for commercial applications.

Isolation and Purification of Taxol from Plant Tissue Culture Broth and Needle Extract: Taxol, a promising anti-cancer agent, was first found in extracts from the bark of the Pacific yew tree. Because of increasing demand for taxol and limited availability of the bark, many studies have been devoted to finding alternative sources. Plant tissue culture and Taxus natural plant tissues are among the most promising alternatives. Dr. Wang and her students have developed a low pressure liquid chromatography process for the separation of taxol directly from plant tissue culture broth (Wu et al. 1996). In addition, a separation process which consists of extraction, concentration, low pressure liquid chromatography, and preparative HPLC has also been developed for the isolation and purification of taxol from Taxus needles. Their current processes can achieve high recovery (90%) and high purity (~95%). Ongoing research aims to apply simulated moving bed chromatography to improve the purity level and to further reduce the recovery and purification cost (Wu, et al. J. of Chromatography, 1999).

Simulated Moving Bed Chromatography for Biochemical Purification: In simulated moving bed chromatography, a series of columns containing a specific adsorbent are connected to form a circuit, which is divided into four zones by two inlet (feed and desorbent) and two outlet (product and by-product) ports. The four ports are periodically moved along the fluid flow direction to allow the feed to enter the region where the solute bands overlap and the products to be drawn from the regions where the bands are separated. The periodic port movement ensures high product purity and high yield in this process. It also simulates periodic counter current movement of the sorbent with respect to the ports, resulting in high sorbent utilization and high mass transfer rates. Since a major portion of the unseparated mixtures is automatically recycled within the circuit, SMB has much higher yield and lower desorbent consumption than corresponding batch chromatography processes.

SMB, however, has not been widely used for large-scale biochemical purifications for the following reasons: (1) The SMB design is difficult, because it involves specifying a minimum of ten parameters (column diameter, four zone lengths, four flow rates, and an average port movement velocity). (2) Existing SMB's are designed for binary splits. Multicomponent separation in SMB is not yet well understood from the literature.

Dr. Wang's group has recently developed a standing wave analysis for continuous moving bed systems. For linear isotherm systems, simple algebraic equations are derived from the analysis to link product purity and recovery to zone lengths, bed movement velocity, flow rates, column capacity factors, and mass transfer coefficients (Ma and Wang, 1997). Once product purity and recovery are specified for a given system, the zone flow rates and bed movement velocity that provide the highest throughput and the lowest solvent consumption can be determined from the solutions. The study shows that in a given system, there is a trade-off between product purity and throughput. Moreover, if bed volume and product purities are fixed, the longer the separation zone lengths, the higher the throughput. Dynamic simulations based on a detailed rate model that considers axial dispersion, film mass transfer, and intraparticle diffusion are developed and they are used to compare the column profiles and effluent histories of CMB and simulated moving bed (SMB). The comparison shows that the standing wave design equations derived for CMB systems are applicable to SMB systems with eight or more columns.

Based on these fundamental studies, Dr. Wang's group has proposed a systematic model-based design approach for SMB design (Wu et,al. 1998). In this approach, isotherm and mass transfer parameters are first estimated from batch equilibrium tests, pulse tests, and frontal chromatography tests. These parameters are used in the standing wave analysis to generate zone flow rates and step time. Rate model simulation are then used to generate column profiles and effluent histories to make sure that product purities and yield are as expected from the standing wave analysis. A few pilot SMB experiments are carried out to obtain transient column profiles and effluent histories, which in turn are compared with the predictions from fate model simulations. This approach has been used successfully in designing SMB systems for sugar separations (Ma and Wang, 1997, Ma et al. 1998), amino acid separations (Wu, et al. 1997, Wu, et al. 1998), and pacitaxel purification (Wu, et al. 1999).

If isotherm and mass transfer parameters can be estimated accurately, the model-based design approach works well. However precise mass transfer parameters are difficult to obtain for some large scale SMB units. Dr. Wang's group has developed mass transfer design method for such cases (Xie, et al., 2000) In this method, effluent histories of SMB runs based on a design that does not consider mass transfer effects are obtained first. The breakthrough curves of the impurities indicate the propagation speeds of the impurity waves due to the mass transfer effects. Zone flow rates and switching time are modified according to the standing wave analysis to prevent the impurity concentration waves from reaching the product ports. Compared to the model-based design, this method is simpler, requires little computation time and can be applied when mass transfer parameters are either unknown or inaccurate. Results from rate model simulations and pilot SMB experiments show that this method can improve product purity and can be implemented on line without restarting SMB runs. The results indicate a strong potential of this method for on-line control.

A well designed four-zone SMB can achieve a binary split of a mixture into a raffinate product and an extract product with high purity and high yield of both products. Separation of glucose from fructose is a well known example. Standing wave analysis can be used to show that a four-zone SMB can separate a three component mixture into two fractions. The highest affinity solute can be recovered as a pure extract product, while the two other solutes can be recovered together in the raffinate. A four-zone SMB can also recover the lowest affinity solute as a pure raffinate product and the two higher affinity solutes in the extract. However, the solute of intermediate affinity can not be recovered in pure form in a four-zone SMB using a continuos feeding and product withdrawal operation. Dr. Wang and her collaborators have shown recently that a nine-zone SMB which consists of two SMBs coupled in parallel (with the same step time) can achieve continuous separation of a three-component mixture of sulfuric acid, glucose, and acetic acid. All three components can be recovered with high purity (>98%) and high yield (>90%). The nine-zone SMB can also separate a four component mixture of sulfuric acid, glucose, xylose, and acetic acid, into three fractions if the two solutes of intermediate affinities (glucose and xylose) are recovered as one product. Experimental data using synthetic mixtures and biomass hydrolysate show that the standing wave analysis approach also works well for multicomponent separations. The column concentration profiles and product effluent histories are in close agreement with rate model simulations. This study shows that a combination of the standing wave analysis and rate model simulations significantly reduces the number of experiments needed in developing a robust nine-zone SMB with 19 design parameters (nine-zone lengths, nine-zone flow rates, and step time).

Publications

Jin, X., Z. Ma, J. Talbot, and N.-H.L. Wang, "A Model for the Adsorption Equilibria of Solutes with Multiple Adsorption Orientation," *Laugmuir*, 15(9), 3321-3333, 1999

Wu, D.J., Z. Ma, and N.-H. L. Wang, "Optimization of Throughput and Desorbent Consumption in SMB Chromatography for Paclitaxel Purification," *J. of Chromatography*, 855, 71-89 1999, in press A.

Hritzko, B.J., M.J. Ortis-Vega, and N.-H.L. Wang, "Adsorption of N-Phosphono methyliminodiacetic Acid, Iminodiacetic Acid, and Sodium Chloride on Poly-4-Vinylpyridine," *IEC Research*, 38(7), 2754-2764, 1999.

Jin, X., Z. Ma, J. Talbot, and N.-H.L. Wang, "A Model for the Adsorption Equilibria of Solutes with Multiple Adsorption Orientation,' *Laugmuir*, 15(9), 3321-3333, 1999.

Hritzko, B.J., M.J. Ortis-Vega, and N.-H.L. Wang, "Adsorption of N-Phosphono methyliminodiacetic Acid, Iminodiacetic Acid, and Sodium Chloride on Poly-4-Vinylpyridine," *IEC Research*, 38(7), 2754-2764, 1999.

Wu, D.J., Z. Ma, and N.-H. L. Wang, "Optimization of Throughput and Desorbent Consumption in SMB Chromatography for Paclitaxel Purification," *J. of Chromatography,* A, 855, 71-89, 1999.

Hritzko, B.J., Ortis-Vega, and N.-H. L. Wang, "Adsorption of N-Phosphsno Methyliminodiacotz Acid, Iminodiacetic Acid and Sodium Chloride on Poly-4-Vinlypyridine," *I.E.C. Research,* 38(7), 2754-2764, 1999.

Cremasco, M.A., Hritzko, B.J., Farrenburg, C.A. and Wang, N.-H.L. "Amino Acid Separation using a Laboratory-Scale Simulated Moving Bed", *Proceedings of Separations Conference of AIChE'99,* Dallas, Texas, 1999.

Hritzko, B.J.D. Walker, and N.-H.L. Wang, "Design of a Carousel Process for Removing Cesium from SRS Waste Using Crystalline Silicotitanate Ion Exchanger," *AIChE J.*, 46(3), 552-564, 2000.

Xie, Y., D.J. Wu, Z. Ma, and N.-H. L. Wang, "An Extended Standing Wave Design Method for SMB Chromatography; Linear systems," *IEC Research,* 39(6), 1993-2005, 2000.

Cremasco, M. A. (speaker) and Wang, N.-H. L., "Effects of Selectivity on Binary Separation in a Four-Column Simulated Moving Bed for Systems with Linear Isotherms," *Proceedings of XIII Brazilian Congress of Chemical Engineering, CD* ROM, Aguas de Sao Pedro, SP, Brazil, 2000.

Cremasco, M. A. (speaker), Wu, D.J., Hritzko, B. J., and Wang, N.-H. L., "Separation of Taxol in Simulated Moving Bed," *Proceedings of XIII Brazilian Congress of Chemical Engineering,* CD ROM, Aguas de Sao Pedro, SP, Brazil, 2000.

Cremasco, M. A. (speaker), Wu, D.J., and Wang, N.-H. L., "Determination of Taxanes Partition Coefficients and Mass Transfer Parameter," *Proceedings of XIII Brazilian Congress of Chemical Engineering,* CD ROM, Aguas de Sao Pedro, SP, Brazil, 2000.

Cremasco, M. A. (speaker), Hritzko, B. J. and Wang, N.-H. L., "Separation of Two Amino Acids in a Four-Column Simulated Moving Bed: An Experimental Study," *Proceedings of XIII Brazilian Congress of Chemical Engineering,* CD ROM, Aguas de Sao Pedro, SP, Brazil, 2000.

Cremasco, M. A. (speaker), Hritzko, B. J. and Wang, N.-H. L. , "Determination of Bed Porosity, Partition Coefficient and Mass Transfer Parameters of Amino Acids by Moment Analysis of Chromatographic Data," *Proceedings of XIII Brazilian Congress of Chemical Engineering,* CD ROM, Aguas de Sao Pedro, SP, Brazil, 2000.

Xie, Y., E. van de Sandt, T. de Weerd, and N.-H. L. Wang, "Purification of Adipoyl-7-ADCA from Fermentation Broth Using Stepwise Elution with a Synergistically Adsorbed Modulator," *J. of Chromatography*, in press.

Invited Lectures

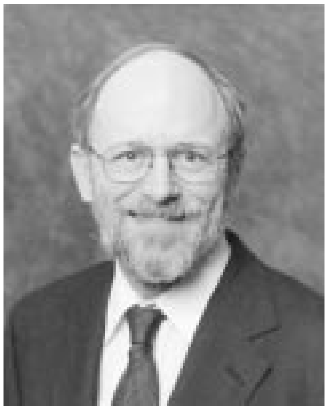
Invited Seminar on "Simulated Moving Bed Chromatography," Nov. 18, 1999.

Invited Seminar on "Simulated Moving Bed Technology for Insulin Purification," E. Lilly, IN., Feb. 19, 2000.

Phillip C. Wankat

1970

Clifton L. Lovell Distinguished Professor of Chemical Engineering



Degrees

BS, Purdue University, 1966

PhD, Princeton University, 1970

MSEd, Purdue University, 1982

Interests

Adsorption and chromatography

Simultaneous fermentation / separation

Distillation

Teaching improvement

Research Areas

New multicomponent gas adsorption cycles: New multicomponent gas separation methods which combine chromatographic operating methods with adsorbent regeneration cycles are being developed. These include elution chromatography cycles for dilute systems and displacement chromatography cycles for concentrated systems. Unusual pressure effects have been observed and analyzed. Vacuum, pressure, steam and thermal swing regeneration methods are being explored.

Other separations research in progress: Studies of simultaneous fermentation / separation have shown that the reaction can be driven to completion with higher overall reaction rates. Methods to improve distillation and make it more energy efficient are being explored. Combined adsorption and reaction is being analyzed.

Awards and Major Appointments

Fellow, AIChE

Union Carbide Lectureship Award, Chem. Engr. Div., ASEE

Publications

Arumugam, B.K., J. F. Banks and P. C. Wankat, "Pressure Effects in Adsorption Systems," *Adsorption,* 5, *261-278, 1999.*

Byrne, M.F. and P.C. Wankat, "Pressure Effects in Adsorbers and Adsorptive Reactors," *Separ. Sci. Technol.,* 35 *(3), 323-351, 2000.*

Gunaseelan, P. and P. C. Wankat, "Dynamic Tray Model to Predict Start-Up Transients in Concentrated Absorbers," *Ind. Engr Chem. Research,* 39, *2525-2533, 2000.*

Wankat, P.C., "Educating Engineering Professors in Education," *J. Engr. Educ.* 88, 471-475, Oct. 1999.

Wankat, P. C., F. S. Oreovicz, and W. N. Delgass, “Integrating Soft Criteria into the ChE Curriculum,” P*roceedings ASEE 2000 Annual Conference*, 2000.

Wankat, P. C. and F. S. Oreovicz, “G. V. (Rex) Reklaitis of “Old Purdue,” *Chemical Engineering Education*, 34, (2), 98-101 & 153, Spring 2000.

Teaching Column Co-authored with F. S. Oreovicz in ASEE PRISM:

“Live! From Lecture Hall 105…,” September 1999, p. 39.

“Lean on Me,” October 1999, p. 31.

“A Problematic Subject,” November 1999, p. 33.

“Fire Up Your Students,” December 1999, p. 34.

“Industrial Role Models,” January 2000, p. 33.

“Memories are Made of This,” February 2000, p. 33.

“More than Words,” March 2000, p. 38.

“By the Book,” April 2000, p. 43.

Invited Lectures

“Teaching Efficiently and Well,” Florida State University/Florida A&M University, Tallahassee, FL, December 10, 1999, and University of Kentucky, Lexington, KY, March 1, 2000.

“The Strange Behavior of Concentrated Absorbers,” New Mexico State University, Las Cruces, NM, October 8, 1999.

Meeting Presentations

Wankat, P. C., F. S. Oreovicz, and W. N. Delgass, “Integrating Soft Criteria into the ChE Curriculum,” ASEE 2000 Annual Conference, St. Louis, MO, June 2000.