A Program in

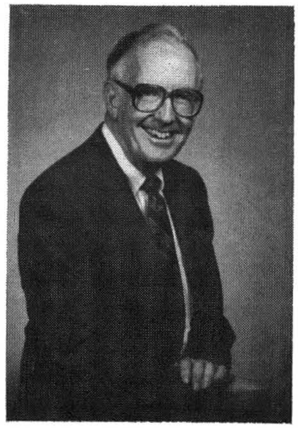
SEPARATIONS RESEARCH

JAMES R. FAIR
The University of Texas
Austin, TX 78712

ALL CHEMICAL ENGINEERS understand the importance of separation processes in the manufacture of chemical products. Raw materials must be purified, catalyst poisons eliminated, unreacted materials separated for recycle, and end-products refined to meet specifications. Further, waste streams must undergo separations before they can be discharged into the environment. Separation processes pervade not only the classical chemical/petroleum process industries but other ones as well, such as electronics, food and biological, metals, and so on. Investment in separation equipment represents a large fraction of the industry total, and the processes consume very large amounts of energy. It is not surprising that there is much interest in developing improved methods for separating mixtures, not just for improved economics but also for simply enabling isolation of a material that is tightly bound in some parent mixture. It is surprising, however, that there is not more easily-identifiable research of a generic type that can support the needs of an industry so dependent on separations.

In fact, there is a great deal of research in progress that supports the development of improved industrial separation processes. In academia, such research covers areas of thermodynamics, transport processes in various media, and reaction selectivity. In industry, the research is often directed toward specific problems that occur in the development of new processes or products. In many respects, there has been too little collaboration between the academicians and the industrialists who share common interests in separations ranging from the fundamental to the applied. This paper describes one attempt to foster greater industry-university collaboration in the separations technology area, the attempt being identified as our Separations Research Program at The University of Texas at Austin.

The research areas targeted were: distillation, adsorption, liquid-liquid extraction, supercritical fluid extraction, membrane processes for separating both gaseous and liquid mixtures, chromatographic separations, electrochemical separation methods, and separations employing chemical reactions.



James R. Fair joined the chemical engineering faculty at The University of Texas in 1979, after many years with Monsanto Company. At Texas he holds the Ernest & Virginia Cockrell Chair and also is Head of the Separations Research Program. He has received numerous awards from the AIChE and was honored as an Eminent Chemical Engineer at the Diamond Jubilee meeting in November 1983. He is a Fellow of AIChE and a member of National Academy of Engineering. He holds BS, MS and PhD degrees from Georgia Institute of Technology and the Universities of Michigan and Texas, as well as an honorary ScD degree from Washington University.

DEVELOPMENT OF THE PROGRAM

A number of UT faculty had been conducting separations-related research for several years when in 1983 they were invited to participate in an industry-funded consortium sponsored by the Center for Energy Studies at UT. The center had a line-item budget from the State of Texas and had as one of its purposes the development of new programs that could impact the efficiency of energy usage by industry. Since the chemical and petroleum industries represent two of the three largest energy-consuming segments of the total industry, and since within them separations are the largest energy-users, it was logical for the center to be interested in industrial separation processes. This led to a seed money grant that enabled the hiring of a full-time program manager, Dr. J. L. Humphrey, to pursue the planning and organization of the consortium. At the same time, a large (145,000 square feet) new research facility was approved by the UT administration, and arrangements were made for the separations work to utilize a significant amount of the space.

The research areas targeted were: distillation, adsorption, liquid-liquid extraction, supercritical fluid extraction, membrane processes for separating both gaseous and liquid mixtures, chromatographic separations, electrochemical separation methods, and separations employing chemical reactions. All of these areas had some coverage by faculty in the chemical engineering and chemistry departments. The industries targeted were: chemical, petroleum refining, gas processing, biological, pharmaceutical, food, and textile. Informal talks were held with UT faculty members, university administration, and representatives of a number of companies. A charter was written, and the plan was further developed and published as an 89-page prospectus. This document was mailed widely to industry, and during the developmental period twenty-two companies visited the UT campus to learn more about the proposed program. In May 1983 an informational meeting was held, and 101 representatives from sixty companies attended. A research participation agreement was drawn up and mailed to companies with an invitation to join the program. Formal operation was to begin in January 1984. It should be mentioned that the cost of the prospectus, the informational meeting, and the preparation of state-of-the-art reports on the several separations areas was underwritten by the Electric Power Research Institute through a grant.

Since the chemical and petroleum industries represent two of the three largest energy-consuming segments of the total industry, and since within them separations are the largest energy-users, it was logical for the center to be interested in industrial separation processes.

TABLE 1
Participants—Separations Research Program*

ABCOR, Inc./Koch Engineering
Air Products and Chemicals, Inc.
Albany International Corp.
Aluminum Company of America
Amoco Oil Company
ARCO Petroleum Products Company
The BOC Group, Inc.
Celanese Chemical Company
Combustion Engineering, Inc.
Dow Chemical Company
Dow Corning Corporation
E. I. duPont de Nemours & Co.
Ethyl Corporation
Exxon Research & Engineering Co.
Glitsch, Inc.
B. F. Goodrich Company
Hoffman-La Roche, Inc.
M. W. Kellogg Company
Koppers Company, Inc.
Monsanto Company
Neste Oy
Norton Company
Nutter Engineering/Chem-Pro Corporation
Osmonics, Inc.
Perry Gas Companies, Inc./Separex Corporation
Phillips Petroleum Company
Rohm & Haas Company
Shell Development Company
A. E. Staley Manufacturing Co.
Standard Oil of Ohio
Texaco, Inc.
Union Carbide Corporation

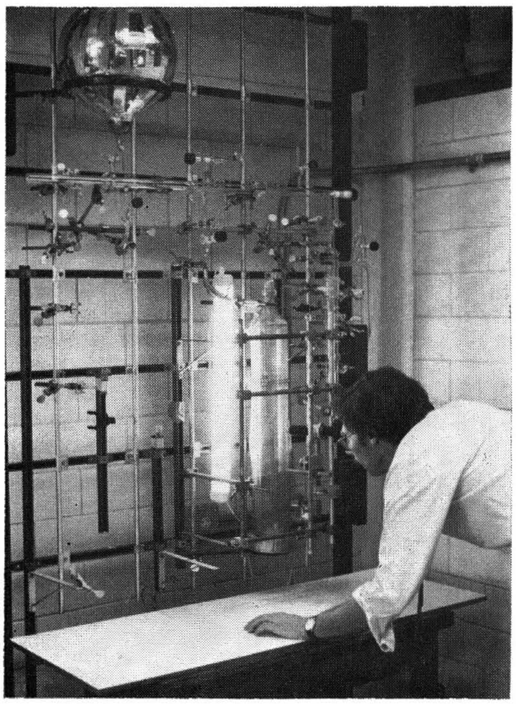
*As of June 1984

At this writing, thirty-two companies have signed two-year participation agreements. They are listed in Table 1.

CURRENT RESEARCH AREAS

The plan was for the research to be supervised largely by regular UT faculty members. Thus, it was necessary for the research area coverage to be compatible with the interests of these people. It was recognized that additional areas could be covered by faculty yet to be hired, or by full-time research scientists and engineers, but these were deferred until a later time when resources and industry interests could justify the expansion. In the following sections brief sketches will describe the current work in progress.

Membrane Separations. This work is divided into the separation of gaseous and liquid mixtures. For gases, direction is under D. R. Paul and W. J. Koros. Both of these people have had active programs in membrane separations for several years, Dr. Paul at UT and Dr. Koros at North Carolina State University. Arrangements were made for Koros to move to UT as a full-time researcher initially, followed by a faculty appointment. It is clear that the use of membranes for gas separation is an industrial reality, with the promise of a large expansion of the areas of application. It is equally clear that many important questions regarding application cannot be answered with today's knowledge, and thus there is the opportunity for more rapid expansion of membrane technology through the support of generic research. The current program has thrusts in the following directions: pure gas sorption and transport, mixed gas sorption and transport, membrane durability, separation of vapors, asymmetric



SRP researcher William J. Koros measures the weight gained by a tiny membrane sample as it sorbs, or takes in, gas. A weight gain of 500 millionths of a gram indicates a highly sorbent material.

membrane formation and characterization, and module simulation/performance. As might be expected, emphases such as the foregoing can shift as more knowledge is gained.

The liquid-mixture membrane program is under the direction of D. R. Lloyd, who began his research in this area at Virginia Polytechnic Institute and State University before moving to UT a few years ago. The program includes the synthesis of polymers, the preparation of sheet- and hollow-fiber membranes, transport studies, and the investigation of possible applications in the petrochemical, biochemical, pharmaceutical, biomedical, and genetic industries. The unifying theme of the research is the need to understand the physicochemical factors that govern the separation process.

Distillation. This old friend, and its associates absorption and stripping, is being studied under the direction of J. R. Fair. As is well known, it is the dominant separation method in the process industries and for many good reasons is likely to remain so. The work at UT is directed primarily to the mass transfer efficiency of common types of contacting devices for distillation columns. Of the several segments of distillation technology (phase equilibria, mass and energy balances, efficiency, and equipment design), understanding of the mass transfer process is in the lowest stage of development. Two particular devices are being studied: the crossflow sieve tray and high-efficiency packing. The sieve tray is widely used and is uniquely amenable to mechanistic modeling. The high-efficiency packing types, only recently developed, are making possible large energy savings in vacuum fractionations. The ultimate goal of this work is to have the form of mechanistic models that enable the reliable prediction of performance for both new and retrofitted distillation columns.

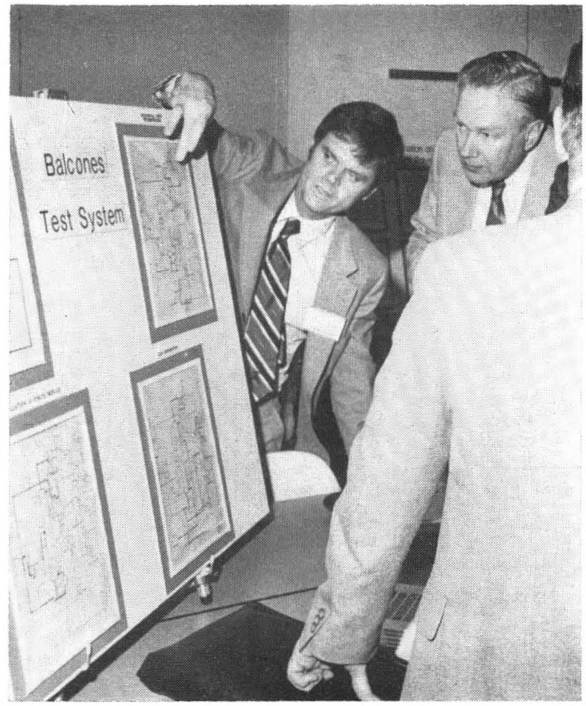
Supercritical Fluid Extraction. This work is under the direction of K. P. Johnston. Supercritical fluid extraction (SFE) is a hybrid process that uses benefits from both distillation and liquid extraction. The process has the additional advantage that slight changes in temperature and pressure near the critical point cause extremely large changes in the solvent density and thus its dissolving power. In comparison with conventional separation processes, SFE offers considerable flexibility for an extractive separation through the control of pressure, temperature, choice of solvent and co-solvent ("entrainer"). There are a few SFE processes that have reached commercialization, but in general the method still awaits better understanding of phase behavior as well as the transport processes that take place in SFE equipment. The program at UT is directed toward the acquisition of fundamental thermodynamic data and the development of predictive models that can guide solvent selection and processing conditions. Of particular interest is the use of cosolvents which in small amount can greatly enhance the separation factors.

Liquid-Liquid Extraction. This work is under the direction of J. R. Fair and J. L. Humphrey. Liquid-liquid extraction (LLE) is another old friend, though not nearly as old as distillation. It has gained increased attention recently as an alternative to distillation that for some cases can result in distinct energy savings. For temperature-labile mixtures, LLE can also offer advantages if the labile species do not undergo high temperature conditions in the solvent stripper. As for distillation, little is known about the mass transfer processes that take place in LLE equipment, and this is partly due to the dominance of proprietary-type extraction devices in commercial practice. Under study at UT are sieve tray extractors and high-efficiency packed columns, both of which are non-proprietary and amenable to mechanistic modeling. It is expected that with the new understanding gained there will be resulting developments in more energy-efficient extraction device design.

In a related area, work is underway to determine the mass transfer characteristics of a continuous-flow supercritical fluid extraction system using a counterflow solvent/feed arrangement.

Adsorption. Drs. Fair and Humphrey are also directing work in this area. Interest in the area is high because of breakthroughs in the application of pressure-swing adsorption to separating gas mixtures such as air into their components without excessive thermal gradients. There are two areas of initial study at UT: mechanisms of thermal and pressure regeneration steps for conventional fixed bed gas adsorbers, and breakthrough relationships for liquid-phase adsorption. There is future interest in the study of moving bed and fluid bed adsorption processes. Progress in adsorption technology has been largely through the development of improved adsorbents such as zeolite and carbon molecular sieves. The work at UT is centered on the kinetics of adsorption and desorption on and from these adsorbents as well as the more traditional adsorbents (where new process applications may be envisioned).

Electric-Based Processes. This work comes under the direction of A. J. Bard of the UT chemistry department. Two areas are currently being studied: electrochemistry in critical aqueous solutions and electrically controlled adsorption. Fundamental research on electrochemical processes in critical aqueous solutions has not been performed previously. Thermodynamic (PVT) and conductance studies have illustrated that the structure of water solutions changes dramatically near the critical point (375°C and 220 atmospheres for pure water). Since the dielectric constant of water decreases to that of a "normal" fluid at high temperatures and pressures, critical and supercritical water becomes a good solvent for nonionic organic species. However, a wide range of supercritical temperatures and pressures is accessible for which water is still a good electrolytic solvent. The electrochemical study of these systems therefore provides a unique opportunity to examine selectively soluble, electroactive species *in situ*.



At poster session representatives from companies listen to program manager J. L. Humphrey describe the separations test facilities to be installed in the new research laboratories.

With respect to electrosorption, the extent of adsorption of substances at the solid/liquid interface depends upon the potential difference across this interface. Thus, the adsorption of organic species on conductive carbon particles can be controlled by the potential applied. This type of separation has not been exploited, mainly because the fundamental data have not been obtained and because of construction problems associated with large-scale adsorbers where a uniform applied potential could be used.

Separations with Chemical Reactions. This program represents an expansion of work started several years ago at UT by G. T. Rochelle, the director of the present work. His quite comprehensive program has dealt largely with the removal of sulfur dioxide from stack gases, commonly called flue gas desulfurization (FGD). The technology of FGD dominates commercial approaches to pollution abatement in fossil-fired

Newer programs deal with the more general area of acid gas removal from gas mixtures and involves basic absorption/reaction modeling studies.

power plants but is expensive, presents operating problems, and produces by-products of limited industrial use. However, it is unlikely to be displaced by other technologies and by its nature suggests that there are many possible improvements. The program at UT has involved enhancement of SO_2 absorption by buffer additives to the $CaCO_3$ slurry scrubbing medium, and has produced mechanistic models for the total diffusion/reaction process. Studies have included the use of dry CaO and "dry" $Ca(OH)_2$ scrubbing media. Simulation work is underway that encompasses the entire process, including regeneration and recycle.

Newer programs deal with the more general area of acid gas removal from gas mixtures and involves basic absorption/reaction modeling studies. Mass transfer in such separations is frequently enhanced by fast chemical reactions and at the very least is accompanied by nonlinear equilibria associated with chemical reactions. Thus, technical quantification of such separations can require measurements of chemical kinetics, equilibria, and mass transfer at representative conditions.

Chromatographic Separation Processes. The use of high-pressure liquid chromatography (HPLC) or gel-permeation chromatography (GPC) for the separation of macromolecular solutions is being studied under the direction of D. R. Lloyd. Aqueous and organic solutions containing synthetic polymers, natural polymers, proteins, pharmaceuticals, and the like are under investigation. The objective here is to study the design considerations that are required to scale up from laboratory to pilot plant. It is clear that this work will have an important bearing on developing biotechnology-type processes.

OPERATION OF THE PROGRAM

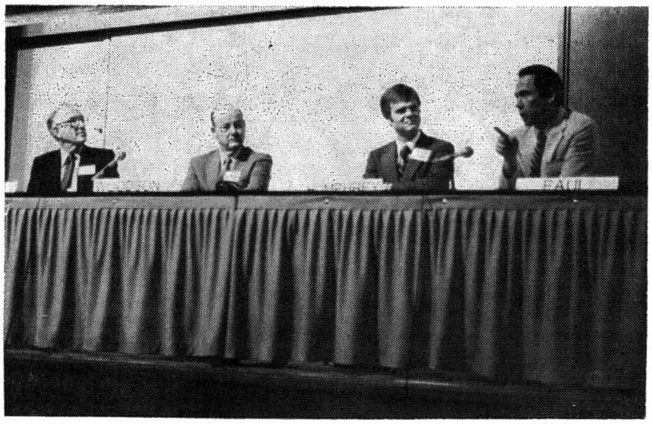
The Separations Research Program is administered by a program head, J. R. Fair, and a program manager, J. L. Humphrey. One representative from each participating company makes up the SRP Industrial Advisory Committee, which meets twice a year to review and advise the program. Separate study groups meet twice yearly to review individual programs in detail; for example, in May 1984 there were separate study group meetings for membranes, distillation, extraction (conventional and supercritical), and chemical reaction separations. The Industrial Advisory Committee receives overviews of programs, whereas the study groups interact closely with faculty, graduate students and, very importantly, with themselves. An effort is made to obtain inputs from the companies that can influence the directions that some programs can take, even though the principal investigators (faculty/staff) retain final control over specific research studies. An example response from the companies to a questionnaire is shown in Table 2.

A question often asked both by academicians and industry people, with regard to consortia of this type, is "What advantage does a participant have over a non-participant, since the research results will eventually be placed in the public domain through theses, dissertations and published articles?" The response to this question can be quite positive, and follows these lines: (1) the participant receives results early, in the way of progress reports, discussions with the researchers, theses and dissertations that can be delayed for publication; (2) the participant receives a royalty-free license to practice any patents resulting from the program; (3) the participant has a mechanism

TABLE 2
Research Topics—Participating Company Interest (26 companies reporting)

	Degree of Interest			Weighted
	High	Mod.	Low	Rating*
Separation of gas mixtures by membranes	19	6	1	44
Separation of liquid mixtures by membranes	17	8	1	42
Supercritical fluid extraction	16	8	2	40
Distillation/absorption /stripping	14	7	5	35
Liquid/liquid extraction	10	12	4	32
Adsorption	11	9	6	31
Separation by chemical reaction	9	7	10	25
Electrochemical separation methods	7	7	12	21

*Weighted rating: high = 2, moderate = 1, low = 0



Panel discussion at Industrial Advisory Committee meeting, with members, from left, James R. Fair, program head; Herbert H. Woodson, director, Center for Energy Studies; Jimmy L. Humphrey, program manager; Donald R. Paul, principal investigator and chairman, Department of Chemical Engineering.

for keeping up to date in separations areas where there is not justification for doing so in-house—for example, in an area of only peripheral interest presently but possibly more active in the future; (4) the participant benefits from interaction of its people with those in other organizations with kindred interests. In some ways, the last-named benefit can be the greatest of them all, if the participant works it carefully.

FUTURE DIRECTIONS

We expect the separations field to continue in the forefront of chemical processing technology, along with the allied areas of reaction engineering and transport processes. Developing interest in specialty chemicals, such as those in the biotechnology and electronics industry segments, carries with it the critical need for recovery and purification, often under non-classical operating conditions. Tonnage chemicals will remain under continuous pressure to reduce costs and conserve energy, and this means retrofitting a like separation technique, substituting a new separation technique, or adopting novel combinations of separating methods. Much of the time-honored technology, for example in distillation, is still not well understood and thus may be difficult to exploit economically. In summary, chemical engineers will continue to deal heavily with separation problems, and we expect to provide them with some answers.

The future of the Separations Research Program at The University of Texas also seems bright. Along with the new research laboratory space will come new equipment provided by the university, some of it of a fairly large scale. A number of companies have recently expressed interest in becoming participants. Plans are developing for the use of visiting scholars and full-time research personnel. We have outside grants and contracts in the separations field that serve to leverage the funding provided by the industrial participants. Importantly, the entire program is being staffed with excellent graduate students, and the learning experience for them and the principal investigators is, indeed, the *raison d'etre* for the entire effort. □

ChE books received

Gas Tables: International Version, Joseph H. Keenan, Jing Chao, Joseph Kaye. John Wiley & Sons, Somerset, NJ 08873; 211 pages, $37.95 (1983)

Metering Pumps: Selection and Application, James P. Poynton. Marcel Dekker, Inc., New York 10016; 216 pages, $29.75 (1983)

Chemical Grouting, Reuben H. Karol. Marcel Dekker, Inc., New York 10016; 344 pages, $45.00 (1983)

Basic Chemical Thermodynamics, Third Edition, E. Brian Smith. Oxford University Press, New York 10016; 160 pages, $21.95 (1983)

Los Alamos Explosives Performance Data, Charles L. Mader, James N. Johnson, Sharon L. Crane. University of California Press, Berkeley, CA; 811 pages, $45.00 (1983)

Practical Quality Management in the Chemical Process Industry, Morton E. Bader. Marcel Dekker, Inc., New York 10016; 160 pages, $27.50 (1983)

Fourth Symposium on Biotechnology in Energy Production and Conservation, Charles D. Scott, Editor; John Wiley & Sons, Inc., Somerset, NJ 08873; 495 pages, $65.00 (1983)

NMR and Chemistry: An Introduction to the Fourier Transform-Multinuclear Era, Second Edition, J. W. Akitt. Chapman & Hall, 733 Third Avenue, New York, NY 10017; 263 pages, $16.95 (paperback) (1983)

Waste Heat: Utilization and Management, S. Sengupta and S. S. Lee; Hemisphere Publishing Co., New York 10036; 1010 pages $125.00 (1983)

Journal: *Particulate Science and Technology*, Vol. 1, No. 1, J. K. Beddow, Editor; Hemisphere Publishing Co., New York, NY 10036; $27.50/year indiv. rate.

Prudent Practices for Disposal of Chemicals in Laboratories, Nat. Academy Press, 2101 Constitution Ave., Washington, DC 20418; 282 pages, $16.50 (1983)

The Chemistry and Technology of Coal, James G. Speight, Marcel Dekker, New York 10016; 544 pages, $69.75 (1983)