

EDITORIAL AND BUSINESS ADDRESS:

Chemical Engineering Education
Department of Chemical Engineering
University of Florida • Gainesville, FL 32611
PHONE and FAX : 352-392-0861
e-mail: *cee@che.ufl.edu*

EDITOR

Tim Anderson

ASSOCIATE EDITOR

Phillip C. Wankat

MANAGING EDITOR

Carole Yocum

PROBLEM EDITOR

James O. Wilkes, U. Michigan

LEARNING IN INDUSTRY EDITOR

William J. Koros, Georgia Institute of Technology

PUBLICATIONS BOARD

• **CHAIRMAN** •

E. Dendy Sloan, Jr.
Colorado School of Mines

• **MEMBERS** •

Pablo Debenedetti
Princeton University

Dianne Dorland
Rowan University

Thomas F. Edgar
University of Texas at Austin

Richard M. Felder
North Carolina State University

Bruce A. Finlayson
University of Washington

H. Scott Fogler
University of Michigan

William J. Koros
Georgia Institute of Technology

David F. Ollis
North Carolina State University

Ronald W. Rousseau
Georgia Institute of Technology

Stanley I. Sandler
University of Delaware

Richard C. Seagrave
Iowa State University

C. Stewart Slater
Rowan University

James E. Stice
University of Texas at Austin

Donald R. Woods
McMaster University

Chemical Engineering Education

Volume 37

Number 1

Winter 2003

► **DEPARTMENT**

2 Vanderbilt University, *M. Douglas LeVan*

► **EDUCATOR**

8 Robert Hesketh of Rowan University, *C. Stewart Slater*

► **CLASSROOM**

- 14 Introducing the Stochastic Simulation of Chemical Reactions: Using the Gillespie Algorithm and MATLAB,
Joaquin Martínez-Urreaga, José Mira, Camino González-Fernández
- 20 Construction and Visualization of VLE Envelopes in Mathcad,
Jasper L. Dickson, John A. Hart, IV, Wei-Yin Chen

► **CURRICULUM**

- 24 Frontiers of Chemical Engineering: A Chemical Engineering Freshman Seminar,
Frank M. Bowman, R. Robert Balcarcel, G. Kane Jennings, Bridget R. Rogers

► **RANDOM THOUGHTS**

- 30 How to Survive Engineering School
Richard M. Felder

► **MEMBRANES IN CHE EDUCATION**

- 32 Introduction
- 33 Analysis of Membrane Processes in the Introduction-to-ChE Course,
Andrew L. Zydney
- 38 A Press RO System: An Interdisciplinary Reverse Osmosis Project for First-Year Engineering Students,
S. Scott Moor, Edmond P. Saliklis, Scott R. Hummel, Yih-Choung Yu
- 46 A Compendium of Open-Ended Membrane Problems in the Curriculum,
G. Glenn Lipscomb
- 52 Exploring the Potential of Electrodialysis,
Stephanie Farrell, Robert P. Hesketh, C. Stewart Slater
- 60 Tools for Teaching Gas Separation Using Polymers,
David T. Coker, Rajeev Prabhakar, Benny D. Freeman
- 68 Membrane Projects with an Industrial Focus in the Curriculum,
Stephanie Farrell, Robert P. Hesketh, Mariano J. Savelski, Kevin D. Dahm, C. Stewart Slater
- 74 A Simple Analysis for Gas Separation Membrane Experiments,
Richard A. Davis, Orville C. Sandall

44 Book Review

45 Letter to the Editor

51 Stirred Pots

CHEMICAL ENGINEERING EDUCATION (ISSN 0009-2479) is published quarterly by the Chemical Engineering Division, American Society for Engineering Education, and is edited at the University of Florida. Correspondence regarding editorial matter, circulation, and changes of address should be sent to CEE, Chemical Engineering Department, University of Florida, Gainesville, FL 32611-6005. Copyright © 2003 by the Chemical Engineering Division, American Society for Engineering Education. The statements and opinions expressed in this periodical are those of the writers and not necessarily those of the CHE Division, ASEE, which body assumes no responsibility for them. Defective copies replaced if notified within 120 days of publication. Write for information on subscription costs and for back copy costs and availability. POSTMASTER: Send address changes to Chemical Engineering Education, Chemical Engineering Department, University of Florida, Gainesville, FL 32611-6005. Periodicals Postage Paid at Gainesville, Florida and additional post offices.

ChE at...

Vanderbilt University

M. DOUGLAS LEVAN

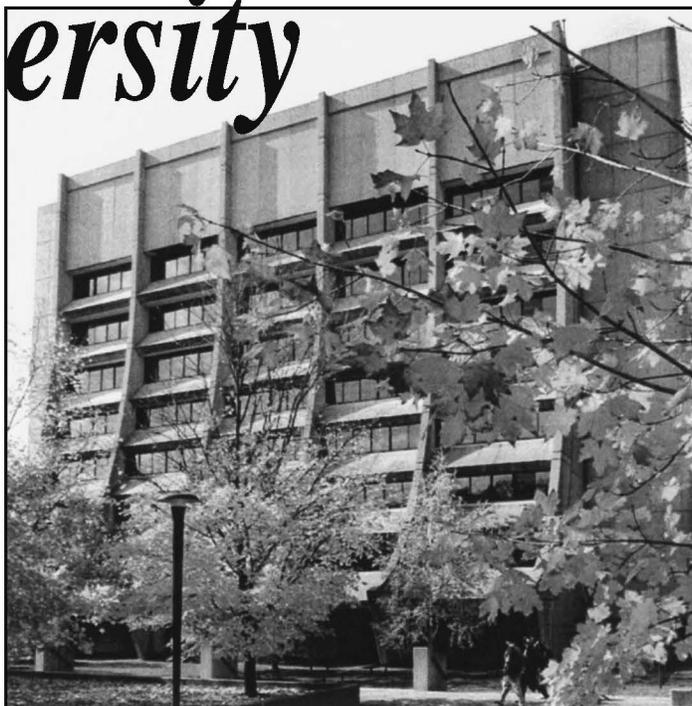
Vanderbilt University • Nashville, TN 37235

Like our discipline, the Department of Chemical Engineering at Vanderbilt University is experiencing a significant expansion beyond its traditional roots toward advanced materials, bioengineering, and other product and application areas. To respond to changes in the field and to take a strong leadership role in research developments in the future, the Department has concentrated on building expertise through faculty recruitment, revising both undergraduate and graduate curricula, and cultivating ambitious interdisciplinary research thrusts. The University's established world-class research prominence in medicine, biology, and environmental studies augments its advantages in reaching its future goals.

VANDERBILT UNIVERSITY

Established in 1873, Vanderbilt University has a long-standing tradition for academic excellence. Cornelius Vanderbilt, "The Commodore," contributed approximately one million dollars of his personal fortune to build a university that could help repair the post-Civil-War rifts among geographical areas of the nation. The University continues to cultivate a tradition of collegiality, interdisciplinary teamwork, and cohesion.

The University, now a national arboretum, is located on 330 park-like acres one and one-half miles from downtown Nashville. It has ten schools, which provide a full range of undergraduate, graduate, and professional programs. There are four schools with undergraduate programs: the School of Engineering, the College of Arts and Science, Peabody College (education), and the Blair School of Music. The Graduate School confers MA, MS,

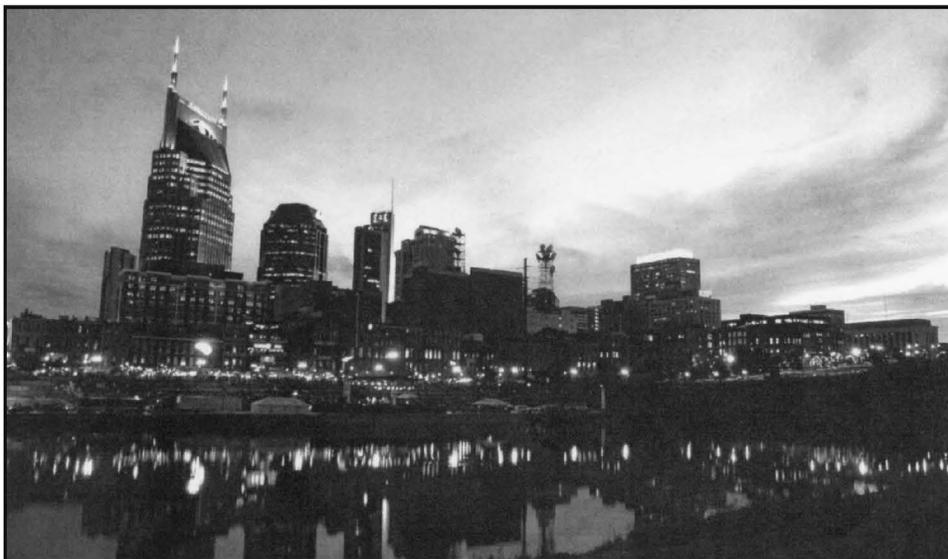


Olin Hall, home of Chemical Engineering at Vanderbilt.

and PhD degrees. The PhD is offered in 39 disciplines. In addition, there are schools of medicine, nursing, management, law, and divinity. Vanderbilt has about 1,900 full-time faculty members and a diverse student body with 6,200 undergraduates and 4,300 graduate and professional students.

Vanderbilt's Chancellor, Gordon Gee, joined the University two years ago after having been President of West Virginia University, the University of Colorado, Ohio State University, and Brown University. Changes have been occurring throughout the University. A residential college system for undergraduates is being strongly considered, and graduate research is an area of considerable focus. The Board of Trust, the University's governing body, has contributed significant funds for several new interdisciplinary research initiatives.

Nashville is called the "Athens of the South" and "Music City



Nashville from across the Cumberland River.

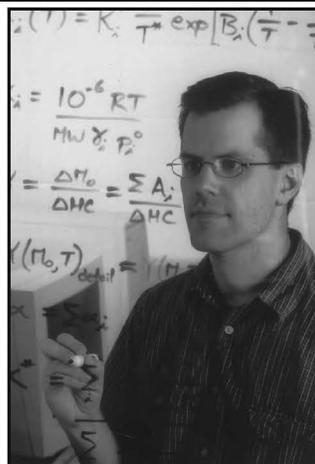
USA” and is the capital of Tennessee. The city and surrounding area support a wide range of activities with performing arts and museums, professional sports teams, and many outdoor activities. Nashville is one of the South’s major focal points for banking, healthcare, insurance, publishing, and entertainment. The Nashville area is home to more than a dozen colleges and universities. Vanderbilt is a major contributor to the intellectual life of Nashville.

THE SCHOOL OF ENGINEERING

In 1874, the year following the founding donation by Cornelius Vanderbilt to the University, engineering was announced as one of ten schools within the Department of Philosophy, Science, and Literature. Engineering classes began in 1879 in drafting, surveying, applied mechanics, structures, water supply, sanitary engineering, and mechanical power. The first Bachelor of Engineering degree was awarded in 1880. Engineering was organized as a department in 1886 and became a school again in 1915, when departments were renamed schools and schools were renamed departments.

Graduate work in the School of Engineering began with chemical engineering. An MS program in chemical engineering was approved in 1943, and the first two MS degrees were awarded in 1946. The first PhD program in engineering to be approved by the Graduate School was in chemical engineering in 1962. The first PhD conferred in engineering went to a chemical engineering student in 1964.

Kenneth F. Galloway joined Vanderbilt in Fall 1996 as Dean of the School of Engineering and Professor of Electrical Engineering. Dean Galloway restructured the School by consolidating some departmental administrative structures. The School now has five Departments: Biomedical Engineering, Chemical Engineering, Civil



Professor Bowman

and Environmental Engineering, Electrical Engineering and Computer Science, and Mechanical Engineering. The Department of Electrical Engineering and Computer Science also offers a degree in Computer Engineering. The School also offers degrees through programs in Engineering Science, Management of Technology, and an Interdisciplinary Program in Materials Science.

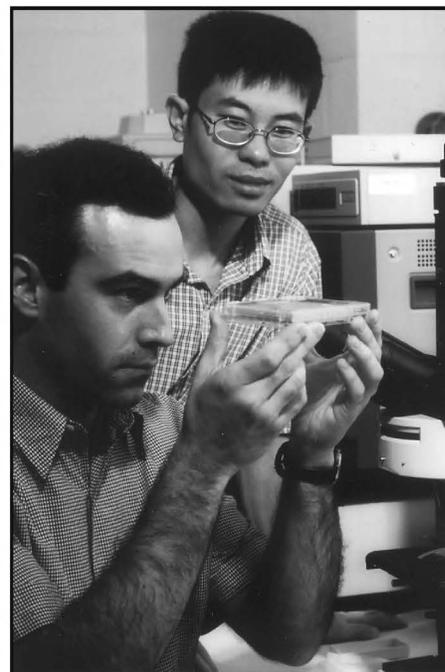
Dean Galloway encouraged growth of research programs. Sponsored research activity within the School has more than doubled since 1996, and research expenditures currently average \$300,000 per faculty member.

The Dean also began a vigorous program of fund raising to improve facilities within the School. A new centerpiece of the School, Featheringill Hall, was formally dedicated in September 2002. It has a large three-story atrium and many areas for small-group interactions. Undergraduates throughout Vanderbilt have voted it the best building on campus.

... the Department of Chemical Engineering at Vanderbilt University is experiencing a significant expansion beyond its traditional roots toward advanced materials, bioengineering, and other product and application areas.



▲ *Vanderbilt's Chemical Engineering Class of 2003.*
Professor Balcarcel with PhD candidate Yuansheng Yang. ►



THE DEPARTMENT OF CHEMICAL ENGINEERING

A Chemical Engineering Program was first announced at Vanderbilt in 1903 as a joint program between engineering and chemistry. A Department of Chemical Engineering was established in 1938 with the first head appointed in 1939.

The Department has had seven Chairs. The early ones were Roy S. Hanslick (1939-1941), E. E. Litkenhous (1941-1961), and W. Dennis Threadgill (1961-1972). E. E. Litkenhous had influence far outside the field of chemical engineering; in 1930, while still an undergraduate at the University of Louisville, he developed a system for rating athletic teams and predicting the outcome of a sporting event based on a "points spread"—this basic system is still in use today.

The School was reorganized in 1972 into a grid system with John A. Roth as Chairman of the Division of Chemical, Fluid, and Thermal Sciences, which was comprised of chemical engineering and mechanical engineering; Thomas M. Goldbold (1972-1975) was Director of the Chemical Engineering Program. In 1975, the School returned to a normal departmental structure.

Recent Chairs have been W. Dennis Threadgill (1975-1980), Karl B. Schnelle, Jr. (1980-1988), Thomas M. Godbold (Acting Chair, 1988-1989), Tomlinson Fort (1989-1996), and M. Douglas LeVan (1997-present).

The current home of the Department is Olin Hall, a gift of the Olin Foundation, which opened in 1974. The building is occupied by the Department of Chemical Engineering, most of the Department of Mechanical Engineering, and much of the Interdisciplinary Materials Science Program. The Department occupies approximately 20,000 square feet,

including space for a high-bay undergraduate unit operations laboratory.

The Department provides an intimate environment for undergraduate and graduate students. Each faculty member cares a great deal about education and student welfare. Classes are small and are all taught by faculty members. Advising is done face-to-face with faculty members.

We have many distinguished alumni. Our graduates hold positions of major responsibility in large corporations, in small entrepreneurial and consulting firms, and in federal and state government agencies. Some PhDs continue their research in post-doctoral positions or enter the teaching profession.

CURRENT FACULTY

M. Douglas LeVan joined the Department as Chair in 1997. At mid-year, the tenured/tenure-track faculty was all tenured and consisted of Professors Robert J. Bayuzick, Kenneth A. Debelak, Tomlinson Fort, M. Douglas LeVan, John A. Roth, Karl B. Schnelle, Jr., and Robert D. Tanner. Each had well over 15 years of university teaching experience. We also had two experienced research faculty, Professors William H. Hofmeister and Ales Prokop. A clear opportunity existed to hire new faculty.

Three research thrust areas were identified: materials, bioengineering, and environmental engineering. All are interdisciplinary and important at Vanderbilt. We sought (and continue to seek) candidates who can contribute fundamentally and broadly to one or more of these focus areas. We also sought faculty with indications of excellent teaching abili-

ties; at Vanderbilt, teaching performance is a strong consideration in promotion and tenure decisions.

Beginning in January 1998, we added four faculty at the assistant-professor level: Frank M. Bowman (Ph.D., California Institute of Technology, 1997) has research interests in atmospheric chemistry and gas-aerosol transport; G. Kane Jennings (Ph.D., Massachusetts Institute of Technology, 1998) works on surface modification and experimental molecular engineering; Bridget R. Rogers (Ph.D., Arizona State University, 1998) focuses on nucleation and microstructure evolution of thin films and microelectronic materials processing; and R. Robert Balcarcel (Ph.D., Massachusetts Institute of Technology, 1999) who studies biological cell life cycles, metabolism, and apoptosis for recombinant therapeutic protein production, cancer therapies, and environmental sensing. All of our new faculty have established significant external funding for their research programs. Professors Bow-

man and Rogers have won NSF CAREER awards. Professor Jennings won the School's teaching award last year.

Our newest faculty member is Peter T. Cummings, who joined us in August 2002 as the John R. Hall Professor of Chemical Engineering. This chaired position was endowed by the Ashland Foundation in honor of John R. Hall, a graduate of the Department, former Chairman and CEO of Ashland, Inc., and recent President of the Board of Trust of Vanderbilt University. Prof. Cummings is acknowledged as an international expert in molecular simulation and computational nanoscience and nanoengineering. He has retained his role at Oak Ridge National Laboratory as Director of the Nanomaterials Theory Institute within the Center for Nanophase Materials Sciences.

Current departmental faculty are listed in Table 1. The special team-teaching role of Professor Julie E. Sharp deserves

TABLE 1
Current Chemical Engineering Faculty at Vanderbilt University

■ **R. Robert Balcarcel**

Assistant Professor (PhD, Massachusetts Institute of Technology)
Biotechnology and bioengineering; mammalian cell cultures; cell life cycles; pharmaceutical production

■ **Robert J. Bayuzick**

Professor (PhD, Vanderbilt University)
Solidification; nucleation; evolution of microstructure; microgravity science; physical metallurgy; containerless processing; oxide superconductor processing

■ **Frank M. Bowman**

Assistant Professor (PhD, California Institute of Technology)
Air pollution; atmospheric chemistry mechanisms; gas-aerosol transport; modeling complex chemical reaction systems

■ **Peter T. Cummings**

John R. Hall Professor (PhD, University of Melbourne)
Computational nanoscience and nanoengineering; molecular modeling of fluid and amorphous systems; computational materials science; parallel computing

■ **Kenneth A. Debelak**

Associate Professor (PhD, University of Kentucky)
Development of plant-wide control algorithms; intelligent process control; activity modeling; effect of changing particle structures in gas-solid reactions; environmentally benign chemical processes; mixing in bioreactors

■ **Tomlinson Fort**

Centennial Professor, Emeritus (PhD, University of Tennessee)
Capillarity; insoluble monolayers/L-B films; adsorption; contact angles and wetting; polymer interfaces; spreading on liquid surfaces; fine particles; flow in porous media

■ **William H. Hofmeister**

Research Associate Professor (PhD, Vanderbilt University)
Materials science and engineering; nucleation and solidification kinetics; microgravity science; high-speed thermal imaging; biological applications of materials science

■ **G. Kane Jennings**

Assistant Professor (PhD, Massachusetts Institute of Technology)
Surface modification; experimental molecular engineering; corrosion inhibition; microelectronics processing

■ **M. Douglas LeVan**

Centennial Professor and Chair (PhD, University of California, Berkeley)
Fixed-bed adsorption; adsorption equilibria; adsorption processes (pressure-swing adsorption, temperature-swing adsorption, adsorptive refrigeration); process design

■ **Ales Prokop**

Research Professor (PhD, Czechoslovak Academy of Sciences)
Bioengineering; bioartificial liver and pancreas; cell encapsulation and immunosolation devices; biocompatible nanotechnology; protein recovery

■ **Bridget R. Rogers**

Assistant Professor (PhD, Arizona State University)
Nucleation and microstructure evolution of thin films; fundamentals of thin film processing for microelectronic applications (mass transport, kinetics, and effects of substrate topography on CVD, sputter deposition and etch processes)

■ **John A. Roth**

Professor (PhD, University of Louisville)
Chemical reactor design; industrial wastewater treatment; sorption processes; chemical oxidation for waste treatment; hazardous waste management; electrochemistry

■ **Karl B. Schnelle, Jr.**

Professor (PhD, Carnegie Mellon University)
Turbulent transport in the environment; control of toxic emissions and SO₂ and NO_x from coal fired boilers; solution thermodynamics; applications of process simulation to microcomputers; supercritical extraction applied to soil remediation

■ **Julie E. Sharp**

Associate Professor of the Practice of Technical Communication (PhD, Vanderbilt University)
Written and oral technical communications; technical reporting; Kolb learning style theory in engineering education

■ **Robert D. Tanner**

Professor (PhD, Case Western Reserve University)
In situ bubble fractionation of excreted proteins from growing baker's yeast; selective protein recovery from a semi-solid air fluidized bed fermentation process; bubble and foam fractionation of proteins.

mention. A practice was started by Professors Debelak and Roth of developing written communication skills in design and laboratory courses through the team-teaching efforts of an expert in technical communications. Their efforts won an ASEE best paper award in 1983. Dr. Sharp has been involved with the Department as the expert in technical communications since 1982. Each semester she co-teaches the undergraduate laboratory courses, where she instructs

students in written and oral communications, and in addition she teaches two sections of a technical communications course for the School, for which she serves as coordinator. She is active within the ASEE and regularly publishes her research on learning styles. She has been instrumental in the consideration of Kolb learning styles within the School of Engineering. Her efforts have won praise from alumni and ABET.

In addition to those shown in Table 1, five faculty currently have secondary appointments in the Department. Professors Todd D. Giorgio, Thomas R. Harris, K. Arthur Overholser, and Robert J. Roselli (all former faculty in the Department of Chemical Engineering) have their primary appointments in the Department of Biomedical Engineering. Professor David S. Kosson has his primary appointment in the Department of Civil and Environmental Engineering.

In addition, the Department is fortunate to have the services of staff members Margarita Talavera, Mary M. Gilleran, Anita K. Patterson, and Mark V. Holmes.

UNDERGRADUATE PROGRAM

The undergraduate program in chemical engineering was accredited by the Engineers' Council for Professional Development (ECPD) in 1952. Accreditation by the Accreditation Board for Engineering and Technology (ABET) followed beginning in the 1980s as ECPD was replaced. The most recent accreditation visit occurred in October 2001.

The undergraduate curriculum was revised for the 1998-1999 academic year and again for the 2002-2003 academic year. Both of these curricula are on our website. The changes for 1998-99 were made to present material in a more logical order, to change computer languages, and to increase efficiency. We retained a 3-hour engineering economy course, but collapsed two 3-hour senior design courses into a single 4-hour capstone course. Graduation requirements were reduced to 128 hours.



Professor Rogers with BS/MS student Virginia Wahlig.

The changes for the current academic year involved improving the structure of our thermodynamics sequence, eliminating engineering courses (but not physics courses) in statics-dynamics and electrical circuits, and adding flexibility. We are now teaching all of thermodynamics, not relying on the Department of Chemistry. We are also increasing the exposure of our sophomores to simulation; instead of teaching just Aspen, we now also apply additional

programming and numerical problem-solving methods to chemical engineering problems.

The new open curriculum makes it easy for students to minor or pursue their own chosen direction. There are six humanities-social science electives spread uniformly throughout the curriculum. We have moved all technical and open electives into the junior and senior years, and as a result, students have a technical elective each semester of the junior and senior years plus two open electives in the senior year. The Department encourages minors in environmental engineering, materials science and engineering, and management of technology; these require 15 hours. Students also minor in chemistry, mathematics, economics, etc. The Department is offering a new concentration in biotechnology that requires 13 hours. Additionally, a special, intensive program leads to a dual degree in chemical and biomedical engineering.

For the last four years, the School of Engineering has offered elective seminar courses to entering freshmen. The Department has participated heavily, offering several courses. Our regular offering, however, has been the course "Frontiers in Chemical Engineering," which has been team-taught every year by our assistant professors based on their research interests. (This course is the subject of an article published in this issue of *Chemical Engineering Education*.)

Our undergraduates have research opportunities also. Each year many of them work side-by-side with graduate students in our research laboratories. In the summers, external and School support has been available to provide research experiences for undergraduates.

We have an active AIChE student chapter with a long history. A Chemical Engineering Club, formed in 1936, became the Tau Alpha Tau Society in 1940 and then the Vanderbilt Chapter of the American Institute of Chemical Engineers in 1947. Students participate in a wide variety of activities, including Rube Goldberg competitions. Last year eight under-

graduates attended the AIChE Student Conference in Puerto Rico. For the 2002 Annual AIChE Meeting, the Department supported a trip for 12 undergraduates to attend.

GRADUATE PROGRAM AND RESEARCH

A majority of our graduate students are PhD students. Most are supported in their first year as teaching assistants, although some support for new students as research assistants is usually available. After the first academic year, almost all students are supported as research assistants from research grants for the duration of their studies. Some multi-year “topping” awards are also available.

Graduate course requirements were changed for the 1999-2000 academic year and again for the 2002-2003 academic year. For 1999-2000, we revised our graduate core course requirements, moving to a more research-oriented chemical engineering science core. For 2002-2003, we reduced coursework requirements for PhD students and made some modifications to our core course structure. We now offer six core courses: applied mathematics for chemical engineers, thermodynamics, transport phenomena, chemical kinetics, simulation, and separation science and engineering.

An MS student must take 24 hours of coursework, a graduate school requirement. This includes five core courses. A thesis is required. (The Master of Engineering, an advanced professional degree, is offered by the School of Engineering.)

We require a PhD student to take a minimum of 30 hours of coursework beyond the bachelor's degree. This includes the six core courses. Many students take more than 30 hours of coursework, but this load is designed to allow students to spend the majority of their studies on original research for the dissertation. PhD students work with their research advisor under the guidance of a PhD committee towards fulfilling all requirements for the degree.

Research laboratories within the Department are equipped for experimental and computational investigations of materials, bioengineering, environmental engineering, adsorption and surface chemistry, chemical reaction engineering, and process modeling and control. Interdisciplinary research opportunities exist with researchers in other departments in the School of Engineering, the natural sciences, and medicine. Our faculty participate in the Interdisciplinary Program in Materials Science and in an NSF-sponsored Engineering Research Center for Bioengineering Educational Technologies. We also participate in two new University-supported interdisciplinary research initiatives—the Vanderbilt Institute for Nanoscale Science and Engineering (VINSE) and the Vanderbilt Institute for Integrative Bioengineering Research and Education (VIIBRE). Activities are currently developing within the Vanderbilt Institute for Environmental Risk and Resources Management (VIERRM).

We currently have an annual Tis Lahiri Memorial Seminar, named after a former graduate student and supported by an endowment. This seminar has an educational flavor. Recent speakers include H. Scott Fogler, Richard M. Felder, Phillip C. Wankat, Ronald W. Rousseau, John M. Prausnitz, Edward L. Cussler, and Arthur W. Westerberg.

We also have an active Chemical Engineering Graduate Student Association (ChEGSA) that represents graduate student interests and sponsors a variety of social events. They have had great leadership and help the Department in many ways.

OUR FUTURE

The Chemical Engineering Department has changed considerably in the last six years. Nine of the fourteen full-time faculty members listed in Table 1 were not in the Department in late 1996. We have been working toward improved undergraduate and graduate curricula and expanding our research activities. The changes will continue.

Our curricula and research programs reflect the broadening of the chemical engineering profession from its chemical and petrochemical heritage toward advanced materials, bioengineering, environmental concerns, and other application-based and product areas. Vanderbilt University as a whole is strong in biological research, with a world-class research hospital; this creates broad opportunities for collaborative research on biologically related topics.

We seek advice on our programs in many ways. A principal avenue is through our Departmental External Advisory Committee. We also seek advice from alumni and corporate friends through a newsletter, “The Catalyst,” edited by Professors Schnelle and Sharp. The Chair has formed an Undergraduate Student Council, which provides him with advice on the undergraduate program, and he serves as advisor to ChEGSA.

Essentially all Departments want to improve not only their rankings but also their quality and visibility. We are certainly no exception. We have been working on improvements from all angles. We recognize the many opportunities that we have at Vanderbilt.

Information: More information on the Department is available at <http://www/vuse.vanderbilt.edu/~cheinfo/che.htm>. Questions should be directed to cheinfo@vuse.vanderbilt.edu.

Acknowledgements: Photographs were taken by David Crenshaw and Darryl Nelson. Kenneth A. Debelak, Vivian F. Cooper-Capps, and Julie E. Sharp provided many helpful comments.

Reference: Jacobs, D., “102 Years: A Story of the First Century of Vanderbilt University School of Engineering,” Vanderbilt University Alumni Association, Nashville, 1975.

□

Robert Hesketh

of Rowan University

C. STEWART SLATER

Rowan University • Glassboro, NJ 08028

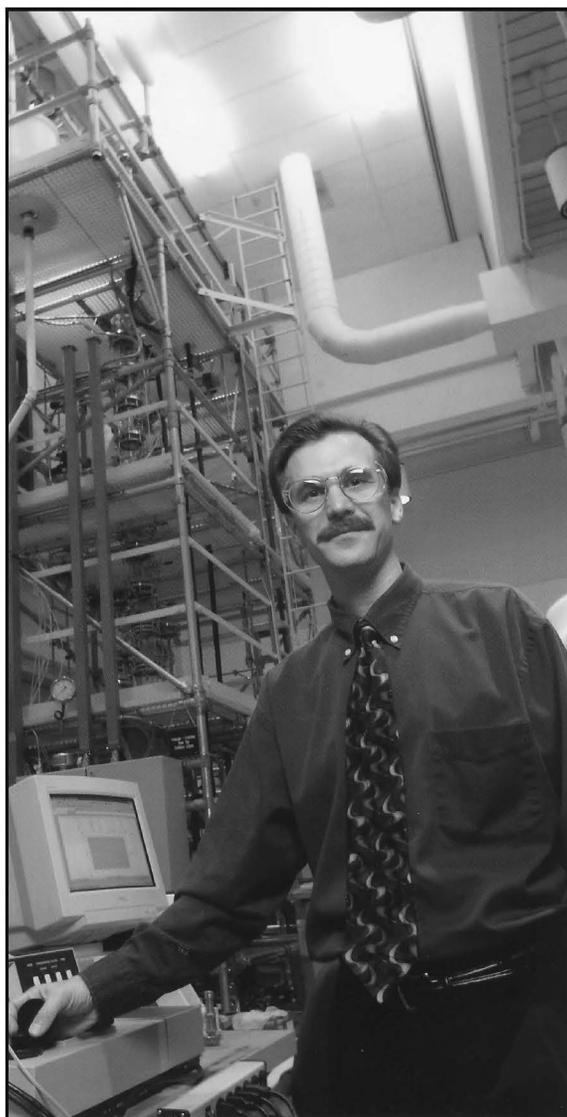
I first met Robert Hesketh at the 1992 Chemical Engineering Summer School in Bozeman, Montana. Phil Wankat and I led a workshop that he attended, and I immediately noticed his enthusiasm for engineering education. As a result of that meeting, he and I later co-authored an article on separations for *CEE*.^[1] Little did I know that I would eventually have the opportunity to hire him as one of the founding members of the Rowan Chemical Engineering Department!

During Robert's faculty interview at Rowan we were impressed with his enthusiasm and his ideas for the freshman engineering program. We knew that his ideas on the use of a coffee machine would work as a basis for our hands-on approach to engineering education at Rowan. We felt he was a perfect fit for the new engineering education program at Rowan, and his dedication to teaching has since been rewarded by several educational awards from ASEE, including the 2002 Robert G. Quinn Award, the 1999 Ray W. Fahien Award, the 1998 Dow Outstanding New Faculty Award, the 2001, 1999, and 1998 Joseph J. Martin Awards, and four other teaching awards. To date he has obtained over \$2 million in external funding from federal, state and industrial sources.

As one of the founding faculty members of the College of Engineering and Chemical Engineering Department at Rowan University, Robert has spearheaded an effort to develop the industrial component of the four-year sequence of the multidisciplinary engineering clinic. In addition, he has created several courses that integrate experiments and lectures in an inductive framework within chemical engineering. He has made many major contributions in laboratory methods that demonstrate chemical engineering practice and principles, the most notable of which uses the coffee maker. He has helped advance the state-of-the-art in laboratory-based education nationally through his many publications, presentations, and seminars at ASEE and workshops supported by NSF.

ROBERT'S EARLY YEARS

What were the major influences in Robert's early years? His mother, Joyce, claims it was the time she spent with him in his crucial developmental years. "He was always happy and singing," she says. Robert



Hesketh in front of the distillation column he helped to design for Rowan University's Chemical Engineering Department.

was born into a family with music and engineering skills on September 28, 1960, near Philadelphia, Pennsylvania. His mother is an accomplished musician with specialties in French horn, piano, organ and harp. His father, Howard, received three degrees in chemical engineering from Pennsylvania State University—State College and is also an accomplished violinist. After earning his Master's degree, Howard served in the army and later returned to DuPont, where he became a senior chemical engineer. He returned to college for his PhD in chemical engineering after working for Beryllium Corporation and Bell Laboratories of Western Electric. In 1970 he accepted a faculty position at Southern Illinois University. During his years at SIU he wrote 18 books in the areas of air pollution and hazardous waste management. Based on his industrial experience, Robert's dad always had a special appreciation for the practical side of engineering.

Robert's enthusiastic personality is reflected by the activities of his early childhood: playing the cello, Boy Scouts, running, and academics. He started playing cello in fourth grade and joined the family ensemble, together with brothers Howard and Ryan and sisters Joy and Melody. There are many theories on the effect of classical music on improving math skills^[2] and it appears that Robert benefited, as evidenced by his receiving the O. K. Bowen Award for Mathematics upon graduation from Carbondale Community High School. He believes that playing a musical instrument also develops a philosophy of practice-makes-perfect. He feels that while it is often impossible to solve a complex problem right at the beginning, just as it is impossible to master a new orchestral piece of music on first reading, through music he learned at an early age how to break the music or a problem into smaller, more manageable, pieces to work on. Music was one of the aspects of Robert's life that gave him confidence in who he is today.

Robert was a nontraditional sports enthusiast. His dad believed that physical activities are an essential part of life, so he began running with his father at the SIU playing fields and eventually set his high school's record in the mile with a time of 4:29 minutes. He also led his cross-country team for the last two years in high school. Again, these early experiences helped Robert develop his work ethic. By practicing (in this case running) every day he was able to drop his half-mile, mile, and two-mile times a few seconds each race. His dad also had plenty of work around the house for Robert to attend to, including installing a swimming pool, building several new houses, mowing the multi-acre lawn, etc. Robert was raised with the philosophy that one needs to work hard to become excellent.

Robert and his brothers developed a love for the outdoors in Boy Scouts. His father was the Scout Master and led a monthly expedition into the forests of Southern Illinois. Many adventures were had by Robert and his family such as 20-

mile hikes, camping in below freezing weather, and backpacking on extended weekends. Robert later became an Eagle Scout, the highest rank obtainable in Scouting. One of his merit badges was in orienteering, where he was able to combine his passion for running through the woods with his problem-solving abilities. He tells me that he still enjoys standing alone in the woods with a map and a compass asking him-

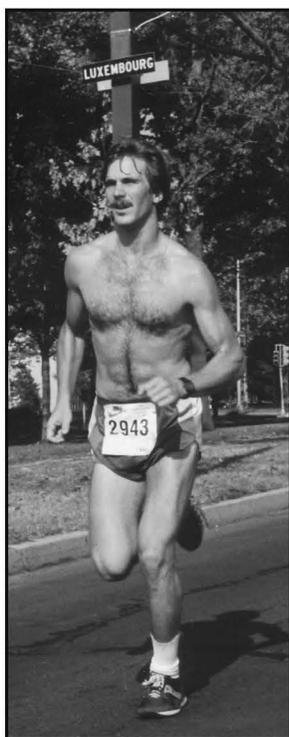
Robert has spearheaded an effort to develop the industrial component of the four-year sequence of the multidisciplinary engineering clinic [and]has created several courses that integrate experiments and lectures in an inductive framework. . .

self, "Where am I now?"! Robert became very successful at orienteering and traveled around the country on weekends to compete in national competitions. The highlight of his orienteering was competing on the U.S. Team at the 1984 University World Championships in Jönköping, Sweden.

Robert started working on environmental projects as a result of his father's work in air pollution control. In the 1970s, Robert's dad started a pilot plant project at the SIU power plant to show that sulfur dioxide emissions from coal could be controlled using venturi scrubbers. Robert and his brothers became a team and assisted their dad on stack tests. In many cases these tests were done either in freezing conditions on the top of a building or in the middle of summer at elevated rooftop temperatures.

UNIVERSITY LIFE

Robert had two requisites in selecting a college: running and chemical engineering. He was good at math, chemistry, and physics and was a natural for chemical engineering. Robert's dad said that he could go to any university in the country, but agreed only to pay an amount of tuition equal to SIU's! The result was that Robert went to SIU for two years and then transferred to the University of Illinois at Champaign-Urbana. While at SIU, Robert continued working with his father by conducting developmental work to support a patent on the catenary grid scrubber. This work resulted in Robert's first publication as an undergraduate and gave him practical experience in designing experiments—he learned that duct tape was excellent for temporary seals on large clear plastic sections of piping! In addition, Robert's father wrote his first textbook in 1972 titled, *Understanding & Controlling Air Pollution*.^[3] It would eventually be used in over fifty universities as a text in air-pollution control and would be updated several times.^[4] Robert was extremely fortunate to watch how his father produced a text, and he worked as an office assistant, typing portions of the copy that were sent to the publisher.



▲ *Running in the Philadelphia Half-Marathon in 1983.*



◀ *Robert, far right holding the dog, at the start of a 1974 backpacking trip (brother Ryan at other end).*

Robert and Fiona Cutting their cello wedding cake, 1990. ▼



▶ *Hands-on house construction of parent's house in Carbondale, 1978.*



◀ *Hiking with Alexander, Natasha, and Fiona in Rocky Mountain National Park. Longs Peak in background, 2002.*

Robert continued his work on environmental engineering problems through two summers of employment in Orlando, Florida, for an environmental engineering consulting firm, Cross-Tessitore and Associates. During this time Robert experienced not only the rigors of environmental audits and assessments, but also the Florida life style of Frank Cross. He felt fortunate to be able to live with the Cross family, who introduced him to white-water kayaking!

In 1982 Robert graduated with a BS with Distinction in Chemical Engineering from the University of Illinois and started graduate school at the University of Delaware. At the University of Delaware, Robert had a special opportunity to work with T. W. Fraser Russell^[5] and Arthur W. Etchells, who is now a DuPont Fellow distinguished by his work in mixing. Working with both Fraser Russell and Art Etchells furthered Robert's appreciation for the practical side of engineering. In this work, Robert developed a correlation for bubble size in turbulent fluid flow that has been cited in over 25 journal articles and is currently being used in the chemical industry for the design of multiphase reactors and piping networks. Both Fraser and Art have helped Robert immensely throughout his career, from shaping and guiding his research to giving him advice on career moves. He recalls one incidence when he was struggling with a bubble breakage func-

tion for a population balance model; he had found numerous complicated models and was trying to figure out which was the best. Fraser, with the wisdom of experience, looked at him and asked, "Have you tried a first-order rate?" Fraser's ability to look for the simple solution to problems remains a cornerstone in Robert's teaching philosophy.

CAMBRIDGE UNIVERSITY

After completing graduate school, Robert had both a job offer with a major pharmaceutical company and an offer of postdoctoral work at Cambridge University in England. Robert was destined for academics, however, and chose to work with Professor and Department Head, John F. Davidson, at Cambridge University. There, he added very fast chemical kinetics to multiphase fluid flow by working on combustion problems in fluidized beds. This work continued his environmental theme of working with coal combustion that results in lower emissions of pollutants than conventional burners.

Robert enjoyed his stay in England from 1987 to 1990, and while there he also decided to improve his musical abilities by taking cello lessons. Attending a concert in 1987, he compared a list of cello teachers with the concert program and found a match; not only for cello lessons, but for the person who later became the love of his life—Fiona L. Stafford! Rob-

ert became one of Fiona's biggest fans. Their wedding in 1990 was notable in that the cello section of the Cambridge Philharmonic Society played before the wedding and their cake was in the shape of a cello! As a special treat for Robert's relatives, he held the wedding rehearsal dinner at Trinity College, where they got a real taste of Cambridge University life.

Robert's passion for engineering education had its genesis at Cambridge. The English love tea, which is served twice a day to all the faculty, staff and students, but Robert wanted real coffee (not the jars of instant had by all other postgrads) and formed a coffee club. It was highly successful until the coffee machine plugged up. So, Robert and his future best man, A. B. Pandit, took the coffee machine apart and cleaned out the tubular heat exchanger. He learned two things: that Cambridge has very hard water and that coffee machines are fascinating.

TULSA UNIVERSITY

Robert's next decision was whether to accept a job offer from a British university or one from Tulsa University in Oklahoma. He had introduced Fiona to San Francisco at the 1989 AIChE annual meeting and apparently convinced her that the rest of the United States was just like San Francisco, so Tulsa won out.

At Tulsa Robert was profoundly influenced in engineering education by his colleagues Richard Thompson, Ramon Cerro, and Martin Abraham. As Department Chair, Rich Thompson introduced Robert to the American Society of Engineering Education by sending him to his first Chemical Engineering Summer School in Montana. The friendships he formed at this first summer school helped guide him as an engineering educator. Rich Felder and Rebecca Brent are still major influences on his teaching style. He has attended at least four effective-teaching workshops and has avidly tried new teaching strategies from each workshop. Based on these workshops, he has employed cooperative learning and an inductive teaching style in his classes. He has also gained important aspects of teaching from educational leaders such as Jim Stice (instructional objectives) and Don Woods (problem-based learning).

Robert also developed a successful teaching and research program at Tulsa and ultimately received three teaching awards, including Professor of the Year in the College of Engineering and Applied Sciences. By the end of his tenure in Tulsa, he had obtained \$670,000 in external funding, including NSF Research Initiation and DuPont Young Professor awards. An outlet for Robert's teaching enthusiasm was found in a series of three NSF Young Scholars Programs at Tulsa,

where he worked with Martin Abraham, John Henshaw (ME), and Keith Wisecarver. In these programs Robert expanded his coffee-machine experience into a series of young scholars experiments and as an outreach tool for student recruitment. At Tulsa Robert also was influenced by the work of Ramon Cerro in both his hands-on laboratory experiments as well as his love of theory.

He is one of the founding professors of the new and innovative engineering clinic. His forward-looking ideas on measurement, design, and course content were incorporated into the engineering clinic starting from the time of his first interview at Rowan University.

A NEW STYLE OF ENGINEERING EDUCATION: ROWAN

Robert is a leader in teaching innovations at Rowan. He is one of the founding professors of the new and innovative engineering clinic. His forward-looking ideas on measurement, design, and course content were incorporated into the engineering clinic starting from the time of his first interview at Rowan University. After observing Robert's excellent leadership skills, Dean James Tracey chose him to be the Freshman Engineering Clinic Coordinator. The engineering clinic at Rowan is unique to engineering education in that engineers are actively engaged in hands-on engineering science and practice through the interdisciplinary clinic for eight semesters.

ENGINEERING CLINIC SEQUENCE

As a founding faculty member of the College of Engineering, Robert has taken a leading role in developing the engineering clinic program—one of the most innovative vehicles for educating engineers. Starting from the novel hands-on freshman semesters in measurement and reverse engineering, he has influenced each subsequent engineering clinic. In the sophomore clinic, he started the detailed planning of the original linkage between the writing faculty and the engineering projects. This planning was further developed by Drs. Anthony Marchese and Jim Newell. The junior and senior clinics have been developed into industrially related engineering projects. Robert brought the first industrially funded project and helped formulate the Clinic Affiliates program where industry is asked to sponsor engineering clinic projects for the junior and senior years. The upper-level engineering clinic has been vertically integrated by having juniors, seniors, and graduate students work on projects funded by industry and the government. He has also worked on integrating the Rowan hallmarks into the syllabus of the clinic. None of these achievements would have been possible without the energetic, innovative, idea-generating faculty of the engineering college.

Robert works with every member of the chemical engineering faculty on industrial and classroom projects. He serves as a mentor for faculty to bring in these projects and has

worked with our chemical engineering faculty on almost every industrial project. As a result, his industrial involvement has included relationships with companies such as Johnson Matthey, Sony Music, Givaudan-Roure, Campbell Soup Co., Pepperidge Farm, Value Recovery, General Mills, and DuPont. Because of this industrial involvement, Robert has had the opportunity to work in fields such as supercritical fluid extraction, microfiltration, liquid-liquid extraction, electrochemical separations such as plating and electrodialysis, adsorption, and ion exchange. He says that the clinic experience is one of the greatest joys of his work at Rowan University.

FRESHMAN ENGINEERING CLINIC

In the Freshman year of the clinic, Robert uses a common consumer product, the coffee machine, as a vehicle for illustrating engineering science and practice. It contains examples of engineering principles from many disciplines. For example, chemical and mechanical engineers are required to design heaters, condensers, and systems for multiphase transport of fluids, and to fabricate plastic and glass components. The process of leaching the organic compounds from the coffee beans uses principles from mass transfer, which is unique to chemical engineering. Automation of processes requires concepts from electrical, mechanical, and chemical engineering. Finally, engineering decisions are required to select the components of a system and place them within an affordable, compact unit that can be easily used by the consumer. This innovative example has been adopted for use at many other institutions. Robert has continued his development of the freshman clinic with Dr. Stephanie Farrell in grants from the National Science Foundation on reaction engineering and drug delivery.

The first year the coffee machine was used, the students not only reverse engineered the unit, but also designed a new system. This is the only project I am aware of where the students actually used what they were making so that they could do an “all-nighter” to ready their final presentations in freshman clinic!

Another innovation Robert incorporated into the freshman clinic is a module on process measurements using the university’s cogeneration facility. He worked with the plant’s director to set up tours for each of the five sections (115 students). On the tour, students took readings of pressure, temperature, and flow from gauges, thermometers, and the plant’s data-acquisition system. They used these measurements to

calculate material and energy balances on two heat exchangers. First, the students used their readings as input for a chemical process simulation, using HYSYS, to determine the heat duty for each heat exchanger. Then for homework they manually calculated the heat duty using all of the engineering equations used by the simulator. This experience was a simulation of the day in the life of a chemical process engineer—truly a unique experience for freshmen.

COOPERATIVE LEARNING

Robert uses the technique of cooperative learning in his courses. He creatively employs cooperative learning in lectures and in homework and semester design projects. In the classroom, students form small groups and within a short period of time solve engineering problems. Robert creatively works with these groups to help them focus on the problem during this session. Using cooperative learning in the classroom creates an active learning experience for students and improves their retention of the material over a pure lecture format. In group homework and design problems he has employed a variety of assessment tools to make each person in the group accountable for achieving all the objectives. This technique is at the forefront of engineering education methods and Robert’s use of it shows that he is at the leading edge of teaching pedagogy.

INDUCTIVE LEARNING

Robert has been transforming his courses so that both the content and the lecture format are in an inductive order. With the inductive order of presentation the professor starts with an experiment, demonstration, or the results of an experiment and finishes the lecture with the derivation and solution of equations describing these results. The second concept is placing the course content in an inductive order. For example, heat transfer could be taught starting with heat exchangers and overall heat transfer coefficients followed by sections on the factors that contribute to the overall heat transfer coefficient, such as conduction and convection. Finally this area of transport could end with coverage of unsteady-state heat transfer. Each of the lectures presented in this novel topical order can be done in an inductive manner, starting from experimental observations and ending with a derivation and solution of the governing equation. Robert has been working with Stephanie Farrell on converting lectures, courses, and labs to an inductive order for fluid



Robert examining the internals of a coffee machine.

mechanics, heat transfer, and transport.

GREEN ENGINEERING

Robert came full circle with respect to his dad's textbooks. After helping with the production of an earlier version, he finally taught a course in air pollution control using his father's 1996 textbook.^[6] In addition to this course, Robert is currently conducting research on methods to reduce the emissions from diesel engines in school buses, with funding from the New Jersey Department of Transportation. The chief problem in this area is particulate emissions, and his dad's text, *Fine Particulates in Gaseous Media*,^[7] has been very useful.

Robert is currently leading an effort to integrate green engineering into the undergraduate curriculum. Green engineering is the design, commercialization, and use of processes and products that are feasible and economical, while minimizing generation of pollution at the source and risk to human health and the environment. This way of thinking embraces the concept that decisions to protect human health and the environment can have the greatest impact and cost effectiveness when applied early to the design and development phase of a process or product. With the help of Kathryn Hollar, Robert just received a three-year grant from the EPA to oversee the development of course-specific modules in green engineering and is looking for faculty who will help him with this endeavor.

WORKSHOP LEADER

Using hands-on experiments, Robert has presented his ideas on education at national meetings and workshops. At the 1997 ASEE Chemical Engineering Summer School for university faculty, he co-led a one-day workshop on Undergraduate Laboratories. At this workshop he led participants through heat transfer, pressure measurement, and coffee strength experiments. He also gave a presentation on innovative teaching techniques in the laboratory. In the summers of 1998 and 1999, Robert and I led a series of workshops based on a grant we wrote together titled, "A Multidisciplinary Workshop on Novel Process Science and Engineering Principles for College Faculty." For this workshop Robert developed new experiments in batch processing (a breadmaker), reaction engineering (catalytic oxidation of VOCs), and polymers (fluidized bed coating), and continued to develop experiments using the coffeemaker. These experiments were conducted by participating faculty from around the country through support from the NSF Undergraduate Faculty Enhancement Program. At the 1998 AIChE annual meeting Robert helped Phil Wankat and myself direct a workshop on teaching effectiveness where he presented a session on active learning techniques in lecture courses and had faculty perform an experiment with the instrumented coffee machine. Most recently Robert co-led a workshop on Innovative Laboratory Experiments with Stephanie Farrell and myself at the 2002 ASEE

Chemical Engineering Summer School in Boulder, Colorado.

PROFESSIONAL SOCIETY SERVICE

Robert is highly active in both ASEE and AIChE. He has published and presented his work in ASEE's *Chemical Engineering Education*, the proceedings of the Annual Conference, and at ASEE zone and regional meetings. He has chaired sessions in education for both ASEE and AIChE. Most notably, he organized the first ever Topical Conference on Education at an AIChE annual meeting titled, "Chemical Engineering Education in the New Millennium." Currently he is the chair of Group 4—Education in AIChE and was previously Vice-Chair of 4 and Chair of 4a—Undergraduate Education. In addition to this service work, Robert has helped formulate the Chem-E-Car competition and has served as the competition's emcee since the races began.

THE MOUNTAINS

Robert retains his passion for music and the outdoors. His family has grown from two cellos to four with the addition of Alexander (5 years old) and Natasha (9 years old). They also love to travel as a family to the Rocky Mountain National Park on hiking expeditions. They have gone to the mountains nearly every summer since getting the "mountain bug" in 1992 at the Bozeman Chemical Engineering Summer School. Robert enjoys hikes with his family, and last summer their longest hike was by Odessa Lake (with an elevation of 10,020 ft and total distance of 9.5 miles) and the most thrilling was climbing up a waterfall to Sky Pond (for a total distance of 9.2 miles).

Robert is destined to climb higher mountains not only in Colorado, but also in his professional life. Throughout his life he has uniquely mixed chemical engineering with his love of music and the outdoors. His educational innovations have touched the lives of numerous students, not only at Rowan and Tulsa, but also at many schools throughout the country that have adopted these methods. He is a trusted friend and a key member of the Rowan chemical engineering team.

REFERENCES

1. Wankat, P. C., R. P. Hesketh, K. H. Schulz, and C. S. Slater, "Separations - What to Teach Undergraduates." *Chem. Eng. Educ.*, **28** (1) 12 (1994)
2. Shaw, G. L., *Keeping Mozart in Mind*, Academic Press, September (1999)
3. Hesketh, Howard E., *Understanding & Controlling Air Pollution*, Ann Arbor Science Publishers, Inc. Ann Arbor MI, (1972 and 1974)
4. Hesketh, Howard E., *Air Pollution Control*, Ann Arbor Science Publishers, Inc. Ann Arbor MI, (1979 and 1981)
5. "T. W. Fraser Russell—An Appreciation by his Colleagues," *Chem. Eng. Educ.*, **31**(2) 74 (1997)
6. Hesketh, Howard E., *Air Pollution Control: Traditional and Hazardous Pollutants*, Technomic Publishing Co., Inc., Lancaster, PA (1991 and 1996)
7. Hesketh, H. E., *Fine Particles in Gaseous Media*, 2nd Ed., Lewis Publishers, Chelsea, Michigan (1986) □

INTRODUCING THE STOCHASTIC SIMULATION OF CHEMICAL REACTIONS

Using the Gillespie Algorithm and MATLAB

JOAQUÍN MARTÍNEZ-URREAGA, JOSÉ MIRA, CAMINO GONZÁLEZ-FERNÁNDEZ
Universidad Politécnica de Madrid • José Gutiérrez Abascal-2 • 28006 Madrid, Spain

There are two main approaches to numerically model and simulate the time evolution of chemical reacting systems. In the deterministic approach, the set of differential equations describing the time evolution of the concentrations is solved using either analytical or numerical methods such as Euler or Runge-Kutta. It is assumed that the complete time evolution of the reacting system is contained in the solution of the set of equations, *i.e.*, given a set of initial conditions, only one trajectory is possible. In this paper, a trajectory is a concentration-time curve. It corresponds to a reacting species in a given experiment and describes the time evolution of the reacting system in such an experiment.

In the stochastic approach, each individual reaction is considered a random event that can take place with a certain probability. Thus the time evolution of the concentrations depends on a series of consecutive probabilistic events. Given a set of initial conditions, there are many possible trajectories, each with its own probability and with the sum of probabilities adding up to one. These trajectories may be drawn by using the probabilistic rate law.

The increasing interest of stochastic methods has been pointed out by Schieber in this journal.^[1] More recently, Scappin and Canu^[2] have reviewed the use of stochastic models for simulating the dynamics of complex chemical systems and have shown that these models allow for easy identification of the main reaction paths in reacting systems involving hundreds of elementary steps.

In addition, several other authors^[3,4] have pointed out that deterministic models cannot accurately simulate the dynamics of systems in which the time evolution depends on the behavior of a very small number of molecules. Interesting examples of such systems are individual cells in living or-

ganisms. McAdams and Arkin^[4] have pointed out that

... Even in clonal cell populations and under the most uniform experimental conditions, considerable variation is observed in the rates of development, morphology, and the concentration of each molecular species in each cell. These fluctuations ... play a fundamental role in the evolution of the living systems. ...

These fluctuations may be predicted and explained by the stochastic models but not by the deterministic ones.

Traditionally, the deterministic methods are by far the most commonly used in modeling the time evolution of chemical



Joaquín Martínez Urreaga is Associate Professor in the Department of Industrial Chemical Engineering at the Universidad Politécnica de Madrid, Spain. He received his MSc (1982) and PhD (1988) from the Universidad de Zaragoza (Spain). His current fields of interest include teaching chemistry and research on interfaces and degradation in materials.

José Mira obtained a Masters Degree in Engineering in 1986 and in 1995 a PhD in Applied Statistics, both from the Universidad Politécnica de Madrid. He is presently an Associate Professor at that University.



Camino González-Fernández obtained her degree in Nuclear Engineering in 1987 and her PhD in 1993, both from the Universidad Politécnica de Madrid. She is Associate Professor in the Department of Statistics at the Universidad Politécnica de Madrid. Her current fields of interest include teaching and research on applied statistics.

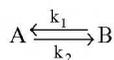
reacting systems. The above remarks, however, may justify the usefulness of introducing undergraduate students to the use of stochastic methods to model chemical reactions.

In order to achieve better understanding of the fundamentals of the stochastic simulation of chemical reactions, it is interesting that students develop their own software tools to carry out the simulation. We present here the basics of the stochastic simulation of a well-known, simple process—the AB equilibrium process—compared to the deterministic simulation of the same process. In the stochastic simulation, we follow the numerical method developed by Gillespie.^[5] Both simulations are carried out with MATLAB, a numerical computation package of increasing use in chemical engineering education.

This example may prove useful for studying how the predictions of the stochastic model relate to the deterministic predictions (and to real-life experiences). To extend the stochastic simulation to other chemical processes, the students can either develop the corresponding MATLAB software, taking as a starting point the MATLAB software supplied in this paper, or they can use commercial simulation software. Two of these commercial programs (freely downloadable from the Internet) are noted in this paper.

SIMULATION OF THE AB EQUILIBRIUM PROCESS

We have chosen as our example the process



because

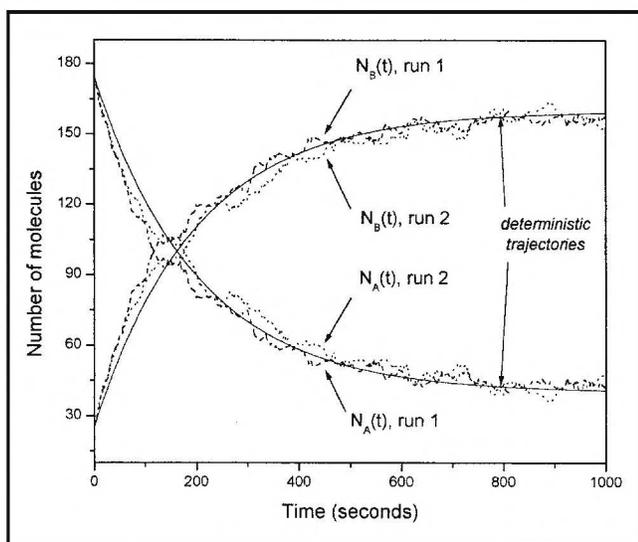


Figure 1. Deterministic (solid) and stochastic (dash, dot) trajectories for the AB equilibrium process. The stochastic trajectories were obtained in two consecutive runs. Initial conditions were

$$N_A(0) = 175; N_B(0) = 25; k_1 = 4 \times 10^{-3} \text{ s}^{-1}; k_2 = 1 \times 10^{-3} \text{ s}^{-1}.$$

- It describes various real processes, such as the hydrolysis of lactone to γ -hydroxybutyric acid in strong hydrochloric acid.^[6]
- It has been previously treated by different authors.^[6,7]
- It is simple enough to be modeled by the undergraduate students. In order to make the modeling easier, we will assume an isothermal process at constant volume.

Deterministic Simulation

The differential rate laws can be written as

$$\frac{dN_A(t)}{dt} = k_2 N_B(t) - k_1 N_A(t) \quad (1)$$

$$\frac{dN_B(t)}{dt} = k_1 N_A(t) - k_2 N_B(t) \quad (2)$$

where $N_A(t)$ and $N_B(t)$ are the numbers of molecules after a given reaction time t , and k_1 and k_2 are the direct and reverse reaction rate constants.

Once the initial values of $N_A(t)$ and $N_B(t)$, ($N_A(0)$ and $N_B(0)$) are specified, it is assumed that the solution of these differential equations describes the complete time evolution of the reacting system. Figure 1 shows an example of the time evolution of $N_A(t)$ and $N_B(t)$ predicted by this approach for $N_A(0) = 175$, $N_B(0) = 25$, $k_1 = 0.004 \text{ s}^{-1}$ and $k_2 = 0.001 \text{ s}^{-1}$. These trajectories were calculated using the MATLAB programs listed in Appendices 1 and 2. In the deterministic approach, given a set of initial conditions, all runs will give the same trajectory.

The equilibrium values of N_A and N_B ($N_{A,eq}$ and $N_{B,eq}$) may be easily calculated by the students. At equilibrium,

$$k_1 N_{A,eq} = k_2 N_{B,eq} \quad (3)$$

Using the mass balance, we obtain

$$N_{A,eq} = [N_A(0) + N_B(0)] / [1 + (k_1 / k_2)] \quad (4)$$

In our case, $N_{A,eq} = 200/5 = 40$ and $N_{B,eq} = 160$.

Stochastic Simulation

As mentioned above, the stochastic simulation of a chemical reacting system is rather different from the deterministic one. Each reaction is a random event that can take place with a given probability, which is a function of the reaction rate constants and the number of molecules. There are many possible trajectories, which we can draw by using the probabilistic rate law. Thus the development of the stochastic simulation requires a deep foundation of the probability theory. A complete description of the stochastic treatment of the AB equilibrium process can be found in a text by Steinfeld, Francisco, and Hase.^[7]

In this paper we describe the development of a MATLAB application for the generation of stochastic trajectories by using the Gillespie algorithm.^[5] Gillespie developed an el-

egant and efficient algorithm that uses Monte Carlo techniques to carry out the numerical stochastic simulation of any given chemical reacting system and demonstrated that this simulation gives an accurate description of the time evolution of the system.

In the Gillespie algorithm, the probability of each reaction is obtained by multiplying the reaction rate constant by the number of combinations of molecules that can lead to the reaction. For the AB process, the numbers of combinations are

$$\binom{N_A}{1} = N_A \quad \text{and} \quad \binom{N_B}{1} = N_B$$

respectively. In order to develop this algorithm, we first must define

► dt

a time interval so small that either only one reaction or no reaction at all can occur in the interval $(t, t+dt)$ (*i.e.*, $dN_A(t) = N_A(t+dt) - N_A(t)$ can only take the values -1, 0, and 1).

► k_1, k_2

k_1 is defined so that $k_1 dt$ is the probability that any A molecule will react to give a B molecule in $(t, t+dt)$ and similarly for k_2 .

► $W_+[N_A(t)], W_-[N_A(t)]$

two positive functions such that $W_+[N_A(t)]dt$ and $W_-[N_A(t)]dt$ are the probabilities that, given that the number of molecules of A at time t is $N_A(t)$, at time $t+dt$ the number of molecules $N_A(t+dt)$ is equal to $N_A(t)+1$ and $N_A(t)-1$, respectively. $W_+[N_A(t)]dt$ and $W_-[N_A(t)]dt$ are conditional probabilities (conditional on the value of $N_A(t)$) and play an essential role in defining the stochastic model. In our example, taking into account the above definitions of k_1 and k_2 , these functions are

$$W_+[N_A(t)] = k_2 N_B(t) \quad (5)$$

$$W_-[N_A(t)] = k_1 N_A(t) \quad (6)$$

After defining the initial conditions, $N_i(0)$ and the constant k_i , the Gillespie algorithm generates time steps of variable length, depending on the probabilities of the reactions and on the random nature of the process (a random number is used to generate the time steps). Subsequently, a second random number is generated to determine which of the two possible reactions occurs, taking into account the reaction probabilities. Next, the $N_i(t)$ values are updated according to the stoichiometry and the process is repeated.

In order to determine the above reaction probabilities and time steps, we need to define

► $a[N_A(t)]$

a non-negative function such that $a[N_A(t)]dt$ is the probability that the number of molecules of A, which

takes the value $N_A(t)$ at time t , suffers a unitary increment (positive or negative) in the differential interval $(t, t+dt)$. It verifies

$$a[N_A(t)] = W_+[N_A(t)] + W_-[N_A(t)] \quad (7)$$

► $w_{\pm}[N_X(t)]$

probability that the process, which has suffered an increment of one on either sense, does it positively or negatively (+1 for w_+ and -1 for w_-). These are also conditional probabilities (conditional on the fact that a reaction has taken place). Evidently

$$w_+[N_X(t)] + w_-[N_X(t)] = 1 \quad (8)$$

$$w_{\pm}[N_X(t)] = \frac{W_{\pm}[N_X(t)]}{a[N_X(t)]} \quad (9)$$

► u

random time step. It is the random variable "time to the next reaction given that the number of molecules of A at time t is $N_A(t)$."

► $p_o[N_A(t), u]$

complementary distribution function for u. Probability that the number of molecules of X, which takes the value $N_A(t)$ in time t , does not suffer any changes in $(t, t+u)$. It can be shown^[5] that

$$p_o[N_A(t), u] = \exp\{-a[N_A(t)u]\} \quad (10)$$

The distribution of u is an exponential with mean $1/a[N_A(t)]$. Using the Monte Carlo method, we can generate a suitable value of the random number u using^[5,7]

$$u = \left\{ 1 / a[N_A(t)] \right\} \log(1/r) \quad (11)$$

where r is a random number of the uniform distribution between 0 and 1. Note that the random time step decreases in average as the probability that any chemical change takes place in the time interval increases.

Thus the algorithm of generation of stochastic trajectories can be written

1. Initialize $t=0$. Introduce the initial values $N_A(0)$ and $N_B(0)$, k_1 and k_2 . Define the total number of reactions Z.
2. Generate a value of u: first a random number r is generated from the uniform distribution in (0,1) and then $u = \{1/a[N_A(t)]\} \log(1/r)$.
3. Generate a second number r' from the uniform distribution in (0,1). This random number determines which reaction will occur, based on conditional probabilities. If $w_-[N_A(t)] > r'$, then take $v = -1$ and if not, $v = 1$.
4. Update the process: $t = t + u$; $N_A(t+u) = N_A(t) + v$
5. If the total number of reactions $i < Z$, go back to step

2. If $i \geq Z$, then stop.

An example of the MATLAB program (stochasticab.m), which implements the above algorithm for the simulation of the AB equilibrium process, is listed in Appendix 3. We emphasize the practical importance of using a random number generator as good as possible to achieve an accurate simulation, including those processes having a wide range of rate constant magnitudes. In this work we have used the random number generation algorithm provided by MATLAB, which is applied extensively in statistical research.

DISCUSSION

Figure 1 shows the trajectories calculated by the above stochastic algorithm in two consecutive runs, as well as the deter-

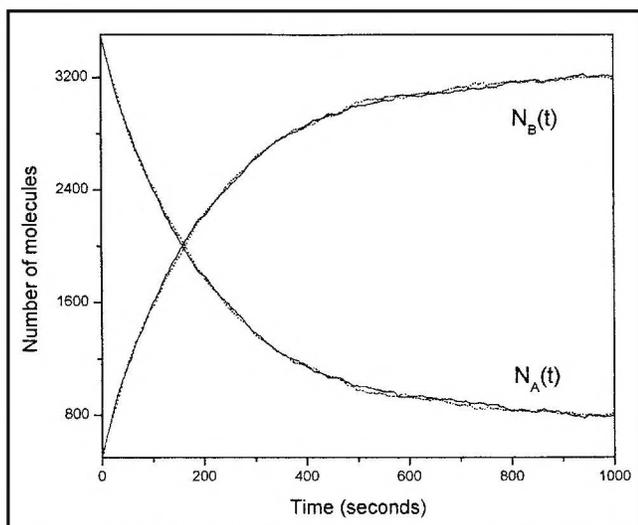


Figure 2. Stochastic trajectories (two runs) with $N_A(0) = 3500$ and $N_B(0) = 500$; k_1 and k_2 are the same as in Figure 1.

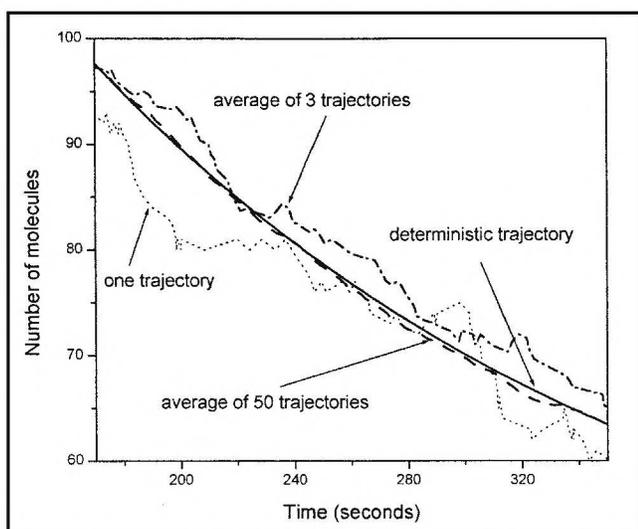


Figure 3. Deterministic and stochastic (single and averages) trajectories $[N_A(t)]$ for the AB process. The initial conditions are the same as in Figure 1.

ministic trajectories, using the same initial values in all cases. These trajectories can be used to carry out a comparative study on the two simulation approaches—stochastic and deterministic.

We can see that there are clear differences. The stochastic trajectories show important fluctuations. Moreover, two consecutive runs predict different trajectories, although the initial conditions are the same ones, *i.e.*, we cannot assure the value of $N_A(t)$ at each time point. On the other hand, the deterministic simulation will always predict the same trajectory, given a set of initial conditions, and it does not present fluctuations in the time evolution. When these results are analyzed, some interesting questions arise. For instance, do these fluctuations (also called stochastic noise) have some physical meaning? Is it possible that we cannot predict with certainty the value of $N_A(t)$ at each time point in a real-life experience?

The students should know that the fluctuations are a real consequence of the probabilistic nature of each chemical reaction. Some interesting real experiments showing stochastic effects have been presented by de Levie.^[3] We can't see these fluctuations in most real-life experiments, however. Which are the factors that determine the importance of the fluctuations? In order to develop an answer, the students can repeat the simulations and vary the input conditions.

Figure 2 shows two new trajectories obtained through the stochastic algorithm, but using a much larger number of initial molecules than in Figure 1, namely $N_A(0) = 3500$ and $N_B(0) = 500$. It can be seen that the fluctuations are only important when the process starts with a small number of molecules. As the initial number of molecules increases, the fluctuations decrease and the stochastic trajectory approaches the deterministic one. This result was explained by Gillespie^[5] showing that the relative fluctuations in $N_A(t)$ around the mean value of $N_A(t)$ ($\langle N_A(t) \rangle$), which can be obtained from repeated runs) are approximately of the order of $(\langle N_A(t) \rangle)^{1/2} / \langle N_A(t) \rangle$.

This is an important result, as it explains how the fluctuations are not important in most real-life experiments. When we work with 10^{20} molecules, the relative fluctuations ($\sim 10^{-10}$), *i.e.*, the uncertainties in the value of N_A , are absolutely negligible. In that case, a deterministic model allows an adequate representation of most processes (with some exceptions—see below).

In many microscopic systems, however, the intrinsic fluctuations are important. For instance, some biochemical reactions taking place in individual cells of living organisms depend on ten or less molecules. In that case, the fluctuations can play a fundamental role in the behavior of the system. Deterministic models cannot adequately describe such behavior.

Figure 3 can be used to explain the relationship between deterministic and stochastic trajectories. It can be seen how

the average of stochastic trajectories approaches the deterministic trajectory as the number of averaged trajectories increases (*i.e.*, the deterministic trajectories can be explained as the average behavior of the whole set of possible stochastic trajectories).

Finally, students can see that both the stochastic and deterministic approaches predict the same final state for the AB equilibrium process, but this is not evident in all cases, even at a macroscopic scale. There are processes with more than one possible stable final state. These processes will evolve toward one of the possible final states, each evolution having a probability that depends on the initial conditions. This is an infrequent behavior in nature, which can be explained and predicted using a stochastic approach.^[5]

EXTENDING THE SIMULATION TO OTHER REACTIONS: COMMERCIAL PROGRAMS

Once the students understand the fundamentals of the stochastic simulation of chemical reactions, the application to the simulation of other chemical processes can be carried out using commercial simulation programs or even by developing new MATLAB software similar to the programs presented here. The key point of this development is obtaining the functions $W_+[N_A(t)]$ and $W_-[N_A(t)]$, which represent the sources and wells of A molecules in each chemical process.

The commercial programs save user time since he/she only has to provide a suitable mechanism and the set of initial data. Moreover, most of these programs include a built-in collection of developed (and interesting) examples. Of the several commercial packages available, we will focus on two high-quality programs that can be freely downloaded from the Internet.

Chemical Kinetics Simulator (CKS 1.01 currently available in versions for OS 2.2.x and higher, Apple Macintosh and Power Macintosh, and Microsoft Windows, 3.1/Windows, 95/Windows NT) was developed at IBM's Almaden Research Center in San Jose, California, and can be downloaded from its homepage.^[8] It is an easy-to-use program (with an excellent tutorial) that allows the accurate stochastic simulation of chemical reactions, including those in which changes in volume, pressure, or temperature are expected. For instance, it may work with explosions. The simulations included in the package may also be useful as learning tools. Some examples of these simulations are the copolymerization of two monomers, a catalytic process in a batch reactor, and the simulation of gas phase reactions in a CVD reactor.

StochSim is a stochastic simulator with a marked focus on biochemical processes. In this case the examples included simulate, for instance the Michaelis-Menten enzyme kinetics and the Lotka Volterra process. It was written by Carl Firth at the University of Cambridge. The currently available version 1.4^[9] consists of a platform-independent core simula-

tion engine encapsulating the stochastic algorithm and a separate graphical user interface. The stochastic algorithm used in this program is rather different from the Gillespie algorithm; here each molecule is represented as a separate software object. This is advantageous for simulating processes in which the physical and chemical properties of the reacting molecules change in the course of the reaction.^[10]

CONCLUSIONS

Stochastic models are playing an increasing role in the simulation of chemical and biochemical processes, as they allow adequate prediction of the so-called stochastic effects, including the intrinsic fluctuations of the system. These fluctuations can play a fundamental role in the evolution of the living systems and, in general, in the behavior of many microscopic systems.

In this paper the Gillespie algorithm is proposed as a suitable tool for introducing undergraduate students to the basics of the stochastic simulation of chemical reactions. Application of the Gillespie algorithm to a simple and well-known reaction, the AB equilibrium process, is presented. Using this algorithm, the students can develop their own MATLAB programs to carry out the stochastic simulations of the AB process and then use the results to analyze the main differences between the stochastic and the deterministic modeling of a chemical reaction.

Two examples of MATLAB programs are presented. Students can also easily adapt these two programs to other reaction schemes. Finally, two commercial simulation programs (freely downloadable from the Internet) are proposed as additional tools for extending the stochastic simulation to other chemical processes.

ACKNOWLEDGMENTS

The authors are grateful to the referees for their helpful comments and suggestions.

REFERENCES

1. Schieber, J.D., "Applied Stochastic for Engineering," *Chem. Eng. Ed.*, **27**(4), 170 (1993)
2. Scappin, M., and P. Canu, "Analysis of Reaction Mechanisms through Stochastic Simulation," *Chem. Eng. Sci.*, **56**, 5157 (2001)
3. De Levie, R., "Stochastics: The Basis of Chemical Dynamics," *J. Chem. Ed.*, **77**(6), 771 (2000)
4. McAdams, H.H., and A. Arkin, "It's a Noisy Business! Genetic Regulation at the Nanomolar Scale," *Trends in Genetics*, **15**(2), 65 (1999)
5. Gillespie, D., *Markov Processes: An Introduction for Physical Scientists*, Academic Press, Inc., New York, NY (1984)
6. Fahidy, T.Z., "Solving Chemical Kinetics Problems by the Markov Chain Approach," *Chem. Eng. Ed.*, **27**(1), 42 (1993)
7. Steinfeld, J.I., J.S. Francisco, and W.L. Hase, *Chemical Kinetics and Dynamics*, Prentice Hall, Englewood Cliffs, NJ (1989)
8. CKS home page: <<http://www.almaden.ibm.com/st/msim/>> (Available Sept. 2002)
9. Download StochSim: <<ftp://ftp.cds.caltech.edu/pub/dbray/>> (Available Sept. 2002)

10. StochSim homepage: <<http://www.zoo.cam.ac.uk/comp-cell/StochSim.html>> (Available Sept. 2002)

APPENDIX 1

Program *deterab.m* for deterministic simulation

```
% This program performs the deterministic simulation of the
AB chemical % process
% k1 y k2 are the direct and reverse reaction rate constants
% na0 and nb0 are the initial numbers of molecules
% tfinal is the total reaction time
k1=4.e-3;
k2=1.e-03;
h=k1;
l=k2;
na0=175;
nb0=25;
tfinal=1000;
timestep=1;
time=0;timestep:tfinal;
[T,Y]=ode45('fisomer',time,[na0],[l,na0,nb0,k1,k2]);
matrix=[T Y na0+nb0)-Y];
save figure 1.dat matrix/ascii;%save results
plot(T(1:500),Y(1:500),T(1:500),na0+nb0-Y(1:500));
% plot curves
```

APPENDIX 2

Auxiliary function *fisomer* for deterministic simulation

```
function F = fisomer(time,Y,flag,na0,nb0,k1,k2)
h=k1;
l=k2;
F=(-h*Y)+(1*(na0+nb0-Y));
```

APPENDIX 3

Program *stochasticab.m* for stochastic simulation

```
% This program performs the stochastic simulation of the
```

```
AB process
% k1 y k2 are the direct and reverse reaction rate constants
% na0 and nb0 are the initial numbers of molecules
% Z is the total number of reactions
% numtray is the number of trajectories to be generated
```

```
k1=5.e-3;
k2=1.e-03;
h=k1;
l=k2;
na0=175;
nb0=25;
Z=500;
numtray=2;

% in this example we generate and plot just two trajectories
unif=rand(numtray,N,2);

na=na0;
nb=nb0;
t=0;
x(1:numtray,1)=ones(numtray,1)*na0;
xb(1:numtray,1)=ones(numtray,1)*nb0;
for m=1:numtray;
na=na0;
nb=nb0;
t=0
for i=2:N;
Wplus(i)=1*nb;
Wminus(i)=h*na;
a=Wplus(i)+Wminus(i);
wplus(i)=1*nb/((h*na)+(1*nb));
wminus(i)=(h*na)/((h*na)+(1*nb));
u(i)=(1/a)*log(1/unif(m,i,1));
if wminus(i)>unif(m,i,2)
v=-1;
else
v=1;
end;
na=na+v;
nb=nb-v;
t=t+u(i);
x(m,i)=na;
xb(m,i)=nb;
time(m,i)=t;
end;
% close loop for each trajectory
end;
% close loop for number of trajectories
matrix(:,(i-1)*3+1)=time(m,:);
plot(time(1,:),x(1,:),time(2,:),x(2,:),time(1,:),xb(1,:),time(2,:),xb(2,:))
% plot two trajectories
matrix=[time(1,:) x(1,:) xb(1,:) time(2,:) x(2,:) xb(2,:)'];
save figure2.dat matrix/ascii;

% save results
□
```

CONSTRUCTION AND VISUALIZATION OF VLE ENVELOPES IN MATHCAD

JASPER L. DICKSON, JOHN A. HART, IV, WEI-YIN CHEN
University of Mississippi • University, MS 38677-1848

One of the major objectives of a thermodynamics course is to introduce the modeling of vapor-liquid equilibrium (VLE). Over the past 25 years, Professor Kenneth Jolls has developed visual aides to graphically demonstrate various thermodynamic functions and phase diagrams. According to Dr. Jolls, "One of the problems with thermodynamics is that, to many students, it has no solid beginning. It doesn't start with concrete notions."^[1] The development and implementation of three-dimensional graphics facilitate the cognition of important building blocks of chemical engineering thermodynamics. Its significance is also reflected by the fact that P-xy-T phase diagrams are shown on the covers of the newest editions of the two popular textbooks on chemical engineering thermodynamics.^[2,3]

There have been various engines used to generate three-dimensional graphs. In Dr. Jolls's earliest attempts to display the steam tables graphically, a simple, locally developed 3-D graphing program was used to generate the plots.^[1,4,5] Since that time, he has used more sophisticated software to produce more complicated plots. For example, he used the graphing package MOVIE.BYU^[1] to produce the three-dimensional surfaces of the Peng-Robinson equation of state (PR EOS). Using these drawings, the unstable, metastable, and stable zones can easily be illustrated. He has also developed three-dimensional graphs for the ideal and the van der Waals gases as well as the Joule-Thomson expansion coefficient.^[1]

Several commercial software packages have been developed over the years for various computational applications in teaching, including the construction of three-dimensional diagrams. At the University of Mississippi, Mathcad is introduced early in the chemical engineering curriculum and is used as one of the computational tools for courses at different levels; it is also selected as the principal computational workhorse for courses on thermodynamics.

Using limited P-x and P-xy data of a benzene/cyclopentane

system, this paper demonstrates the construction of three-dimensional, P-xy-T, phase envelopes based on two independent procedures in Mathcad; both examples have served as the templates in our pedagogical process. In the first approach, the phase envelope is constructed based on Barker's algorithm along with the Wilson equations and virial EOS for the estimations of the activity coefficients and fugacity coefficients, respectively. In the second approach, the phase diagram is constructed based on the Peng-Robinson equation of state along with the one- and two-parameter models of the van der Waals mixing rule. Regression of three sets of P-xy data at three different temperatures yields the parameters in these governing equations. Using these parameters, the P-xy-T envelopes were generated and extended to the mixture's critical region.

MODEL DEVELOPMENT AND DISCUSSION

The experimental data used for the VLE modeling was obtained from Hermsen and Prausnitz.^[6] The data included total pressures and liquid-phase compositions for the benzene/cyclopentane system at three temperatures: 25°C, 35°C, and 45°C. The component properties were obtained from Reid, et al.^[7]

Jasper L. Dickson received his MS and BS in Chemical Engineering from the University of Mississippi. He is currently pursuing a PhD in Chemical Engineering at the University of Texas at Austin. His research interests have been in the area of colloid science.

John A. Hart, IV is a graduate student at the Department of Chemical Engineering of the University of Mississippi. He has received his BS in Forensic Chemistry and his BS in Chemical Engineering from the University of Mississippi also. His research interest is environmental remediation.

Wei-Yin Chen is Professor of Chemical Engineering at the University of Mississippi. His teaching and research interests have been in reaction engineering, thermodynamics, and mathematical modeling. He received a PhD in Chemical Engineering from the City University of New York, an MS in Chemical Engineering from the Polytechnic Institute of New York, an MS in Applied Mathematics and Statistics from the State University of New York at Stony Brook, and a BS in Chemical Engineering from Tunghai University.

Model 1 **Barker's Algorithm**

To construct the phase envelope using Barker's algorithm,^[8] the two temperature-dependent parameters in a model for the activity coefficient were recovered through regression, a Mathcad solve block (see Table 1). The "Given-MinErr" solve block in Table 1 consists of a powerful, built-in regression procedure in Mathcad for recovering parameters. To avoid possible experimental errors in the vapor-phase compositions, these data are not used in the estimation of activity coefficient in Barker's algorithm.^[3,8] The term denoted by Psat_prime in Table 1 represents the ratio of the fugacity of the pure liquid of interest to the fugacity coefficient of that component in the vapor mixture under equilibrium, or f_i^l / ϕ_i . This ratio determines the partial pressure, y_i^p , through the equation governing the phase equilibrium:

$$\phi_i y_i P = \gamma_i x_i f_i^l \quad \text{for } i=1,2 \quad (1)$$

The fugacity of liquid can be related to its properties at its saturation point; thus, the ratio mentioned above can also be visualized as the product of the saturation pressure, the Poynting factor, and the ratio of the fugacity of the pure component of interest at its saturation pressure to the fugacity coefficient of that component in the vapor mixture. When the second virial coefficients are used in estimation of the non-idealities, or the fugacities, Psat_prime can be expressed as^[8]

$$P_i^{\text{sat}'} \equiv \frac{f_i^l}{\phi_i} \approx P_i^{\text{sat}} \exp \left[\frac{(v_i^l - B_{ii})(P - P_i^{\text{sat}}) - P y_j^2 \delta_{12}}{RT} \right] \quad (2)$$

TABLE 1	
Given-MinErr Block for Barker's Algorithm	
initial guesses:	$\begin{bmatrix} \Lambda_{12} \\ \Lambda_{21} \end{bmatrix} := \begin{bmatrix} 800 \\ 100 \end{bmatrix} \frac{\text{joule}}{\text{mole}}$
Given	
	$\sum_i [P_{\text{experimental}} - (x_1 \gamma_1(\Lambda_{12}, \Lambda_{21}) \cdot \text{Psat1_prime} + x_2 \gamma_2(\Lambda_{12}, \Lambda_{21}) \cdot \text{Psat2_prime})] = 0$
	$\begin{bmatrix} \Lambda_{12} \\ \Lambda_{21} \end{bmatrix} := \text{MinErr}(\Lambda_{12}, \Lambda_{21})$

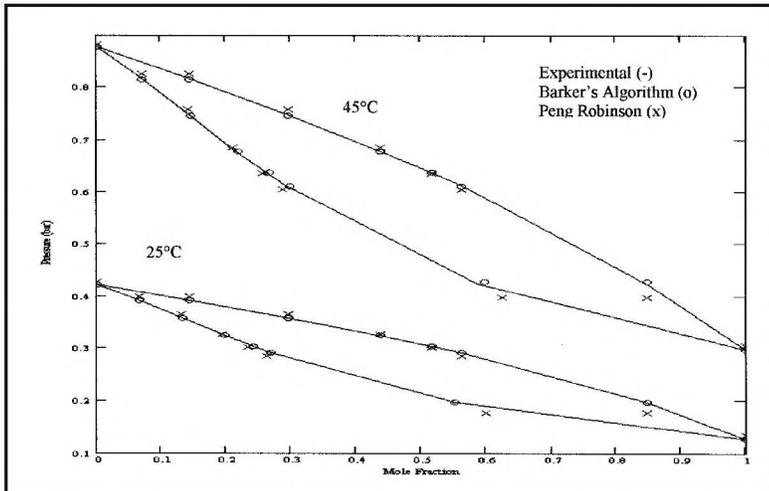


Figure 1. Model Fits.

where B_{ii} denotes the second virial coefficient, and

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}$$

In this example, the Wilson equation was used for the estimation of the activity coefficient, and regression yielded the two parameters of Wilson equations for the activity coefficients, $\Lambda_{12}(T)$ and $\Lambda_{21}(T)$. After the recoveries of these parameters at three temperatures, regression was conducted to recover the parameter associated with the exponential dependence of temperature.

Once the functions of $\Lambda_{12}(T)$ and $\Lambda_{21}(T)$ were generated, the total system pressures at various compositions were determined by summing the partial pressures. Vapor-phase compositions, y_j 's, were estimated after the total pressures were obtained. The vapor-phase compositions, y_j 's, are used only for comparison after total pressures are obtained because the aforementioned activity coefficient conforms to the Gibbs-Duhem equation. Since the vapor-phase compositions were not known initially, the vapor-phase compositions, y_j 's in Eq. (2), were set equal to zero in Psat_prime for the initial regression for Λ_{ij} . With a set of coarse estimations of y_j 's in hand, a second round of regression was performed using the full version of Psat_prime.^[8] The inclusion of y_j 's only slightly altered the values of Λ_{12} and Λ_{21} in this example. Using these new values of Λ_{12} and Λ_{21} , the refined total pressure and vapor phase compositions were calculated.

Figure 1 presents the comparisons of the experimentally measured and predicted P-xy data from both Barker's algorithm and the EOS model. Since the number of traces in Mathcad is limited to sixteen, only two groups of the data at 25°C and 45°C are shown.

Figures 2 and 3 (next page) represent the three-dimensional P-xy-T phase envelopes. The former illustrates the phase envelope around the experimental conditions, and the latter illustrates the phase envelope extended to the mixture's critical region through the temperature dependence of $\Lambda_{12}(T)$ and $\Lambda_{21}(T)$ in the Wilson equation.

For extrapolation, an expression similar to the one in the "Given-MinErr" solve block in Table 1 was used to calculate the system pressure at various temperatures. Once the system pressure was known, the vapor phase mole fraction was calculated in the same manner as above. A surface plot graph was then inserted into the Mathcad worksheet. Smoother phase envelopes can be constructed if more data sets at different temperature levels are included. Figures 2 and 3 present results

from only three and four sets of P-xy data, respectively. Mathcad, unfortunately, does not allow titles to be included for the axes of the 3-D graphs. Vertical axes in these figures represent pressure in bar, and the two horizontal axes represent temperature K and mole fraction.

It is interesting to note that the envelope observed in Figure 2 becomes much thinner as the temperature is extended to the critical region. As the temperature approaches the critical temperature for the mixture, the phase diagram begins to converge. A three-dimensional figure in Mathcad can be rotated to illustrate the features of curvatures by dragging the mouse.

Model 2

Peng-Robinson EOS with van der Waals Mixing Rules

To demonstrate Mathcad's ability to process more complicated algorithms, the same system was modeled with Peng-Robinson EOS and the van der Waals mixing rules.^[9] Both the one- and two-parameter models for the van der Waals mixing rule were included in the computation. When a cubic EOS is used for estimating the properties of both the vapor and the liquid, the fugacity coefficient of component *i* in a liquid mixture can be defined in the same manner as that for the vapor phase. Therefore, the equation governing the phase equilibrium can be expressed as

$$\phi_i^v y_i = \phi_i^l x_i \quad \text{for } i=1,2 \quad (3)$$

where the fugacity coefficients in both phases of the mixture were estimated by

$$\ln \phi_i = \frac{b_i}{b} \left(\frac{PV}{RT} - 1 \right) - \ln \frac{P(V-b)}{RT} - \frac{a}{2\sqrt{2}bRT} \left[\frac{2\sum_j y_j a_{ji}}{a} - \frac{b_i}{b} \right] \ln \frac{V + (1 + \sqrt{2})b}{V + (1 - \sqrt{2})b} \quad (4)$$

Mole fractions, y_i 's, in the above equation were replaced by x_i 's when the fugacity coefficients of component *i* in the liquid were estimated. Moreover, the parameters of the PR EOS for mixtures *a* and *b* were related to their counterparts for the pure component, mole fractions in the phase of interest, and the binary interaction parameters, k_{ij} . When the one-parameter van der Waals mixing rule is implemented, k_{ij} is the only adjustable parameter in the model. When the two-parameter mixing rule is used, it is expressed as^[9]

$$k_{ij} = K_{ij} x_i + K_{ji} x_j \quad (5)$$

and K_{ij} and K_{ji} are adjustable parameters in the model.

To find the mole volumes of the mixture in the individual phases, the PR EOS was expanded in volume and solved for the three roots by using the built-

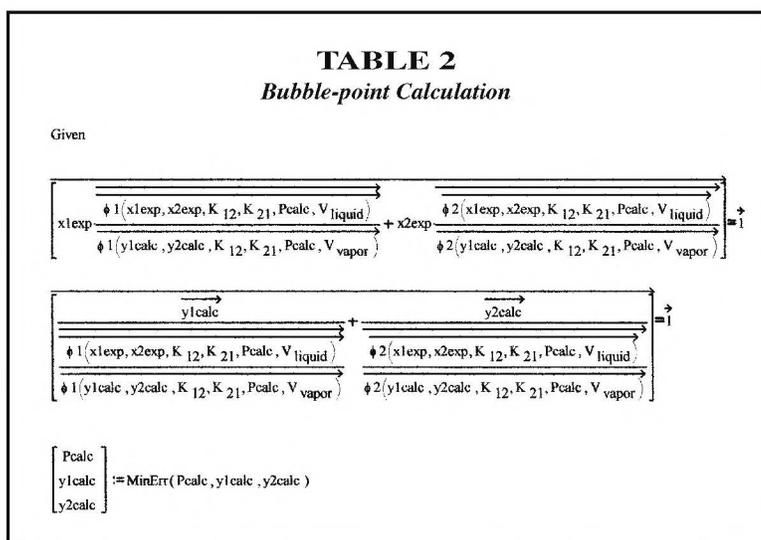
in command "polyroots." The maximum and minimum roots correspond to the vapor and liquid volumes, respectively.

To find the parameters k_{ij} or K_{ij} by regression, a "Given-MinnErr" block similar to Table 1 was executed. The equation below the Given command, however, was replaced by minimizing the sum of the differences between the left-hand side and right-hand side of Eq. (3). Once the values for k_{ij} and K_{ij} 's were obtained, the system pressure and vapor phase compositions were determined by a bubble point calculation (see Table 2.) The two equations shown in Table 2 state that the sum of the mole fractions must be equal to one. They also suggest the efficiency of using vector notations for handling data for multiple points in Mathcad. It should be mentioned that, since the experimental data concerning the vapor-phase composition are not readily available, the outputs from Barker's algorithm were used as experimentally measured data for y_i .

The fit from the two-parameter PR EOS is presented in Figure 1. Calculations for Barker's algorithm took a shorter processing time and produced a better fit. The extended processing time for the PR EOS was primarily due to the bubble point calculation.

As with Barker's algorithm, it was desirable to use the PR EOS to predict the system pressure and vapor-phase composition near the mixture's critical temperature. To accomplish this extension, the values for k_{ij} or K_{ij} 's were assumed to be temperature independent. Vapor-phase compositions were estimated using a bubble point calculation. The key to the extension was the estimation of the vapor- and liquid-mole volumes. In the development of the P-xy diagram, the ex-

TABLE 2
Bubble-point Calculation



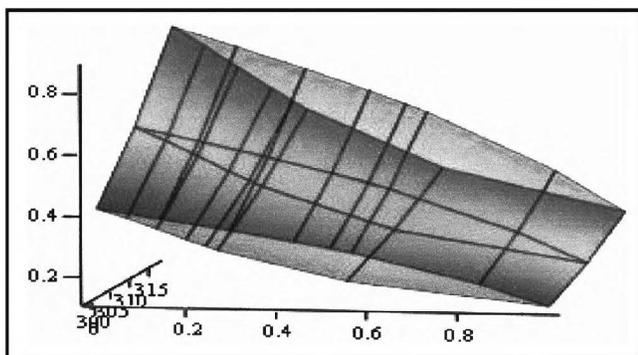


Figure 2. Phase envelope developed by Barker's algorithm.

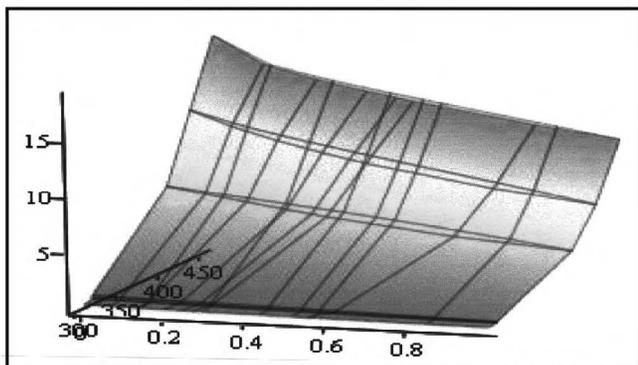


Figure 3. Extended phase envelope developed by Barker's algorithm.

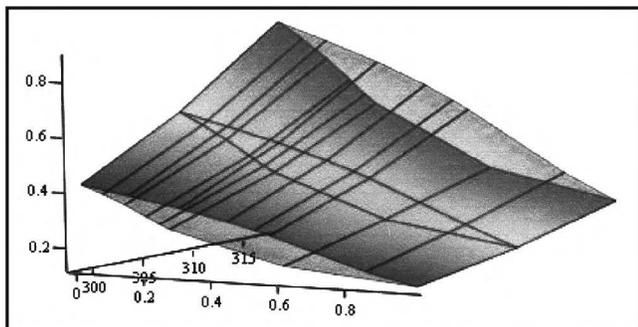


Figure 4. Phase envelope developed by Peng-Robinson equation of state and two-parameter van der Waals mixing rule.

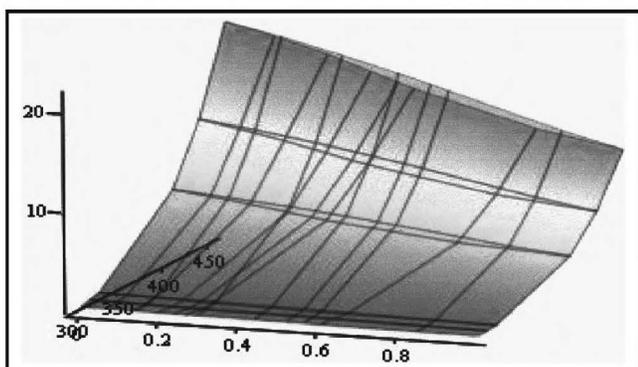


Figure 5. Extended phase envelope developed by Peng-Robinson equation of state and two-parameter van der Waals mixing rule.

perimentally measured pressure was used to calculate the vapor and liquid molar volumes. Since the pressure is not known as the phase envelope is extended, however, this method could not be used. To solve this problem, the vapor and liquid volumes were expressed as functions of pressure in the worksheet. Therefore, every time the pressure was altered in the iterative process, the vapor and liquid volumes were recalculated. The phase envelopes developed from these procedures, one for the region where the experimental data were collected and the other near the critical region, are shown in Figures 4 and 5, respectively.

The Mathcad worksheets for Barker's algorithm and those for the PR EOS discussed above have been used in our thermodynamics classes. Recoveries of parameters at various temperatures are split into several files for convenience and speedy results. They have been posted on the web under the index "Mathcad Programs for Thermodynamics" at <www.olemiss.edu/~cmchengs/>

CONCLUSIONS

Vapor-liquid equilibrium data were modeled in Mathcad using both Barker's algorithm and the Peng-Robinson cubic equation of state model. Using the experimental data at three temperatures, Mathcad was capable of calculating the necessary parameters for each of the two models. Once the parameters were determined, Mathcad was used to predict the system pressure and the vapor- and liquid-phase compositions. Both models yielded reasonable fits with the experimental data. The three-dimensional P-xy-T phase diagrams were then extended to the mixture's critical region. The data reduction procedures described herein are representative for students who are learning VLE for the first time; moreover, the three-dimensional phase envelopes give students concrete notions concerning the phase behaviors.

REFERENCES

1. Jolls, K.R., "Visualization in Classical Thermodynamics," *Proc. ABET Ann. Meet.*, p. 28 (1996)
2. Sandler, S.I., *Chemical and Engineering Thermodynamics*, 3rd ed., Wiley, New York (1999)
3. Smith, J.M., H.C. van Ness, and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th ed. McGraw-Hill, New York (2001)
4. Balbuena, P.B., "An Eye for the Abstract," *Science*, **286**, p. 430 (1999)
5. Jolls, K.R., and K.S. Tian, "Fluid-Phase Equilibria from a Chemical Process Simulator," Paper presented at the Annual Meeting of the ASEE, Milwaukee, WI (1997)
6. Hermesen, R.W., and J.M. Prausnitz, "Thermodynamics Properties of the Benzene and Cyclopentane System," *Chem. Eng. Science*, **18**, p. 485 (1963)
7. Reid, R.C., J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York (1987)
8. Prausnitz, J.M., R.N. Lichtenthaler, and E.G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, New Jersey, p. 236 (1999)
9. Orbey, H., and S.I. Sandler, *Modeling Vapor-Liquid Equilibria, Cubic Equations of State, and Their Mixing Rules*, Cambridge University Press, New York (1998) □

FRONTIERS OF CHEMICAL ENGINEERING

A Chemical Engineering Freshman Seminar

FRANK M. BOWMAN, R. ROBERT BALCARCEL, G. KANE JENNINGS, BRIDGET R. ROGERS
Vanderbilt University • Nashville, TN 37235-1604

In this paper we will describe a new seminar elective for freshman engineering students titled “Frontiers of Chemical Engineering.” We have designed the seminar to introduce freshmen to the field and profession of chemical engineering by using examples from cutting-edge research to illustrate fundamental concepts. Exposing students to chemical engineering in their first semester provides an earlier chance for them to catch the excitement of chemical engineering and should help them make better-informed decisions regarding their educational plans.

Chemical engineering students at many universities receive little, if any, exposure to chemical engineering as freshmen. For example, at Vanderbilt University freshman chemical engineering majors primarily take large lecture courses in math, physics, chemistry, and general engineering. Their sophomore year consists of only a single chemical engineering course each term, along with organic chemistry, math, and physics. This traditional curriculum leaves students with few opportunities to interact with professors in their major until their junior and senior years. Additionally, the large introductory lecture courses of the freshman year, which often provide little opportunity for student involvement, set a pattern of expectation, hopefully incorrect, for the learning and teaching methods to be used throughout the remainder of their program.

Compounding these problems, most freshmen have a poor understanding of the engineering profession in general and chemical engineering in particular. Often, students do not begin to see the big picture of the chemical engineering profession until the senior capstone design course. Consequently, they form impressions of chemical engineering, make decisions on which major to pursue, and set expectations for the college learning environment early in the college career—all based almost entirely on non-engineering courses and professors.

We feel that our chemical engineering profession has an obligation to educate prospective chemical engineering students regarding the broad applicability of chemical engineering principles, the multitude of available career paths, and the many other opportunities that our graduates normally receive. Such information should be made available to students as early as possible—certainly to new students in the first semester of their freshman year.

Many engineering programs across the country have modified their freshman curricula to address these challenges. A variety of approaches has been used, including general engineering courses, design-based courses,^[1-4] orientation courses,^[5-8] and seminars.^[9-11] General engineering courses bring together students from all engineering majors to provide a consistent grounding in basic engineering principles and skills, such as engineering problem solving, communication tools and skills, basic computer literacy, mathematical

Frank Bowman is Assistant Professor of Chemical Engineering at Vanderbilt University. He received his BS from Brigham Young University in 1991 and his PhD from Caltech in 1997, both in chemical engineering. His research interests include atmospheric aerosol modeling and chemical mechanism analysis.

Robert Balcarcel is Assistant Professor of Chemical Engineering at Vanderbilt University. He received his BS from the University of California, Berkeley, in 1993 and his PhD from MIT in 1999, both in chemical engineering. His research interests include improvement and metabolic engineering of mammalian cell cultures for biopharmaceutical production and analysis of chemical and biological agents.

Kane Jennings is Assistant Professor of Chemical Engineering at Vanderbilt University. He received his BS in chemical engineering from Auburn University in 1993, an MS in chemical engineering practice from MIT in 1996, and a PhD in chemical engineering from MIT in 1998. His research is focused on ultrathin organic films.

Bridget Rogers is Assistant Professor of Chemical Engineering at Vanderbilt University. She received her PhD and MS degrees from Arizona State University and her BS degree from the University of Colorado, Boulder, all in chemical engineering. Her research program focuses on film formation, microstructure evolution, and material properties of UHV-CVD deposited high permittivity dielectric thin films.

modeling, and computer programming. Design-based courses use real-world, hands-on experiences to introduce the engineering design process, teamwork, and engineering problem-solving skills. Orientation-type courses help students make the transition from high school to college and introduce them to the engineering profession, including topics such as campus policies and resources, time management and study skills, exposure to various engineering disciplines and job functions, and professional ethics. Seminar courses foster student/engineering faculty interactions using small-group discussions on a variety of engineering related topics.

FRESHMAN ENGINEERING AT VANDERBILT

The Vanderbilt University School of Engineering has recently introduced a variety of freshman seminar electives for the purpose of providing students greater access to engineering faculty, helping them make more informed career choices, and developing diverse learning and problem-solving skills.^[1] These seminars are one-semester-hour courses, taught entirely by full-time professors, with a limited student enrollment (typically 10-15 students). Faculty involvement is voluntary and professors are free to teach on anything within their area of expertise. In the academic year 2001-2002, approximately half of the freshman engineering students participated in a freshman seminar. Both student and faculty response to the program has been very favorable. These seminars complement the existing freshman engineering curriculum. Within

We have designed the seminar to introduce freshmen to the field and profession of chemical engineering by using examples from cutting-edge research to illustrate fundamental concepts.

the School of Engineering, the choice of engineering major is formally delayed until the beginning of the sophomore year. All freshman engineering students take a common general engineering course (“Introduction to Computing in Engineering”—teamwork skills, engineering method, computer tools) and a C++- or Matlab-based programming course (“Programming and Problem Solving”).

COURSE DESCRIPTION

As part of the seminar program, we have developed and teach a “Frontiers in Chemical Engineering” seminar. Each professor spends three to four weeks teaching a unit that is focused on his or her research area. During the past three years we have used examples from the modern topics of biopharmaceutical production, semiconductor fabrication, atmospheric particle formation, and molecular self-assembly to introduce the profession and principles of chemical engineering to the students.

In designing the course, we have identified the four main elements listed in Table 1. The first three items are specific academic objectives that help guide the selection of course content (what is taught). The last item is more general and defines the desired learning environment (how the course is taught). Within the individual research units, each of these elements is repeated. The goal is for students to see several different fields within chemical engineering, to see different applications of the same principles, and to interact with different faculty members.

Real-world applications that are familiar to students are used to motivate interest in each of the research topics. For example, biopharmaceutical production is introduced as a way to treat diseases such as diabetes or to decrease transplant rejections. The unit on atmospheric particles is started by asking the question, “Why do we care about particles in the atmosphere?”, which leads to discussions of how particles influence global climate, the ozone hole, and human health. Molecular self-assembly is explored as a process that can create coatings for applications such as corrosion protection of naval ships, chemical and biological sensors, biocompatible medical devices, and water-resistant fabrics. The section on semiconductor fabrication includes a discussion of how solid state transistors work and an exercise that involves role playing a process engineer evaluating a problem costing the company \$250,000 per day. The role-playing exercise emphasizes

TABLE 1
Objectives for Freshman Chemical Engineering Seminar

- ▶ **Demonstrate What Chemical Engineering Is**
Enable students to
 - Explain what a chemical engineer does
 - Identify products that chemical engineers make
 - Identify companies that employ chemical engineers
- ▶ **Touch on Chemical Engineering Principles**
Introduce students to the chemical engineering principles of
 - Material balances
 - Chemical and phase equilibrium
 - Mass transfer
 - Reaction kinetics
- ▶ **Introduce the Frontiers of Chemical Engineering**
Provide students with an introduction to the nontraditional chemical engineering topics of
 - Biopharmaceutical production
 - Molecular self-assembly
 - Atmospheric particles
 - Semiconductor fabrication
- ▶ **Get the Freshmen Off to a Good Start**
 - Excite them about engineering and chemical engineering
 - Provide an opportunity for them to get to know each other
 - Introduce them to chemical engineering faculty
 - Prepare and encourage them to participate in undergraduate research

the need for teamwork as well as the need to be informed about how the unit processes of a production flow affect those preceding and following it.

The class meets for 75 minutes once a week for a total of 15 weeks. An outline of course topics from the fall 2001 seminar is shown in Table 2. When the course was taught in fall 2000, the semiconductor fabrication unit was not included, and the other research units were each expanded to four weeks. The design of the course is such that different research units can rotate or be replaced from year to year depending on faculty availability and interest.

Class sessions take a variety of forms. The “Chemical Engineering” and “Tying it All Together” sessions at the beginning and end of the semester are taught by all of the professors. As part of the first class, small groups of three to four students and a professor work to develop lists of chemical-engineering-related products and companies. For the last class, similar groups create lists of the research topics discussed and match them up with the underlying chemical engineering principles (see Table 3).

Homework assignments are given out each week. They contain a mixture of writing, data analysis and interpretation, mathematical calculation, and experimental design. Students are encouraged to collaborate on the homework but are required to submit individual assignments. The homework contributes 70% to the course grade, with a comprehensive final exam worth 30%.

The seminar enrolled 9 students in 1999, 11 students in 2000, and 13 students in 2001. Each year, approximately half the students intended to major in chemical engineering, with the other half divided among the other engineering majors or undecided.

Research Units

The research units are taught by individual professors and are structured to take advantage of their respective research programs. Each of the units is described below. The semiconductor manufacturing and biopharmaceutical production units are discussed in greater detail to illustrate the level at which material is presented. While each research unit focuses on a specific research area, an important objective is to illustrate the underlying chemical engineering principles that are common to all areas. Table 3 summarizes four of the main principles that are highlighted throughout the course and examples of how they are presented in the different research units.

For the atmospheric particles unit, students spend most of the class period working in groups with a computer model that simulates gas-particle equilibrium and growth. They use the model to run simulated experiments and try to discover how variables such as particle size, number concentration, vapor pressure, temperature, and diffusivity influence particle growth. These computer exercises are supplemented

with discussions of student-selected current issues in atmospheric pollution such as global warming, the ozone hole, and urban smog.

To teach students about molecular self-assembly, the instructor uses a hands-on demonstration involving the formation of a self-assembled monolayer to convey introductory chemical engineering concepts in both thermodynamics and kinetics. Since chemical engineers should ultimately develop a molecular perspective, this unit also emphasizes how molecular-level effects can influence macroscopic surface properties. For example, the students find it extremely interesting and intuitive that a hydroxyl-terminated self-assembled monolayer is wet by water while a methyl-terminated monolayer repels water. The instructor also discusses the potential applications of these monolayer films to introduce students to fundamental concepts in separations and mass transfer.

While studying semiconductor fabrication, students are introduced to the unit operations of a typical process flow for a complementary metal-oxide-semiconductor (CMOS) transistor. A video tape is used to help students visualize the clean-room environment and the process equipment used in microelectronics manufacturing. After viewing the video, the class participates in a group exercise focused on one of the process steps. In 2001 we focused on chemical vapor deposition (CVD). This exercise started with a brief lecture of the mechanisms involved in CVD—transport of reactants into the reactor, diffusion of reactants to the substrate’s surface, reaction, surface diffusion of adatoms to form islands lead-

TABLE 2
Course Topics

Week Topic

- | | |
|-------------------------------------|---|
| 1 | Chemical Engineering, Profession and Curriculum |
| <i>Semiconductor Manufacturing</i> | |
| 2 | Microelectronic Device Processing |
| 3 | Silicon Oxidation |
| 4 | Chemical Vapor Deposition |
| <i>Atmospheric Particles</i> | |
| 5 | Particles in the Atmosphere |
| 6 | Why do Particles Grow? |
| 7 | How Fast do Particles Grow? |
| <i>Biopharmaceutical Production</i> | |
| 8 | Biotechnology and Cell Culture |
| 9 | Producing a Therapeutic Protein: Part I |
| 10 | Producing a Therapeutic Protein: Part II |
| <i>Molecular Self-Assembly</i> | |
| 11 | Chemistry of the Kitchen Sink: An Introduction to Self-Assembly |
| 12 | Self-Assembled Monolayer Films |
| 13 | Use of Molecular Films in Corrosion Prevention |
| 14 | Tying it All Together |
| 15 | Final Exam |

ing to film formation, and desorption of reaction byproducts. This lecture highlighted many chemical engineering concepts, such as fluid dynamics, molecular transport, and reaction kinetics.

Following the lecture the students broke up into groups to discuss three questions related to CVD:

- *What process parameters might be important to CVD and what might they affect?*
- *What properties of the film that is formed might determine how it is used in a device?*
- *Sometimes the precursors exist as liquids at room temperature. How might they be introduced into the reactor in order*

TABLE 3
Examples of Chemical Engineering Principles

1. Material Balances

Atmospheric particles

- when gases condense to form particles in the atmosphere, the total mass in the system remains constant

Biopharmaceutical production

- differential mole and cell balances for batch bioprocesses cultivating mammalian cells

Semiconductor manufacturing

- mass balances used in deriving models for silicon oxidation and CVD

2. Mass Transfer

Atmospheric particles

- particle growth depends on particle surface area, and the concentration gradient between the particle surface and bulk gas

Semiconductor manufacturing

- reactants diffuse to the substrate surface in both CVD and silicon oxidation processes
- surface diffusion of adatoms in CVD

Molecular self-assembly

- mass transfer of oxygen and water through a molecular film to an underlying metal surface

3. Reaction Kinetics

Biopharmaceutical production

- growth, death, and production rate constants are specified as first order with respect to viable cell concentration

Semiconductor manufacturing

- silicon oxidation described by first-order kinetics

Molecular self-assembly

- how long will it take for a self-assembled monolayer to form?

4. Chemical and Phase Equilibrium

Molecular self-assembly

- thermodynamic driving forces for molecular self-assembly, *i.e.*, when will a self-assembled monolayer form?

Atmospheric particles

- particles form in the atmosphere when the gas phase becomes supersaturated
- the saturation concentration (vapor pressure) depends on temperature and liquid phase composition (Raoult's law)

to participate in the reaction?

The intent of this exercise was to encourage the students to think beyond what was presented in the video and brief lecture and to incorporate basic concepts that they had been exposed to in high school chemistry and physics.

Another class session is used to focus on a different process step, silicon oxidation. Again, a brief lecture is used to highlight some of the chemical engineering concepts involved in the process, including oxidant transport to the surface, oxidant transport through the growing oxide layer, and reaction between the oxidant and silicon at the oxide/silicon interface. The Deal-Grove^[12] model of silicon oxidation is used as the basis for this discussion. Development of the Deal-Grove model was motivated by the lack of a comprehensive model that could fit all published silicon oxidation data. Previous proposed models would only fit a small subset of the published data. Therefore, we discussed how silicon oxidation data could be used to validate proposed models. Additionally, we discussed what experiments would be used to collect these data.

As a homework assignment, the students are given published silicon oxidation data and are asked to evaluate two proposed models for this process. They are asked to determine parameters for the proposed models based on the data they are given and are also asked to comment on how well each model fits the experimental data. In addition to this assignment, the students are guided through an internet search to learn more about the industry as well as the chemical engineers who helped mold the industry into what it is today. Specifically, they are given a list of terms related to semiconductor processes to define. They are also asked to find out who Andrew Grove is and what he, as a chemical engineer, has done in the semiconductor processing arena.

During the biopharmaceutical production unit, the instructor introduces students to biotechnology and cell culture and guides them through a discussion of the various factors that influence the production of therapeutic proteins and their cost. A lecture-based teaching method is enhanced by frequent "break-out" sessions where students are asked to generate as many possible explanations for a given effect or to calculate a specific item for further discussion.

In the first class session of the unit, the terms biotechnology, bioengineering, biochemical engineering, biomedical engineering, and biomechanics are all defined. The chemical engineering principles taught in each of the core chemical engineering courses are highlighted and examples from biotechnology are described (cell balances-material balances, bioreactors-reactor design, solubility of oxygen in culture medium-phase equilibria, control of pH-process control, etc.). Biopharmaceutical production is then introduced as a way to treat diseases such as diabetes or to decrease transplant rejections. Several biotech companies, such as Genentech, Genzyme, and Amgen, are listed as well as

The challenge is in selecting and presenting the appropriate material to both challenge and excite freshmen without scaring them with concepts they are not prepared to learn.

some of their main products and applications.

As part of their first biopharmaceutical assignment, students do an internet search to find additional biotechnology companies and products that were not mentioned during the lecture. They are also asked to consider engineering ethics by explaining which types of interventions—chemical, therapeutic protein, adult gene therapy (inserted genes are not passed to the next generation), and embryonic gene therapy (genes are presumably passed to their offspring)—they consider to be acceptable. Their viewpoints are discussed in subsequent class sessions.

The remaining classes in the unit look at designing a process to produce a therapeutic protein, such as one that could dramatically reduce the symptoms of Alzheimer's disease. Students are asked to estimate the demand, production requirements, and cost to produce this protein. The amount of product needed from an upstream batch process must be that needed to meet the market plus the amount lost during separations steps. Efficiency of separation is assumed to be 70%. Reactor volume is then determined based on the estimated market need for product (X kg/year) and assuming a given achievable concentration of product at the end of a batch (1 g/L). Height and diameter of the vessel are determined given a desired H:D ratio.

Material balances and kinetics are used to formulate differential mole and cell balances for batch bioprocesses cultivating mammalian cells. "Accumulation = In - Out + Generation - Consumption" is formulated and translated to an equation with appropriate nomenclature. Growth, death, and production rate constants are specified as first order with respect to viable cell concentration. Equations are integrated and used to estimate final cell concentration and product given growth, death, and production rate constants, or to determine average rate constants given cell concentration and production data. Students are shown how to use Excel for numerical integration using the trapezoid rule.

Students use this model to determine how many days it will take for the bioreactor to reach a maximum product con-

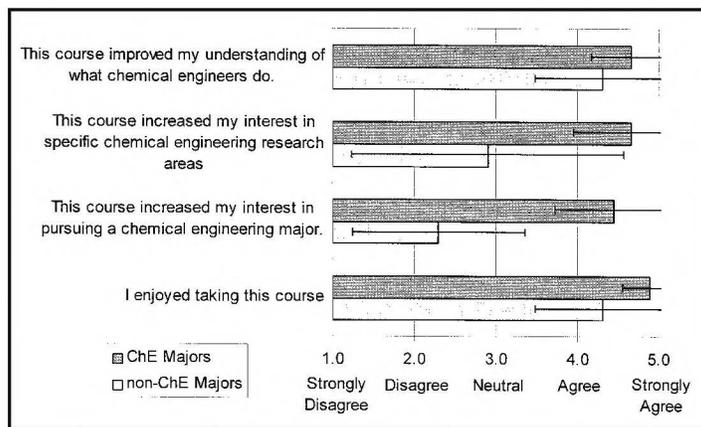


Figure 1. Student responses to end-of-course survey.

centration and to understand the effect of the various reaction rate parameters on production time and cost. The cost of biopharmaceuticals is explained as being high due to the low yield from the primary process batch and the high costs of the elaborate separation scheme needed to achieve "ready-for-injection" purity. Students estimate a reduction in cost associated with increasing the product yield by keeping cells

alive longer and/or genetically engineering them to produce more product per cell.

COURSE ASSESSMENT

Course objectives, as defined by the professors, are summarized in Table 1. Student-defined objectives for the course are much more focused. In beginning- and end-of-course surveys, in response to the question, "Why did you enroll in this course?" students without exception stated two things: "To learn about chemical engineering" and "To see if I wanted to be a chemical engineer."

Achievement of these professor- and student-defined objectives was assessed with anonymous surveys at the beginning and end of the semester. Responses to several questions from the 1999 and 2000 end-of-course survey are shown in Figure 1. The 2001 survey used different wording and, while not directly comparable, showed similar results to the surveys in the first two years. Virtually all students, whether chemical engineering majors or non-majors, agreed or strongly agreed that the course improved their understanding of what chemical engineers do, with slightly higher ratings from chemical engineering majors. This indicates that the first objective of both professors and students—to learn about chemical engineers and chemical engineering—is being met.

Much larger differences between majors and non-majors were observed on questions regarding interest in chemical engineering. After taking the course, chemical engineering majors were more interested in both specific chemical engineering research areas and in continuing to pursue a chemical engineering major. Non-majors had widely divergent responses to the question on chemical engineering research ar-

eas, either strongly disagreeing or strongly agreeing that the course increased their interest. Concerning pursuit of a chemical engineering major, the course tended to make non-majors less interested. These results suggest that the course has been more effective at confirming students original selection of a major rather than recruiting non-majors into chemical engineering. Written student comments support this view, with chemical engineering majors saying, "Now I am sure this is what I want to major in," and non-majors saying "I found out that I do not want to be a chemical engineer and that other fields interest me more."

Both sets of students tended to agree or strongly agree that they enjoyed taking the course, with exceptionally favorable responses from the chemical engineering majors. That non-majors, despite a demonstrated preference for other engineering majors, enjoyed the course is taken as a sign that the course is providing the desired positive experience for freshman engineering students.

Faculty response to the seminar has also been favorable. We have appreciated the opportunity to get to know our students early in their college careers. As we encounter them in other courses, we find that we have already established a relationship with them, which helps us connect better with the entire class. Presumably, this experience is reciprocated, and students also feel more comfortable interacting with us. An additional benefit has been that several students have expressed interest in our individual research programs, and some have begun working as undergraduate research assistants in our research labs.

The overall time commitment for preparing and teaching the seminar, particularly when divided among three or four professors, is quite reasonable. But it was noted that preparation time for each class period was higher for this course compared to semester-long courses. The challenge is in selecting and presenting the appropriate material to both challenge and excite freshmen without scaring them with concepts they are not prepared to learn.

AREAS FOR IMPROVEMENT

We have identified a few areas for improvement in upcoming years. Greater coordination between the individual research units is needed so that the seminar is a coherent, integrated course and not merely a collection of unrelated mini-seminars. Related to this, initially we noted a deficiency in meeting the objective of introducing basic chemical engineering principles, so in 2001, greater emphasis was placed on common underlying ideas in each research unit to help tie the course together and provide a better understanding of these principles.

Assessment surveys need to be refined to better measure achievement of the stated course objectives. The progress of past seminar students should be followed to determine what, if any, impact the course may have had on their college experience. Unfortunately, due to the limited and voluntary en-

rollment, accurate comparison to a control group of students who didn't take the seminar is not practical.

The first time the course was taught, we found two- or three-week units to be too short. Three to four weeks for each research area was better, because it allowed more time to explore the research topic. A certain amount of background material is essential when introducing unfamiliar subjects, but our goal is to achieve sufficient depth to intellectually challenge the students. Part of this challenge is inherent in making graduate-level research topics accessible to a freshman audience.

Overall, we feel the course has been quite successful. Students have learned more about chemical engineering, and by exposure to our different research areas they have gained a clearer view of the wide scope of opportunities available to them. Perhaps most importantly, freshman engineering students have had the opportunity to begin their college experience working closely with other engineering students and with engineering faculty. The experience has proved enjoyable and beneficial for all involved. The format of the course is flexible and should be easily adaptable to other chemical engineering departments.

ACKNOWLEDGMENTS

Frank Bowman would like to thank the National Science Foundation for supporting development of the educational aerosol computer model under Grant ATM-9985108.

REFERENCES

1. Ambrose, S.A., and C.H. Amon, "Systematic Design of a First-Year Mechanical Engineering Course at Carnegie Mellon University," *J. Eng. Ed.*, **86**, 173 (1997)
2. Carlson, B., *et al.*, "A Motivational First-Year Electronics Lab Course," *J. Eng. Ed.*, **86**, 357 (1997)
3. Sheppard, S., and R. Jenison, "Examples of Freshman Design Education," *Int. J. Eng. Ed.*, **13**, 248 (1997)
4. Burton, J.D., and D.M. White, "Selecting a Model for Freshman Engineering Design," *J. Eng. Ed.*, **88**, 327 (1999)
5. Landis, R.B., "Improving Student Success Through a Model 'Introduction to Engineering' Course," *Proc. 1992 ASEE Ann. Conf.*, Toledo, OH (1992)
6. Hatton, D.M., P.C. Wankat, and W.K. LeBold, "The Effects of an Orientation Course on the Attitudes of Freshmen Engineering Students," *J. Eng. Ed.*, **87**, 23 (1998)
7. Porter, R.L., and H. Fuller, "A New 'Contact-Based' First Year Engineering Course," *J. Eng. Ed.*, **87**, 399 (1998)
8. Budny, D., "The Freshman Seminar: Assisting the Freshman Engineering Student's Transition from High School to College," *Proc. 2001 ASEE Ann. Conf.*, Albuquerque, NM (2001)
9. Merritt, T.R., E.M. Murman, and D.L. Friedman, "Engaging Freshmen Through Advisor Seminars," *J. Eng. Ed.*, **86**, 29 (1997)
10. Richardson, C., "Freshman Retention in Engineering Technology Programs at Rochester Institute of Technology," *Proc. 1997 ASEE Ann. Conf.*, Milwaukee, WI (1997)
11. Overholser, K.A., "Engineering Freshman Seminars," *Proc. 2001 ASEE Ann. Conf.*, Albuquerque, NM (2001)
12. Deal, B.E., and A.S. Grove, "General Relationship for the Thermal Oxidation of Silicon," *J. Appl. Phys.*, **36**, 3770 (1965) □

Random Thoughts . . .

HOW TO SURVIVE ENGINEERING SCHOOL

RICHARD M. FELDER

North Carolina State University • Raleigh, NC 27695

Dear Engineering Student:

Don't take the title of this column literally. Despite the incomprehensible lectures, endless homework, and impossible tests, studying engineering has rarely been fatal. Nevertheless, things may not always go quite the way you would like—classes with absurd amounts of work and test averages in the 50s are facts of life in engineering. I had lots of classes like that when I was where you are now, and I complained about them just as loudly. Unfortunately, while complaining may make you feel better, it won't do a thing for your grades.

I'd like to propose several better ways to help yourself. First, though, let me suggest that the real problem may not be that professor who's making your life miserable. It is that over the years you may have unconsciously bought into a message that goes like this: *"My teachers know everything I need to know to be an engineer. Their job is to tell it to me in lectures, and my job is to soak it up and then repeat it on exams. If I can do that, I've learned it."*

Wrong! That approach may have worked in high school but it begins to fail in college, and once you get into the plant or research lab, it stops working completely. Out there, there are no professors, lectures, or texts with worked-out examples, and the problems don't come neatly packaged with all the information needed to solve them. In fact, often the hardest part of a real problem is figuring out exactly what the problem is.

But you also need to remember this. Around the world, hundreds of thousands of engineers—most no smarter than you, many not as smart—who once struggled with their own confusing instructors and unreadable texts and didn't understand entropy any better than you do, are out there doing just fine. Every day they figure out what they need to know to solve their problems, and then they solve them. If they could learn to do that, so can you. What I'd like to do here is give

you five simple tips to help you start learning it now. If you find yourself struggling in classes, give the tips a try. If they work (and I'm pretty sure that they will), you'll have an easier time in school and hit the ground running in your first job.

TIP 1

Figure out what might make course material clearer and try to get it in class.

Do you ever find yourself expressing one of these common complaints? *"I need practical, real-world applications before I can understand something, but all we get in class is theory."* *"I want to understand how things work, but all we get are facts to memorize and formulas to substitute into."* *"I understand what I see—pictures, diagrams, demonstrations—better than what I hear and read, but all we get are words and formulas."*

If you do, pay attention to yourself—identifying what you're missing in a course is the first step toward getting it. The obvious next step is to ask your professor, in or out of class, for whatever it may be. Most professors genuinely want their students to learn—that's why they became professors—and often complain that their students rarely ask questions except "Are we responsible for this on the test?" So if you don't understand something, try asking for something that



Richard M. Felder is Hoechst Celanese Professor Emeritus of Chemical Engineering at North Carolina State University. He received his BChE from City College of CUNY and his PhD from Princeton. He is coauthor of the text *Elementary Principles of Chemical Processes* (Wiley, 2000) and codirector of the ASEE National Effective Teaching Institute

might clarify it. “Could you give an example of how you would use that formula?” “Could you sketch what that (device, solution, plot) might look like?” “Where did that equation you just wrote come from?” Even if you’re afraid a question may sound stupid, ask it anyway. I guarantee that others in the class are equally confused and will be grateful to you for having the courage to speak up. And if you need more help, go to the professor’s office and ask for it.

Caution, however. Even instructors who really want to help will get annoyed if they think you’re trying to get them to do your homework for you. *Never ask your instructor for help on a problem until you have made a serious effort to solve it by yourself.* When you ask, be prepared to show what you tried and how far you got. Bring in your flow charts and free body diagrams and calculations, including the ones that didn’t work. The more you bring in, the more likely you are to get the help you need.

TIP 2
Read

Some textbooks try to clarify difficult material by giving practical illustrations and explanations. Check out those parts of your text if you’re having trouble rather than just searching for solved examples that look like the homework problems. Another good strategy is to look at a second reference on the same subject—a different text, a handbook, or a Web site. Even if you can’t find the crystal-clear explanations and examples you’d like, just reading about the same topic in two different places can make a big difference in understanding.

TIP 3
Work with other students

When you work alone and get stuck on something, you may be tempted to give up, where in a group someone can usually find a way past the difficulty. Working with others may also show you better ways to solve problems than the way you have been using. Here are two ideas for making groupwork effective.

▶ *Outline problem solutions by yourself first and then work out the details in your group.* Someone in every group is generally fastest at figuring out how to start problem solutions and does it for every problem. If that student isn’t you, you may have to figure it out for the first time on the test, which is not a particularly good time to do it. Outlining the solutions before meeting with the group is the way to avoid this disaster.

▶ *Get group members—especially the weaker ones—to*

explain all completed problem solutions before ending a problem-solving session. If everyone can do that, the session worked.

TIP 4
Consult experts

Sometimes you’ll run into a problem that completely stumps you and everyone you’re working with. When practicing engineers run into such problems, as they all do occasionally, they consult experts. You also have experts available to you. Your course instructor is an obvious candidate, but that doesn’t always work out. Other potential consultants include graduate teaching assistants, other professors who teach the same course, students who have previously taken the course, smart classmates, and tutors. No matter whom you go to, though, go early: waiting until two days before the final exam probably won’t cut it.

TIP 5
Believe that you have what it takes to be a good engineer.

If this advice is hard for you to take now, you’re probably suffering from what psychologists refer to as the *Impostor Phenomenon*, which is like a tape that plays inside people’s heads. If you’re an engineering student looking around at your classmates, the tape goes something like this: “*These people are good—they understand all this stuff. They really belong here...but I don’t. Over the years I’ve somehow managed to fool them all—my family, my friends, my teachers. They all think I’m smart enough to be here, but I know better...and the very next hard test or hard question I get in class will finally reveal me as the impostor I am.*” And what would happen next is too horrible to contemplate, so at that point you just rewind and replay the tape.

What you don’t know is that almost everyone else in the class is playing the same tape, and the student in the front row with the straight-A average is playing it louder than anyone else. Furthermore, the tape is usually wrong. If you survived your first year of engineering school, you almost certainly have what it takes to be an engineer. Just remember all your predecessors who had the same self-doubts you have now and did just fine. You do belong here, and you’ll get through it just like they did. Try to relax and enjoy the trip.^[1]

Sincerely,
Richard Felder

1. For more about student survival skills and the *Impostor Phenomenon*, see <www.ncsu.edu/felder-public/Student_handouts.html>

All of the *Random Thoughts* columns are now available on the World Wide Web at http://www.ncsu.edu/effective_teaching and at <http://che.ufl.edu/~cee/>

INTRODUCTION

TO SPECIAL SECTION ON

MEMBRANES IN CHEMICAL ENGINEERING EDUCATION

Andrew L. Zydney

The Pennsylvania State University • University Park, PA 16802

When I was an undergraduate studying chemical engineering, there really was no significant membrane industry worth mentioning. That has certainly changed. Today, the membrane industry has sales of several billion dollars a year. This includes major applications in the treatment of kidney disease by hemodialysis, the separation of commodity gases such as oxygen and nitrogen, the purification of therapeutic proteins and pharmaceuticals, and the treatment and desalination of natural and industrial waters.

About two years ago, the North American Membrane Society conducted a survey to determine the extent to which membrane science and technology was covered in the undergraduate chemical engineering curriculum. This survey revealed a number of programs with significant membrane-related material, including specific laboratory experiments, open-ended design problems, and significant sections in both core and elective ChE courses. In most cases, however, the teaching was done by only one or two “experts,” typically faculty who had significant personal experience in the membrane field. Departments that had no faculty working on membranes tended to have little if any coverage of membrane problems within their undergraduate programs.

Motivated in large part by the results of this survey, the Membrane-Based Separations Area and the Education Division of the AIChE decided to co-sponsor a session on *Membranes in the Chemical Engineering Curriculum* at the 2001 Annual Meeting. The session was an enormous success, with a series of fascinating presentations covering a wide range of membrane problems within the undergraduate curriculum. The papers presented in this issue of *Chemical Engineering Education* are a direct result of this session, and I would like to personally thank Tim Anderson for his encouragement and support in putting this special issue together.

The papers that follow have been organized “chronologically,” beginning with examples of how to introduce

membrane technology in the *Introduction to Chemical Engineering* course and then moving through examples in mass transfer, separations, the undergraduate laboratory, and senior design. The specific problems/examples cover the full range of membrane applications, including problems in

- 1) *Design of appropriate hemodialysis therapy for the treatment of kidney disease*
- 2) *Optimization of gas separations using hollow fiber modules*
- 3) *Removal of impurities from therapeutic proteins using membrane diafiltration*
- 4) *Desalination of salt water by reverse osmosis or electrodialysis*
- 5) *Recovery of precious metals from spent catalysts*
- 6) *Concentration of apple juice using ultrafiltration*
- 7) *Production of ethylene in a ceramic membrane reactor*

Our hope is that these papers will provide faculty with examples that they can use in their classes so that all chemical engineering undergraduates can be exposed to some of the important principles and applications of membrane technology. The authors have tried, wherever possible, to provide sufficient details and references so that faculty can use these examples in their teaching. In addition, all of the authors have indicated they would be happy to answer questions about the problems, and several of the papers contain URLs that provide links to more detailed descriptions of the process simulators or lab experiments.

The North American Membrane Society (NAMS) will also be hosting an education section on its website (www.membranes.org), and anyone who is using these (or other) membrane problems within their courses is strongly encouraged to contact NAMS so that this information can be disseminated as effectively as possible throughout the chemical engineering community.

ANALYSIS OF MEMBRANE PROCESSES

In the Introduction-to-ChE Course

ANDREW L. ZYDNEY

University of Delaware • Newark, DE 19716

The introductory course in most chemical engineering departments is designed to meet a broad range of educational goals. They typically include: 1) providing information that will enable students to determine if chemical engineering is the “correct” major for them; 2) providing a foundation for subsequent courses in the curriculum; and 3) teaching significant chemical engineering principles, particularly in the area of mass balances.^[1] Traditional introductory courses, *e.g.*, those based on the classical book by Felder and Rousseau,^[2] focus primarily on the use of steady-state mass (and energy) balances to describe the behavior of a wide range of chemical processes. These courses often include a small section on transient processes at the end of the semester, such as Chapter 11 in the Felder and Rousseau^[2] text or Chapter 7 of Himmelblau.^[3] Russell and Denn^[4] take a very different approach, emphasizing transient balance equations right from the beginning. This approach has the advantage of allowing the instructor to focus on the key concepts of “rate” and characteristic times, an aspect that is often lost in courses that emphasize steady-state processes.

One of the challenges of introducing students to transient mass balances is a lack of interesting and effective problems that analyze the behavior of non-reacting systems (batch reactor problems provide a very effective introduction to time-dependent reacting systems). Russell and Denn^[4] devote more than an entire chapter to the analysis of draining and filling tanks—a problem that illustrates the important concepts but one that generates very little excitement and enthusiasm among the students. Himmelblau^[3] also uses the tank draining problem as a primary example, along with problems on diluting a salt solution with water. Felder and Rousseau^[2] try to make the tank draining problem a little more interesting by examining the water level in a reservoir during a period of drought and the water volume in a storage tank that has a leak. But students often see these problems as artificial, in part because of the seemingly arbitrary functions given

for the rate of inflow and outflow, and they provide little opportunity for the students to think about process design considerations.

The University of Delaware uses the text by Russell and Denn^[4] as the basis for its introductory chemical engineering course, which is taught in the spring semester of the freshman year. The course is divided into three main sections:

- *Transient mass balances in nonreacting systems*
- *Transient mass balances in reacting systems, including the analysis of batch reactors and CSTRs*
- *Interfacial mass transfer*

The traditional material in this course has been supplemented with a series of membrane problems specifically designed to illustrate the key concepts involved in the analysis of transient mass balances. These membrane problems are “real,” they are easy for students to relate to, they tend to be much more interesting than the traditional tank draining and filling problem, they provide a much better introduction to the range of problems and application areas of interest to chemical engineers, and they give students an opportunity to think about real design issues, even when they are freshmen.

APPLE JUICE CONCENTRATION USING REVERSE OSMOSIS

Apple juice can be concentrated by a reverse osmosis system



Andrew Zydney is currently Professor and Endowed Chair in the Department of Chemical Engineering at The Pennsylvania State University. He received his PhD from MIT in 1985 and was a faculty member at the University of Delaware from 1985 to 2001. He has been actively involved in membrane research for more than twenty years, with emphasis on biotechnological and biomedical applications.

Membranes in ChE Education

using the fed-batch process shown in Figure 1. Fresh juice is fed to a recycle tank, with the juice from the recycle tank then passing through the reverse osmosis unit where water is removed through the membrane. The concentrated juice is returned to the recycle tank—the system is designed to operate so that the volume in the recycle tank remains constant throughout the process. At the end of the process, a concentrated juice product is obtained in the recycle tank. It can be frozen and sold as “apple juice concentrate” or the concentrated juice can be shipped and then reconstituted at a remote site by simply adding water. This latter process can lead to significant cost-savings since a much smaller volume of juice needs to be shipped across the country. One of the concerns with this process is that the membrane is never “perfect,” meaning that there will be a small loss of flavor components through the membrane during the concentration process. This is why many juice companies will specifically advertise on the label that their juice is “not from concentrate.” Cheryan and Alvarez^[5] provide a more detailed discussion of membrane processes for juice concentration.

The goal of the problem is to evaluate the fraction of flavor components that are lost during a process designed to take 10,000 L of fresh juice and produce 500 L of apple juice concentrate. To simplify the analysis, we assume that the concentration of flavor components in the filtrate stream collected through the membrane is equal to a certain fraction (S) of the flavor concentration in the stream that enters the membrane unit. This latter assumption is simply the definition of the membrane sieving coefficient. This type of constitutive relation must be determined experimentally, playing a role analogous to the rate expression in batch reactor problems.^[4]

The problem is solved by writing both total and component mass balances around the recycle tank and the reverse osmosis unit (shown by the dashed line in Figure 1):

$$\frac{d(\rho V)}{dt} = \rho_{\text{feed}} Q_{\text{feed}} - \rho_{\text{filtrate}} Q_{\text{filtrate}} \quad (1)$$

$$\frac{d(V C)}{dt} = Q_{\text{feed}} C_{\text{feed}} - S Q_{\text{filtrate}} C \quad (2)$$

where C is the concentration of the flavor components in the feed tank. If we make the assumption of a constant (uniform) density, then the total mass balance simply reduces to $Q_{\text{filtrate}} = Q_{\text{feed}}$ since V is constant. This conclusion is also valid for a juice in which the density is a linear function of the flavor concentration.^[4] The component mass balance is then readily integrated to give

$$\ln \left[\frac{C_{\text{feed}} - S C}{(1 - S) C_{\text{feed}}} \right] = - \left(\frac{S Q_{\text{feed}} t}{V} \right) \quad (3)$$

where the concentration of flavor components in the recycle tank at the start of the process is equal to C_{feed} . This equation can be easily solved for the final concentration of flavor components, with t evaluated as the time required to process 10,000 L of juice (or in this case, to add 9,500 L of juice to the 500 L initially present in the recycle tank). The overall flavor recovery is then evaluated as the ratio of the final mass of flavor components in the juice (VC_{final}) to the initial mass of flavor components

$$\text{Recovery} = \frac{VC_{\text{final}}}{V_{\text{total}} C_{\text{feed}}} = \frac{V - V(1 - S) \exp \left[-S \left(\frac{V_{\text{total}} - V}{V} \right) \right]}{S V_{\text{total}}} \quad (4)$$

where V_{total} is the total amount of juice (in this case, 10,000 L).

In addition to solving the mass balance equations, there are a number of interesting design issues that the students can begin to think about, such as what would happen to the final concentration of flavor components in the recycle tank if it were poorly mixed. For example, if the recycle stream is returned to the top of the recycle tank, then the concentration of flavor components will be lower in the bottom of the tank (near the tank exit), which will reduce the amount of flavor that is lost through the membrane. Although this situation cannot be modeled quantitatively this early in the curriculum, the qualitative behavior of the system is quite easy to explain. The discussion of mixing provides a great opportunity for the instructor to talk about the residence time in the recycle tank and the different design approaches that can be used to achieve good mixing in a large tank.

The students can also be asked to consider what (if any) difference would occur if the juice concentration were accomplished using a batch process instead of the fed-batch system shown in Figure 1. In this case, all of the juice is placed in a single large tank, the feed stream entering the

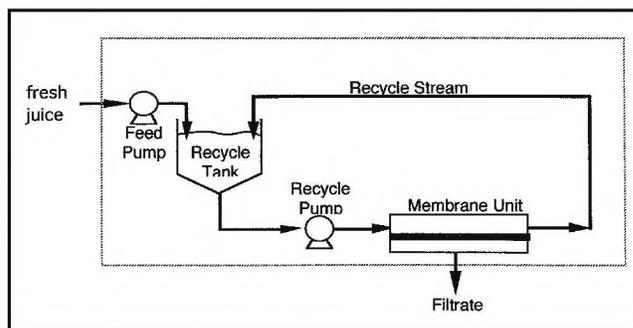


Figure 1. Fed-batch system for producing apple juice concentrate.

tank is eliminated, and the volume in the tank decreases with time as fluid is removed through the membrane. This problem can either be analyzed qualitatively based on physical insights about the batch process, or the students can develop and solve the mass balance equations for the batch system (easily assigned as a homework problem after presenting the fed-batch analysis in class). The final expression for the flavor recovery in the batch system is simply

$$\text{Recovery} = \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right)^S \quad (5)$$

It is relatively easy to show that there is always less flavor lost using the batch process. This is because the concentration of flavor components in the recycle tank in the fed-batch process increases much more rapidly than that in the batch system due to the smaller volume in the recycle tank, leading to a greater passage of flavor components through the membrane. Given that result, the students can think about why one might still decide to use a fed-batch process for the juice concentration. One practical reason is that it can be difficult to maintain a well-mixed solution as one goes from an initial volume of 10,000 L to a final volume of 500 L in the batch process. The lack of mixing not only affects the flavor loss, it also affects the filtrate flow rate that can be achieved in the membrane unit. The batch process also requires the use of a very large (and expensive) feed tank. In addition, the fed-batch process provides greater design flexibility for use in multiple processes in a single commercial facility.

IMPURITY REMOVAL FROM RECOMBINANT THERAPEUTIC PROTEINS

The biotechnology industry now produces a wide range of therapeutic proteins using recombinant gene technology. The DNA of interest is cloned into an appropriate microorganism or mammalian cell line, enabling those cells to produce the desired protein using their natural metabolic processes. Current commercial recombinant products include: insulin for the treatment of diabetes, tissue plasminogen activator used as an anti-clotting agent for the treatment of stroke and heart attack, human growth hormone for the treatment of dwarfism, and erythropoietin as a red blood cell stimulating agent for the treatment of anemia. A nice review of recombinant gene technology is provided by Glick and Pasternak.^[6]

One of the critical issues in the production of therapeutic proteins is the high degree of purification that must be achieved, particularly since these molecules are typically given directly into the bloodstream by intravenous injection. The bulk of the purification is typically done using some combination of affinity, ion exchange, and/or hydrophobic inter-

The traditional material in this course has been supplemented with a series of membrane problems specifically designed to illustrate the key concepts involved in the analysis of transient mass balances.

action chromatography. Small impurities (e.g., buffer components and excess salt), however, are generally removed by membrane diafiltration. Van Reis and Zydney^[7] provide a nice review of the principles of diafiltration for bioprocessing applications.

The diafiltration process looks very similar to the apple juice concentration shown in Figure 1. The membrane is nearly fully retentive to the protein of interest, but allows relatively unhindered passage of the small impurity through the membrane. The solution containing the therapeutic protein is contained in the recycle tank, and a protein- and impurity-free buffer solution is continually added to the tank to maintain a constant solution volume while the impurity is washed through the membrane.

The transient mass balance for the constant volume diafiltration process is

$$V \frac{dC}{dt} = -SQ_{\text{filtrate}}C \quad (6)$$

where S , the membrane sieving coefficient, is equal to the ratio of the impurity concentration in the filtrate solution to that in the feed. Equation (6) can be integrated to give a simple decaying exponential relating the impurity concentration at time t to the initial concentration of the impurity in the protein solution. The results are more conveniently expressed in terms of the total volume of protein-free buffer that must be used to reduce the impurity concentration to a desired target level

$$\frac{C_{\text{final}}}{C_{\text{initial}}} = \exp\left(-\frac{SV_{\text{buffer}}}{V}\right) \quad (7)$$

The membrane diafiltration can be used in combination with an ultrafiltration process to achieve protein concentration and impurity removal in a single processing step.^[7]

This same diafiltration process is also used as part of a viral inactivation step. For example, an appropriate solvent or detergent is first added to the protein solution to achieve a concentration that is sufficient to inactivate nearly all viruses. The solvent/detergent is then removed by diafiltration, typically to a target of less than 10 ppm (parts per million). This is an ideal opportunity to talk about product safety issues,

Membranes in ChE Education

including the need to achieve essentially complete virus removal/inactivation while at the same time avoiding denaturation of the recombinant protein product and minimizing potential complications from the presence of trace amounts of any viral inactivation agents. It is important for students to recognize that even though the membrane diafiltration is very effective at removing residual solvents and detergents, it is impossible to achieve 100% removal of these components using a finite volume of diafiltration buffer—the exponential decay provides an asymptotic approach to zero concentration.

UREA REMOVAL DURING HEMODIALYSIS

Another interesting membrane problem that is readily incorporated into the introductory mass balance course is analysis of urea removal during hemodialysis.^[8] Hemodialysis is currently used to treat chronic kidney failure in more than 500,000 patients around the world—patients who would die within about two weeks without the availability of this type of artificial kidney. Urea removal in hemodialysis can first be examined by analyzing a transient batch process for removing urea from blood across a semi-permeable membrane (top panel in Figure 2). The dialysate contains all the key salts and sugars normally found in plasma to insure that these components aren't removed during the dialysis. The membrane is impermeable to all blood cells and proteins, but it allows urea to be removed at a rate that is proportional to the concentration difference between the blood and the dialysate solution

$$\dot{m}_{\text{transfer}} = k_m A [C_{\text{blood}} - C_{\text{dialysate}}] \quad (8)$$

where k_m is the membrane mass transfer coefficient (or permeability) and A is the membrane area. Component mass balances are written for the urea concentration in the blood and in the total system (blood plus dialysate)

$$V_{\text{blood}} \frac{dC_{\text{blood}}}{dt} = -k_m A [C_{\text{blood}} - C_{\text{dialysate}}] \quad (9)$$

$$V_{\text{blood}} \frac{dC_{\text{blood}}}{dt} + V_{\text{dialysate}} \frac{dC_{\text{dialysate}}}{dt} = 0 \quad (10)$$

where we have assumed that the volumes of the blood and dialysate compartments remain constant during the dialysis. The system mass balance (Eq. 10) is directly integrated to develop an expression for $C_{\text{dialysate}}$ in terms of C_{blood} . If presented in class, it is helpful to ask the student what will happen at long times before actually solving the equations. Many students don't appreciate that the system will approach steady state with $C_{\text{blood}} = C_{\text{dialysate}}$. The steady-state solution can easily be developed by setting the derivatives equal to zero and solving the resulting algebraic equations. The full solution is

readily developed by integration of Eq. (9) to give

$$\ln \left[\frac{C_{\text{blood}}}{C_{\text{blood},0}} \left(1 + \frac{V_{\text{blood}}}{V_{\text{dialysate}}} \right) - \frac{V_{\text{blood}}}{V_{\text{dialysate}}} \right] = -k_m A t \left(\frac{1}{V_{\text{blood}}} + \frac{1}{V_{\text{dialysate}}} \right) \quad (11)$$

where $C_{\text{blood},0}$ is the urea concentration in the blood at the start of the dialysis. It is easy to show that Eq. (11) approaches the steady-state solution in the limit of $t \rightarrow \infty$ as required.

After analyzing the transient hemodialysis system, the students can think about why this isn't the way hemodialysis is actually performed clinically. Most students recognize the problem of having a large portion of the patient's blood outside of the body, and some will even appreciate the logistical challenge of insuring that the right blood is returned to the right patient. It thus becomes relatively easy to motivate the need for using a continuous-flow system for hemodialysis (bottom panel of Figure 2). A simple solution for this problem can be developed by assuming that the urea concentrations are at steady state and that the blood and dialysate solutions are both well-mixed. The steady-state assumption can often be confusing since the urea concentration in the patient's blood clearly decreases with time during the hemodialysis. But the time constant for concentration changes in the dialyzer is so much shorter than the time constant for the body due to the small extracorporeal volume, that it is appropriate to use this type of pseudo-

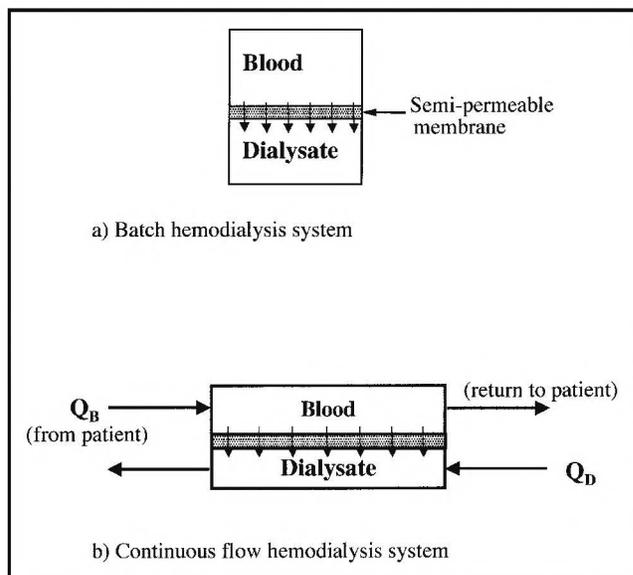


Figure 2. Hemodialysis systems for urea removal. Top panel shows a batch system; bottom panel shows continuous-flow process.

steady-state approximation. The final result is

$$\frac{C_{\text{Bout}}}{C_{\text{Bin}}} = \frac{Q_B \left(1 + \frac{k_m A}{Q_D} \right)}{Q_B \left(1 + \frac{k_m A}{Q_D} \right) + k_m A} \quad (12)$$

where C_{Bout} and C_{Bin} are the urea concentrations in the blood leaving and entering the dialyzer, and Q_B and Q_D are the blood and dialysate flow rates. More sophisticated solutions can be developed for countercurrent flow if the students are able to handle the concepts and mathematics required for analysis of the position-dependent differential mass balances in this system.^[8]

Although the well-mixed analysis provides a simple analytical expression, most students don't immediately appreciate the implications of the final result. For example, the analysis clearly shows that the outlet urea concentration in the blood doesn't go to zero as the membrane area becomes infinite. In addition, this equation seems to imply that increasing the blood flow rate is detrimental since it increases the urea concentration in the blood stream that is returned to the patient (although it also increases the rate of urea removal from the body). This leads nicely into a discussion of the key design criteria for the dialyzer.

It is also relatively easy to couple analysis of the hemodialyzer with the transient mass balances describing the urea concentration within the body (treated as a well-mixed "tank"). The resulting equations can be used to examine the performance of a clinical dialysis session at reducing the urea concentration to a safe level. Current clinical practice is for patients with complete kidney failure to undergo four-hour dialysis sessions three times a week, 52 weeks a year. The total cost of providing hemodialysis in the United States is approximately \$15 billion per year, essentially all of which is paid by the Federal government. This is a great opportunity for a discussion about some of the ethical and economic issues involved in the development and delivery of expensive new medical technologies, an issue that is likely to become even more important in the coming years.

Another hemodialysis design issue that can be worth discussing is the importance of minimizing the extracorporeal blood volume while maintaining a large surface area for mass transfer. Current clinical dialyzers use a parallel array of more than 10,000 narrow hollow fiber membranes (inner diameter of about 200 μm) to achieve a surface area of close to two square meters. Smaller diameter fibers, approaching the 6-8 μm diameter of the blood capillaries within the kidney, would further increase the ratio of surface area to blood volume. Blood clotting becomes a major problem in these very nar-

row fibers, however, even in the presence of a strong anti-coagulant like heparin. This leads nicely into a discussion of biomaterials and some of the issues involved in the development of truly biocompatible polymeric materials that still maintain the desired mechanical and mass transport characteristics needed for this type of biomedical device.

SUMMARY

The membrane problems described in this paper provide an attractive set of examples for introducing students to key concepts in the analysis of transient material balances in non-reacting systems. Related problems can also be developed for the analysis of gas separation membrane processes (*e.g.*, the production of oxygen from air) and on the behavior of membrane reactors (*e.g.*, the use of palladium membranes to remove hydrogen and thereby improve product yield in equilibrium-limited dehydrogenation reactions).

All of these membrane problems are of real commercial interest, they provide students some exposure to new application areas of chemical engineering, and they give the instructor an opportunity to introduce basic concepts of process design at a very early stage in the curriculum.

Student response to these problems in the Introduction to Chemical Engineering course at the University of Delaware has been outstanding. They definitely appreciate being able to analyze real-world problems even as freshmen, and they clearly enjoy the opportunity to begin thinking about process design issues. In addition, these membrane examples give students a perspective into the kinds of problems and processes that they will encounter throughout their undergraduate chemical engineering education.

REFERENCES

1. Solen, K.A., and J. Harb, "An Introductory ChE Course for First-Year Students," *Chem. Eng. Ed.*, **32**(1), 52 (1998)
2. Felder, R.M., and R.W. Rousseau, *Elementary Principles of Chemical Processes*, 3rd ed., John Wiley & Sons, Inc., New York, NY (2000)
3. Himmelblau, D.M., *Basic Principles and Calculations in Chemical Engineering*, 6th ed., Prentice Hall, Upper Saddle River, NJ (1996)
4. Russell, T.W.F., and M.M. Denn, *Introduction to Chemical Engineering Analysis*, John Wiley & Sons, Inc., New York, NY (1972)
5. Cheryan, M., and J. Alvarez, "Food and Beverage Industry Applications," in *Membrane Separations Technology: Principles and Applications*, R.D. Noble and S. A. Sterns, eds., Elsevier, Amsterdam (1995)
6. Glock, B.R., and J.J. Pasternak, *Molecular Biotechnology: Principles and Applications of Recombinant DNA*, 2nd ed., American Society for Microbiology Press, Washington, DC (1998)
7. van Reis, R., and A.L. Zydney, "Protein Ultrafiltration," in *Encyclopedia of Bioprocess Technology: Fermentation, Biocatalysis, and Bioseparation*, M.C. Flickinger and S.W. Drew, eds., pp 2197-2214, John Wiley & Sons, Inc., New York, NY (1999)
8. Galletti, P.M., C.K. Colton, and M.J. Lysaght, "Artificial Kidney," in *The Biomedical Engineering Handbook*, Vol. II, 2nd ed., J.D. Bronzino, ed., CRC Press, Boca Raton, FL (2000) □

A PRESS RO SYSTEM

An Interdisciplinary Reverse Osmosis Project for First-Year Engineering Students

S. SCOTT MOOR, EDMOND P. SALIKLIS, SCOTT R. HUMMEL, YIH-CHOUNG YU
Lafayette College • Easton, PA 18042

Attempting to create a project that includes chemical, civil, electrical, and mechanical engineering is a challenging task. At Lafayette College we try to include such a project in our Introduction to Engineering course. While finding electro-mechanical projects is relatively easy, it is difficult to include the process nature of chemical engineering in projects that are typically product oriented.

Among engineering programs that use an introduction-to-engineering course, a wide range of projects and laboratories is used. At the 2002 ASEE annual meeting, several mechanical or electro-mechanical projects were described, including a sundial, wind power for a ski resort public-transit system, and an orbital sander.^[1-3] At Rowan University, the Freshman Clinic provides a year-long lab experience with multidisciplinary experiments that use measurement as the theme.^[4,5] They use a wide range of approaches and projects, including reverse engineering, engineering analysis of the human body,^[6] and the production of beer.^[7] Recently, they included a project that involves using a membrane fuel cell to charge batteries for a LEGO® Mindstorms robot.^[8]

Many programs rotate through several different labs that illustrate different disciplines in order to include chemical engineering. At Notre Dame, a year-long introductory course uses four projects with the LEGO Mindstorms brick—control of pH is one of these four projects.^[9] North Carolina State uses a series of laboratories, one of which is a reverse osmosis experiment.^[10] At Virginia Tech several laboratories and projects are used with one laboratory being focused on a simple mass balance,^[11] while Drexel University's E⁴ program uses a laboratory focused on measurements to introduce students to engineering.^[12] The environmental engineering program at the University of Dayton uses a sand-and-charcoal filter where students analyze both the filtration process and

the support structure.^[13] In very few cases does one project include concepts from both chemical engineering and other branches of engineering.

For many years, C.S. Slater (Rowan University) has developed and advocated several reverse osmosis experiments based on PUR brand portable RO systems.^[15,14] Both the University of Minnesota at Duluth and Manhattan College have also developed laboratories based on the PUR systems.^[15,16]

We have developed a project based on a simple dead-end reverse osmosis (RO) test system at Lafayette College. The equipment consists of a cylindrical vessel with a small piston-and-lever arm used to create the pressure. Each discipline examines different issues with the device: in the chemi-

S. Scott Moor is Assistant Professor of Chemical Engineering at Lafayette College. He received a BS and MS in Chemical Engineering from M.I.T. in 1978. After a decade in industry he returned to academia at the University of California, Berkeley, where he received a PhD in Chemical Engineering and an MA in Statistics in 1995. His current research focuses on educational materials development and on the visualization of fluid and transport dynamics in Wurster coating, in fluidized beds, and in spray drying.

Edmond Saliklis is Assistant Professor in the Department of Civil and Environmental Engineering at Lafayette College. He received his BS from the University of Illinois-Chicago in 1984, his MS from Syracuse University in 1988, and his PhD from the University of Wisconsin-Madison in 1992, all in Civil Engineering. His current research focuses on the mechanics of thin wood-based plates and thin concrete and masonry shells.

Scott Hummel is Assistant Professor of Mechanical Engineering at Lafayette College. He earned a BS at the University of Hartford in 1988, an MS at Stevens Institute of Technology in 1996, and a PhD at Lehigh University in 1998. His current research focuses on the wear properties of nonlubricated stainless steel components and on the LENS rapid prototyping process.

Yih-Choung Yu is Assistant Professor of Electrical and Computer Engineering at Lafayette College. He received a BSEE degree from Chinese Culture University in Taipei, Taiwan, in 1987, an MSEE degree from the State University of New York at Binghamton in 1992, and a PhD degree from the University of Pittsburgh. His research interests include control applications for bioengineering and medical device development.

Membranes in ChE Education

cal engineering portion of the course, we study the theory and practice of reverse osmosis; in the civil engineering portion, the focus is on the hoop stresses in our cylindrical pressure vessel and the use of RO in water treating; in the mechanical engineering portion, students examine the mechanical advantage needed to create the necessary pressure for RO; and in the electrical engineering portion, students study and construct the circuit to monitor the strains on the surface of the vessel.

A MULTIDISCIPLINARY COURSE

The "Introduction to Engineering" course, where we use this project, is a complex interdisciplinary course. It consists of five segments, or blocks, covering 1) engineering economics and management, 2) chemical engineering, 3) civil engineering, 4) electrical and computer engineering, and 5) mechanical engineering. Figure 1 diagrams the structure of the course. Engineering economics and management are covered in the first and last weeks of the class. During the middle weeks of the term, students rotate through four three-week

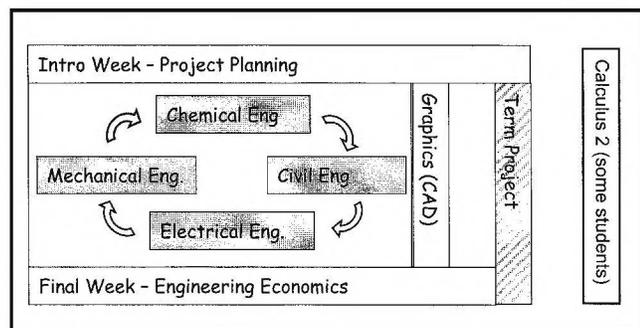


Figure 1. Structure of Introduction to Engineering course at Lafayette College.

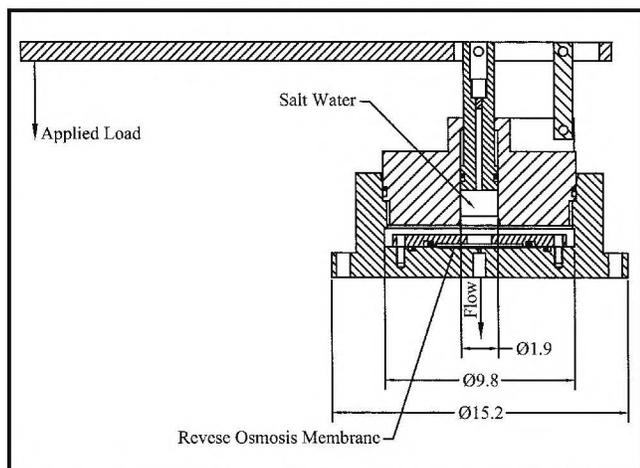


Figure 2. A cut-away view of the press RO system (dimensions are in cm).

blocks covering each of the main engineering disciplines. These blocks include both lecture and laboratory experiences. Concurrently throughout the term, students are learning computer-aided drafting (CAD) and working in teams on the RO project. One laboratory period in each disciplinary block is devoted to RO experiments.

The learning objectives are that upon completion of this course, students will have

- 1) An ability to apply engineering equations to solve a variety of practical engineering problems
- 2) An ability to design and conduct experiments as well as an ability to analyze, interpret, and document experimental data
- 3) An introduction to the various aspects of engineering design that include initial sizing or planning of a component or system, modeling, drawing, testing, cost-estimating, and redesigning the component or system
- 4) A firm introduction to engineering graphics and proper protocol on engineering drawings
- 5) An ability to function on multidisciplinary teams
- 6) Experience in communicating technical information
- 7) A knowledge of the engineering departments at Lafayette College and possible career tracks upon graduation

THE PRESS RO SYSTEM

Figure 2 is a diagram of the basic design of our system. An approximately 5-cm diameter membrane is held in the bottom of the device by a clamp ring with two O-rings for sealing. One O-ring seals the clamp ring to the bottom of the device and the other seals the clamp ring to the top of the membrane. There is a small chamber above the clamp ring that holds the salt water that we are purifying. A 1.9-cm diameter piston is used to pressurize the water reservoir with a lever arm to amplify the force applied. The small piston area combined with the lever arm produces a mechanical advantage of approximately 14 to 1. Weights are hung from the lever arm to apply a constant load. The product water flows out the bottom of the unit. The major components of the system are constructed of aluminum. The material cost is approximately \$35/unit. A picture of the ready-to-run press RO system is shown in Figure 3. While a cross-flow configuration is the norm for RO systems, we chose to use a dead-end system because of the engineering principles it allowed us to illustrate. This configuration allows us to create the necessary pressure using simple and understandable lever and hydraulic principles. The cylindrical shape of the pump allows for simple structural strain calculations.

The project addresses all of the course goals listed in the previous section. It is particularly important in addressing experimentation (goal 2), design (goal 3), working in multidisciplinary teams (goal 5), and communication (goal

Membranes in ChE Education

6). It also provides concrete examples of the application of each of the engineering disciplines (goal 7). It is hoped that the project will be interesting, enjoyable, and accessible to our first-year students.

CHEMICAL ENGINEERING BLOCK

This project provides a wealth of chemical engineering topics, including osmotic pressure, equilibrium, flux, rate based separation, and fluid processing. The general concepts of osmotic pressure and solution equilibrium are discussed. The van't Hoff equation is used to estimate osmotic pressure

$$\Pi = CRT \quad (1)$$

where Π is the osmotic pressure, C is the molar concentration of ions, R is the universal gas constant, and T is the absolute temperature. This equation assumes a dilute ideal solution that follows Raoult's law. For the solutions, we are using (0-14 g/l NaCl), the van't Hoff equation predicts 3-5% high and is adequate for our needs.^[17] Wankat presents the theory for more accurate estimations of osmotic pressure for other situations.^[18]

There is some disagreement on the exact mechanism for reverse osmosis, but the solution-diffusion theory is the most widely accepted.^[18,19] In this picture of membrane function, the membrane has no true pores. Rather, the membrane is treated as a separate phase. The solvent and solute dissolve in and diffuse through the membrane.

Students are then introduced to the concept of flux and its proportionality to driving force. We present the simplified case of the driving force as the pressure above osmotic. The resulting equation for flux is

$$J_w = \frac{q}{S} = A(\Delta P - \sigma \Delta \Pi) \quad (2)$$

where J_w is the volumetric flux of water through the membrane, q is the total flow through the membrane, A is the water permeability constant, σ is the Staverman coefficient, S is the membrane area, and ΔP is the applied pressure across the membrane.^[19] Assuming that the Staverman coefficient equals one in Eq. (2) implies that the solute is perfectly excluded. This is a simplification of the real case, but it is frequently used.^[5,17,18,20]

Equation (3) shows a simple and common model for the solute (salt) flux through the membrane under a concentration gradient:

$$J_s = B(C_{\text{feed}} - C_{\text{product}}) \quad (3)$$

where J_s is the molar flux of solvent, B is the salt permeability constant, and the driving force ($C_{\text{feed}} - C_{\text{product}}$) is the salt concentration difference across the membrane. Again, a more

complete version of the theory would include a second reflection coefficient.^[19] Using the first two equations, students are able to complete a design problem determining a pressure drop and membrane area that will meet a given purification need. For these simple first-pass sizing problems, we assume that the solute flux will be negligible.

The concepts behind these equations and their simplifications are explained to the students. We then ask them to evaluate how well these concepts (particularly the simplifications) are playing out in our experimental system. A short section in Perry's on reverse osmosis and nanofiltration provides some helpful conceptual background in a brief presentation.^[20] The issues considered include the nature of membranes, recovery, concentration polarization, pretreatment, rate-based separations, and cartridge configurations.

Concentration polarization is a particularly important issue. The salt concentration near the membrane is increased because salt is being transported to the membrane by bulk flow, but then it is being retained by the membrane. This increase in concentration near the membrane affects the osmotic pressure and the potential flux of solute. A mass diffusion model is required to estimate this effect.^[18,21-23]

Students experiment on the press RO system, examining the impact of pressure and salt concentration on the purified water flow rate. They determine the water permeability con-

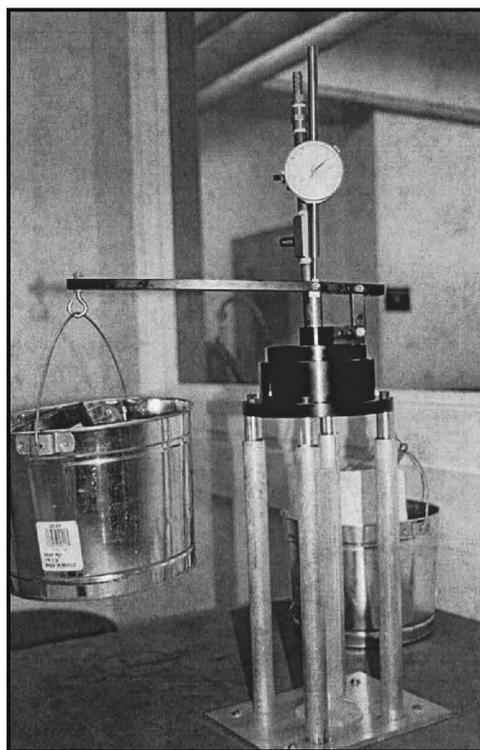


Figure 3. A press RO system ready to run.

stant in these experiments.

Figures 4 and 5 show experimental sets of data. The first series is a nice linear relationship—a reliable upper-class student assistant prepared this series. The second series, which is not so nicely linear, was the initial attempt of some first-year students. The difference in results arises from how carefully the apparatus was assembled and how consistently it was operated. The students soon realized that they must have disciplined laboratory procedures in order to get the best results. With a “good” set of data, such as the first series, it is possible to use the x-intercept to estimate the experimental osmotic pressure. For poor results such as those in the second series, the results of this extrapolation are too variable and the students must calculate the osmotic pressure, fix the x-intercept, and then simply estimate the slope of the line. This procedure yields reasonable results even for poor data. In both approaches, the slope is the water permeability constant, A .

The biggest weakness of these RO devices is their dead-end configuration and the likelihood of significant concentration polarization. In fact, plots of flux versus time show

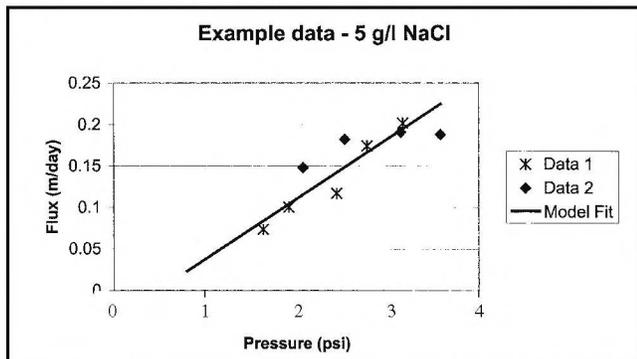


Figure 4. Example flux data for 5 g/l sodium chloride. An upper-class laboratory assistant took the data labeled data 1. An inexperienced first-year team took the data labeled data 2. See the text for an explanation of how the model fit line was generated.

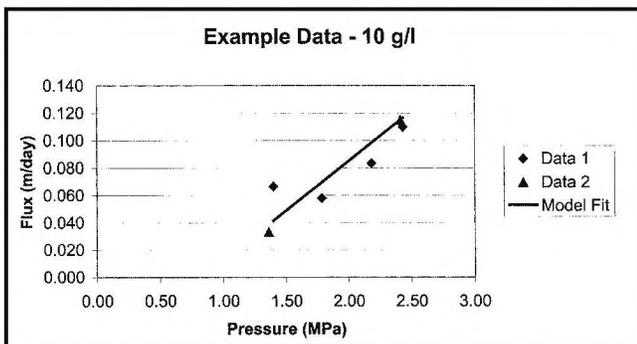


Figure 5. Example flux data for 10 g/l sodium chloride. The series labels have the same meaning as in Figure 4.

steadily decreasing flux rates throughout our experiments. To allow some standardization, students take flux data from 20 to 40 minutes during their experiments and calculate an average flux during this period. Students are also able to measure the conductivity of the salt solution before and after passing through the membrane. In our dead-end unit, a 75% reduction in salt concentration is typically achieved. This concentration reduction is substantial, but not perfect, and leads to a discussion of the rate-based nature of the RO separation. Finally, we can also address the practical issues of how membranes are implemented, including the use of cross-flow filtration and spiral-wound cartridges. Throughout, we provide practical examples of RO implementation, from emergency RO water purifiers^[24] to a new two-million-gallon per day RO desalination plant recently installed in Cape May, New Jersey.^[25]

CIVIL ENGINEERING BLOCK

Two civil engineering lab exercises familiarize the students with elementary pressure vessel design. The equation describing hoop stress for thick-walled pressure vessels is

$$\sigma_{\text{thick}} = \frac{p}{k^2 - 1} \left(1 + \frac{r_{\text{outer}}^2}{r^2} \right) \quad (4)$$

where σ_{thick} is the thick-walled hoop stress at any given radius, r is the specific radius, r_{inner} and r_{outer} are the inner and outer diameters respectively, p is the vessel internal pressure, and k is the ratio $r_{\text{outer}}/r_{\text{inner}}$. During the first lab, students program this equation in Mathematica[®] and perform parametric studies of the influence of changing wall thickness. They compare the results of the thick-walled equation to those of the simpler thin-walled equation

$$\sigma_{\text{thin}} = p \left(\frac{r_{\text{outer}}}{t} \right) \quad (5)$$

where σ_{thin} is the thin-walled hoop stress and t is the wall thickness. Finally, in the first lab they are given Hooke’s Law, which relates stress to strain.

In the second lab, the students are given the opportunity to quantify experimentally the strains on the outer surface of our RO system cylinder by means of strain gages. The outer diameter of several RO system cylinders has been reduced, creating vessels of several wall thicknesses. The students plot vessel pressure versus hoop strain. They then calculate the stress by means of the previously presented Hooke’s Law formulation and are thus able to compare theoretical strains to experimental strains.

Another exercise requires them to analyze the stress and the deflection in the lever arm of the pump. Experimental

Membranes in ChE Education

investigations of the bent arm are compared to theoretical predictions. This exercise provides an opportunity to discuss structural design strategies and specific design codes in general terms. Finally, one civil engineering lecture is devoted to hydrology. During this lecture, RO systems are discussed.

MECHANICAL ENGINEERING BLOCK

One of the mechanical design considerations of the reverse osmosis unit is generating a high pressure, 10 to 20 bar, across the membrane with a relatively low applied load, 5 to 10 kg, on the input handle. The design problem is solved through the use of a mechanical linkage and a piston-cylinder arrangement. This enables low forces applied to the piston to generate relatively large pressure inside the chamber. In addition, the piston is made part of a slider-crank mechanism to further increase the pressure inside the chamber for a given applied load. The pivot points of the mechanism are determined by the students as part of their design recommendations for the project. Students examine hydrostatics, lever arm mechanical advantage, and the use of a load cell to measure force.

ELECTRICAL ENGINEERING BLOCK

During the electrical engineering block, students use lab time to construct and experiment with a Wheatstone bridge to read the strain gauges used in the civil engineering block. Their lab experience includes bread boarding and calibrating a basic circuit. From their experiments and circuit analysis, they are expected to select appropriate resistance values for their bridge. In these labs they learn practical skills in constructing electrical circuits and are required to make some circuit design decisions. In lectures, students learn the basic circuit principles that allow them to understand how the circuit works.

ENGINEERING ECONOMICS AND MANAGEMENT BLOCK

During the first week of the term, students are introduced to some basic scheduling concepts and asked to apply them to planning their work on the project. They need to schedule experimentation, analysis, and report preparation. During the final week of the term they learn basic engineering economics and are given a problem to analyze on the economics of RO desalination.

USE IN A MATHEMATICS COURSE

In our apparatus, the volume pushed through the membrane is small relative to the total volume of salt water feed (less than 5%). This allows us to assume the concentration of salt is essentially constant. If, however, the volume change is allowed to be significant and the separation assumed to be perfect (*i.e.*, no salt passes the membrane), a mass balance yields the following interesting differential equation for flow through the membrane:

$$\frac{dx}{dt} = \phi A \left(\Delta P - \frac{C_0 V_0 RT}{V_0 - x} \right) \quad (6)$$

where x is the volume of pure water produced, C_0 is the initial concentration of the salt feed, and V_0 is the initial volume of salt solution in the device. This equation is complex but still separable. It is being used as an example problem in our Calculus 2 class. The basic differential equation and its derivation are presented in class, and students are asked to solve the equation analytically as a homework problem. Then they come to a computer lab session where they use Mathematica to explore

this differential equation and make some design trade-offs. This is part of an institutional effort to connect our calculus classes to applications in other courses. Students who have advanced placement in calculus are in this Calculus 2 class at the same time that they are taking Introduction to Engineering.

THE PROJECT

Groups of 4 to 5 students each work on the RO project throughout the semester in four phases. The first phase is an orientation to the project and reverse osmosis. The project nature, structure, and expectations are introduced. During the second phase, students carry out their first experiments with the press RO system. They learn assembly and operation of the pumps and complete an initial trial and data analysis. During the third phase, they learn how to install the membranes in their pumps and complete another set of trials. During this phase, each group runs a different condition and posts their data to the course website. The groups are expected to download and analyze the complete data set. From this data, students must determine what the flux coefficient is for the membrane they have been using.

The final phase of the project is a time for student-directed open-ended trials and design work. Students are expected to extend the work they have done so far. Many options are

A dead-end RO system provides the basis for a truly interdisciplinary project that provides a wealth of problems and examples for many different branches of engineering...it connect[s] a calculus course to the engineering curriculum.

Membranes in ChE Education

given for this extension: they can take additional data to answer questions arising from their earlier analysis; they can run experiments with a different membrane, different seals, or a different technique; they can vary the salt used. Students are asked to consider how they would improve the test apparatus.

In addition, each group is given a unique RO sizing problem. An example problem is

A small and exclusive island resort requires an improved water supply for the roughly 150 people who are there at any given time. The resort estimates it will need 30 gallons/person each day. There is a large brackish water supply on the island with a salt concentration of 13 g/l as NaCl.

Students are expected to use the water permeability constant that they determined from their experiments to calculate possible pressures and membrane areas. They are expected to consider the economic ramifications of their choices. In this simplified analysis, the operating costs are considered to be the cost of creating pressure. This cost is determined by calculating the energy required for pumping. We use the basic formula

$$\text{power} = \frac{\Delta P Q}{\eta} \quad (7)$$

to determine the power required. Students assume that they are using a cross-flow configuration and that they are able to recover the pressure energy of the waste stream. ΔP is the pressure increase across the pump, Q is the volumetric flow rate, η is the pump efficiency (we use 0.80), and power is the power required. The capital cost of the plant is considered to be a function of membrane area. Students are given the following scale-up formula to estimate the capital cost:

$$C = (4500\$ / \text{m}^{1.5}) A^{0.75} \quad (8)$$

where C is the estimated capital cost (in \$), and A is the membrane area (in m^2). In their economic sections they have been taught to calculate net present value and are expected to consider the optimum trade-off between capital and operating costs.

ASSESSMENT AND COMMENTS

The project was evaluated based on re-examining final project reports from half of the student groups involved in the class (16 out of 32 groups) and based on instructors' observations. Reports were re-examined with a particular focus on the students' demonstration of experimentation skills (goal 2) and design skills (goal 3). Throughout this analysis it is difficult to separate the project impact from the course as a whole.

The chance for students to experiment with the system

throughout the term was one of the strengths of this project. The final reports included an analysis of flux experiments at different concentrations and pressures, plus student-designed studies. In reviewing the final reports, 88% of the groups analyzed flux experiments completely and correctly. A review of the student-designed studies showed that 79% met our expectation of solid creative experiments that fit the time and equipment constraints. Students completed a wide range of additional experiments, including testing an alternative membrane; using calcium chloride instead of sodium chloride; examining variations in flux decline with time and concentration; studying an alternative clamping mechanism that has a longer back diffusion path; and examining hold-up volume by comparing piston stroke movement to volume collected.

Reports included two different engineering design sections: the specific RO sizing problem and suggested design improvements for the RO press. As pertains to the sizing problem, in 80% of the cases, the basic RO analysis was correct, but as we move to more advanced analysis, the number of student groups mastering the concepts drops off. The idea of an economic trade off between pressure and membrane area was clearly understood by 63% of the groups. A majority (56%) completed the expected economic estimates, but only a third included an analysis of the time value of money. All of the percentages were a bit lower than we had hoped.

The students' work on design improvements to the test pumps showed mixed results. In almost all cases (fourteen reports), the students had solid initial proposals for how to improve our apparatus, but the detailing of their designs was weak. In only five cases did the students complete detailed design calculations and make their designs specific. Suggested improvements included

- *Modifying the lever arm to reduce deflection (change the material and/or dimensions)*
- *Increasing the piston stroke to increase the volume of water pumped per stroke*
- *Implementing a cross-flow configuration*
- *Adding agitation to the system to reduce concentration polarization*
- *Adding additional instrumentation to the units*

This project was designed from the beginning to be multidisciplinary. Almost all student reports mention aspects from all four BS engineering disciplines. The instructors found that they needed each other's skills to design and understand this project. We freely pointed this out to the students.

CONCLUSION

A dead-end RO system provides the basis for a truly interdisciplinary project that provides a wealth of problems and

examples for many different branches of engineering. In addition, it is used to connect a calculus course to the engineering curriculum. The project provided a particularly good introduction to engineering experimentation. Student design work on the project was good, but could be strengthened—particularly in the details of full design calculations and economic analysis.

REFERENCES

- Johnson, R., and L. Anneberg, "Sundials Make Interesting Freshman Design Projects," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 2793 (2002)
- Soysal, O.A., "Project Based Learning of Energy Conversion Principles at Freshman Level," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 2533 (2002)
- Ochs, J.B., T.A. Watkins, and B.W. Boothe, "Cultivating an Entrepreneurial Spirit through Cross-Disciplinary Student Teams in Freshman Projects Course," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 3454 (2002)
- Hesketh, R.P., K. Jahan, A.J. Marchese, T.R. Chandrupatla, R.A. Dusseau, C.S. Slater, and J.L. Schmalzel, "Multidisciplinary Experimental Experiences in the Freshman Clinic at Rowan University," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 2326 (1997)
- Hesketh, R.P., and C.S. Slater, "Innovative and Economical Bench-Scale Process Engineering Experiments," *Int. J. Eng. Ed.*, **16**(4), 327 (2000)
- Farrell, S., R. Hesketh, K. Hollar, M. Savelski, C.S. Slater, R. Spect, "Don't Waste Your Breath," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 1613 (2002)
- Farrell, S., R.P. Hesketh, J.A. Newell, and C.S. Slater, "Introducing Freshmen to Reverse Process Engineering and Design through Investigation of the Brewing Process," *Int. J. Eng. Ed.*, **17**(6), 588 (2001)
- Hollar, K., F. Lau, L. Head, K. Jahan, E. Constans, P. von Lockette, and B. Pietrucha, "Bugbots! A Multidisciplinary Design Project for Engineering Students," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 2426 (2002)
- Brockman, J.B., T.E. Fuja, and S.M. Batill, "A Multidisciplinary Course Sequence for First-Year Engineering Students," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 2253 (2002)
- Beaudoin, D.L., and D.F. Ollis, "A Product and Process Engineering Laboratory for Freshmen," *J. Eng. Ed.*, **84**(3), 279 (1995)
- Connor, J.B., and J.C. Malzahn Kampe, "First-Year Engineering at Virginia Polytechnic Institute and State University: A Changing Approach," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 2553 (2002)
- Quinn, R.G., "E¹ Introductory Engineering Test, Design, and Simulation Laboratory," *J. Eng. Ed.*, **82**(4), 223 (1993)
- Safferman, S.I., M. Zoghi, and D.H. Farhey, "First-Year Civil and Environmental Engineering Design Experience," *J. Eng. Ed.*, **90**(4), 645 (2001)
- Slater, C.S., and J.D. Paccione, "A Reverse Osmosis System for an Advanced Separation Process Laboratory," *Chem. Eng. Ed.*, **22**, 138 (1987)
- Lodge, K.B., R.A. Davis, D. Dorland, and D.N. Baria, "Experiments in Waste Processing for Undergraduates," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 2513 (1997)
- Assif-Anid, N.M., and H. C. Hollein, "Incorporating Biotechnology in the Chemical Engineering Curriculum," *Proc. Conf. Amer. Soc. Eng. Ed.*, Session 2276 (2002)
- Baker, R.W., E.L. Cussler, W. Eykamp, W.J. Koros, R.L. Riley, and H. Strathman, *Membrane Separation Systems: Research and Development Needs Assessment, Final Report*, Contract Number DE-AC01-88ER30133, U.S. Department of Energy (1990)
- Wankat, P.C., "Membranes," Part III in *Rate Controlled Separations*, Klauer, Amsterdam (1990)
- Cussler, E.L., "Membranes," Chapter 17 in *Diffusion: Mass Transfer in Fluid Systems*, 2nd ed., Cambridge University Press (1997)
- Eykamp, W., "Reverse Osmosis and Nanofiltration," in *Perry's Chemical Engineers' Handbook*, 7th ed., R.H. Perry, D.W. Green, and J.O. Maloney, eds., pp. 22-48 thru 22-52, McGraw-Hill (1997)
- McCabe, W.L., J.C. Smith, and P. Harriott, "Membrane Separation Processes," Chapter 26 in *Unit Operations of Chemical Engineering*, 6th ed., McGraw-Hill, 857 (2001)
- Mahlab, D., N. Ben Joseph, and G. Belfort, "Interferometric Measurement of Concentration Polarization Profile for Dissolved Species in Unstirred Batch Hyperfiltration (Reverse Osmosis)," *Chem. Eng. Comm.*, **6**, 225 (1980)
- Ho, W.S.W., and K.K. Sirkar, *Membrane Handbook*, Van Nostrand Reinhold (1992)
- Proctor & Gamble, *PUR Survivor 06*, at http://www.purwater.com/L3_mar_end_06.shtml, retrieved 7/2002
- Avedissian, E., *Cap May's Desalination Plant's No Albatross!*, at <http://www.capemay.com/Desalination.html>, retrieved 7/2002 □

ChE book review

Modeling of Chemical Kinetics and Reactor Design

by A. Kayode Coker

2nd edition; 1095 pages plus CD-ROM; US \$195. ISBN 0-88415-481-5 (2001)

Published by Butterworth-Heinemann, 225 Wildwood Avenue,

This book is intended as a reference volume by the author. Educators will find the book useful for several topics that are not covered by textbooks or other reference volumes.

In addition to standard chapters on residence time distribution and reactor models for non-ideal flow, there is an extensive chapter (91 pages) on mixing in tanks, mix-

ing by static elements, and heat transfer in agitated tanks.

There is also a chapter (47 pages) that introduces the use of computational fluid dynamic simulators for studying mixing and flow in reactors. That chapter discusses examples of mixing and reaction in a stirred tank and flow in a radial flow catalyst bed. On the CD, there are beautiful and informative color images of transient mixing and

reaction of a competitive-consecutive reaction in a stirred tank.

Other chapters in the book, which aren't covered or are covered only briefly by other books, include a chapter (80 pages) on biochemical reactions and reactors. There is an extensive chapter (134 pages) on safety, including descriptions of calorimeters used to characterize reactions, calculations of vent sizes, and a brief discussion of HAZOP analysis. Scale-up of reactors is considered in a chapter (47 pages) that discusses the use of dimensional similitude in combination with reactor models.

Another strong point of the book is the numerous examples that are worked in detail. Many of these example problems are supplemented by Excel spreadsheets and computer programs on the CD.

The CD also has a unit conversion program and PDF files with explanations of numerical methods and a cross-reference between examples in the book and supporting material on the CD. Source code (Fortran 77) for all of the software programs on the CD is included along with the executables. Unfortunately, temporary files produced during compilation (object, make, compiler interface) are also included, which (in addition to the lack of sub-folders in each chapter's folder) makes finding the file needed to run the program harder than necessary. A DOS program is available for calculating heats of reaction at reaction temperature with input of stoichiometry, standard heats of formation, and heat capacity formula coefficients.

Other programs are Windows double-clickable executables that display text output in the output window and write output files to disk. A recommendation for future editions is to change the file extensions to ".txt" from those used for the input ("dat") and output ("res") so that they can be accessed easily by double-clicking.

There are several topics that are not covered by the book. Other than brief mention and sketches in a chapter mentioning types of reactors, there is nothing on multiple-phase reaction systems. There is nothing on reaction-diffusion in porous catalysts or non-catalytic solids. There is brief discussion on pressure drop but none on the effect of pressure drop of gases on reaction rate. There are a couple brief discussions of selectivity and yield in two-reaction systems, but nothing on more complex multiple-reaction systems. The thermodynamics section would benefit from a worked example on reaction equilibrium composition. There are no end-of-chapter problems that can be used for student assignments.

Other chapters in the book cover standard material such as reaction mechanisms, analysis of kinetic data, design and comparison of the "ideal" reactor types, thermal effects, and residence time distribution.

Richard K. Herz

*Chemical Engineering Program and
Mechanical & Aerospace Eng. Dept.
University of California, San Diego*

ChE *letter to the editor*

To the Editor:

Reference is made to the article by Ang and Braatz, "Experimental Projects for the Process Control Laboratory" [CEE, 36(3), p. 182, 2002]. The exercise that has to do with "dye concentration" can also be done with the control of a hot-water stream instead of a dye stream flowing into the tank. Just as a colorimeter indicates the amount of dye stream, so too can thermocoupling indicate the amount of hot-water stream; otherwise the experimental apparatus would be the same.

We find a convenience in not needing to deal with a dye stream disposal problem at the "Drain" indicated in their figure. Our water stream is collected and reused.

Dale L. Schruben
Texas A&M Kingsville

Author's Response

We agree that control of temperature using a hot-water stream is safe, with no waste disposal issues—which is why this is used in many control apparatuses (e.g., as in apparatuses 5, 7, and 10 described in the article). An advantage of the dye concentration control experiment is that students can directly visualize the open- and closed-loop dynamics and the extent of nonideal mixing, as they observe the color changes in the tank.

Before constructing any apparatus, Materials Safety Data Sheets should be consulted for safety and disposal considerations for all chemicals that are intended for use in the experiments. The instructional value of a particular apparatus with particular chemicals should be weighed against capital and operating costs and any safety or disposal issues. There are many internet resources for viewing MSDSs (e.g., see <<http://www.ilpi.com/msds/#Internet>>).

Richard D. Braatz
University of Illinois

A COMPENDIUM OF OPEN-ENDED MEMBRANE PROBLEMS IN THE CURRICULUM

G. GLENN LIPSCOMB

University of Toledo • Toledo, OH 43606-3390

Membrane separation processes have infiltrated both the academic and industrial worlds. Commercial successes have engendered a wealth of research activity and collaboration on projects ranging from nitrogen production to hemodialysis. Coverage of membrane topics in the undergraduate curriculum has lagged, however, as authors and educators wait to see if membrane processes are “for real.”

In this paper we present three design projects that have been used in chemical engineering classes to introduce membrane processes. The first project requires students to specify a treatment plan for individuals undergoing hemodialysis. The second and third projects highlight the manufacturing process used to produce hollow fiber membranes. One requires the design of a water distribution system for spinline quench baths, while the other seeks to recover solvent from the dilute, aqueous waste stream produced by the process. These projects do not require extensive knowledge of membrane transport phenomena, modules, or processes, but they do require application of fundamental chemical engineering principles for design purposes while simultaneously providing an introduction to the manufacture and use of membranes.

Project 1

Hemodialysis Treatment (Mass and Energy Balances)

This design problem, given to freshmen and sophomores in mass and energy balances classes, builds upon the hemodialysis problem in Felder and Rousseau.^[1] Instructors might encourage students to look up the dialysis process on the equipment CD that accompanies Felder and Rousseau or in the *Membrane Handbook*.^[2] Hemodialysis replaces kidney function for individuals who have experienced total or partial kidney failure. The preferred treatment is a kidney trans-

plant, but hemodialysis (or other replacement therapy such as peritoneal dialysis) is required when a donor is not available or the failure is expected to be temporary.

Hemodialysis only partially replaces kidney function. The primary goals are removal of cell metabolism waste products and maintenance of the body's water balance. Typically, three times per week a patient will spend three to four hours in a clinic connected to a dialysis machine. Blood is taken from the patient and passed through an artificial kidney (hemodialyzer) where water and wastes are removed before being returned to the patient.

Within the hemodialyzer, the patient's blood flows through the lumen of 10,000 to 15,000 hollow fiber membranes while simultaneously dialysate is pumped around the exterior of the fibers. The dialysate serves as a reservoir for accumulation of metabolism wastes as they diffuse across the porous fiber wall. The incoming dialysate stream possesses a composition similar to blood plasma, excluding the wastes, to minimize loss of electrolytes and other low molecular weight plasma components. Large components such as red blood cells and albumin cannot diffuse or flow across the wall because the pores are too small.

For the design problem, students are asked to specify a treatment schedule (the time required for treatment, t_d , and the time interval between treatments, t_b) for a patient weighing

G. Glenn Lipscomb is Professor of Chemical and Environmental Engineering at the University of Toledo. After graduating from the University of California at Berkeley, he worked for three years in Dow Chemical's Western Division Applied Science and Technology Laboratory in Walnut Creek, CA. He was part of the team that developed Dow's second-generation oxygen/nitrogen membrane separation system. His research interests lie primarily in module design and membrane formation.



Membranes in ChE Education

135 lb_m. They are given the above background information on kidney function, hollow fiber hemodialyzers, and the dialysis process. They are also given the following information for the specific hemodialyzers and treatment processes they are to consider:

- During treatment, blood and dialysate flow rates are held constant
- The inlet blood flow rate equals the outlet blood flow rate
- Blood cannot be withdrawn from the body at a rate greater than 400 ml/min
- Dialysate cannot be introduced into the artificial kidney at a rate greater than 800 ml/min
- The available artificial kidneys possess 1 m² of membrane area and a mass transfer coefficient of 0.010 cm/min

To simplify the analysis, urea is taken as a model waste solute—the only one for which mass balances are required to determine dialysis efficacy. Urea is produced by the body at a rate roughly given by $r = 0.11 * M$ g/day, where M is the body mass in kilograms.^[3] The goal of treatment is to keep urea levels below 3 g/L—normal concentrations are approximately 0.5 g/L.

Students are instructed to treat urea-containing fluid within the body like fluid within a single, well-stirred tank (CSTR). The fluid volume in liters is related to mass by $V = 0.58 * M$.^[3] They are also encouraged to consider what happens when a patient is undergoing therapy (Figure 1 shows a schematic of the treatment process) separately from what happens between treatments. During treatment, urea is removed (students are told to neglect urea generation during treatment) while urea is produced by the body between treatments. Finally, students are given the following equation to describe the performance of the hemodialyzer:^[2]

$$Q_b(c_b - c_{b,o}) = Q_b c_b \left\{ \frac{1 - \exp[-N(1-Z)]}{1 - Z \exp[-N(1-Z)]} \right\} \quad (1)$$

where Q_b is the blood flow rate, c_b is the inlet blood urea concentration, $c_{b,o}$ is the outlet concentration, $N = (kA)/Q_b$,

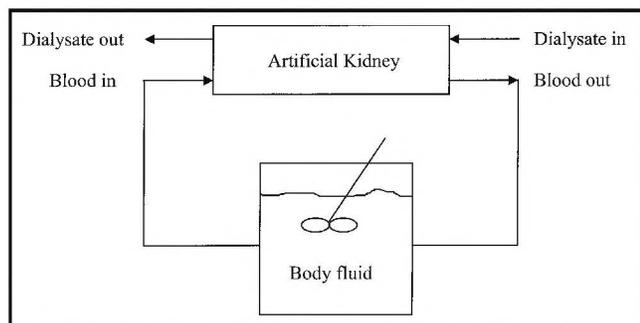


Figure 1. Schematic of hemodialysis treatment process.

$Z = Q_b/Q_d$, k is the mass transfer coefficient, A is the membrane area in the module, and Q_d is the dialysate flow rate. Equation (1) provides the relationship between c_b and $c_{b,o}$ in terms of membrane properties and process conditions that is required in mass balances.

The analysis requires application of transient mass balances.

These projects do not require extensive knowledge of membrane transport phenomena, modules, or processes, but they do require application of fundamental chemical engineering principles for design purposes . . .

A urea mass balance around the body (tank) during the treatment time leads to the differential equation

$$\frac{d(c_b V)}{dt} = Q_b(c_{b,o} - c_b) \quad (2)$$

where c_b is the blood urea concentration leaving the body (which equals the concentration entering the hemodialyzer), V is the urea distribution volume of the body (body fluid volume), Q_b is the rate at which blood is withdrawn from the body (which equals the rate it enters the artificial kidney), and $c_{b,o}$ is the blood urea concentration entering the body (which equals the concentration leaving the hemodialyzer).

Assuming k , A , Q_b , Q_d , and V do not change with time, substituting Eq. (1) into Eq. (2) gives a differential equation that can be readily integrated to give

$$c_b = c_{b,d} \exp(-t / \tau) \quad (3)$$

where $c_{b,d}$ is the blood concentration at the beginning of treatment and τ is given by

$$\tau = \left(\frac{V}{Q_b} \right) \left\{ \frac{1 - Z \exp[-N(1-Z)]}{1 - \exp[-N(1-Z)]} \right\} \quad (4)$$

In between dialysis treatments, the material balance for urea in the body is given by

$$\frac{d(c_b V)}{dt} = r \quad (5)$$

which one can readily integrate, assuming r is constant, to give

$$c_b - c_{b,b} = \frac{rt}{V} \quad (6)$$

where $c_{b,b}$ is the blood concentration at the beginning of the period between treatments. Therefore, the design equations

Membranes in ChE Education

that relate concentration to treatment time, t_d , and time between treatments, t_b , are

$$c_{b,b} = c_{b,d} \exp(-t_d / \tau) \quad (7)$$

$$c_{b,d} = c_{b,b} + rt_b / V \quad (8)$$

Given values for M , kA , Q_b , and Q_d , these two equations involve four unknowns: $c_{b,b}$, $c_{b,d}$, t_d , and t_b . Therefore, one must specify two more variables before the problem is fully specified and the remaining dependent variables can be calculated. A spreadsheet can be used to rapidly solve the equations for a range of values for each variable. A typical solution is illustrated in Figure 2.

With this analysis, students are asked to answer the following questions:

- How long should each dialysis treatment last?
- What are the desired flow rates of blood and dialysate?
- What is the body fluid urea concentration at the beginning of treatment? At the end of treatment?
- How much dialysate is used during each treatment?
- How long can a person wait between treatments? Specify a practical treatment schedule; for example, it is not practical for a patient to visit the clinic every 2.3 days, so patients typically are scheduled at the same time on specific days during the week.
- Is the assumption of no urea generation during dialysis a good one?

Students are encouraged to minimize the time required for each treatment (to reduce treatment costs and improve patient well being), maximize the time between treatments (also to reduce treatment costs and improve patient well being), and minimize the amount of dialysate used (to reduce dialysate costs). One cannot achieve all of these goals simultaneously!

Past experiences with this problem have been positive. The subject intrigues students—the problem also challenges them. The challenge comes not from the mathematics involved but from setting up the equations from the problem statement and identifying the constants, independent variables, and dependent variables in each. This is often their first experience with an unstructured, open-ended design problem—one that requires arbitrarily specifying some variables to calculate others and to synthesize a solution from information presented not in order of use and in a variety of unit systems.

Additionally, the problem involves processes and concepts that may not be familiar to them. With a little guidance and encouragement, though, they can obtain a solution. The primary negative feedback is that the students didn't want to

work in groups and be assigned a group grade despite attempts to address these issues using approaches described in the literature.^[4] We believe such criticism is common to group projects in classes across the curriculum and is not related to the membrane content of the problem.

Project 2

Hollow Fiber Spinning Plant Water Distribution System Design (Fluid Mechanics)

Polymeric membranes in the form of fine hollow fibers are used almost exclusively to form modules for gas separations and hemodialysis. The fibers are produced in a spinning process similar to that used to produce textile and structural fibers.

In this process, the polymer is mixed with one or more solvents to form a “spin dope.” The spin dope is pumped through a spinneret to form a hollow liquid cylinder; a single extruder may feed multiple spinnerets while a single spinneret may produce from 10 to over 100 filaments. A second liquid or gas stream is fed to the spinneret to fill the cylinders and keep them from collapsing. The filaments pass through an air gap (“draw zone”) and then one or more liquid baths (“quench baths”) to induce a desired wall structure and extract solvent. The most commonly used liquid is water. The filaments produced by a single spinneret travel through the process in a group referred to as a “tow.” Figure 3 illustrates the process.

The membranes produced by this process commonly possess a porous wall in which pore size depends on position in the wall. Typically, the smallest pores are adjacent to one wall

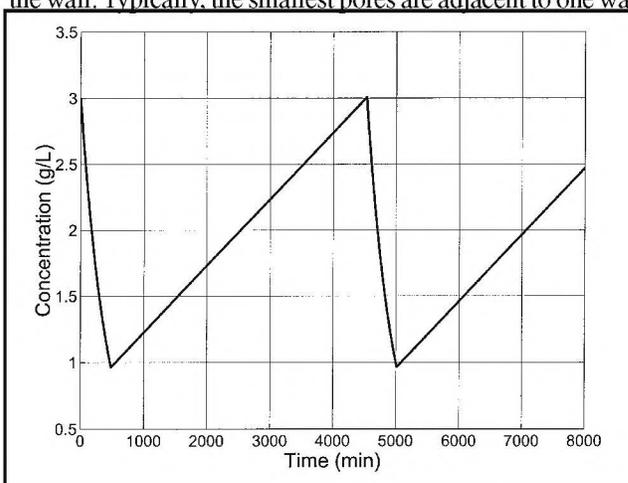


Figure 2. Urea concentration changes during treatment and between treatments for $Q_b = 400$ ml/min, $Q_d = 800$ ml/min, $c_{b,d} = 1.5$ g/L, and $t_d = 240$ min. For these conditions, $c_{b,b} = 0.85$ g/L and $t_b = 4900$ min (3.4 days).

Membranes in ChE Education

and the largest adjacent to the other wall. Fibers range in size from approximately 100 to 400 microns outer diameter and 75 to 300 microns inner diameter, while pore sizes range from Angstroms (molecular size) to microns.

Students in fluid mechanics classes were asked to design a water distribution system for the water baths. The circulation loop contains an adsorption column to remove solvent since

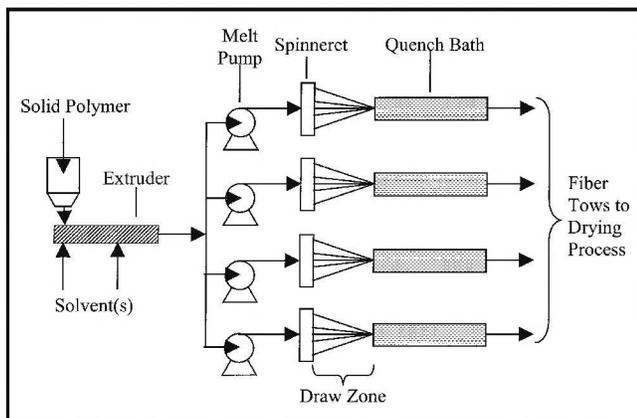


Figure 3. Schematic of a typical fiber spinning plant with a single quench bath.

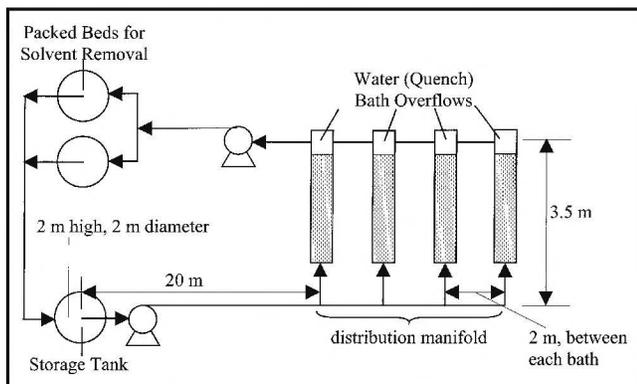


Figure 4. Water distribution system in a fiber spinning plant.

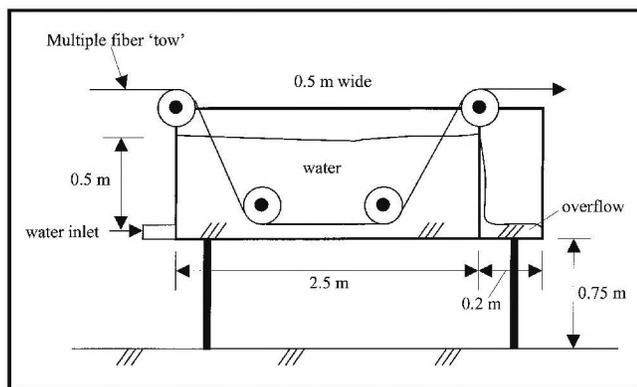


Figure 5. Bath schematic.

the solvent concentration in the baths must be kept below some critical level to produce “good” fiber. Figure 4 illustrates the water distribution system, while Figure 5 illustrates the dimensions of each water bath.

For the analysis, a range of water flows was specified that would ensure the solvent concentration remains below the maximum allowable value. Simplified packed bed performance and design guidelines were given for sizing purposes. Additionally, constraints on the piping, pumps, pump location, and the storage tank were specified. These are summarized in Table 1.

The students were asked to provide

- A piping diagram
- Pump placement and horsepower
- Packed bed dimensions and packing requirements
- An inventory of required equipment

The analysis consists primarily of application of macroscopic momentum balances (*i.e.*, the Bernoulli equation), basic pump sizing principles, and mass balances. The equipment inventory for a typical design is provided in Table 2 (next page).

Student response to the problem was positive. Unsolicited

TABLE 1

Design Constraints for Water Distribution System

- Water flow rates range from 1 - 2 m³/hr and solvent concentration cannot exceed 1% by weight.
- Centrifugal pumps are available in integral horsepower ratings from 1 to 10 hp and increments of 5 hp above 10 hp. Assume 80% efficiency and NPSH = 2 m.
- Use 12-gauge stainless steel tubing and at most two sizes: one for the supply and one for the return.
- Minimum working distance between pump and tank is 0.5 m.
- Neglect pressure changes in the distribution manifold.
- Account for entrance and exit losses for all tanks.
- All fitting losses may be approximated by an increase in the required straight pipe length of 10% except for the specific ones mentioned above.
- The water stream is always near 25°C.
- The viscosity and density of the water stream do not change until the solvent concentration exceeds 10%.
- The packed beds are mounted vertically and flow is upward. The bottom of each bed is 0.5 m off the ground. The stream exiting from the packed bed empties into the top of the storage tanks.
- Packing is 1-cm diameter spheres ($\rho = 2000 \text{ kg/m}^3$), bed void fraction ranges from 0.45 to 0.55, packing adsorbs 1 kg solvent/kg packing, and exiting water stream is solvent free until packing is saturated.
- Cylindrical beds are available in 0.5 m, 1 m, 1.5 m, and 2 m diameters. Use an aspect ratio of 3.

Membranes in ChE Education

comments on course evaluation forms included “I liked the group project” and “The design project was a good idea except for the whole group work thing.” As with the previous problem, students were not comfortable working in groups despite attempts to address their concerns.

Project 3

Hollow Fiber Spinning Plant Solvent Recovery (Senior Design)

In the senior design class, students were asked to design a separation system to recover solvent from the water leaving the quench baths for recycle within the process. The economics of membrane manufacture can be very sensitive to solvent losses and environmental costs associated with waste disposal. Consequently, this problem might be used as a pollution prevention example in the design course.

The spinning process for this problem is illustrated in Figure 6. The primary difference between this process and the process illustrated in Figure 3 is that two quench baths in series are used to remove the solvent. Students were given essential process specifications (see Table 3) and asked to design the recovery process. A fiber spinning process with similar characteristics is described in the patent literature.^[5]

Each student group had to provide the following design information:

- What is the required makeup water flow rate for each bath? At what rate is water removed from each bath for treatment?
- What are the design specifications for each unit operation in the solvent recovery process?
- Provide a complete PFD for the process, including a table of stream and unit operation properties.
- Estimate process costs and compare to the cost of simply returning the wastewater to the city sewer system at a concentration of less than 0.1 weight percent organics.

As one might expect, most groups considered distillation processes. Common process simulators (e.g., ChemCAD) can be used for the design of individual columns and column trains. Consideration of other unit operations such as reverse osmosis, pervaporation, or adsorption requires hand calculations and contact with potential vendors.

The separation process design is complicated by the tight requirements on the water effluent from the first bath—total solvent concentration less than 1% by weight. For the given process specifications, a minimum of approximately 120 lb_m/min of water

TABLE 2
Typical Equipment Inventory for Water Distribution System

- 5-hp centrifugal pump (160 psig discharge) for water supply to baths from storage tank
- 6-hp centrifugal pump (210 psig discharge) for water return to storage tank from baths
- 230 ft 7/8 in OD 12-gauge stainless steel tubing
- Four stainless steel 7/8-in tees
- Ten globe valves
- Two vessels (1m x 3m) for packed beds
- 2 m³ packing for packed beds
- One vessel (2m x 2m) for the storage tank (illustrated in Figure 4)
- Four water baths (illustrated in Figure 5)

TABLE 3
Fiber Spinning Process Specifications

- The spin dope consists of 32.5 weight percent N-methyl pyrrolidone (C₄H₉NO), 15.5 weight percent ethylene glycol, and the balance polycarbonate.
- The spin dope is extruded at a rate of 5 lb_m/min. This is fed to three spinnerets that each produce 60 fibers.
- The 180 liquid filaments enter into a water bath maintained at 5°C and spend approximately 5 seconds in the bath.
- Upon exiting from the first bath, approximately 65% of the ethylene glycol is removed and 45% of the N-methyl pyrrolidone. An equal volume of water replaces the organic solvents.
- The total solvent composition of the first bath must be kept below one weight percent.
- The fiber enters a second bath maintained at a temperature of 85°C and spends approximately 10 minutes in the bath.
- Upon exiting from the second bath, virtually all of the organic solvents have been removed and replaced by an equal volume of water.
- The total solvent composition of the second bath must be kept below 10 weight percent.
- Makeup water for the baths comes from city water lines but must be distilled to purify it.
- Makeup water should be returned at the temperature of the bath. However, you do not have to provide temperature control for either bath.
- To reuse the solvents, the water content must be less than one weight percent.

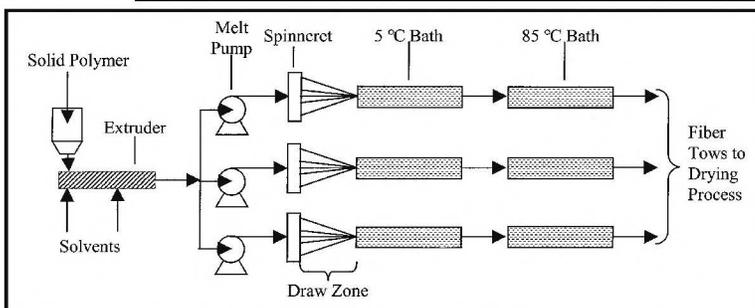


Figure 6. Schematic of a typical fiber spinning plant with two quench baths.

Membranes in ChE Education

must be fed to the first bath. Some of the effluent from the first bath can be used as the feed water to the second, but the water flow through the second bath is an order of magnitude less (about 12 lb_m/min), so most of the dilute effluent from the first bath must be sent to the separation process.

One can recover solvent from the combined bath effluents at sufficiently high purity (less than 1 weight percent water) to permit reuse with a single modest column (five stages and reflux ratio of 2). Water recovery to permit reuse in the first bath is more problematic. Large columns with high reflux ratios are required to increase water purity above 99%, the maximum allowed concentration of the effluent from the first bath; use of multiple columns is undesirable since water (the highest concentration component) goes overhead in each column. Therefore, most designs send some water to waste treatment and replace it with fresh water. The trade-offs between the cost of water disposal, cost of solvent lost in the wastewater, and column energy and capital costs dictate the final design. Instructors may use cost information from standard design texts (e.g., Turton, *et al.*^[6]) to evaluate the trade-off. Other configurations that students have considered include sending the effluent from each bath to separate columns and sending only the effluent from the second bath (with the highest solvent concentration) to a column. In the latter configuration, all of the effluent from the first bath is sent to waste treatment.

CONCLUSIONS

Three design problems that illustrate hollow fiber membrane manufacturing processes and use of membranes in separation processes are described. The problems have been used in classes that range from the freshman/sophomore to senior years in the curriculum. These problems are unique in their emphasis on membrane manufacture. Upon request, detailed problem statements and sample solutions can be provided.

REFERENCES

1. Felder, R.M., and R.W. Rousseau, *Elementary Principles of Chemical Processes*, 3rd ed., John Wiley & Sons, New York, NY (2000)
2. Kessler, S.B., and E. Klein, "Dialysis," in *Membrane Handbook*, W.S. Ho and K.K. Sirkar, eds., Van Nostrand Reinhold, New York NY (1992)
3. Galletti, P.M., C.K. Colton, and M.J. Lysaght, "Artificial Kidney," in *The Biomedical Engineering Handbook*, J.D. Bronzino, ed., CRC Press, Boca Raton, FL (1995)
4. Felder, R.M., and R. Brent, "Cooperative Learning in Technical Courses: Procedures, Pitfalls, and Payoffs," ERIC Document Reproduction Service, ED 377038 (1994) Available on-line at <<http://www2.ncsu.edu/unity/lockers/users/f/felder/public/Papers/Coopreport.html>>
5. Sanders, E.S., D.O. Clark, J.A. Jensvold, H.N. Beck, G.G. Lipscomb, and F.L. Coan, Process for Preparing POWADIR Membranes from Tetrahlobisphenol A Polycarbonates, US Patent 4,772,392, issued Sept. 20, 1988.
6. Turton, R., R.C. Bailie, W.B. Whiting, and J.A. Shaeiwitz, *Analysis, Synthesis, and Design of Chemical Processes*, Prentice Hall, Upper Saddle River, NJ (1998) □

ChE stirred pots

After reading David Lindley's book *Boltzmann's Atom*, Professor Robert R. Hudgins (University of Waterloo) was inspired to pen his thoughts on two subjects very familiar to chemical engineers. He shares those thoughts here...

Ludwig Boltzmann's Disorder

Herr Doktor Boltzmann has a vision rare
Of gases as a flight of tiny balls
In random 3-D motion that would dare
Allow him to explain their force on walls.

Ernst Mach insists that physics must be strict
And not be mocked, since atoms are not real.
Observables alone cannot be tricked;
Thereby, vague theories shall be brought to heel.

But Boltzmann's disarray achieves a feat—
Bold inferences drawn from how atoms fly.
He reinterprets what is meant by heat,
And temperature and pressure by the bye.

At length, chaotic motion proves its worth,
As entropy's conceived and has its birth.

Gibbs' Phase Rule

J. Willard Gibbs, the pedant in this tale,
Reflecting on an elemental state
Of matter at his alma mater, Yale,
Took to his books and never sought a mate.

In love with equilibrium he stayed
(No doubt both metaphorical and real).
When do P phases coexist? He played
With arguments with consecrated zeal.

As countrymen pursued uncivil war
'Round F degrees of freedom for their slaves,
Gibbs solved, with C components of savoir,
A theorem that, when understood, draws raves.

Robust and brief ('twould make a fine tattoo),
Proclaims **F equals C less P plus two.**

EXPLORING THE POTENTIAL OF ELECTRODIALYSIS

STEPHANIE FARRELL, ROBERT P. HESKETH, C. STEWART SLATER
Rowan University • Glassboro, NJ 08028

Electrodialysis is an electrochemical membrane separation technique for ionic solutions that has been used in industry for several decades.^[1] It can be used in the separation and concentration of salts, acids, and bases from aqueous solutions, the separation of monovalent ions from multivalent ions, and the separation of ionic compounds from uncharged molecules. It can be used for either electrolyte reduction in feed streams or recovery of ions from dilute streams.^[2-4] Industrial applications encompass several industries and include the production of potable water from brackish water, removal of metals from wastewater, demineralization of whey, deacidification of fruit juices, and the removal of organic acids from fermentation broth.^[1,2-5] Additional examples of the applications of electrodialysis are given in Table 1.

As a selective transport technique, electrodialysis uses an ion-selective membrane as a physical barrier through which ions are transported away from a feed solution. An energy-intensive phase change is unnecessary, in contrast to the common separation techniques of distillation and freezing.^[6] The use of an organic solvent, as is often required with other selective transport techniques such as liquid extraction, is avoided with electrodialysis. In addition, electrodialysis is typically performed under mild temperature conditions, making it particularly attractive for food, beverage, and pharmaceutical applications that deal with heat labile substances.

In typical chemical engineering undergraduate curricula, students are exposed to traditional separations methods with a heavy emphasis on operations such as distillation, extraction, and absorption. The need for incorporation of membrane technology into the chemical engineering curriculum has attracted recent attention.^[7-9]

The membrane separation processes mentioned above employ “traditional” driving forces such as concentration and

pressure gradients, in contrast to electrodialysis, which uses electrical potential to drive the separation. The first treatment of electrodialysis in the educational literature appeared in 1931.^[10] In this work, Kendall and Gebauer-Fuelnegg present three reasons why electrodialysis remains among the “neglected methods” of organic chemistry: 1) its treatment in textbooks is inadequate, 2) its advantages and applicability are not generally recognized, and 3) simple and efficient types of electrodialyzers are not generally available. While bench-scale electrodialysis equipment is now readily available from various manufacturers, electrodialysis is not commonly addressed in chemical engineering curricula, due primarily to the first two reasons presented above. Several reference books include excellent treatment of electrodialysis theory and applications,^[1,3-5,11] but this material is not easily “distilled” into material that can be introduced in the undergraduate classroom or laboratory, particularly if the professor has limited experience with membrane separations.

Increasing interest in electrochemical education is reflected by recent publications that address electrochemical reactors for synthesis and pollution control.^[12-17] Kendall and Gebauer-

Stephanie Farrell is Associate Professor of Chemical Engineering at Rowan University. She received her BS in 1986 from the University of Pennsylvania, her MS in 1992 from Stevens Institute of Technology, and her PhD in 1996 from New Jersey Institute of Technology. Her teaching and research interests are in controlled drug delivery and biomedical engineering.

Robert Hesketh is Professor of Chemical Engineering at Rowan University. He received his BS in 1982 from the University of Illinois and his PhD from the University of Delaware in 1987. His research is in the areas of reaction engineering, novel separations, and green engineering.

C. Stewart Slater is Chair of the Chemical Engineering Department at Rowan University. He is a two-time recipient of the Martin Award, and other awards include the Westinghouse, Carlson, and Dow. He is the founding chair of the innovative, hands-on undergraduate-focused chemical engineering program at Rowan. He is on the editorial board of Chemical Engineering Education and The International Journal of Engineering Education.

Fuelneegg^[10] made a strong case for inclusion of electro dialysis in the chemistry curriculum and described inexpensive laboratory set-ups for simple and rapid laboratory investigations. Literature that specifically explores electro dialysis in chemical engineering and chemistry education is scarce, however. Garcia-Garcia, *et al.*, have developed an exciting experiment for the desalting of an amino acid solu-

tion using electro dialysis as an alternative to precipitation using organic solvents.^[18]

This paper describes a hands-on investigation of electro dialysis that introduces the basic principles and applications of electro dialysis technology. The effects of various process operating conditions on the system performance are explored experimentally. Emphasis is given to data analysis and engineering calculations related to rate of ion transfer, Faraday's law, efficiency, energy consumption, and separation performance. These experiments can be implemented in core chemical engineering courses such as unit operations and separation processes, or in elective or graduate-level courses in green/environmental engineering, wastewater treatment, electrochemical engineering, pharmaceutical engineering, and food engineering. Through these experiments, students are not only exposed to an innovative membrane separation experiment, but they also gain a greater knowledge of experimental skills and calculations relevant to the membrane field.

TABLE 1
Industrial Applications of Electro dialysis

Electrolyte reduction	<ul style="list-style-type: none"> • Potable water from brackish water • Nitrate removal for drinking water • Boiler water, cooling tower water, effluent steam desalting • Cheese whey demineralization • Fruit juice deacidification • Sugar and molasses desalting • Potassium tartrate removal from wine • Blood plasma protein recovery • Demineralization of amino acid solutions in the food industry • Acid removal from organic products
Electrolyte recovery	<ul style="list-style-type: none"> • Edible salt production from seawater • Ag(I) salts from photographic waste • Zn(II) from galvanizing rinse water • Organic salts from fermentation broth • Amino acids from protein hydrolysates • Salts, acids, and alkali from industrial rinse waters
Miscellaneous	<ul style="list-style-type: none"> • Conversion of organic salts into acid and base (bipolar membrane ED) • Salt splitting

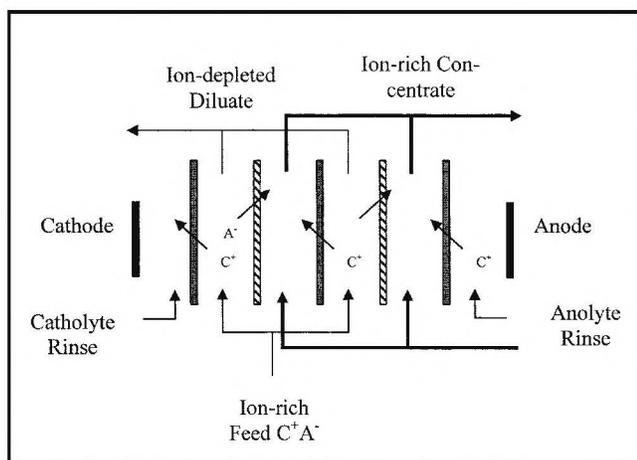


Figure 1. The principles of electro dialysis.

FUNDAMENTALS

The principle that governs electro dialysis is an electrical potential difference across an alternating series of cation and anion exchange membranes between an anode and a cathode. The feed solution containing both positive and negative ions enters the membrane stack to which a voltage is applied, thus causing the migration of the ions toward their respective electrodes. The cation exchange membranes allow the transfer of cations but inhibit the transfer of anions. Conversely, anion exchange membranes allow the transfer of anions but inhibit the transfer of cations. The result is alternating compartments containing streams of dilute ion concentration (diluate) and streams rich in ion concentration (concentrate) exiting the stack. An ionic rinse solution is circulated past the electrodes to maintain conductivity of the membrane stack while preventing potentially corrosive ions from the feed solution from contacting the electrodes. This concept is illustrated in Figure 1 with a feed solution of a salt (C^+A^-) in aqueous solution.

The electro dialysis membrane stack comprises electrodes and membranes separated by gaskets and spacers. The spacers are turbulence-promoting support mesh used to create the compartments through which the solutions flow. Uniform flow distribution and prevention of internal leakage through spacer and gasket design are critical to system performance. Stack design is discussed by Strathmann.^[3]

Material balances can be written for streams entering and exiting the membrane stack, as ions are transported from the feed stream to the concentrate stream. The molar rate of transfer of an ionic species to a stream passing through the mem-

Membranes in ChE Education

brane stack is

$$\dot{m}^i = F_2^i C_2^i - F_1^i C_1^i \quad (1)$$

where the subscript 2 is the stream exiting the stack and 1 is the stream entering the stack, superscript *i* represents either the feed or concentrate stream, *F* is volumetric flowrate, and

The electrodialysis system is easy to operate and the students can perform the suggested experiments in a typical undergraduate laboratory period. The experiments can be used in a variety of undergraduate classes, including a unit operations laboratory or separations course.

C is concentration of the species being transported. In batch recirculation mode, the streams exiting the stack are returned directly to the well-mixed reservoir vessels. The solutions in the reservoir vessels are then fed to the stack. The unsteady-state material balance on the reservoir vessel is

$$\frac{d}{dt}(V^i C_1^i) = F_1^i C_1^i - F_2^i C_2^i \quad (2)$$

Equating Eqs. (1) and (2) yields an expression for the molar rate of change in the reservoir vessels in terms of measured reservoir volume *V*^{*i*} and concentration

$$\dot{m} = -\frac{d}{dt}(V^i C_1^i) \quad (3)$$

Transfer of ions to and from the rinse solutions does take place, and this rate of transfer is found by an overall balance on the three streams (feed, rinse, and concentrate):

$$\dot{m}^r + \dot{m}^c + \dot{m}^f = 0 \quad (4)$$

Electrodialysis is commonly performed in either constant-voltage or constant-current mode. Calculations relating voltage and current to power consumption and efficiency are of critical interest, and basic equations that will be used for process evaluation are presented here.

The cell voltage and current within a membrane stack are related through Ohm's Law

$$\mathcal{V} = I \times R \quad (5)$$

where \mathcal{V} is the voltage (V), *I* is the current (A), and *R* is the resistance of the membrane stack (). The resistance of the membrane stack is due to the friction of the ions with the membranes and the aqueous solution while being transferred from one solution to another.^[5] At high voltages, the system does not follow Ohm's Law, and the interested reader is re-

ferred to standard texts such as Mulder^[1] for the description of other regimes.

The power consumption necessary for the removal of ions from the feed solution is proportional to the current and the stack resistance. The necessary power, *P*(J/s), is represented by

$$P = I^2 R \quad (6)$$

This equation does not account for power necessary to pump the feed, rinse, or diluate streams.^[1]

Combination of Eqs. (5) and (6) results in a power expression in terms of measured variables voltage and current, and the number of membrane pairs in the stack, *n*,

$$P = \mathcal{V}' n I \quad (7)$$

Current is the rate of charge passed through the stack

$$I = \frac{dc}{dt} \quad (8)$$

where *c* = charge passed (Coul) and *t* is time (s). For a system operated at constant voltage, the power consumption will change throughout the run as the current changes. The power is defined as the rate of energy consumption

$$P = \frac{dE}{dt} \quad (9)$$

To determine the total energy consumed in time *t*, Eqs. (7) and (8) are substituted into Eq. (9), which is integrated from time 0 to *t* to obtain

$$E = n \mathcal{V}' c \quad (10)$$

The efficiency of the membrane stack is a measure of the system's ability to use the current effectively in the removal of ions. The minimum (theoretical) charge, *c*_{min}, required to transfer *m* moles of ions through the membrane stack is expressed by Faraday's Law

$$c_{\min} = z m \mathcal{F} \quad (11)$$

where *z* is the valence and \mathcal{F} is Faraday's Constant (96,500 c/mol). The efficiency, η , of the stack compares the minimum theoretical charge to the actual charge required to transport ions through a stack having *n* membrane pairs^[3]

$$\eta = \frac{c_{\min}}{nc} \quad (12)$$

An efficiency of less than one indicates that not all of the charge passed by the electrodialysis system was used to transfer ions from one stream to another. Potential causes of a less-than-perfect efficiency include less-than-perfect ion selectivity of the membranes, the potential of parallel current paths within the membrane stack, and the transfer of water

Membranes in ChE Education

molecules by osmosis and ion hydration.^[6] The efficiency will change with feed and concentrate solution concentrations throughout a batch run, since the rates of water transfer by osmosis and ion hydration are concentration-dependent.^[3]

In an electro dialysis system with the feed stream containing monovalent and divalent ions, the selectivity of a specific membrane of one ion over another can be calculated. The selectivity, α , is taken to be the ratio of the number of moles transferred from the feed vessel of each ion j and k , m^j and m^k .^[19]

$$\alpha = \frac{m^j}{m^k} \quad (13)$$

Equation (13) is applicable when the ion species j and k are equal in the feed vessel. In a batch electro dialysis system, the feed concentrations change with time, and Eq. (13) for overall selectivity throughout the run is used to quantify the selective transport of ions.

There is a wide range of important theoretical concepts and practical issues related to electro dialysis that are beyond the scope of this paper. Selective transport theory is presented in various references^[3,5,6] and Strathman^[5] offers a practical treatment of design and cost estimates that would allow estimation of membrane area and required energy for a desired plant capacity. Additional practical considerations of electro dialysis operations include limiting current density, boundary layer effects, and concentration polarization, osmosis, and electroosmosis effects. For treatment of these topics, the reader should consult references 1,3,4,5,6, and 11.

ELECTRODIALYSIS SYSTEM DESCRIPTION

The laboratory-scale electro dialysis system in our experiments was purchased from Electrosynthesis Corporation in Lancaster, New York. The major components of the system are the electro dialysis cell, an electrochemical process control unit, and system instrumentation. The basic features of the electro dialysis system in our laboratory are summarized in Table 2. The entire system was purchased for approximately \$30,000. A perfectly adequate electro dialysis system could be constructed for well under \$10,000 by purchasing a fabricated electro dialysis cell for about \$3,200 (electrodes, cell body, membranes, gaskets, and spacers) and assembling the other components and instrumentation in-house.

The Electrosynthesis Model ED-1 electro dialysis cell features a platinum-on-titanium anode and 316 stainless steel cathode, polypropylene cell body, and individual membrane area of 0.01 m². Multiple pairs of membranes allow a total membrane area up to 0.2 m². The cell stack includes turbulence-promoting mesh spacers and gaskets. A photograph of the electro dialysis cell is shown in Farrell, *et al.*,^[20] in this issue of *CEE* (Figure 2b).

The Boss Model 710 electrochemical process control system features a digital coulometer, digital temperature monitor, four independent pump and flow control loops, and digital indicators for temperature, cell potential, current, process charge, and setpoints. Safety features include process shutdown for exceeding flow, voltage, temperature, or charge limits.

The system is fully instrumented with in-line conductivity/

TABLE 2
Basic Features of the Electro dialysis System

Cell body • Polypropylene
Number of membranes • 10 pairs
Individual effective membrane area • 0.1 m ²
Spacers • Polypropylene mesh, 0.75 mm intermembrane gap, 2.0 mm electrode chamber gap
Gaskets • Epoxy-Cured EPDM
Anode • Platinized titanium
Cathode • 316 stainless steel
Reservoir • Custom 2-L glass
Conductivity/Temperature measurement • Amel K-1 glass, polypropylene probes with Amel SIRIO meters
Charge, Current, Voltage, Temperature, Flow measurement/display • The Boss electrochemical process control system
Pumps • March model BC-3CP-MD centrifugal, polypropylene and ceramic with viton o-rings
Flow sensors • Teflon impeller style, Cole-Parmer Model U-33110-05
Tubing, compression fittings, valves • Polypropylene, 1/2-inch diameter

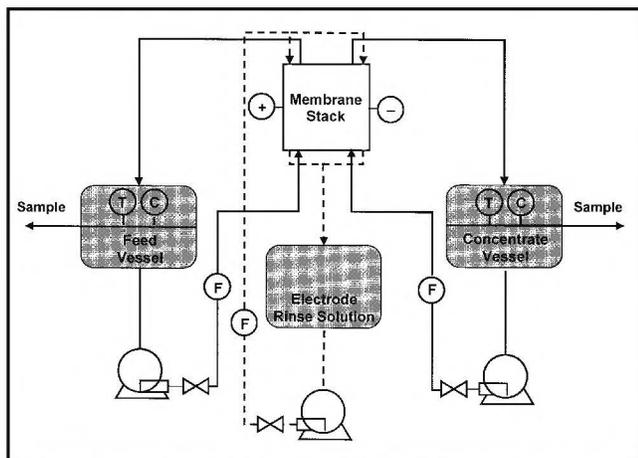


Figure 2. Scheme of the experimental electro dialysis system employed for the separation runs. T, C, F are Temperature, Conductivity, and Flowrate on-line analyzers.

Membranes in ChE Education

temperature probes (K-1, AMEL, Milan, Italy), programmable microprocessor conductivity/resistivity indicator (model SIRIO, AMEL s.r.l., Milan, Italy), Teflon impeller flow sensor (model U-33110-05, Cole Parmer, Vernon Hills, IL) with ratemeter/totalizer (model DP78A, Omega Engineering, Inc., Stamford, CT). Determination of cation concentrations for mixed monovalent-divalent cation solutions was made using ion selective electrodes (divalent cation electrode Model 93-32 and ammonium electrode model 93-18 with sensing module, Thermo Orion, Beverly, MA).

The electro dialysis process is shown schematically in Figure 2, and a photograph of the system is shown in the companion paper by Farrell, *et al.*, (Figure 2a).^[20] The system is operated in batch recirculation mode. Continuous and batch modes of operation, along with their relative advantages and disadvantages, are described by Shaffer and Mintz.^[6]

ION EXCHANGE MEMBRANES

The performance of ion-permeable membranes used in electrochemical processes depends on several properties. The desirable characteristics of membranes used in electro dialysis applications include^[5,21] selectivity between ions of opposite charge, high ionic conductivity, low electrical conduction, long-term chemical stability, mechanical strength, and resistance to fouling. These characteristics are determined by the membrane matrix polymer and the fixed ionic moiety that effects the ion selectivity of the membrane. Strathmann^[5] describes the challenges of optimization of these properties. Polymer materials such as polystyrene, polyethylene, and polysulfone are often chosen for the membrane matrix and

are often cross-linked to ensure stability. Fixed ionic moieties such as SO_3^- , COO^- , PO_3^{2-} , HPO_2^- , AsO_3^{2-} , and SeO_3^- are commonly used for cation exchange membranes, and NH_3^+ , RNH_2^+ , R_3N^+ , R_2N^+ , R_3P^+ , R_2S^+ , are common choices for anion-exchange membranes.^[5]

There are several manufacturers of ion-selective membranes for a variety of electrochemical process applications. Table 3 provides information on the materials and features of several ion exchange membranes used in electro dialysis applications. Detailed information on membrane manufacturers and membrane characteristics is provided in reference books^[3,21] and directly from the manufacturers. Membrane replacement costs are on the order of \$100/m².

Tokuyama Soda Neosepta[®] ion-exchange membranes are used in our experiments. Two Neosepta cation exchange membranes, CMX and CMS, were investigated, while the same anion exchange membranes, Neosepta AMX, were used in all experiments. Neosepta AMX and CMX membranes are standard grade, general-purpose polystyrene-based ion exchange membranes. Neosepta CMS membranes have a thin cationic charged layer on the membrane surface that increases the selectivity between monovalent cations (*i.e.*, NH_4^+) and multivalent cations (*i.e.*, Mg^{2+}). Neosepta membranes have high ionic selectivity, low electric resistance, and a low diffusion coefficient for solute or solvent. They exhibit high mechanical strength and high dimensional stability, and are highly resistant to chemical attack.

EXPERIMENTAL

Ammonium cations and chloride anions are contaminating

TABLE 3
Ion Exchange Membranes Used in Electro dialysis Applications
(Information from References 3, 21, and Membrane Manufacturers)

Manufacturer	Tradename	Material	Special Features	Location
Solvay		Perfluorinated film with fixed pyridine (anion-permeable) or sulfonic acid (cation-permeable)		France
FuMA-Tech		Polyetherketones, polysulfone, polyphenylene oxide		Germany
Tokuyama Soda	Neosepta [®]	Styrene-divinyl benzene	Robust high mechanical strength; Moderate electrical resistance	Japan
Asahi Glass	Selemiom [®]	Polystyrene-based	Very low electrical resistance	Japan
Asahi Chemical	Aciplex [®]	Styrene-divinyl benzene/PVC backing		Japan
Ionics, Inc.		Heterogeneous polystyrene-based/acrylic fabric, with fixed sulfonate (cation-permeable) and quarternary ammonium cations (anion-permeable)	Rugged, low resistance, high selectivity, chemically stable, low fouling	MA, USA
Dupont Co.	Nafion [®]	Perfluorinated sulfuric acid polymer	Cation permeable	NC, USA
Sybron	Ionac [®]	Heterogeneous resin-PVDF/fabric	High mechanical strength	NJ, USA

Membranes in ChE Education

species that are commonly present in industrial process streams. In this investigation, we considered removal of ammonium chloride from an aqueous stream. Experiments were performed to study the effect of the following parameters in the removal of NH_4Cl from water: the initial concentration of the concentrate vessel, the applied cell voltage, and the selection of the membranes. Additional experiments could be conducted to investigate other process parameters such as number of membrane pairs, flow rate, feed concentration, and temperature (within the limits of the membranes). The system performance was evaluated using efficiency, selectivity, power, and energy consumption calculations.

The membrane stack was constructed with five pairs of cation and anion exchange membranes, with a cation exchange membrane adjacent to each electrode as described above. A solution of 0.5 M ammonium sulfate was used as

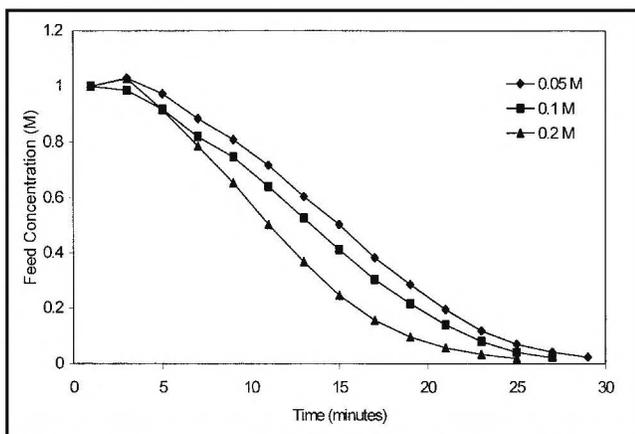


Figure 3. Effect of initial concentrate concentration at constant voltage. Process operating conditions: 13 V, 1 M feed (initial), AMX/CMX membranes.

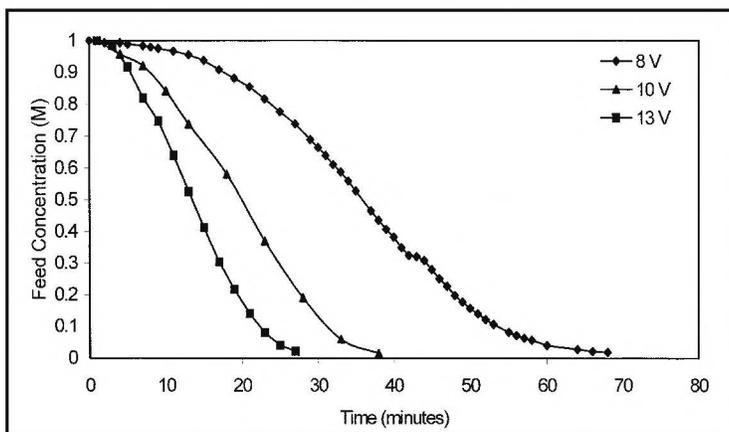
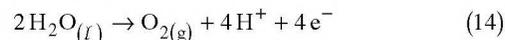
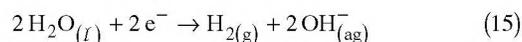


Figure 4. Effect of voltage on the feed concentration. Process operating conditions: 1 M feed (initial), 0.1 concentrate (initial), and AMX/CMX membranes.

the anolyte/catholyte rinse solution in order to prevent generation of chlorine or hypochlorite, which would be hazardous. The feed solution was aqueous NH_4Cl or $\text{NH}_4\text{Cl}/\text{MgCl}_2$ with a total initial salt concentration of approximately 1.0 M. The concentrate stream was an aqueous NH_4Cl with an initial concentration between 0.05 and 0.2 M (specified for each run). At the anode, the expected predominant reaction in this system with a neutral solution is the formation of oxygen



At the cathode, the formation of hydrogen gas is the predominant reaction in neutral solution



The system was operated in a constant voltage, batch recirculation mode. Flowrates were 0.5 L/min for the feed and concentrate streams, and 0.7 L/min for the combined anolyte and catholyte streams. The following data were collected at regular intervals of ten minutes or less: liquid volume in each vessel, conductivity of each stream, current, charge passed, and temperature. Completion of experiments took between 70 and 90 minutes, depending on the applied voltage and other operating parameters. The experiment was considered complete when the current dropped to approximately 1.0 A. The ion concentrations were determined using conductivity measurements.

Initial concentration of the concentrate vessel is important because it is a key parameter in the resistance of the membrane stack. If the concentrate stream initially has an extremely low ion concentration, water splitting may occur in order to provide the ions necessary to carry the current. (Water splitting generates hydrogen ions and hydroxyl ions, which are capable of migrating through the cation- or anion-selective membranes, respectively; this may result in pH changes in the diluate and concentrate compartments.) Thus, the concentrate stream is usually “primed” with a low electrolyte concentration to facilitate transport of the desired ions from the feed stream. To illustrate this, the system performance is compared using different initial concentrate vessel concentrations. The effect of the initial ion concentration in the concentrate stream is shown in Figure 3.

These runs were performed at a constant voltage of 13 V using a 1.0 M NH_4Cl feed and 0.5 M $(\text{NH}_4)_2\text{SO}_4$ rinse, and the initial concentrate concentration was varied from 0.05 M to 0.2 M NH_4Cl . The figure shows the decline in the feed ion concentration throughout the course of the runs. The rate of ion transport increases with increasing initial concentrate concentration. At

Membranes in ChE Education

higher concentrate concentrations, the ionic conductivity of the membrane increases, effecting a higher current for a given voltage drop across the cell stack and thus resulting in a higher rate of transport of the ionic species.

Applied cell voltage is a critical operating condition in electrodialysis processes. As the cell voltage is increased, the ion concentration in the feed vessel is depleted more rapidly, thus reducing the duration of the experiments. Increasing the cell voltage, however, increases the energy consumption of the unit according to Eq. (10). An interesting investigation can be performed by varying the voltage and comparing the system performance and energy consumption.

To study the effect of voltage, the voltage was varied between 8 and 13 volts, based on manufacturer recommendations.^[22] The system operated in the Ohmic region within this voltage range. The results of ammonium chloride removal at different voltages are shown in Figure 4, which plots the feed ion concentration throughout the run. This figure shows that at higher cell voltages, the feed ion concentration is depleted more rapidly than at lower cell voltages. As the concentrate concentration increases at the start of the run, the current increases and a higher ion transport rate is observed. This can be observed through the change in the slope of the curves in Figure 4 (about 5-10 minutes into the run).

Using Eqs. (11) and (12), students can calculate the efficiency of the membrane stack in the removal of ions at the various cell voltages. At the conditions shown in Figure 4, overall efficiencies of close to 100% were obtained for the 8 V and 10V runs, while the efficiency of the 13 V run was approximately 85%. The lower efficiency of the 13 V run was accompanied by an increase in temperature due to finite membrane resistance, which could damage the ion-selective membranes if cooling is not provided. Similarly, the calculated energy consumption for the 13 V run was significantly higher than that for the 8 V or 10 V run, as shown in Table 4. The experimental results for efficiency and energy consumption could be used to estimate the energy requirements and membrane area necessary to achieve this deionization task for a given plant capacity and to obtain a rough estimation of process costs.

A third parameter for students to investigate is the type of membrane used in the stack. There are numerous types of specialized membranes available for a variety of separation applications. Some general features of available commercial membranes include size selective, charge selective, and specific-ion selective membranes. The objective of this experiment is to compare the selectivities of two types of cation exchange membranes—a general-purpose membrane (CMX) and a monocation-selective membrane (CMS).

For the purpose of this experiment, divalent cations (Mg^{2+}) and monocations (NH_4^+) were provided in a feed solution of 0.55 M $MgCl_2$ and 0.55 M NH_4Cl . The initial concentrate concentration was 0.2 M NH_4Cl and the system was operated at 10 V. Samples were extracted from the feed and concentrate vessels initially and at ten-minute intervals. They were stored for analysis with ion selective probes.

The monocation-selective membranes reduce the migration of the divalent magnesium ions from the feed vessel to the concentrate vessel. The concentration of the ammonium ions and magnesium ions in the feed vessel can be plotted as a function of time for either set of membranes. Figure 5 shows the slow decline of magnesium ions in the feed vessel in comparison with the rapid decline of the ammonium ions in an experiment with the CMS membranes. Comparing the performance of CMS membranes to CMX membranes, the enhanced retention of magnesium in the feed using the CMS membranes is also shown in Figure 5. (At early times, the expected difference in magnesium ion removal rates for the two membranes is not apparent. This is probably due to sys-

TABLE 4
Comparison of Total Energy Consumption for Runs at Three Different Applied Voltages

Time (min)	Voltage (V)	Energy Consumption (kJ)
68	8	722
38	10	816
25	13	962

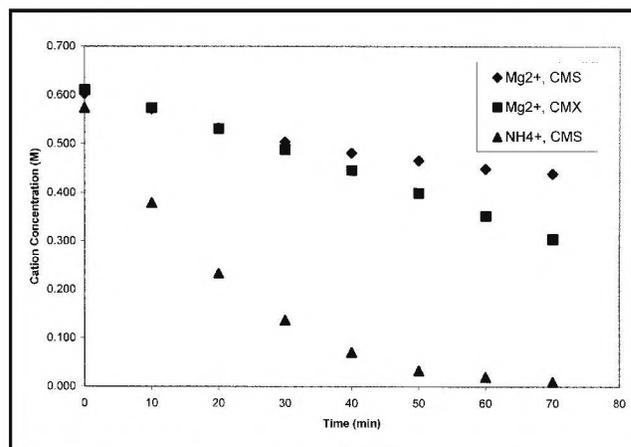


Figure 5. Removal of ammonium and magnesium ions using CMX and CMS cation exchange membranes. Process operating conditions: 10 V, 0.5 M $MgCl_2$, and 0.5 M NH_4Cl feed (initial), 0.2 M concentrate (initial).

tem equilibration and run-to-run variations that are most apparent at start-up. The difference in removal rates for the two runs is evident after 20 minutes.)

The overall selectivity throughout the run, for ammonium relative to magnesium, is calculated using Eq. (13), using the total number moles of each ion removed from the feed at the completion of a 70-minute run. The total number of moles of each ion transferred from the feed is determined by integrating Eq. (3) for the duration of the run.

For the general-purpose CMX membrane, the overall selectivity was 1.04, indicating that the average removal rates of ammonium and magnesium are approximately equal. For the monocation-selective membrane, the overall selectivity was 2.8, indicating that the CMS membrane selectively enhances the removal of monovalent ammonium ions from the feed.

CONCLUSIONS

We have developed an experimental investigation of the practical engineering aspects of electrodialysis. Students investigate the effects of operating parameters such as concentrate concentration and applied voltage. Membrane selection is explored through comparison of two cation exchange membranes for the selective removal of competing cations.

Additional experiments could be conducted to investigate other process parameters such as the number of membrane pairs, flow rate, feed concentration, and temperature (within the limits of the membranes). Data analysis and calculations emphasize practical engineering considerations such as energy consumption, efficiency, and selectivity.

The electrodialysis system is easy to operate and the students can perform the suggested experiments in a typical undergraduate laboratory period. These experiments can be used in a variety of undergraduate classes, including a unit operations laboratory or separations course. Advanced courses that would be enhanced with electrodialysis experiments are specialized topics courses such as green/environmental engineering, wastewater treatment, electrochemical engineering, pharmaceutical engineering, and food engineering.

ACKNOWLEDGMENTS

Support for the laboratory development activity described in this paper was provided for by Johnson Matthey, Inc., a grant (DUE 9850535) from the National Science Foundation, and the Chemical Engineering Department at Rowan University. The authors gratefully acknowledge the work of Rowan engineering students, particularly Natalie Deflece and Craig Rogers, in conducting experiments.

REFERENCES

1. Mulder, M., *Basic Principles of Membrane Technology*, 2nd ed., Kluwer Academic Publishers, Dordrecht, Holland (1996)
2. Electrosynthesis Company promotional literature at <www.electrosynthesis.com> accessed May 6, 2001
3. Strathmann, H., "Electrodialysis" in *Synthetic Membranes: Science, Engineering, and Applications*, P.M. Bungay, H.K. Lonsdale, and M.N.D. de Pinho, eds., Reidel Publishing Company, Dordrecht, Holland (1986)
4. Davis, T.A., "Electrodialysis," in *Handbook of Industrial Membrane Technology*, M.C. Porter, ed., Noyes Publications, Park Ridge, NJ (1990)
5. Strathmann, H. "Electrodialysis," in *Membrane Handbook*, W.S. Ho and K.K. Sirkar, eds., Van Nostrand Reinhold, New York, NY (1992)
6. Shaffer, L.H., and M.S. Mintz, *Principles of Desalination*, Academic Press, Inc., New York, NY (1980)
7. Slater, C.S., "Teaching the Engineering Aspects of Membrane Process Technology," *J. Membr. Sci.*, **62**, 239 (1991)
8. Slater, C.S., and H.C. Hollein, "Educational Initiatives in Teaching Membrane Technology," *Desal.*, **90**, 291 (1993)
9. Slater, C.S., "Education on Membrane Science and Technology" in *Membrane Processes in Separation and Purification*, J.G. Crespo and K.W. Boddeker, eds., Kluwer Academic Publishers, Dordrecht, Netherlands, pg. 479 (1994)
10. Kendall, A.I., and E. Gebauer-Fuelnegg, "Electrodialysis with Simple Apparatus," *J. Chem. Ed.*, **8**, 1634 (1931)
11. Lacey, R.E., "Basis of Electromembrane Processes" in *Industrial Processing with Membranes*, R.E. Lacey and S. Loeb, eds., John Wiley and Sons, New York, NY (1972)
12. Ottewill, G., and F. Walsh, "Education Topics Number 2: The Speed of Metal Deposition and Dissolution," *Trans. Inst. Met. Finish*, **77**(5), 209 (1999)
13. Walsh, F., and G. Ottewill, "Education Topic Number 3: Electrochemical Cell Reactions," *Trans. Inst. Met. Finish*, **77**(4), 169 (1999)
14. Walsh, F., and D. Robinson, "Electrochemical Filter-Press Reactors: Technology Designed for Versatility and Efficiency," *Electrochemical Soc. Interface*, **7**(2), 40 (1998)
15. Walsh, F., and G. Ottewill, "Electrochemical Cells," *Chem. Rev.*, **5**(4), 2 (1996)
16. Trinidad, P., and F. Walsh, "Conversion Expressions for Electrochemical Reactors Which Operate Under Mass Transport Controlled Reaction Conditions: Part 1. Batch Reactor, PFR, and CSTR," *Int. J. Eng. Ed.*, **14**(6), 431 (1998)
17. Expósito, E., M.J. Inglés, J. Iniesta, J. González-García, P. Bonete, V. García-García, and V. Montiel, "Removal of Heavy Metals in Wastewater by Electrochemical Treatment," *Chem. Eng. Ed.*, **33**(2), 172 (1999)
18. García-García, V., V. Montiel, J. González-García, E. Expósito, J. Iniesta, P. Bonete, and E.M. Inglés, "The Application of Electrodialysis to Desalting an Amino Acid Solution," *J. Chem. Ed.*, **77**(11), 1477 (2000)
19. Wankat, P.C., *Rate Controlled Separations*, Kluwer, Amsterdam (1990)
20. Farrell, S., R.P. Hesketh, M.J. Savelski, K.D. Dahm, and C.S. Slater, "Membrane Projects with an Industrial Focus in the Curriculum," *Chem. Eng. Ed.*, **37**(1), 68 (2003)
21. Davis, T.A., J.D. Genders, and D. Pletcher, *A First Course in Ion Permeable Membranes*, The Electrochemical Consultancy, Hants, England (1997)
22. Personal communication with Duane Mazur, Electrosynthesis Company, June 9, 1999 □

Tools for Teaching GAS SEPARATION USING POLYMERS

DAVID T. COKER, RAJEEV PRABHAKAR*, BENNY D. FREEMAN*
Research Triangle Institute • Research Triangle Park, NC 27709-2194

Gas separation with polymer membranes is rapidly becoming a mainstream separation technology. The most widely practiced separations are enriched nitrogen production from air, hydrogen separation in ammonia plants and refineries, removal of carbon dioxide from natural gas, removal of volatile organic compounds (*e.g.*, ethylene or propylene) from mixtures with light gases (*e.g.*, nitrogen) in polyolefin purge gas purification, and water vapor removal from air.^[1-3] Relative to conventional separation technologies, membranes are low-energy unit operations, since no phase change is required for separation. Additionally, membranes have a small footprint, making them ideal for use in applications on offshore platforms, aboard aircraft, and on refrigerated shipping containers, where space is at a premium or where portability is important. They have no moving parts, making them mechanically robust and increasing their suitability for use in remote locations where reliability is critical.^[3]

Gas separation membranes are often packaged in hollow-fiber modules—a cartoon of such a module is presented in Figure 1. A full-scale industrial module for air separation may contain from 300,000 to 500,000 individual fibers in a tubular housing that is 6 to 12 inches in diameter and approximately 40 inches long. Each fiber will have inside and outside diameters on the order of 150 and 300 micrometers, respectively. For a typical case, the fiber wall, approximately 75 micrometers thick, consists of a very thin, dense separation membrane layer on the order of 500 to 1000 Å (0.05 to 0.1 micrometers) thick, on the outside of the fiber. This thin layer provides, ideally, all of the mass transfer resistance and separation ability of the hollow fiber. The remaining 74.9 to 74.95 micrometers of the fiber wall comprise a porous polymer layer that provides mechanical support for the thin membrane, but offers little or no mass transfer resistance. (To put fiber dimensions in perspective, the diameter of a typical human hair is about 100 micrometers.)

Gas (air in this example) flows under pressure into the module, where it is distributed to the bores of the fibers. In air separation, feed pressures of approximately 10 to 15 bar

are typical. The air gases permeate through the wall of the fibers into the shell of the hollow-fiber module, which is maintained at essentially atmospheric pressure. The gas permeating through the fibers and into the shell is collected and leaves the module as the permeate stream.

Because oxygen, water, and carbon dioxide are more permeable than nitrogen and argon, the gas in the fiber bore is enriched in N₂ and Ar as it moves through the fiber lumens from the feed to the residue end of the module. This process can produce 99+% N₂ in the residue stream.

Such purified nitrogen is widely used for blanketing or inerting applications in, for example, the aviation (fuel tank blanketing), shipping (food container/packaging blanketing), and chemical industries (storage tank and line blanketing or

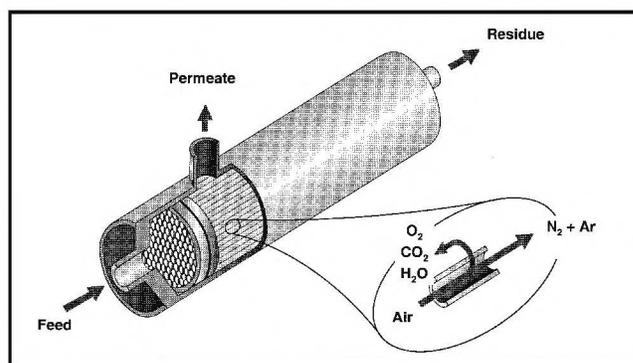


Figure 1. Cartoon of hollow-fiber module used for air separation. From <www.medal.com> and Ref. 4.

David T. Coker provides engineering software services for Research Triangle Institute. He holds a BS in Chemical Engineering (1997) from North Carolina State University.

Rajeev Prabhakar is currently working toward his PhD in chemical engineering at the University of Texas at Austin. His research relates to the development of membrane-based systems for removal of carbon dioxide from natural gas streams. He received his BTEch in chemical engineering from the Indian Institute of Technology (Kharagpur) and his MS from North Carolina State University.

Benny D. Freeman is the Matthew van Winkle Professor of Chemical Engineering at the University of Texas at Austin. His research is in polymers, particularly the sorption, diffusion, and permeation of small molecules through polymers and polymer-based composites.

* University of Texas at Austin, Austin, TX 78758

purging)(see <www.medal.com> for further examples).

This paper presents a brief background section describing the fundamentals of gas transport in polymer membranes and then discusses models of mass transfer in gas separation modules. First, an analytical model for binary gas separation will be described, and it can be used to rapidly develop intuition regarding the effect of membrane process variables on separation performance. Then, a more rigorous model, which is available on the Internet, will be described—this model can be used to perform more realistic simulations and address more complex situations (*e.g.*, multicomponent separations, use of sweep streams to enhance separation efficiency, staging membrane units, recycle, etc.).

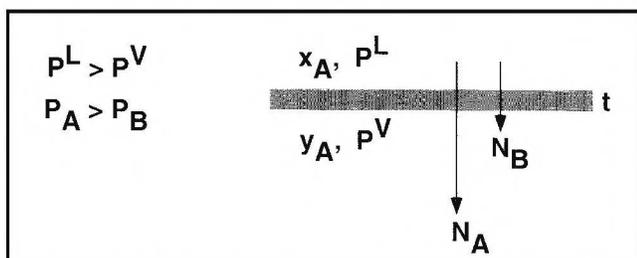


Figure 2. Schematic of a gas separation membrane of thickness t being used to separate a gas mixture of components A and B (O_2 and N_2 , for example). The upstream pressure, P^L , is greater than the downstream pressure, P^V , and the mol fractions of component A on the upstream and downstream sides of the membrane are x_A and y_A , respectively. The steady state fluxes of components A and B through the membrane are N_A and N_B , respectively. By convention, component A is selected so that the permeability of the membrane to component A, P_A , is greater than the permeability of the membrane to component B, P_B .

TABLE 1
Oxygen and Nitrogen Permeability in Selected Polymers*

Polymer	Oxygen Permeability (Barrer)	Nitrogen Permeability (Barrer)	Oxygen/Nitrogen Selectivity
Poly(1-trimethylsilyl-1-propyne)	7600	5400	1.6
Poly(dimethylsiloxane)	638	320	2
Poly(4-methyl-1-pentene)	30	7.1	4.2
Poly(phenylene oxide)	16.8	3.8	4.4
Ethyl cellulose	11.2	3.3	3.4
6FDA-DAF (polyimide)	7.9	1.3	6.2
Polysulfone	1.38	0.239	5.8
Polyaramid	3.1	0.46	6.8
Tetrabromo bis polycarbonate	1.4	0.18	7.8

*These data are from Baker.^[3] The unit for gas permeability, the Barrer, is named after Professor Barrer, one of the pioneers in this area.^[7]
1 Barrer = 10^{-10} cm²(STP)cm/(cm²s cmHg). For permeability values, standard temperature and pressure (STP) are 0°C and 1 atm, respectively.

BACKGROUND

The fundamental mechanism for gas transport across a polymer membrane was described by Sir Thomas Graham more than a century ago.^[5] (This classic article, along with a number of other seminal papers in membrane science, are reproduced in the 100th volume of the *Journal of Membrane Science*.^[6]) This mechanism, known as the solution/diffusion model, postulates a three-step process for gas transport through a polymer: 1) dissolution of the gas into the high-pressure (or high chemical potential) upstream face of the polymer, 2) diffusion of the gas through the polymer, and 3) desorption from the low-pressure (*i.e.*, low chemical potential) downstream face of the polymer. Steps 1 and 3 are very fast relative to step 2, so diffusion through the polymer is the rate-limiting step in mass transport across a membrane.

Figure 2 depicts a dense polymer film (or membrane) of thickness t exposed to a binary mixture of gases A and B. The mole fraction of A on the upstream, or high pressure, side of the membrane is x_A , and the mole fraction of A on the downstream, or low pressure, side of the membrane is y_A . The upstream pressure, P^L , is greater than the downstream pressure, P^V . Because separation membranes are so thin (500-1000Å), the characteristic timescale for gas molecule diffusion through the membrane is very fast, and as a result, industrial gas separation membranes typically operate at steady state. The flux of A across the film, N_A , is^[2]

$$N_A = \frac{P_A}{t} (x_A P^L - y_A P^V) \quad (1)$$

where P_A is the permeability of the polymer to component A. The ratio of permeability to membrane thickness is called the permeance of the membrane to gas A, and this ratio can

be viewed as a mass transfer coefficient that connects the flux (often expressed in cm³[STP] of gas permeated through the membrane per cm² of membrane area per second) with the driving force for transport, which is the partial pressure difference between the upstream and downstream sides of the membrane. (Standard temperature and pressure for permeance are 0°C and 1 atm, respectively.) A similar expression can be written for component B as

$$N_B = \frac{P_B}{t} [(1 - x_A)P^L - (1 - y_A)P^V] \quad (2)$$

For a given gas molecule, every polymer has a different permeability coefficient. Based on the data in Table 1, oxygen permeability, for example, varies by orders of magnitude from one polymer to another. Moreover, in a given polymer, the permeability coefficient will vary from

Membranes in ChE Education

one gas to the next, and it is this property that allows the polymer to separate gas mixtures. The data in Table 1 indicate that oxygen is always more permeable than nitrogen in all polymers, and the ratio of O_2 to N_2 permeability, the selectivity, varies from 1.6 to 7.8 in the materials shown. Typically, as the permeability of a polymer to oxygen increases, its selectivity decreases, and vice versa.^[8,9] In the most widely used gas separation membranes, permeability coefficients often decrease with increasing gas molecule size, so most gas separation membranes are more permeable to small molecules (*e.g.*, H_2) than to larger molecules (*e.g.*, CH_4). There are interesting exceptions to this general rule, and membranes based on such materials may become more commonplace in the near future.^[10-12]

ANALYTICAL CROSSFLOW MODEL

The mole fraction of gas A on the permeate or downstream side of the membrane is given by the flux of component A through the membrane divided by the total gas flux through the membrane

$$y_A = \frac{N_A}{N_A + N_B} = \frac{\frac{P_A}{t}(x_A P^L - y_A P^V)}{\frac{P_A}{t}(x_A P^L - y_A P^V) + \frac{P_B}{t}[(1-x_A)P^L - (1-y_A)P^V]} \quad (3)$$

This expression can be reorganized as follows to permit a direct calculation of permeate purity:

$$y_A = \frac{\left[1 + (\alpha - 1)\left(\frac{1}{R} + x_A\right)\right]}{\frac{2}{R}(1 - \alpha)} \left[\left(1 + \frac{\frac{4}{R}(1 - \alpha)\alpha x_A}{\left[1 + (\alpha - 1)\left(\frac{1}{R} + x_A\right)\right]^2}\right)^{1/2} - 1 \right] \quad (4)$$

where the selectivity, α , is defined as the ratio of permeability coefficients ($\alpha = P_A/P_B$) and the pressure ratio, R , is defined as the ratio of feed to permeate pressure ($R = P^L/P^V$). Equation 4 can be used to determine the effect of feed composition, pressure ratio, and membrane selectivity on the mole fraction of gas produced by a membrane.

There are two limits of Eq. (4) that provide insight into the factors that govern the ultimate separation performance of membranes. It is easier to see these two limits if, instead of using Eq. (4) directly, we use the following equivalent reorganized form of Eq. (3):

$$\frac{y_A}{\alpha(1 - y_A)} = \frac{R x_A - y_A}{R(1 - x_A) - (1 - y_A)} \quad (5)$$

Figure 3 presents the permeate purity as a function of membrane selectivity, and the two limits of interest are shown. The first limit

to be discussed is the pressure ratio limit. As membrane selectivity increases, the permeate mole fraction, y_A , will increase, but y_A can only increase up to the point that the partial pressure of component A on the upstream side ($x_A P^L$) of the membrane equals that on the downstream side ($y_A P^V$). At this point, the driving force for transport of A across the membrane is zero, the flux of component A goes to zero, and there can be no further increase in the mole fraction of component A in the permeate. Therefore, in the limit of very high selectivity (*i.e.*, as $\alpha \rightarrow \infty$ in Eq. 5 and, therefore, Eq. 4), Eq. (5) reduces to

$$y_A = R x_A \quad (6)$$

That is, at high selectivity, the purity of gas produced is limited by the pressure ratio. Of course, the value of y_A can never be greater than unity.

This limit has industrial significance in situations where selectivity is very high and process conditions dictate a small pressure ratio between permeate and feed streams. An example is the removal of hydrogen from mixtures with hydrocarbons in hydrotreaters in refineries.^[3] The hydrocarbons in such a mixture would be methane and higher hydrocarbons, all of which are less permeable than methane in the membranes used for such separations. Typically, H_2 is hundreds of times more permeable than CH_4 and other components in such a mixture.^[2] But typical upstream and downstream pressures would be 120 and 30 bar, respectively,^[3] so the pressure ratio would only be 4. In such a case, having very high selectivity does not result in much

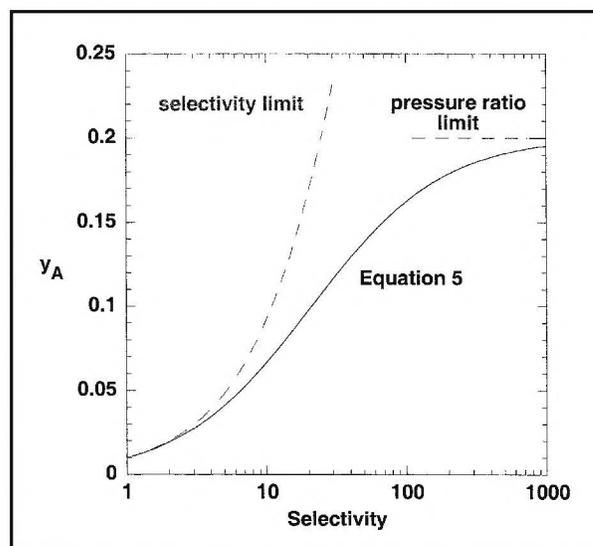


Figure 3. Permeate purity as a function of membrane selectivity for a feed composition, x_A , of 1 mole percent A (99 mol percent B) and a pressure ratio of 20.

higher-purity H_2 in the permeate because the H_2 permeation is at or near the limit where its partial pressure upstream and downstream are almost equal.

Another example is dehydration of gas streams such as air. Typically, water is much more permeable than air gases in polymers used for gas separation, so the amount of water that can be removed from a gas stream is often limited by the ability to keep the partial pressure of water very low in the permeate gas. This is often done by recycling some of the dry residue gas product back across the permeate side of the membrane to dilute the concentration of water being produced in the membrane. Such so-called purge or permeate sweep strategies can markedly reduce the dew point of air produced by dehydration membranes.^[4]

At the other extreme, if the membrane is operated with a vacuum on the permeate side of the membrane (*i.e.*, $R \rightarrow \infty$), then Eq. 5 becomes

$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A} \quad (7)$$

and permeate purity is limited by polymer selectivity. As permeate pressure, P^V , decreases toward zero (or, equivalently, as the ratio of feed to permeate pressure increases to the point that the partial pressures of components A and B in the permeate become very small relative to their partial pressures in the feed), the flux of components A and B approach maximum values based on membrane permeability, thickness, composition, and upstream pressure

$$N_A \rightarrow \frac{P_A}{t} x_A P^L \quad \text{and} \quad N_B \rightarrow \frac{P_B}{t} (1 - x_A) P^L \quad (8)$$

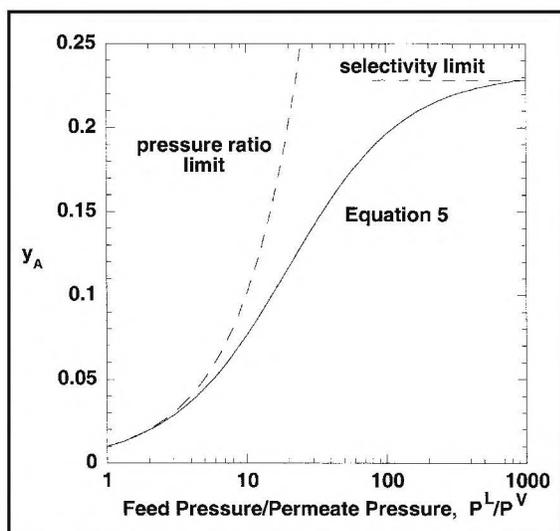


Figure 4. Permeate purity as a function of pressure ratio for a feed composition, x_A , of 1 mole percent A (99 mol percent B) and a selectivity of 30.

When the expressions in Eq. (8) are used to evaluate permeate purity based on $y_A = N_A/(N_A + N_B)$, Eq. (7) is obtained. In this case, the mole fraction of component A in the permeate is then limited by the ability of the membrane to prevent transport of component B across the membrane; that is to say, permeate purity is limited by membrane selectivity. This limit is shown in Figure 3 and also in Figure 4, which presents permeate mole fraction as a function of pressure ratio. This limit is reached when the pressure ratio is very high or the membrane selectivity is low.

An example of practical importance is the separation of N_2 from CH_4 in natural gas wells, a separation that is currently not practiced industrially using membranes because of this issue.^[3] Many natural gas wells are contaminated with nitrogen, which would need to be removed to bring the heating value of the natural gas to pipeline specifications.^[3] But polymer membranes rarely have an N_2/CH_4 selectivity greater than 2. In this case, even for large pressure ratios, the separation of this gas mixture is not good using membranes. For example, when the feed mole fraction of N_2 is 2%, the permeate mole fraction of N_2 is only 3.9%, and at a feed mole fraction of 20%, the permeate mole fraction is only 33%. There is little separation, and most of the low-pressure permeate waste gas is methane. That is (because the separation is poor), there is a large loss of methane into the low-pressure permeate stream with little removal of N_2 from the feed gas.

INTERNET MODEL

The analytical model described above is applicable to separation of binary mixtures only. Moreover, it does not account for the fact that as the feed gas travels through the hollow fibers, its composition changes as selective permeation strips the more permeable components from the feed-gas mixture. A classic extension of this model, due to Weller and Steiner, takes this factor into account.^[1,3] This model, however, is no longer strictly an analytical solution. Moreover, it cannot simulate the countercurrent flow patterns that are used industrially in gas-separation modules. As indicated qualitatively in Figure 1, typical industrial permeators are designed to allow the feed gas and permeate gas to flow countercurrent to one another. Moreover, this model does not allow for separation of multicomponent mixtures of gases, which is a major practical limitation.

The simple model described above has been extended to account for multicomponent gas separation and to simulate countercurrent flow.^[4,14] In this case, the governing mass balance equations are coupled differential equations, and no analytical solution is available. Numerical solutions to this model are available for public use at

<http://membrane.ces.utexas.edu>

Membranes in ChE Education

The basic notion underlying the multicomponent, counter-current simulator developed by Coker, *et al.*, is presented in Figure 5, which shows a diagram of the hollow-fiber module from Figure 1 divided axially into N slices or stages. In a typical simulation, N ranges from a few hundred to several thousand, depending on how rapidly the concentration of the most permeable species changes with axial position along the module. Inside each stage of the membrane, mass transfer occurs according to Eq. (1), which is written analogously for each component.

Using an approach originally developed for staged unit operations such as distillation,^[15] the flow of each component from stage to stage is linked by a mass balance. The set of mass balances for each component on each stage can be written in the form of a family of tridiagonal matrices, which are solved using the Thomas algorithm.^[16] The mass balances are nonlinear, so an iterative solution is required. Moreover, the model allows for pressure in the bore of the hollow fibers to change according to the Hagen-Poiseuille equation, and this introduces another source of nonlinearity into the problem. The details of the solution are provided in the literature.^[4]

The simulation is organized to perform analysis calculations. That is, the membrane permeation characteristics, thickness, fiber inner and outer diameter, fiber length, and number of fibers are all specified via a graphical user interface, shown in Figure 6. The user may select bore-side or shell-side feed. It should be noted that the model is based on plug flow of gas through the module and fibers, so effects associated with gas maldistribution in the module are not captured. The reader is directed to the work of Lipscomb and colleagues for a more detailed description of these effects.^[17]

The so-called “pot length” of the fibers must be specified in the simulation. When membrane fibers are assembled into a module, the membrane bundle is glued or “potted” on both ends in epoxy to provide a leak-free connection between the

fiber bundle and the module housing. Gas can travel down the bore of the fibers in the potted region of the module, which leads to a pressure drop along the bore of the fibers, but because the fibers are covered with epoxy, there is no gas transport across the fiber wall. Typical values of pot length would be 10 cm on each end of a fiber 100 cm long. So, in the case, the “active” length of a fiber (*i.e.*, the length of fiber that is active for mass transfer via permeation) would be 100 cm - 2x10 cm (since the fiber is potted on both ends) = 80 cm.

An on-line databank is available with permeation properties of a few common polymers, such as polysulfone, or the users can supply their own permeation properties. The feed pressure, feed flowrate, feed composition, and permeate pressure are specified by the user. With these inputs, the simulator calculates the concentration, flow and pressure profiles in the module, the residue and permeate composition and flowrate, and the residue pressure. The concentration and flow profiles can be viewed as graphs built into the simulator. A user can establish an account where membrane fiber and module data are stored, so that simulation conditions can be entered and stored for later use. Several example simulations can be downloaded as pdf files.

USING THE INTERNET MODEL FOR TEACHING

Two examples of the use of the model are presented. Other examples are given in the literature.^[4,14] The first case involves a membrane for air drying. The objective is to remove water from air and produce dry air as the residue stream. In conventional gas-separation membranes, water is typically more permeable (by a factor of 50 or more) than air gases such as N_2 and O_2 , so H_2O/N_2 and H_2O/O_2 selectivities are very high. Additionally, the mol fraction of water in air is low. For example, air at 40°C and 10 atmospheres total pressure (conditions that are common for feeding a gas-separation module for air separations), the mole fraction of water at saturation is

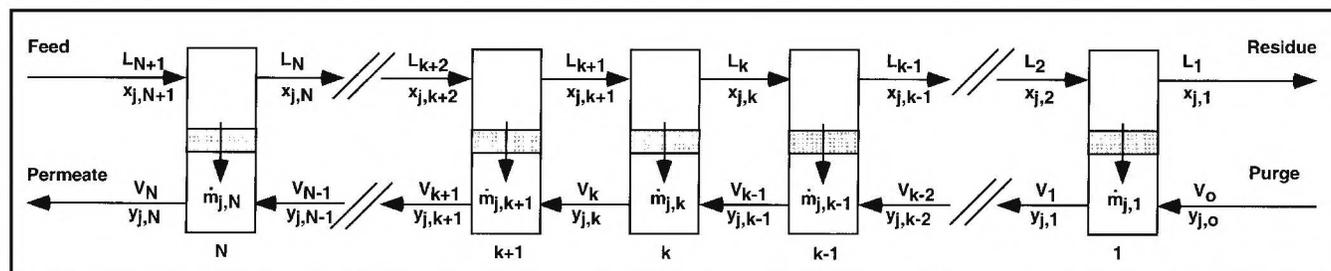


Figure 5. Schematic of hollow-fiber module divided into N stages. In analogy with labeling conventions used in distillation, the flow rate of gas leaving the upstream (*i.e.*, residue) side of stage k is labeled L_k , and the flow rate of gas leaving the downstream (*i.e.*, permeate) side of stage k is labeled V_k . The flow rate of gas of component j that permeates from the upstream to the downstream side of stage k is $\dot{m}_{j,k}$. The mole fractions of component j leaving stage k on the upstream and downstream sides of the membrane are $x_{j,k}$ and $y_{j,k}$, respectively. Adapted from the literature.^[4]

Membranes in ChE Education

0.72%.^[18] These conditions (high selectivity, low feed concentration) lead to pressure-ratio-limited separation, and the amount of water removed from the gas stream is strongly dependent on the downstream partial pressure of water.

If one could lower the downstream partial pressure of water or otherwise accelerate the removal of water from the permeate side of the membrane, then the amount of water that could be removed from the air fed to the module would be enhanced. In practice, this is most often achieved by recycling a small fraction of the dry residue gas to the permeate side of the membrane, as illustrated in Figure 7. This has the benefit of sweeping or purging the permeate of components (*i.e.*, water) that have been preferentially removed by the membrane—this

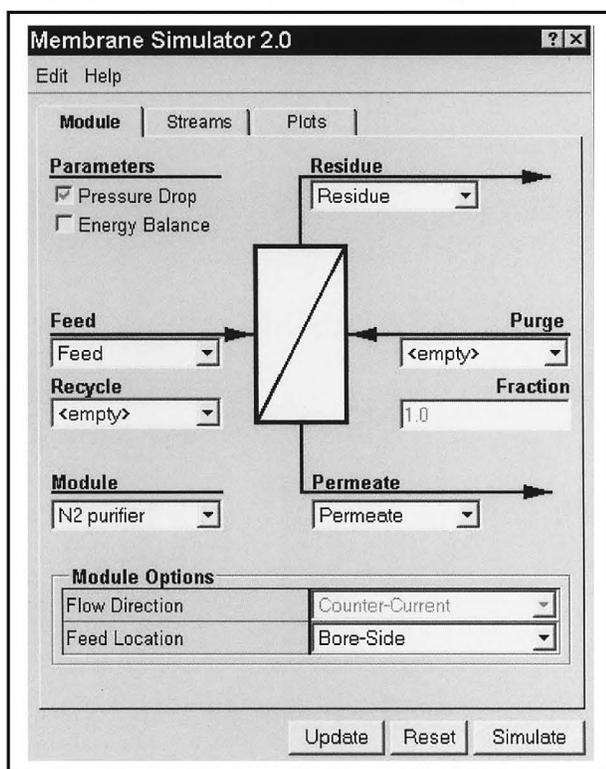


Figure 6. Graphical user interface of the on-line membrane simulator at <http://membrane.ces.utexas.edu>

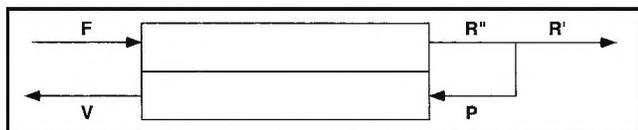


Figure 7. Gas flow configuration in which a portion of the residue stream, P , is returned to the permeate side of the membrane as a sweep or purge stream to increase the driving force for removal of water. Adapted from Coker, et al.^[4] The feed gas flow rate is F , the permeate flow rate is V , and the final residue flow rate of product gas is R' .

recycle stream is often called a purge or sweep stream.

An interesting calculation is to determine the effect of changes in the fraction of the residue stream that is recycled on the water concentration in the product residue gas, usually expressed as the dew point of the residue gas. The general trend, shown in Figure 8, is that using more gas to purge the permeate results in better water removal from the residue (*i.e.*, lower dew point). This results in a smaller amount of the dry product gas being available for use, however, so there is a trade-off between gas dryness and production rate.

Other problems that could be envisioned include replacing the polymer (which is polysulfone in the case of the results presented in Figure 8) with other polymers having different selectivities for water and determining the impact of separation factor on the fraction of residue purge gas needed to achieve a given dewpoint using a standard-size module. A good first approximation of the reduction in the amount of residue gas available for use is the flowrate of residue gas in the absence of purging times the fraction of residue gas removed for purging. This rule-of-thumb is not exact, how-

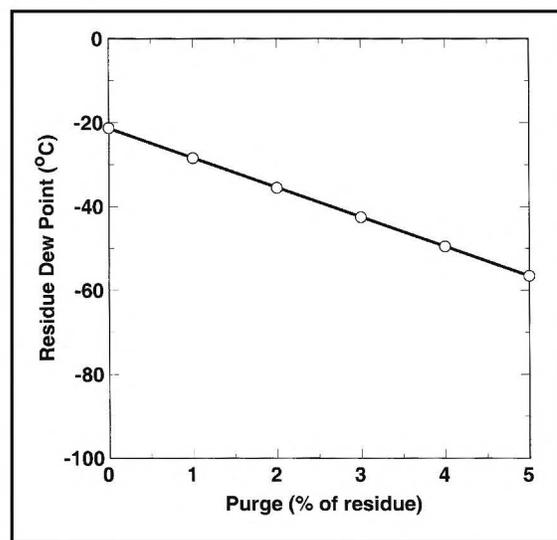


Figure 8. The effect of permeate purge on the dew point of the residue gas obtained by feeding air to a module at 40°C and 10 atm. The permeate pressure is 1 atm, and the permeance of the membrane to water is $1,000 \times 10^{-6} \text{ cm}^3(\text{STP})/(\text{cm}^2 \text{ s cmHg})$. Standard temperature and pressure for permeance, like permeability, are 0°C and 1 atm. The feed air flowrate is 8,000 ft³(60°F, 1 atm)/hr. Specifying gas flowrates at 60°F and 1 atm (rather than at STP) is standard in some process simulators. Other parameters (number and length of fibers, permeance to all other components, etc.) are given in the literature.^[4] The water mole fraction data in the residue stream were converted to dew points using a web-based psychrometric calculator at

<http://www.connel.net/freeware/psychchart.shtml>

Membranes in ChE Education

ever, and it is of interest to allow students to figure out what other factors (*i.e.*, driving force for other components in the feed gas, etc.) might also influence the residue-gas flow rate for such problems.

The second example is hydrogen recovery from a hydrotreatment unit in a refinery. In hydrotreatment, petroleum intermediates are contacted with hydrogen to reduce sulfur, nitrogen, metals, asphaltene, and carbon residue content. This process requires substantial amounts of hydrogen gas, and much of the excess hydrogen can be recycled. Membranes are often used to purify the recycled hydrogen. The major impurities are light hydrocarbons. A typical stream might contain 65 mol % H_2 , 21 mol % CH_4 , and the balance will be other hydrocarbons, such as C_2 and C_3 .^[4]

In the conventional membranes used in this process, hydrogen is by far the most permeable component in the mixture, followed by methane and then by the other hydrocarbons. H_2/CH_4 selectivity values can be of the order of several hundred in commercially used membrane materials.

The objective of this separation is to generate highly purified hydrogen for recycle to the process. Because this is a high-pressure process and because the H_2 product appears in the permeate stream, permeate pressure must be kept as close to the feed pressure as possible to minimize recompression costs. So the pressure ratio is typically not very high. At fixed feed and permeate pressure, the more feed gas that is allowed to permeate through the membrane (by having lower flow rates or larger membrane area, or both), the higher is the recovery of hydrogen in the permeate, but the purity of the permeate stream is lower. So it is instructive to construct so-called purity/recovery curves for this separation.

One example is shown in Figure 9. The curves in this figure were generated by varying the feed flow rate to a module and noting the permeate H_2 purity and flowrate. That is, at very high flow rates, one can produce relatively pure H_2 , but the amount of H_2 recovered in the permeate stream is very low. At the opposite extreme, at very low flow rates, most of the H_2 and CH_4 gas permeates through the membrane, so H_2 recovery is very high, but the purity is quite low. The ideal situation would be to have both high recovery and high purity, but these factors typically work against one another.

Figure 9 also illustrates the impact of pressure ratio on the results. Two pressure scenarios are presented. In both cases, the difference between feed and permeate pressure is identical. The case with lower feed pressure and higher pressure ratio yields superior membrane separation performance, however. Such sensitivity of purity/recovery curves is an indication that the separation is being performed in a pressure-ratio-limited regime.

Other interesting problems include calculating purity/recovery curves for other polymers to understand how the choice of polymer material influences the separation. In this regard, there is a large database of permeability values in the *Polymer Handbook*.^[19] Also, the hydrotreater example as well as the air separation example involve multicomponent mixtures, and one could track the distribution of each of the other components as polymer selectivity, flowrate, feed, or permeate pressure changes. We have used the analytical simulator as well as the Internet version of the simulator in the senior-level design course, and it should be suitable for an undergraduate unit operations course as well.

The Internet simulator allows exploration of the effects of operating the module with bore-side feed or shell-side feed. It is of interest to compare the same separation (*e.g.*, air separation) using bore- and shell-side feed and to explain differences in the separation results. Basically, when the membrane module is fed on the bore side, the permeate gas is collected on the shell side of the module and experiences essentially no pressure drop traveling from one end of the module to the other. There is a slight decrease in pressure along the bore of the fibers, but this decrease is typically small relative to the feed pressure and has a small impact on separation performance.

With shell-side feed, however, the permeate gas flows in the bore of the fibers, and pressures are much lower in the permeate stream than in the residue stream. Small pressure changes along the bore of the fibers, estimated according to the Hagen-Poiseuille relation, can lead to decreases in sepa-

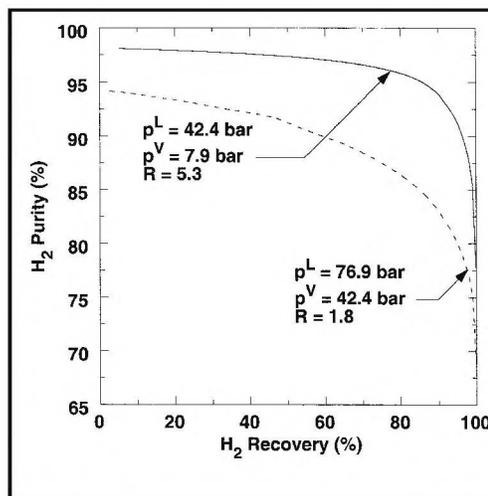


Figure 9. Effect of pressure ratio on H_2 purity and recovery in a hydrotreater application. The membrane properties and module conditions as well as the feed composition are given in Coker, et al.^[4] H_2 recovery in the permeate is the molar flowrate of hydrogen in the permeate divided by the molar flowrate of hydrogen fed to the module.

ration efficiency (lower product purity, less gas permeated per unit area of membrane) relative to bore-side feed.

Additionally, the Internet simulator allows connection of the outlet stream (*e.g.*, residue) from one module as the feed stream to a second module. This feature allows exploration of the effect of connecting modules in series on product gas purity and flowrate. Similarly, the Internet simulator is organized to allow the product gas from one module to be recycled to the feed side of a previous module. Downloadable example files illustrate the use of these features.

If students have access to process simulation tools, comparison with other separation technologies can be interesting. For example, large-scale air separation is currently performed using cryogenic distillation. If one requires only 98% nitrogen for an application (rather than pure nitrogen), current membranes with an O₂/N₂ selectivity of 7 or 8 can readily produce gas at this purity level.

An interesting calculation is to compare capital and operating costs for a cryogenic air-separation plant and a membrane-separation plant to produce nitrogen at such purities. Some variables that could be studied include required product gas flowrate, purity, and pressure. For such rough economic analyses, the installed costs of membranes have been estimated as \$54/m² of membrane surface area.^[20] For a membrane process, the process operating cost is the energy input required to compress air from one atmosphere to the 10-15 atmosphere range normally used for air-separation membranes. Therefore, the higher the purity of the product required, the lower the product recovery and the greater the energy waste due to loss of nitrogen into the low-pressure permeate stream.

Currently, membrane processes do not scale as well as conventional separation technologies. That is, to double the amount of gas being processed by a membrane plant, one needs to install twice as much membrane area, so the capital cost scales linearly with gas flowrate. Processes depending on column-based technology, such as distillation, exhibit much slower increases in capital costs with increasing flow rate, and this factor has led to membranes being used for lower flowrate applications and distillation being used for high-flowrate situations.^[2] One could also explore the effect of new membrane materials development on such a separation. If the O₂/N₂ selectivity of today's membranes could be raised from 7 to 14, how would this influence the capital and operating costs associated with nitrogen production?

CONCLUSION

We have described some basic issues related to the use of polymeric membranes as separation agents, and we have provided two types of tools—one analytical and one Internet-

based—to assist students in gaining intuition into the performance of gas separation membranes. Examples provide some basis for homework or class project activities. Some extensions to the problems discussed in this manuscript would have a significant design component, which might increase their utility.

REFERENCES

1. Zolandz, R.R., and G.K. Fleming, "Gas Permeation" in *Membrane Handbook*, W.S.W. Ho and K.K. Sirkar, eds, Van Nostrand Reinhold, New York, NY, p. 17 (1992)
2. Ghosal, K., and B.D. Freeman, "Gas Separation Using Polymer Membranes: An Overview," *Polym. Adv. Tech.*, **5**(11), 673 (1994)
3. Baker, R.W., *Membrane Technology and Applications*, McGraw-Hill Book Co., New York, NY (2000)
4. Coker, D.T., B.D. Freeman, and G.K. Fleming, "Modeling Multi-component Gas Separation Using Hollow-Fiber Membrane Contactors," *AIChE J.*, **44**(6), 1289 (1998)
5. Graham, T., "On the Absorption and Dialytic Separation of Gases by Colloid Septa. Part I. Action of a Septum of Caoutchouc," *Phil. Mag.*, **32** 401 (1866)
6. Graham, T., "On the Absorption and Dialytic Separation of Gases by Colloid Septa. Part I. Action of a Septum of Caoutchouc," *J. Membrane Sci.*, **100**, 27 (1995)
7. Michaels, A.S., "A Sixty-Year Love Affair with Membranes: Recollections of Richard M. Barrer, Edited and Annotated by Alan S. Michaels," *J. Membrane Sci.*, **109**(1), 1 (1996)
8. Robeson, L.M., "Correlation of Separation Factor Versus Permeability for Polymeric Membranes," *J. Membrane Sci.*, **62**, 165 (1991)
9. Freeman, B.D., "Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes," *Macromolecules*, **32**, 375 (1999)
10. Baker, R.W., and J.G. Wijmans, "Membrane Separation of Organic Vapors from Gas Streams," in *Polymeric Membranes for Gas and Vapor Separations*, D.R. Paul and Y.P. Yampol'skii, eds., CRC Press, Boca Raton, FL (1994)
11. Freeman, B.D., and I. Pinnau, "Separation of Gases Using Solubility-Selective Polymers," *Trends in Poly. Sci.*, **5**(5), 167 (1997)
12. Freeman, B.D., and I. Pinnau, "Polymeric Materials for Gas Separations," in *Polymeric Membranes for Gas and Vapor Separations: Chemistry and Materials Science, ACS Symposium Series Number 733*, B.D. Freeman and I. Pinnau, eds., American Chemical Society, Washington, DC (1999)
13. Weller, S., and W.A. Steiner, "Fractional Permeation Through Membranes," *Chem. Eng. Prog.*, **46**(11), 585 (1950)
14. Coker, D.T., T. Allen, B.D. Freeman, and G.K. Fleming, "Nonisothermal Model for Gas Separation Hollow-Fiber Membranes," *AIChE J.*, **45**(7), 1451 (1999)
15. Stichlmair, J., and J.R. Fair, *Distillation: Principles and Practices*, John Wiley & Sons, New York, NY (1998)
16. King, C.J., *Separation Processes*, McGraw-Hill, New York, NY (1980)
17. Lemanski, J., and G.G. Lipscomb, "Effect of Shell-Side Flows on Hollow-Fiber Membrane Device Performance," *AIChE J.*, **41**(10), 2322 (1995)
18. Felder, R.M., and R.W. Rousseau, *Elementary Principles of Chemical Processes*, John Wiley & Sons, New York, NY (1986)
19. Pauly, S., "Permeability and Diffusion Data," in *Polymer Handbook*, 4th ed., J. Brandrup, E.H. Immergut, and E.A. Grulke, eds., John Wiley and Sons, New York, NY (1999)
20. Baker, R.W., "Future Directions of Membrane Gas Separation Technology," *Ind. Eng. Chem. Res.*, **41**, 1393 (2002) □

MEMBRANE PROJECTS WITH AN INDUSTRIAL FOCUS

In The Curriculum

STEPHANIE FARRELL, ROBERT P. HESKETH, MARIANO J. SAVELSKI,
KEVIN D. DAHM, C. STEWART SLATER
Rowan University • Glassboro, NJ 08028

Educational initiatives are crucial to the continued technical growth and wide-scale commercialization of membrane processes. This paper discusses innovative use of membrane technology in a project-oriented curriculum, building on the prior work of Slater, *et al.*, who developed membrane experiments in a conventional chemical engineering laboratory setting.^[1-7] At Rowan University, the authors have integrated membrane technology throughout the engineering curriculum and involved student teams in a unique multidisciplinary laboratory project experience—the clinics.^[8]

Chemical engineering education is traditionally a process- or systems-oriented curriculum, producing graduates who can apply their process expertise in many industries. Some versatility has been lost over the last several decades due to the overwhelming emphasis on unit operations and design problems pertaining to the petroleum industry. Separation-process needs exist both in the traditional process industries and in emerging areas such as biochemical engineering, specialty chemical manufacture, hazardous waste management, food and beverage processing, microelectronics production, and biomedical engineering.^[9,10] Growth in these technologies will depend on engineers who are well-educated in the field and have a working knowledge of membrane applications in these areas. Education should have a multidisciplinary perspective where students from other fields can apply their expertise to solving membrane-related process problems.^[11]

The need for more instruction in membrane technology and in many other advanced separation processes has been previously addressed.^[12,13] Many schools have graduate courses in advanced mass transfer and some have courses in membrane technology, but introducing it to the undergraduate chemical engineering curriculum is rare. A 1995 study^[14] revealed that only 2.6% of lecture time in an undergraduate mass transfer course is on the subject of membrane processes. ABET's Criteria 2000 specifies many of the outcomes that are included

in this curriculum development: an ability to function in multidisciplinary teams, designing and conducting experiments, understanding safety and environmental issues, analyzing and interpreting data, and using modern engineering tools.^[15]

ROWAN UNIVERSITY'S ENGINEERING CLINIC

Rowan University is a comprehensive regional state university with six colleges: Business Administration, Communications, Education, Engineering, Fine and Performing Arts, and Liberal Arts and Sciences. The College of Engineering was initiated using a major gift in 1992 from the Rowan Foundation.^[16] The engineering program is taking a leadership role by using innovative methods of teaching and learning, as recommended by ASEE,^[17] to prepare students for entry into a

Stephanie Farrell is Associate Professor of Chemical Engineering at Rowan University. She received her BS in 1986 from the University of Pennsylvania, her MS in 1992 from Stevens Institute of Technology, and her PhD in 1996 from New Jersey Institute of Technology. Her teaching and research interests are in controlled drug delivery and biomedical engineering.

Robert Hesketh is Professor of Chemical Engineering at Rowan University. He received his BS in 1982 from the University of Illinois and his PhD from the University of Delaware in 1987. His research is in the areas of reaction engineering, novel separations, and green engineering.

Mariano J. Savelski is Assistant Professor of Chemical Engineering at Rowan University. He received his BS in 1991 from the University of Buenos Aires, his ME in 1994 from the University of Tulsa, and his PhD in 1999 from the University of Oklahoma. His technical research is in the area of process design and optimization with over seven years of industrial experience.

Kevin Dahm is Assistant Professor of Chemical Engineering at Rowan University. He received his PhD in 1998 from Massachusetts Institute of Technology. His primary technical expertise is in chemical kinetics and mechanisms, and his recent educational scholarship focuses on incorporating computing and simulation into the curriculum.

C. Stewart Slater is Professor and Chair of the Department of Chemical Engineering at Rowan University. He received his BS, MS, and PhD from Rutgers University. His research and teaching interests are in separation and purification technology, laboratory development, and investigating novel processes for fields such as bio/pharmaceutical/food engineering and specialty chemical manufacture.

Membranes in ChE Education

rapidly changing and highly competitive marketplace.

To meet these objectives, the four engineering programs of chemical, civil/environmental, electrical/computer, and mechanical engineering have a common engineering “clinic” throughout their programs of study. At the freshman level, students conduct engineering measurements and reverse engineer a process. The sophomore engineering clinic is communications-intensive and also introduces students to the design process of each discipline and to related topics of product/process function. The junior and senior clinics provide an opportunity for the most ambitious part of our project-intensive curriculum—team projects employing modern technologies that tie together many engineering and scientific principles. Institutions that have similarly named engineering “clinics” are Harvey Mudd College and California State Polytechnic University, Pomona.^[18] Our flexible clinic model allows departmental and interdepartmental initiatives that satisfy programmatic and faculty/student/university developmental needs. These clinics also provide an opportunity for industrial involvement in the sponsoring and mentoring of projects.^[18]

This ambitious program takes a leading-edge technology such as membrane processes and uses it as the focal point of curricular innovation in our College of Engineering. We have involved teams of engineering students in process research, development, design, and analysis of experimental systems. Students have gained an understanding of the fundamental aspects of membrane technology, process design, and application to new and emerging fields. Our curriculum is considered to be project-intensive and industrially oriented, with a strong hands-on component. One of the most important attributes obtained through this type of activity is a focus on “soft skills.” Students working on designing, fabricating, and starting up an experimental system have a much richer environment of interacting in a team setting. Team dynamics improve and management skills are incorporated into the project. Students’ informal and formal communication skills are also enhanced. Our Chemical Engineering Industrial Advisory Board has endorsed this concept from the technical side and in preparing students in other areas such as teamwork and communication skills.

PROJECT IMPLEMENTATION

The major focus of the innovative aspects of this project is the junior and senior engineering clinics where multidisciplinary teams (3-4 students/team) work on open-ended projects in various areas, many linked to industry or a faculty grant from a state or federal agency. These projects emanate from a particular discipline, are led by that department’s faculty, and typically involve an industrial mentor.

The teams are matched by the faculty Project Manager (PM) to achieve the best results in the individual projects. Teams may combine various fields of expertise within a classic discipline (environmental, water resources, and structural in CEE; biochemical and polymer in ChE; science with engineering in Chem and ChE) as recommended by the recent report of the NRC.^[8] In some cases, student “consultants” from other disciplines assist on a limited basis, representing the realistic role found in industry. Students are required to produce a written report or paper/journal publication and present an oral report at the end of the semester.



Figure 1. Student conducting membrane separation study of vegetable product stream.

Several selected membrane-oriented clinic projects are summarized below. A full listing of Rowan clinic projects can be obtained at <<http://sun00.rowan.edu/programs/chemical/clinic.html>>.

Advanced Vegetable Processing Technology

In a project sponsored by Campbell Soup Company, a team of students researched cutting-edge technologies, such as novel membrane processes, for processing soups and juices. The multidisciplinary team consisted of two undergraduate chemical engineering students, one civil engineering student, and one biology student. In addition, one master’s student served as PM. Campbell Soup has its corporate R&D facilities in nearby Camden, New Jersey, facilitating frequent progress meetings with the project sponsors.

Through this project, students investigated advanced membrane separation techniques as well as enzymatic, thermal, and physical/mechanical treatment techniques applied to vegetable processing. Their responsibility included HAZOP analysis, project planning, budget formulation and management, literature and patent reviews, experimental design, and development of a proposal for a second phase of the clinic project (see Figure 1). In addition to the engineering expertise the students acquired through this project, they gained

Membranes in ChE Education

familiarity with Food and Drug Administration regulations, good manufacturing practices, and labeling requirements.

Engineers from Campbell's demonstrated a high level of commitment to the project by attending monthly progress meetings where the students gave oral presentations on their progress. This was followed by brainstorming and discussion sessions where the industrial representatives and faculty refocused and fine-tuned the project. This industrial interaction helped maintain a high level of motivation among the students and maintained the focus and a fast pace of productivity. In addition to the progress meetings, the student team also conducted a "lunch-and-learn" seminar at Campbell's to share their research with engineers, scientists, and marketing representatives from the company. The enthusiastic response of the audience at Campbell's reaffirmed the industrial relevance and impact of the team's clinic research project.

Campbell Soup Company is a strong supporter of our program, not only by supporting the clinic project mentioned above, but also by employing both full-time and internship students from our program. In the summer following the vegetable processing project, two undergraduate students accepted summer internships at Campbell's. The students had the rewarding experience of successfully implementing two of the technologies developed at Rowan into Campbell's processing facilities in California and New Jersey.

Metals Purification Processes

Various metals purification projects have been sponsored by Johnson Matthey, Inc. A precious metals "refinery" is operated at West Deptford, New Jersey, which is less than ten minutes from our campus. This close proximity facilitates numerous interactions and projects that we have with Johnson Matthey. The company has sponsored three years of engineering clinic projects with the objective of investigating novel techniques that have the potential to replace current "traditional" refinery process units.

At the refinery, precious metals such as Pt, Pd, and Rh are purified from feed streams containing many unwanted metal species and other impurities. The feed streams are made up of spent catalysts from which precious metals are recovered and recycled to feed stream from mines. In the refinery, there are many dissolution, selective-precipitation, and filtration steps. Using innovative membrane processes, the plant capacity, product purity, and processing costs have the potential to be improved. In essence, students have an opportunity in the engineering clinic to conduct engineering projects that are equivalent in scope to those done by engineers in the plant. Our most successful project resulted in Johnson Matthey adding several new processing units to their refinery.

One of the Johnson Matthey projects involving membranes

was electro dialysis process development for separation of a precious metal chloride salt solution that was contaminated with unwanted acids and salts. The traditional separation and purification steps used in the production of these metal compound solutions include multiple precipitation and dilution steps that are time-consuming and labor intensive and result in a significant loss of product. Development of an alternative separation and purification technique was the aim of this project.

The specific objectives of the projects were

- To design and build an electro dialysis unit for the separation and purification of the desired process stream
- To investigate the performance of electro dialysis in the removal of the salt contaminant from the product on a laboratory scale

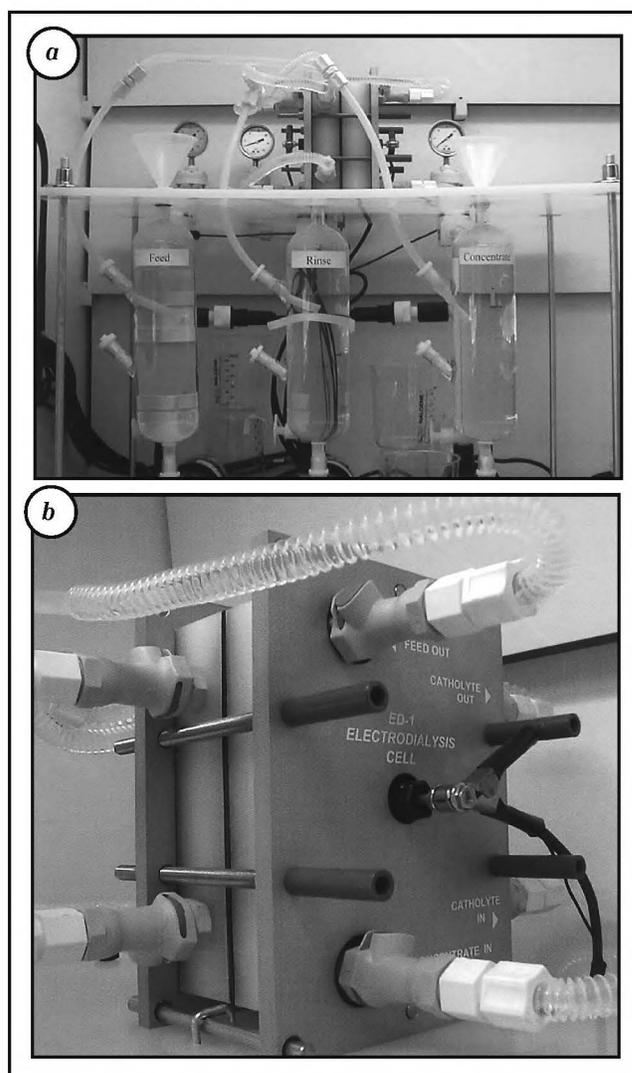


Figure 2. (a) Electro dialysis process system used in precious metals separation clinic project. (b) Electro dialysis cell used in the process system.

Membranes in ChE Education

- To perform an economic analysis of the proposed process in comparison with the traditional technique
- To scale up the process to pilot scale

The potential outcomes include reduction of operating costs, increased product yield, and increased product output by an order of magnitude.

The first phase of the project involved the design and assembly of a laboratory-scale electro dialysis unit and preliminary benchmark testing (see Figures 2a and 2b). The second phase of the project involved investigation of process parameters on the yield and selectivity of the product. Typical student results for the removal of an ammonium chloride contaminant are shown in Figure 3. Subsequent experiments were conducted to investigate the impact of size-selective and charge-selective ion exchange membranes on the retention of desired product. Based on the experimental results, the process was scaled up to pilot scale and an economic investigation was conducted to examine the trade-off between capital costs and operating costs as well as the overall economic feasibility of the process. The process demonstrates the potential for reduced operating costs and increased product yield and selectivity and is currently being evaluated further by Johnson Matthey.

Johnson Matthey has provided significant support to our chemical engineering department and was a “charter member” of the PRIDE program (Partners with Rowan in Developing Engineers). They have employed Rowan chemical engineering students both as interns and as permanent employees.

Ceramic Membrane Reactor System

In this project, a ceramic membrane reactor has been designed and constructed by a team of three undergraduate students. The reactor, used for the production of ethylene from the dehydrogenation of ethane, is modeled after that of Champagne and colleagues.^[19,20] Equilibrium as a reaction constraint and methods to shift equilibrium in favor of desired products are taught in chemistry and chemical reaction engineering courses, but a student rarely uses these techniques in experiments. This reactor, when integrated into an undergraduate

course on reaction engineering, demonstrates the advantages of using advanced membrane technology in combination with reaction kinetics. The basic operational principle behind the ceramic membrane reactor is that removal of a reaction product (hydrogen) through the membrane drives the reaction beyond the equilibrium constraints set by the feed composition and reaction temperature and pressure.

Ethane dehydrogenation was chosen as an example for a number of reasons. The most compelling was that ethylene is a chemical that is familiar to the students, and at over 50 billion pounds per year it is one of the top five chemicals in annual worldwide sales,^[21] making the problem recognizable as a practical one. Another point is that the reaction is very endothermic, and temperatures in excess of 1000 K are needed for the reaction to approach completion. The student team first explored the feasibility of the membrane reactor concept through modeling studies, using the assumption that Knudsen diffusion describes the operation of the membrane. Students modeled the system in HYSYS, using an alternating series of equilibrium reactors and separators to approximate a simultaneous reaction/separation. These studies suggest that the membrane reactor

should be able to achieve a given conversion at temperatures hundreds of degrees Kelvin lower than needed in a conventional plug flow reactor of the same volume. Students readily appreciate the desirability of operating at lower temperatures, both in terms of cost and safety. Thus, this project integrates many process design concepts. The process flow diagram of the system is shown in Figure 4.

The reactor consists of a quartz shell surrounding a platinum-coated ceramic membrane tube. The ceramic membrane was obtained from US Filter and has a pore size of 5nm. Students worked in conjunction with Johnson Matthey and students and faculty from the Department of Chemistry to devise and carry out a workable plan for coating the catalyst tubes using a chloroplatinic acid process. The reactant and product concentrations are measured using an HP 6890 GC/MS. The only other equipment required included Fisher heating tapes, temperature

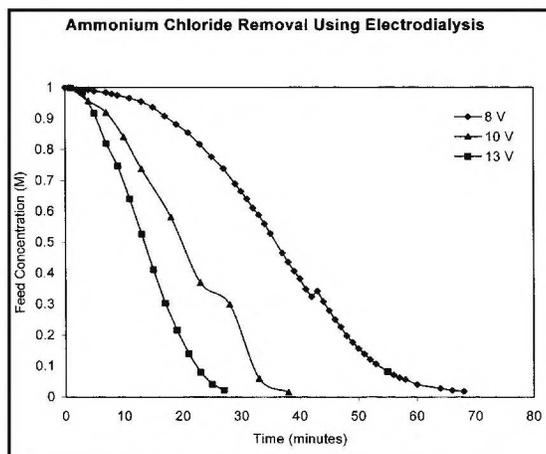


Figure 3. Typical student data showing the effect of voltage on the removal of an ammonium chloride contaminant from a precious metal feed solution.

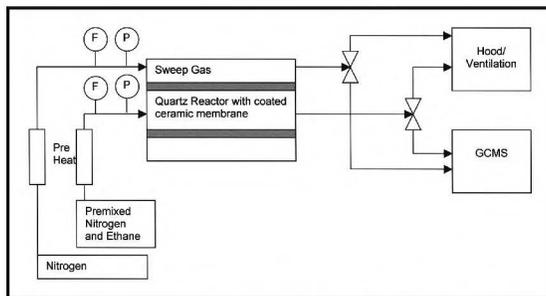


Figure 4. Process flow diagram of the ceramic membrane reactor project.

Membranes in ChE Education

controllers, and mass flow meters. The total cost of the system, including reactor and catalyst (but excluding the GC/MS, which was previously on site) was less than \$2000.

In addition to illustrating important chemical engineering concepts, this setup also demonstrates some interesting practical issues to the students. One point is that although “isothermal reactors” are routinely posed in problems and modeled by undergraduate students, students do not necessarily appreciate the difficulty involved in carrying out a reaction that is truly isothermal. In this case, the reaction is very endothermic and is carried out well above room temperature—both factors that complicate maintaining an isothermal reaction. Another issue is the difficulty of creating gas-tight seals when working with materials (such as the ceramic membrane) that expand significantly with increasing temperature. Working with the chemical engineering lab technician, the students devised a procedure for sealing the reactor after it had al-

ready been brought to temperature. After the experiment is complete, the temperature is maintained and the system is purged with nitrogen before the seal is broken. Throughout the “design-and-build” phase of this project, the student team worked with various technicians in the college, from machining parts to electronic controls.

ASSESSMENT

Of significant importance to chemical engineering educators is satisfying the new EC2000 requirements of ABET, the most vexing of which are the “soft skills” represented by Criterion 3, f-i. The projects mentioned above can effectively satisfy these criteria, and the outcomes can be effectively assessed in a sustainable way. Our program has firsthand experience with this and has used various assessment instruments to verify the results. Table 1 indicates how the membrane projects meet the EC2000 requirements.

TABLE 1
ABET Criterion 3 (a-k) in the Membrane Projects

<u>Criterion</u>	<u>Membrane Project Implementation</u>
a Apply math, science and engineering	<ul style="list-style-type: none"> • Projects apply basic mathematics such as in calculating fluxes. Chemistry is applied in understanding the nature of the solutions to be separated and membrane structure. • Chemical engineering is applied from membrane mass transfer to process transport analysis.
b Design/conduct experiments and analyze data	<ul style="list-style-type: none"> • The membrane projects involve experimentation—students must design the studies to be conducted and collect, correlate, and analyze their experimental results. Modern software tools are used.
c Design process	<ul style="list-style-type: none"> • In most of the projects, the students design the bench-scale process unit to be used. In some of the projects, students present a final scale-up “paper” design for plant implementation that may include multiple sequential processes.
d Function of multidisciplinary teams	<ul style="list-style-type: none"> • Inherent in the Rowan clinic program is that students perform the project in multidisciplinary or multifunctional teams. Each student has a role simulating actual industrial membrane project staffing.
e Formulate/solve engineering problems	<ul style="list-style-type: none"> • While many of the projects have their original problem statements formulated by industry, the student teams may refine the problem and obviously will be the ones solving the process problem.
f Professional and ethical responsibility	<ul style="list-style-type: none"> • Students learn about many aspects, such as safe handling and disposal of chemicals, safety, and process responsibility.
g Communicate effectively	<ul style="list-style-type: none"> • All students must give an oral report and submit a final written report at the end of each semester. • Additionally, students engage in meetings with industrial representatives and present/defend their findings. • Senior Clinic counts as the “writing intensive” part of our curriculum.
h Impact of engineering on society	<ul style="list-style-type: none"> • Through these projects, students learn the impact of membrane technology on society, such as in waste management, water reuse, purification of pharmaceuticals, and energy conservation.
i Life-long learning	<ul style="list-style-type: none"> • The membrane projects have stimulated students to consider continuing their education, and many of them have gone on to pursue Masters or Doctoral degrees.
j Contemporary issues	<ul style="list-style-type: none"> • Membrane processes are used in many contemporary problems facing society, such as environmental management, health care, and the production of potable water.
k Modern engineering tools	<ul style="list-style-type: none"> • Membranes are indeed a modern engineering process and therefore satisfies this broad category. Other modern engineering tools used in the membrane projects include analytical instrumentation, computer data acquisition/control, and computer hardware and software.
l University-specific criteria: Undergraduate research/emerging fields	<ul style="list-style-type: none"> • A unique criteria added at Rowan University was to engage undergraduate students in research in emerging fields, which these membrane projects effectively do.

Student feedback from the clinic projects mentioned above has been extremely positive. The experiential outcomes of our clinic projects have been assessed in several ways. We have conducted student focus groups, and representative comments from students on the membrane projects include: "The clinics gave me industrial hands-on experience that has helped me understand chemical engineering better." "I liked working in a team and having an industrial focus to my project." "I learned project management and research skills through the clinic and was more excited because it was a real industrial problem our group was solving.

Senior exit interviews have also been conducted. The responses from several questions related to the curriculum development described in this paper from twelve graduating seniors involved in the projects are:

- In the area of experimental research methods, can you write literature reviews, design experiments, and present research results? 91.7% Yes; 8.3% Maybe
- In the laboratory, can you make appropriate measurements, record information in a meaningful format, perform necessary analysis, and convey an interpretation of the results to an appropriate audience? 91.7% Yes; 8.3% Maybe
- Can you select a process component based on chemical engineering principles that is of an appropriate size and type to meet desired needs? 91.7% Yes; 8.3% Maybe
- Can you conduct experiments in a safe manner and understand safe practices and hazards? 100% Yes
- Can you interact synergistically with students from other disciplines, backgrounds, and cultures to achieve a common goal? 100% Yes
- In Classroom, design, and laboratory activities, can you identify known variables, formulate key relationships between them, solve engineering problems, and assess the reasonableness of their problem solutions? 100% Yes
- Can you write effective documents, including memos, e-mails, business letters, technical reports, operations manuals, and descriptions of systems, processes, or components? 100% Yes
- Can you give effective oral presentations? 100% Yes
- Are the Junior/Senior Clinic projects a valuable experience in your preparation as a chemical engineer? 100% Yes

SUMMARY

Through the support of NSF and several industries, multidisciplinary student projects were initiated that challenged student teams to solve realistic industrial problems. These projects are versatile and can be modified slightly for use as laboratory experiments to provide the curricular development. The clinic projects help the forward-looking EC2000 curriculum by providing a focal point for ability to function in multidisciplinary teams, ability to design and conduct experiments, understand safety and environmental issues, analyze and interpret data, and use modern engineering tools. In a primarily undergraduate institution such as Rowan University, these projects provide an opportunity for faculty/student scholarship.

ACKNOWLEDGMENTS

Support for the industrial projects mentioned above has been provided by the sponsors, Johnson Matthey, Inc., and Campbell Soup Company, to which our department is grateful. Some support for membrane equipment purchased for these projects was provided by a grant (DUE-9850535) from the National Science Foundation through the Division for Undergraduate Education.

REFERENCES

1. Slater, C.S., "A Manually Operated Reverse Osmosis Experiment," *Int. J. Eng. Ed.*, **10**, 195 (1994)
2. Slater, C.S., "Education on Membrane Science and Technology," in *Membrane Processes in Separation and Purification*, K.W. Boddeker and J.G. Crespo, eds., Kluwer Academic Publishers, Boston MA (1994)
3. Slater, C.S., and H.C. Hollein, "Educational Initiatives in Teaching Membrane Technology," *Desalination*, **90**, 291 (1993)
4. Slater, C.S., C. Vega, and M. Boegel, "Experiments in Gas Permeation Membrane Processes," *Int. J. Eng. Ed.*, **7**, 368 (1992)
5. Slater, C.S., and J.D. Paccione, "A Reverse Osmosis System for an Advanced Separation Process Laboratory," *Chem. Eng. Ed.*, **22**, 138 (1987)
6. Slater, C.S., H.C. Hollein, P.O. Antonecchia, L.S. Mazzella, and J.D. Paccione, "Laboratory Experiences in Membrane Separation Processes," *Int. J. Eng. Ed.*, **5**, 369 (1989)
7. Hollein, H.C., C.S. Slater, R.L. D' Aquino, and A.L. Witt, "Bioseparation via Cross Flow Membrane Filtration," *Chem. Eng. Ed.*, **29**, 86 (1995)
8. Newell, J.A., S. Farrell, R.P. Hesketh, C.S. Slater, "Introducing Emerging Technologies into the Curriculum Through a Multidisciplinary Research Experience," *Chem. Eng. Ed.*, **35**, 296 (2001)
9. Garside, J., and S. Furusaki, *The Expanding World of Chemical Engineering*, Gordon and Breach Science Publishers, Amsterdam, The Netherlands (1994)
10. Hegedus, L.L. (National Research Council, Committee on Critical Technologies), *Critical Technologies: The Role of Chemistry and Chemical Engineering*, National Academy Press, Washington, DC (1992)
11. American Chemical Society, American Institute of Chemical Engineers, The Chemical Manufacturers Association, The Council for Chemical Research, The Synthetic Organic Chemical Manufacturers Association, *Technology Vision 2020*, American Chemical Society, Washington, DC (1996)
12. Wankat, P.C., R.P. Hesketh, K.H. Schulz, and C.S. Slater "Separations: What to Teach Undergraduates," *Chem. Eng. Ed.*, **28**, 12 (1994)
13. King, C.J. (National Research Council, Committee on Separation Science and Technology), *Separation and Purification: Critical Needs and Opportunities*, National Academy Press, Washington, DC (1987)
14. Griffith, J.D., "The Teaching of Undergraduate Mass Transfer," AIChE Annual Meeting Paper 245a, Miami Beach, FL (1995)
15. Engineering Accreditation Commission of the Accreditation Board for Engineering and Technology, "Engineering Criteria 2000," Dec. (1995)
16. Rowan, H.M., and J.C. Smith, *The Fire Within*, Penton Publishers, Cleveland, OH (1995)
17. "Engineering Education for a Changing World," joint project report by the Engineering Deans Council and Corporate Roundtable of the American Society for Engineering Education, Washington, DC (1994)
18. Annon., "The Engineers Are In! The Cal Poly Pomona Engineering Interdisciplinary Clinic," *Chem. Eng. Prog.*, **S5**, November (1995)
19. Champagne, A.M., T.T. Tsotsis, R.G. Minet, and I.A. Webster, "A High Temperature Catalytic Membrane Reactor for Ethane Dehydrogenation," *Chem. Eng. Sci.*, **45**, 2423 (1990)
20. Champagne, A.M., T.T. Tsotsis, R.G. Minet, and E. Wagner, "The Study of Ethane Dehydrogenation in a Catalytic Membrane Reactor," *J. Catal.*, **134**, 713 (1992)
21. <http://www.chemexpo.com/news/> □

A Simple Analysis For GAS SEPARATION MEMBRANE EXPERIMENTS

RICHARD A. DAVIS, ORVILLE C. SANDALL*
University of Minnesota Duluth • Duluth, MN 55812

Membrane applications for gas separations have made rapid advances over the past decade.^[1] In some cases, membrane technologies have been used to enhance or replace more traditional methods of gas purification. The need for educating undergraduate chemical engineering students about membrane-based separations has not gone unnoticed. Newer editions of popular separations textbooks have added chapters on membranes with sections on gas permeation.^[2-4]

Earlier, Davis and Sandall^[5] described an undergraduate laboratory membrane experiment and analysis for separating the components of air. It remains relevant today as one approach to providing students with hands-on experience with this important technology. The experimental objectives included an inverse mass transfer analysis of experimental data for key membrane transport parameters. The original analysis involved solving a set of differential species balances and fitting the results to experimental data by iterative, trial-and-error techniques. They found that the numerical methods required to implement their analysis were beyond the scope of the undergraduate chemical engineering laboratory experience. Consequently, they provided students with True BASIC programs that were used to solve the model equations. Unfortunately, the programs were limited to the specific membrane configuration in the laboratory. Students were unable to explore alternative designs using the validated models without modifying the programs. In the meantime, several popular, modern, computational software applications (such as Excel, Mathcad, Matlab, or Polymath) have emerged that provide readily accessible tools for solving complex problems that involve nonlinear algebraic and differential equations. The drawbacks in the original analysis, along with developments in computational tools, have led to a simpler alternative analysis described in this paper.

EXPERIMENT

Davis and Sandall^[5] provided specific details of the experimental objectives, apparatus, and procedure for a commercial hollow-fiber membrane unit for air separation. The Prism separator developed by Permea

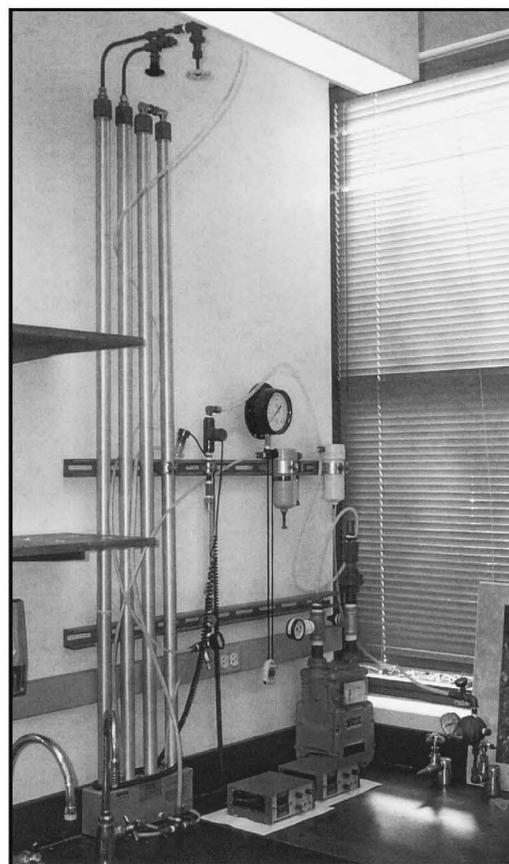


Figure 1. Prism hollow-fiber membrane apparatus.

Richard A. Davis is Associate Professor in the Department of Chemical Engineering at the University of Minnesota Duluth. He earned his BS in Chemical Engineering from Brigham Young University and his PhD from the University of California, Santa Barbara. He teaches a variety of courses in transport phenomena and separations, and his current research interests include process modeling and optimization.

Orville C. Sandall is Professor of Chemical Engineering at the University of California, Santa Barbara. He is a graduate of the University of Alberta (BSc and MSc) and the University of California, Berkeley (PhD). His teaching and research interests are in the areas of mass transfer and separation processes.

* University of California, Santa Barbara, CA 93106

Corporation, shown in Figure 1, consists of four hollow-fiber membrane modules arranged in a series of columns. Each module is a shell-and-tube arrangement of a bundle of hollow-fiber membranes that are capped at the top. High-pressure feed air is introduced to the shell side of the fibers. The permeating gas flows through the hollow-fiber bores and is collected in a manifold at the open end. The pressure drop across the shell side of the membrane unit was found to be negligible.^[5] The permeate streams are open to the atmosphere. The pressure at the closed end of the fiber bores is not directly measurable in the current module arrangements. Information about fiber length, fiber inside diameter, and the number of fibers in the Prism separator bundle is not available, but a conservative estimate of the pressure build-up in the fiber bore was calculated to increase by less than nine percent above atmospheric pressure for the range of experimental operating conditions. For most of the experiments, the pressure build-up was estimated to be less than three percent.

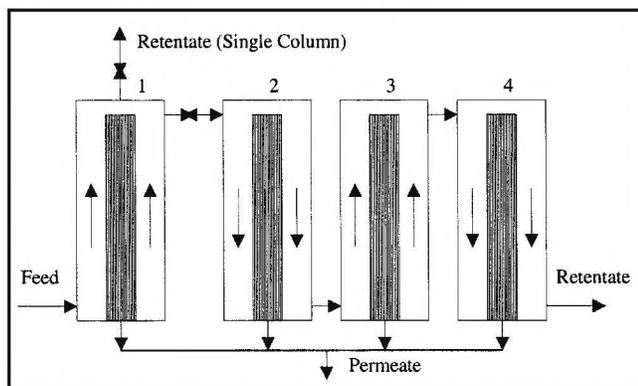


Figure 2. Schematic of single, countercurrent flow column or four columns with alternating flow patterns.

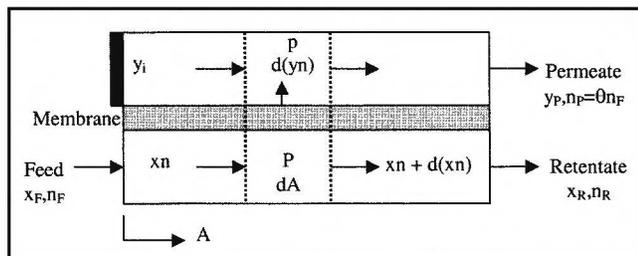


Figure 3. Ideal cocurrent flow pattern

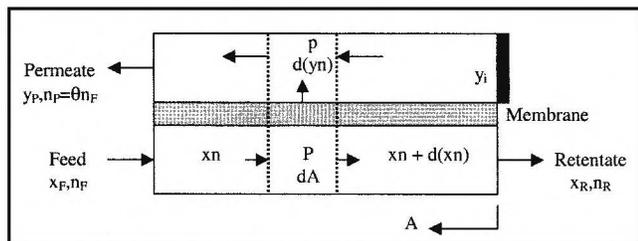


Figure 4. Ideal countercurrent flow pattern.

Modern gas-separation membrane modules introduce the high-pressure feed to the bore side of the fibers to eliminate channeling and maintain a more uniform flow distribution. High-pressure feed to the fiber bores can result in a significant axial pressure drop in the fibers. Although not required for this membrane module, the effects of pressure are included in the analysis for completeness.

As shown in the schematic of Figure 2, the air-flow pattern consists of alternating countercurrent and cocurrent flow through the columns. The composition of the retentate and permeate streams was measured with oxygen analyzers. The flow rate of the retentate stream was measured with a volumetric flow meter. The feed and permeate flow rates may be calculated by mass balances.

The membrane separator may be operated as four columns in series, or as a single column by closing a valve on the tube connecting the retentate and feed streams between the first two columns. The first column operates in countercurrent flow and was used to calibrate the membrane models from a series of runs performed at various feed-flow rates and pressures. The calibrated model was confirmed by favorable comparisons of model predictions with experimental results from the four-column configuration.

THEORY AND ANALYSIS

A differential model of binary gas separation in the membrane experiment was validated by Davis and Sandall and is summarized next. For the conditions of the experiment, it can be shown that a simplification to the equations permits an algebraic solution.

The mathematical model of membrane gas separation was based on several key assumptions. First, the temperature was assumed to be constant. Further, it was assumed that all streams through the shell and permeate sides of the fibers were in plug flow. The air fed to the unit was assumed to be a binary mixture of 79% N_2 and 21% O_2 . All four columns were assumed to have the same dimensions and specific area for mass transfer. Finally, axial pressure drop was ignored for the fiber bore. This assumption is valid for low permeate flow or large transmembrane pressure differences where small changes in permeate pressure are negligible relative to the high feed pressure.

■ Differential Model

Walawender and Stern^[6] derived the differential equations for a binary gas system in countercurrent and cocurrent plug flow patterns, shown ideally in Figures 3 and 4. Details of the derivation are available in several references.^[3,5,6] For a binary gas system, the total mole and O_2 species balances around the separator are

Membranes in ChE Education

$$n_F = n_R + n_p \quad (1)$$

$$x_F n_F = x_R n_R + y_p n_p \quad (2)$$

where n_F , n_R , and n_p are the molar flow rates of the feed, retentate, and permeate streams, respectively, and x_F , x_R , and x_p are the feed, retentate, and permeate O_2 mole fractions, respectively. The species balances around a differential volume element in the membrane give

$$d(xn) = Q_{O_2}'(x_P - y_p)dA \quad (3)$$

$$d[(1-x)n] = Q_{N_2}'[(1-x)P - (1-y)p]dA \quad (4)$$

where Q_j' is the permeance of species j , A is the membrane surface area, and P and p are the average retentate and permeate side pressures, respectively.

For convenience in the analysis, Eqs. (1) to (4) were combined into the following dimensionless equations for countercurrent flow:

$$K_R \frac{dx}{dA^*} = \left(\frac{x-y}{x_R - y_i} \right) \left\{ \alpha^* (1-x)(xr-y) - x[(1-x)r - (1-y)] \right\} \quad (5)$$

$$K_R \frac{dy}{dA^*} = \left(\frac{x-y}{x_R - x} \right) \left\{ \alpha^* (1-y)(xr-y) - y[(1-x)r - (1-y)] \right\} \quad (6)$$

$$K_R \frac{dn^*}{dA^*} = \alpha^* (xr-y) + (1-x)r - (1-y) \quad (7)$$

where y_i is the mole fraction in the permeate at the closed end of the fibers. The dimensionless transport parameters are defined as

$$A^* = A / A_m \quad (8)$$

$$r = P / p \quad (9)$$

$$K_R = n_R / Q_{N_2}' A_m P \quad (10)$$

$$\alpha^* = Q_{O_2}' / Q_{N_2}' \quad (11)$$

$$n^* = n / n_R \quad (12)$$

where A_m is the total membrane area. The ideal separation factor, α^* , was assumed constant, but the dimensionless transport parameter, K_R , was defined as a function of the retentate molar flow rate. The solution to Eq. (7) was used to check the assumptions leading to the algebraic model of the next section. The countercurrent flow equations are integrated from the retentate end of the membrane, subject to the initial conditions

$$\left. \begin{array}{l} x = x_R \\ y = y_i \\ n^* = 1 \end{array} \right\} \text{at } A^* = 0 \quad (13)$$

Note the discontinuity in Eq. (6) at $x = x_R$ requires application of l'Hôpital's rule.^[6]

The dimensionless cocurrent flow model equations are

$$K_F \frac{dx}{dA^*} = \left(\frac{x-y}{y - x_F} \right) \left\{ \alpha^* (1-x)(xr-y) - x[(1-x)r - (1-y)] \right\} \quad (14)$$

$$K_F \frac{dy}{dA^*} = \left(\frac{x-y}{x - x_F} \right) \left\{ \alpha^* (1-y)(xr-y) - y[(1-x)r - (1-y)] \right\} \quad (15)$$

where

$$K_F = \frac{n_F}{Q_{N_2}' A_m P} \quad (16)$$

The cocurrent model equations are integrated from the feed end, subject to the initial conditions

$$\left. \begin{array}{l} x = x_F \\ y = y_i \end{array} \right\} \text{at } A^* = 0 \quad (17)$$

The permeate composition at the capped end of the hollow fibers is calculated from the ratio of Eqs. (3) and (4)

$$\frac{y_i}{1-y_i} = \frac{\alpha^* [xr - y_i]}{[(1-x)r - (1-y_i)]} \quad (18)$$

where, for countercurrent flow, $x = x_R$. For cocurrent flow, $x = x_F$. Equation (18) is quadratic in y_i . Note that there is an error in the denominators of Eqs. (17) and (22) of the paper by Davis and Sandall.^[5] The correct solution to the quadratic equation is

$$y_i = \frac{(\alpha^* - 1)(xr+1) + r - \sqrt{[(\alpha^* - 1)(xr+1) + r]^2 - 4(\alpha^* - 1)\alpha^* xr}}{2(\alpha^* - 1)} \quad (19)$$

Davis and Sandall successfully used the differential model in their analysis of O_2/N_2 separation in the membrane module. At the time, they found that the background required to solve the model equations for α^* and K_R was beyond the scope of an undergraduate student in their laboratory course. Consequently, they developed True BASIC programs that were provided to the students to solve the model equations. Since then, advances in computational software (such as Mathcad) have simplified the process of solving the model

equations. Undergraduate students are now able to develop their own solutions using standard numerical methods for solving systems of nonlinear equations or differential equations that are readily available in these computer tools.

Nevertheless, students are still required to set up a standard method such as Euler's or Runge-Kutta for the initial-value problems in order to find the values for α^* and K_R by inverse analysis of the first column in countercurrent flow. For example, Mathcad and Polymath do not permit their intrinsic capabilities for solving systems of first-order differential equations to be treated as part of another function. An example of programming required in Mathcad for the inverse mass transfer is shown in Figure 5. This type of solution may be intimidating for undergraduate students, depending on their level of experience. This realization, along with the observation that the composition profiles along the membrane were approximately linear, led to the following alternative analysis that avoids the initial-value problem solution requirements entirely.

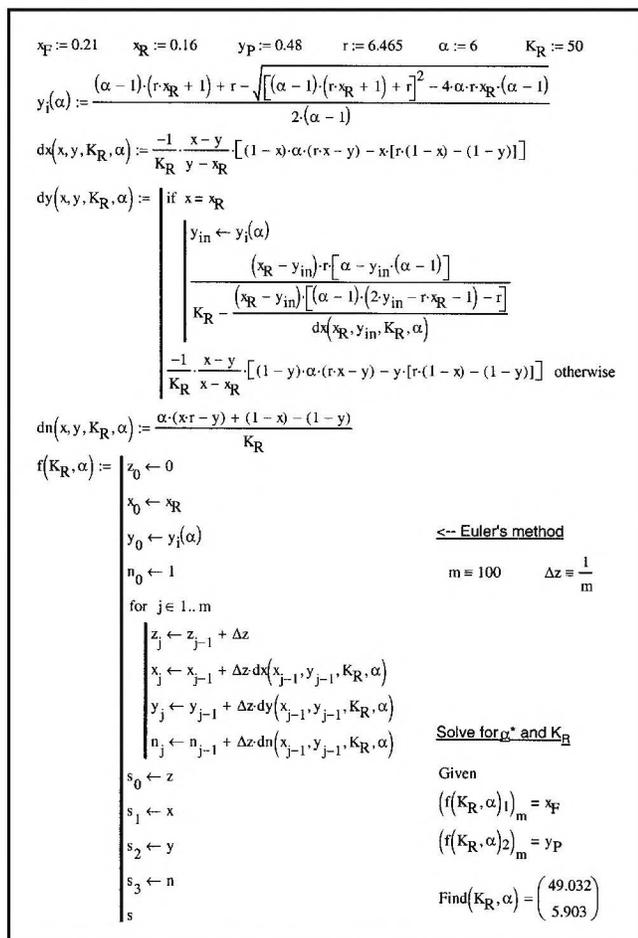


Figure 5. Example of Mathcad programming for inverse mass transfer analysis for α^* and K_R .

Algebraic Model

Boucif, *et al.*,^[7] presented a series solution to the binary component differential model Eqs. (5), (6), (14), and (15) that requires a numerical solution to a pair of third-order polynomial equations. The solution to the series equations agrees with numerical solutions to the differential model when the cut is less than 50%. The series solution does not include axial pressure effects in the feed or permeate gas, however. Hundyil and Koros^[8] presented a more complete analysis of hollow-fiber membrane modules for multicomponent gas separation that includes pressure effects. Their approach is based on a finite-volume element model that requires iterative solutions to a large system of nonlinear algebraic equations. The finite-element approach is recommended when detailed information of pressure, temperature, and composition effects is required.

A simpler, alternative analysis of the membrane unit described here was developed that involves only the solution to a small system of nonlinear algebraic equations and includes pressure effects when necessary. The simpler-model equations are analogous to the shell-and-tube heat-exchanger design equations that are familiar to undergraduate chemical engineering students. The following analysis assumes laminar flow and constant species permeances that are independent of the pressure and composition of the feed or permeate gas. The Hagen-Poiseuille equation is commonly used to calculate axial pressure effects^[9]

$$\frac{dp}{dz} = \frac{128 RT \mu n}{p \pi d_f^4 N_f} \quad (20)$$

where R is the ideal gas constant, T is the gas temperature, μ is the gas viscosity, n is the variable molar flow rate of permeate gas, d_f is the inside fiber bore diameter, and N_f is the number of fibers in a bundle. Other expressions derived from the Hagen-Poiseuille equation have been developed to account for compressibility and flow in porous channels when necessary.^[8,10-12]

It has been observed that when the change in the feed mole fraction of oxygen is less than 50%, the differential balances may be replaced with algebraic expressions involving the logarithmic mean of the transmembrane partial-pressure difference.^[13] In Eq. (3), let

$$\Delta = x_P - y_P \quad (21)$$

The driving force for diffusion across the membrane, Δ , is assumed to be a linear function of the change in the molar flow on the feed side of the membrane

$$\frac{d(xn)}{d\Delta} = \frac{(xn)_R - (xn)_F}{\Delta_R - \Delta_F} \quad (22)$$

Combine eqs. (2), (3), and (22), separate variables and inte-

Membranes in ChE Education

grate

$$y_p n_p \int_{\Delta_F}^{\Delta_R} \frac{d\Delta}{\Delta} = Q_{O_2} (\Delta_R - \Delta_F) \int_0^A dA \quad (23)$$

or

$$y_p n_p = Q_{O_2} (xP - yP)_{lm} A_m \quad (24)$$

where the log-mean difference in O_2 partial pressure across the membrane is defined as

$$(xP - yP)_{lm} = \frac{(xP - yP)_R - (xP - yP)_F}{\ln[(xP - yP)_R / (xP - yP)_F]} \quad (25)$$

A similar result is found for a N_2 flux expression

$$(1 - y_p) n_p = Q_{N_2} [(1 - x)P - (1 - y)P]_{lm} A_m \quad (26)$$

The steady-state binary-gas membrane equations can be written in dimensionless form using the average pressures

$$x_F = x_R(1 - \theta) + y_p \theta \quad (27)$$

$$y_p K_R \theta = (1 - \theta) \alpha^* (x_r - y)_{lm} \quad (28)$$

$$(1 - y_p) K_R \theta = (1 - \theta) [(1 - x)r - (1 - y)]_{lm} \quad (29)$$

where the cut is defined here as the ratio of permeate-to-feed flow rates

$$\theta = n_p / n_f \quad (30)$$

Alternative forms of Eqs. (28) and (29) in terms of K_F are

$$y_p K_F \theta = \alpha^* (x_r - y)_{lm} \quad (31)$$

$$(1 - y_p) K_F \theta = [(1 - x)r - (1 - y)]_{lm} \quad (32)$$

The permeate composition at the closed end of the hollow-fiber membranes is calculated from Eq. (19).

The experimental separation factor was calculated from the measured compositions of the permeate and retentate streams

$$\alpha = \frac{y_p(1 - x_R)}{x_R(1 - y_p)} \quad (33)$$

Under conditions where the change in the feed composition exceeds 50%, the log-mean model can be applied two or more times as necessary across a module such that each cut does not exceed a 50% change in x_F from the previous step. The pressure at the closed end of the fiber bore can be calculated by assuming that the permeate flow rate is a linear function of distance along the fiber

$$n = \frac{n_p z}{L} \quad (34)$$

where L is the fiber length. Equation (20) can be integrated with substitution from Eq. (34) to give an estimate for the permeate pressure at the closed end of the fibers^[9]

$$P_c = \sqrt{P^2 + \frac{128 RT \mu L n_p}{\pi d_f^4 N_f}} \quad (35)$$

■ Solution Method

The algebraic model Eqs. (19) and (27-29) represent a system with four degrees of freedom, or four equations in eight variables: x_F , x_R , y_p , y_r , θ , α^* , K_R , and r . The model was initially calibrated by fixing x_F and r and measuring x_R and y_p , leaving y_r , θ , α^* , and K_R as unknowns in the solution.

The solution of the system of nonlinear algebraic equations requires an iterative, trial-and-error technique, such as Newton's method. The log-mean approximation of the partial-pressure driving force is notoriously difficult to converge under these circumstances. Fortunately, there are good approximations to the log-mean that avoid problems of divergence in the solution. The following form of the Chen approximation was used:^[14]

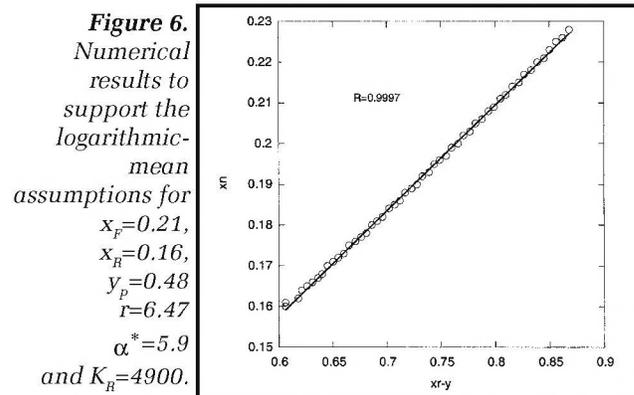
$$\frac{\Delta_2 - \Delta_1}{\ln(\Delta_2 / \Delta_1)} \cong \left[\Delta_1 \Delta_2 \frac{(\Delta_1 + \Delta_2)}{2} \right]^{1/3} \quad (36)$$

Floudas noted that the Chen approximation to the log-mean has the advantage that it becomes zero if either the feed or exit partial-pressure driving forces become zero.^[15]

The four-column configuration requires sequential solution to the countercurrent and cocurrent models. Note that $n_{2F} = n_{1R}$ and $K_{2F} = K_{1R}$ between the first and second columns, and that $n_{4F} = n_{3R}$ and $K_{4F} = K_{3R}$ between the third and fourth columns. The feed flow rates to each column are calculated from the cut for the previous column.

RESULTS AND DISCUSSION

The experimental data of Davis and Sandall^[5] were used to illustrate the analysis procedure. The assumption of Eq. (22) for the log-mean approximation was evaluated by plotting a representative numerical solution to Eq. (7), shown in Figure 6. A linear least-squares regression of the numerical results



Membranes in ChE Education

shows that the assumption of a linear function for Δ is valid for the conditions of this laboratory experiment.

A sample calculation of the single countercurrent flow model calibration using Mathcad is shown in Figure 7. The experimental data and results of the algebraic model are compared with the results from the differential model in Table 1 for α^* and K_R . There are no significant differences in the results between these models.

```

x_F := 0.21  x_R := 0.16  y_P := 0.48  r := 6.465
K_R := 50  alpha := 6  y_i := 0.5  theta := 0.2

Delta_lm(Delta_1, Delta_2) := (Delta_1 * Delta_2 * (Delta_1 + Delta_2) / 2)^(1/3)

Given

x_F = x_R * (1 - theta) + y_P * theta

y_i / (1 - y_i) = alpha * (x_R * r - y_i) / ((1 - x_R) * r - (1 - y_i))

y_P * K_R * theta = (1 - theta) * alpha * Delta_lm(x_F * r - y_P, x_R * r - y_i)

(1 - y_P) * K_R * theta = (1 - theta) * alpha * Delta_lm((1 - x_F) * r - (1 - y_P), (1 - x_R) * r - (1 - y_i))

Find(K_R, alpha, y_i, theta) = (49.024, 5.931, 0.426, 0.156)
    
```

Figure 7. Example of Mathcad calculation for inverse mass transfer analysis using the log-mean model.

TABLE 1							
Calibration Data^[5] and Results for Single Countercurrent Column							
<u>Experimental Data</u>				<u>Differential Model</u>		<u>Algebraic Model</u>	
P(kPa)	n _r × 10 ² (gmol/s)	x _R	y _P	α*	K _R	α*	K _R
377	0.73	0.18	0.43	5.81	31.1	5.82	31.1
377	0.74	0.18	0.43	5.81	31.1	5.82	31.1
377	1.03	0.19	0.44	5.98	49.6	5.98	49.6
377	1.32	0.19	0.44	5.98	49.6	5.98	49.6
377	2.54	0.20	0.44	5.71	98.7	5.71	98.6
515	0.62	0.15	0.45	5.93	26.2	5.97	26.1
515	0.73	0.16	0.46	6.02	33.3	6.05	33.2
515	0.95	0.17	0.47	6.12	43.9	6.14	43.9
515	1.51	0.18	0.47	5.85	58.2	5.86	58.2
515	2.25	0.19	0.48	5.96	92.1	5.96	92.1
653	0.74	0.14	0.46	5.78	31.5	5.84	31.4
653	0.95	0.15	0.47	5.84	38.8	5.88	38.7
653	1.32	0.16	0.48	5.90	49.1	5.93	49.0
653	2.18	0.18	0.49	5.73	85.7	5.74	85.6
653	3.44	0.19	0.5	5.81	135	5.81	135
<i>Average</i>				5.88		5.90	

A linear relationship between the retentate flow rate and K_R is calculated for use in the remaining three column predictions. The linear function is plotted with the results in Figure 5. The result of a linear least-squares regression gives

$$K_R = 4.0 \times 10^3 n_R \quad (37)$$

The average value of α^* was calculated to be 5.9 assuming atmospheric pressure in the fiber bore. An increase in fiber-bore pressure would cause the experimentally determined species permeances to decrease. The axial pressure drop has been found to vary linearly with flow rate, however.^[16] Thus, the slope in Eq. (37) is not affected by the small pressure build-up in the permeate stream.

Separation factors for the four-column configuration were predicted from the sequential calculations of the model for a range of feed pressures and flow rates. The results plotted in Figure 9 show good agreement with the experimental values calculated from the data of Davis and Sandall.

All of these results lend confidence in the algebraic model. Students are able to quickly design alternative configurations and explore the potential performance of competing designs.

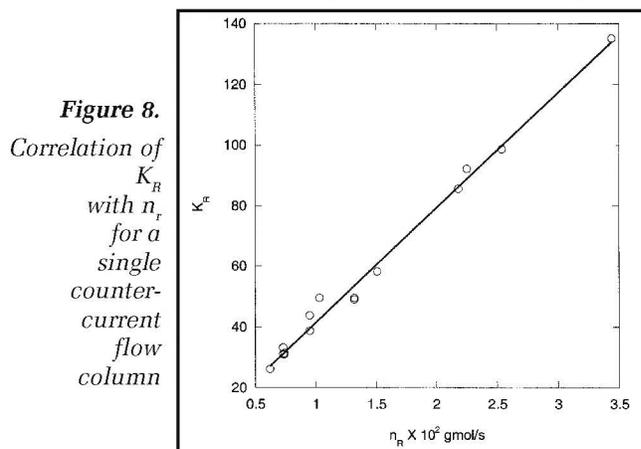


Figure 8. Correlation of K_R with n_r for a single countercurrent flow column

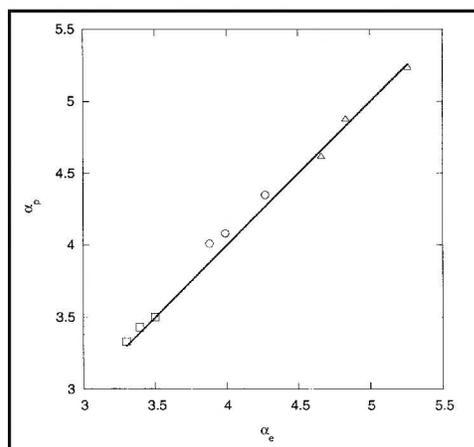


Figure 9. Comparison of predictions with experimental results for air separation in the four-column configuration: □=377kPa, ○=515 kPa, △=653 kPa.

Membranes in ChE Education

For example, students usually start by comparing the performance of cocurrent and countercurrent flow. This leads to a design for one column operating in countercurrent flow with the same membrane surface area as the four columns. The single column design gives a predicted increase of 10% N_2 recovery when compared to the modular design. Students may use the models to predict a dimensionless membrane area, $1/K$, to recover a desired fraction of oxygen fed to the permeator. Other designs include four columns operating in parallel with countercurrent flow or four columns with the feed side in series and the permeate side in parallel.

The Mathcad files used in the analysis are available at <www.d.umn.edu/~rdavis/cee>

CONCLUSIONS

A membrane experiment for investigating gas separation has been in use for over ten years in the undergraduate laboratory at the University of California, Santa Barbara. A simple analysis method was presented that requires only the solution to a system of four algebraic equations. The simpler analysis is equally applicable to newer membrane configurations that introduce the high-pressure feed to the fiber bores in order to maintain better flow patterns in the membrane module. The experimental apparatus was designed to permit single- and four-column investigations of air separation. The single column was used to calibrate the models for binary gas separation. Comparing results for the four-column operation validated the calibrated model. Good model and experimental agreement lend confidence in the model and validate the model assumptions. Students are then able to use the model to develop competing designs for gas separation and optimize their designs for maximizing efficiency of separation. The advantages of the simpler approach are that students can readily set up and solve the model equations without complicated programming. Students are also able to explore alternative designs by building models and comparing the results.

NOMENCLATURE

A	membrane area, m^2
d	diameter, m
K	dimensionless membrane transport parameter
L	fiber length, m
n	molar flow rate, $gmol/s$
N	number of fibers in a bundle
p	permeate side pressure, kPa
P	feed side pressure, kPa
Q'	permeance, $gmol/(s \cdot kPa \cdot m^2)$
R	ideal gas constant, $kPa \cdot m^3/gmol \cdot K$
T	temperature, K
x	feed stream mole fraction of oxygen
y	permeate stream mole fraction of oxygen

z variable fiber length, m

Greek Symbols

α	experimental separation factor
Δ	transmembrane partial pressure, kPa
μ	viscosity, N-m/s
θ	cut of feed to permeate stream

Subscripts/Superscripts

c	closed end of fiber bore
e	experimental
f	fiber
F	feed
i	closed end of permeate stream
lm	log-mean result
m	membrane
N_2	nitrogen
O_2	oxygen
p	predicted
R	retentate
*	dimensionless or ideal parameter

REFERENCES

1. Pandey, P., and R.S. Chauhan, "Membranes for Gas Separation," *Prog. Polym. Sci.*, **26**(6), 853 (2001)
2. McCabe, W.L., J.C. Smith, and P. Harriott, *Unit Operations of Chemical Engineering*, 5th ed., McGraw-Hill, New York, NY (1993)
3. Geankoplis, C., *Transport Processes and Unit Operations*, 3rd ed., Prentice-Hall, Englewood Cliffs, NJ (1993)
4. Seader, J.D., and E.J. Henley, *Separation Process Principles*, John Wiley and Sons, New York, NY (1998)
5. Davis, R.A., and O.C. Sandall, "A Membrane Gas Separation Experiment for the Undergraduate Laboratory," *Chem. Eng. Ed.*, **25**(1), 10 (1991)
6. Walawender, W.P., and S.A. Stern, "Analysis of Membrane Separation Parameters. II: Counter-Current and Cocurrent Flow in a Single Permeation Stage," *Sep. Sci.*, **7**(5), 553 (1972)
7. Boucif, N., S. Majumdar, and K.K. Sirkar, "Series Solutions for a Gas Permeator with Countercurrent and Cocurrent Flow," *Ind. Eng. Chem. Fund.*, **23**, 470 (1984)
8. Thundiyil, M.J., and W.J. Koros, "Mathematical Modeling of Gas Separation Permeators: For Radial Crossflow, Countercurrent, and Cocurrent Hollow Fiber Membrane Modules," *J. Mem. Sci.*, **125**, 275 (1997)
9. Zolanz, R.R., and G.K. Fleming, "Design of Gas Permeation Systems," in *Membrane Handbook*, W.S. Ho and K.K. Sirkar, eds., Van Nostrand Reinhold, New York, NY, p. 66 (1992)
10. Bruining, W.J., "A General Description of Flows and Pressures in Hollow Fiber Membrane Modules," *Chem. Eng. Sci.*, **44**(6), 1441 (1989)
11. Federspiel, W.J., J.L. Williams, and B.G. Hattler, "Gas Flow Dynamics in Hollow-Fiber Membranes," *AIChE J.*, **42**(7), 2094 (1996)
12. Lim, S.P., X. Tan, and K. Li, "Gas/Vapour Separation Using Membranes: Effect of Pressure Drop in Lumen of Hollow Fibers," *Chem. Eng. Sci.*, **55**, 2641 (2000)
13. Mulder, M., *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, Dordrecht, Netherlands (1991)
14. Chen, J.J.J., "Comments on Improvements on a Replacement for the Logarithmic Mean," *Chem. Eng. Sci.*, **42**(10), 2488 (1987)
15. Floudas, C.A., *Nonlinear and Mixed-Integer Optimization*, Oxford University Press, Oxford (1995)
16. Vladislavljevic, G.T., and M.V. Mitrovic, "Pressure Drops and Hydraulic Resistances in a Three-Phase Hollow Fiber Membrane Contactor with Frame Elements," *Chem. Eng. Proc.*, **40**, 3 (2001) □