

CACHE'S ROLE IN COMPUTING IN CHEMICAL REACTION ENGINEERING

H. Scott Fogler
University Of Michigan
Ann Arbor, Michigan 48109

Abstract

Throughout the last 25 years CACHE has either initiated, nurtured, or financially supported projects to enhance courses in chemical reaction engineering and, as a result, has been instrumental in the evolution of chemical reaction engineering education. Five major CACHE-assisted projects involving computer modules, and/or interactive simulations are discussed. Specifically, we focus on early computer programs, the University of Michigan Projects, the Purdue University Modules, POLYMATH, and the University of Washington's Chemical Reactor Design Tool.

Introduction

CACHE has played many roles in the incorporation of computing in Chemical Reaction Engineering (CRE). It has been an initiator of projects, such as the computer programs in chemical reaction engineering (1972), and the set of six CHEMI books on Kinetics (1976-1979), it has been a distributor of programs such as POLYMATH and the Michigan Interactive Kinetics modules. CACHE has also been a mentor and facilitator in the development of these materials, providing both financial, and intellectual resources through collaboration, not only with CACHE trustees, but also with many colleagues in the United States, Canada, and overseas. This paper highlights five areas in which CACHE has played a major role in the advancement of chemical reaction engineering education: the computer programs, the University of Michigan's Interactive Kinetics modules, the Purdue University's Simulations, the University of Washington's Chemical Reactor Design Tool, and POLYMATH.

Early Computer Programs

One of the very first CACHE projects involving the development of computer programs in the areas of chemical reactor design, control design, transport, stoichiometry, and thermodynamics. The programs were written by college faculty and sent on punched cards for evaluation to the appropriate area editor. Professor Matt Reilly was the area editor for kinetics and reactor design, and set the standards for accepting programs by running them in every way possible to try to get them to fail. If a program passed Matt's rigorous testing, a source program listing and sample output were included in the published volume (Reilly, 1972). A list of the programs and

authors is shown in Table 1.

Table 1. CACHE Computer Programs for Chemical Engineering Education: Kinetics (1972)

1. BATCH REACTORS
 - 1.1 Complex Reaction System in a Batch Reactor by Jaime P. Ampaya and Robert G. Rinker
 - 1.2 Batch Decomposition of Acetylated Castor Oil by Joseph J. Perona
 - 1.3 Series of Reactions in a Batch Reactor or in a Sequence of Stirred Tank Reactors by R. Rajagopalan
2. CONTINUOUS STIRRED-TANK REACTORS
 - 2.1 Molecular Weight Distribution in a Polymerization Reactor Sequence by James L. Kuester
 - 2.2 Dynamic Mass and Energy Balances in a CSTR by Ephraim Kehat
3. HOMOGENEOUS TUBULAR REACTORS
 - 3.1 Tubular Reactor Design with Two Consecutive Reactions by E. H. Crum
 - 3.2 Chemical Equilibrium and Reaction Rate Conflict by Billy C. Crynes and Barney L. Ghiglieri
 - 3.2 Plug Flow Reactor with Dispersion by George M. Homsy
4. HETEROGENEOUS CATALYSIS
 - 4.1 Effectiveness Factor for a Spherical Catalyst Pellet by Joseph S. Naworski
 - 4.2 Non-Isothermal Catalyst Pellet by Ran Abed and Robert G. Rinker
 - 4.3 Computer-Administered Programmed Instruction in Effectiveness Factors by James T. Cobb, Jr., and Thomas Gestrich
5. CATALYTIC REACTORS
 - 5.1 Analysis of Catalytic Reactions in a Packed Bed Reactor by Thomas Z. Fahidy
 - 5.2 Design of a Fixed-Bed Reactor by Charles N. Satterfield and Russell L. Jones
 - 5.3 Design of Non-Isothermal Flow Reactor by William J. Hatcher, Jr.
 - 5.4 Adiabatic Catalytic Reactor Design for Methanol Synthesis: High Pressure by Kermit L. Holman
6. REACTOR DESIGN AND OPTIMIZATION
 - 6.1 Air Sparged Reactor Design by Louis L. Edwards
 - 6.2 SO₂ Oxidation Reactor Simulation Program by Donald B. Wilson and Robert L. Hair
 - 6.3 Optimal Selection of a Blend of Two Catalysts in a Tubular Reactor by Michael S. K. Chen
7. EXPERIMENTAL DATA ANALYSIS
 - 7.1 Data Correlation via Non-Linear Regression by George W. Roberts
 - 7.2 Residence-Time Distribution Computation for Flow Processes by William C. Clements, Jr.

The University of Michigan Projects

In 1976, approximately three years after the computer programs listed in Table 1 were published and distributed to chemical engineering departments across the nation, a second project was completed. With the aide of a grant from the Olin Corporation, five interactive programs, listed below, were developed at the University of Michigan by Professor H. Scott Fogler and a junior in chemical engineering, T. Michael Duncan (now a professor at Cornell).

1. Rate Laws
2. Stoichiometry
3. Heterogeneous Catalysis
4. Columbo (Murder in a CSTR)
5. Death by Dying (Analysis of Rate Law Data)

These programs were made available for testing by students in the chemical reaction engineering course during the 1976-77 academic year. The response and enthusiasm for the modules was overwhelming. These modules were demonstrated at the Summer School for Chemical Engineering Faculty held in Snowmass, Colorado during the summer of 1977. The response of the faculty viewing the modules was equally enthusiastic; following the summer school, a number of faculty at different universities requested copies of the modules for use in their classes. At this point, we encountered our first major hurdle. The uniqueness of the University of Michigan computer graphics systems was such that it could not be run easily, even on similar computers at other universities. A few faculty at other universities (in particular, David Himmelblau at the University of Texas and Dick Mah at Northwestern) even hired or encouraged students to modify parts of the code to get the programs to work at their universities, with little or no success. Consequently, the interactive computing modules went into hibernation until the portability problem could be solved.

The introduction of the IBM PC breathed new life into the modules as the portability problem was solved almost overnight. Between 1982 and 1985, four of the modules developed for the mainframe computer were rewritten for the PC, and a heterogeneous catalysis module and three modules from other areas of chemical engineering were distributed by the CACHE Corporation to all departments in the U.S. The four kinetics modules, along with a Kepner-Tregoe plant design module developed by the author (Reilly, 1972), served as the basis for a proposal to the National Science Foundation in the summer of 1987; the proposal was funded a year later (Fogler, 1992). The funds from this grant were used to develop nine modules in chemical reaction engineering and 15 in other areas of chemical engineering. During the five-year development process, we incorporated the pedagogical expertise gained through our interaction with the Center for Research on Learning and Teaching at the University of Michigan, review of the literature, and our previous experiences with interactive computing modules. Extensive testing at the University of Michigan and many other universities has allowed us to distribute modules which, we believe, address important issues that ensure success in interactive computer learning:

- Ease of use
- Maintaining focus on the concepts
- Minimal tediousness
- Promoting learning
- Individual guidance

These modules run on IBM-PCs and compatibles with EGA or better graphics and minimal system requirements of DOS 5.0 or later, a 20Mhz 80386 processor, an 80387 math co-processor and at least 512 KB of RAM. (HETCAT - the Heterogeneous catalysis module -requires

approximately 570 KB of memory to perform properly). The interactive modules in reaction engineering currently available are described below.

KINCHAL1: Kinetics Challenge 1 - Introduction to Kinetics

This module allows the students to test their knowledge of the general mole balance equation and reaction rate laws, as well as types of reactions and reactors. The interaction occurs in the form of an interactive game (see Fig. 1) with timed responses and computer-generated competitors. Twenty questions are selected from a pool of approximately 100 multiple choice questions (see Fig. 2). Students can choose questions from any of four categories (mole balance, reactions, rate laws, and reactor types) and five difficulty levels (100 - 500 points):



Figure 1. Choosing a category in the KINCHAL1 module.

The student has one minute to choose the correct answer. The module responds to the student's choice, either reinforcing the reasoning for a correct answer, or immediately clarifying a misunderstanding if an incorrect answer is entered. If no response is entered within the time limit, or if an incorrect response is entered, the points are lost and one of the computer competitors tries to answer the question.

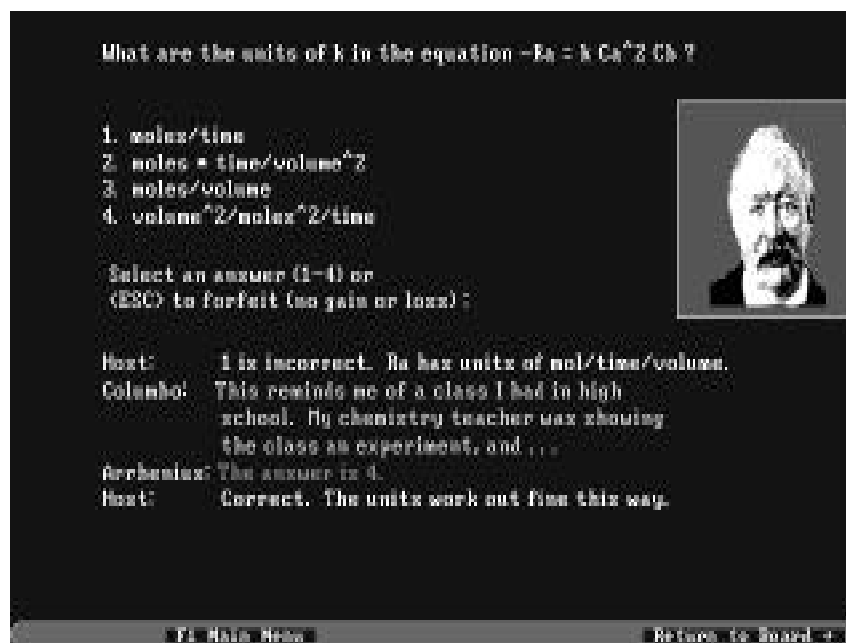


Figure 2. A question and response from the KINCHALI module.

The competitor who last answered a question correctly gets to pick the following category and degree of difficulty (note that this will not necessarily always be the student). In addition to regular questions, one question is randomly assigned as the “Double Challenge,” in which the student has the option of betting points. After all twenty questions have been answered, the contestants with positive scores go on to the “Final Challenge” question, in which they are also allowed to bet points.

STAGING: Reactor Staging and Optimization

In the interaction portion of this module the student must arrange a group of five reactors – CSTRs and PFRs – in the order that will result in at least 75% conversion, while maximizing the product flow rate, for the reaction $A \rightarrow B$. Both the $-F_{A0}/r_A$ vs. X (conversion) graph and the reactor volumes are specified, and many arrangements of reactor order and inlet flow rate can be tested using an interactive simulation.

The student may at any time access a reference section that reviews the derivation of the design equations for PFRs and CSTRs, clarifying the change in conversion down a PFR, and the well-mixedness of the CSTR.

The reactor optimization simulator can also be run independently of the scenario. This allows the professor to present the student with a variety of open-ended problems to be investigated using the simulator.

KINCHAL2: Kinetics Challenge 2 - Stoichiometry and Rate Laws

This module focuses on rate laws and stoichiometry, allowing the student to master the elements of the stoichiometric table. The interactive portion of the module is similar to that in Kinetic Challenge 1. Students can choose from four categories (reactants, products, rate law, potpourri) and four levels of difficulty (200-1,000 points).

The key focus in this module is to provide students with practice so that they will avoid the more prevalent mistakes (expressing the reaction rate law for an irreversible reaction as if it were reversible, and using the ideal gas law for liquid-phase reactions).

COLUMBO: CSTR-Volume Algorithm - A Murder Mystery

The principal purpose of this module is to allow students to practice the algorithm for CSTR design.

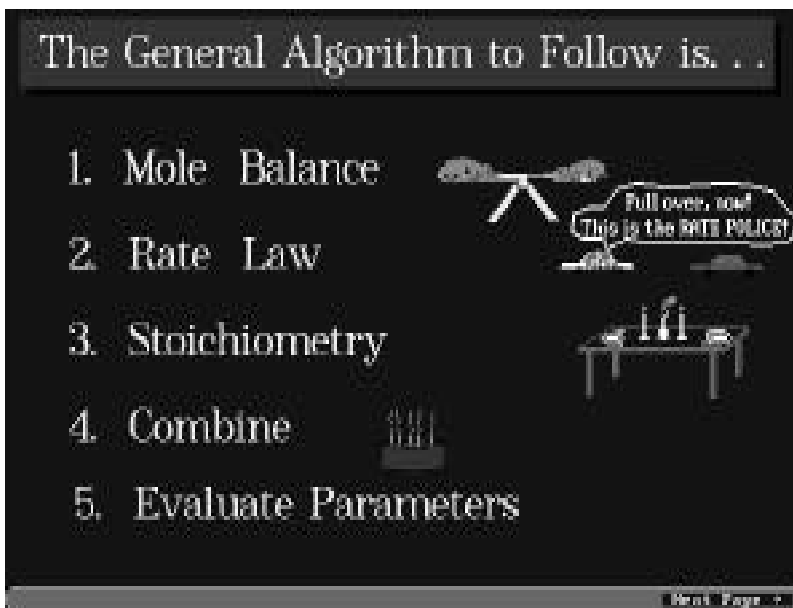


Figure 3. Frame from the COLUMBO module.

In the interactive portion of the module the student must solve a murder mystery, with the aid of Lieutenant Columbo. It seems that overnight there was a slight irregularity in the conversion in the reactor at the Nutmega company (see Fig. 4).

It is feared that one of the employees may have been murdered by a fellow employee, and the body left in the reactor. By analyzing the conversion data and using personnel information and knowledge of CSTR reactor design, the student must determine the identity of both the murderer and the victim. Help may be obtained by questioning the suspects.

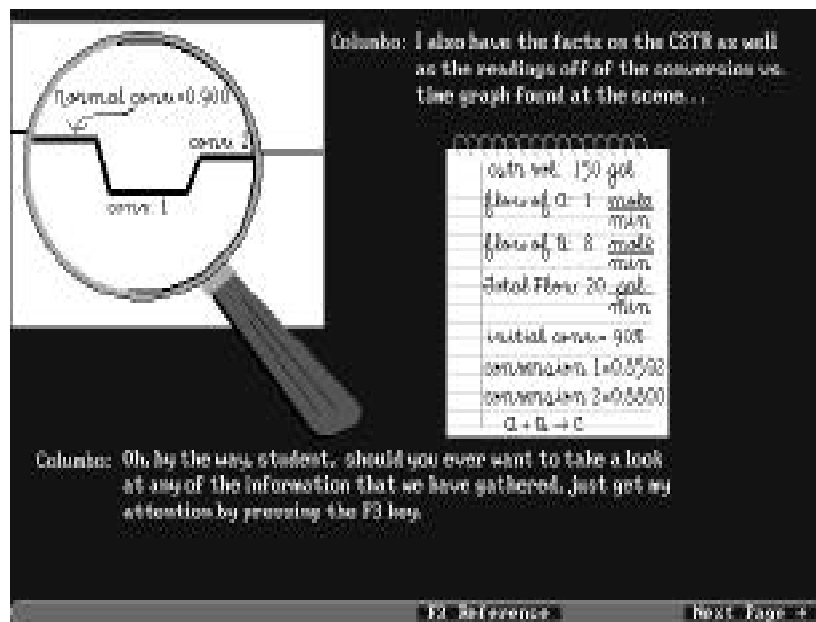


Figure 4. Frame from the COLUMBO module.

TICTAC: Ergun, Arrhenius, and Van't Hoff Equations in Isothermal Reactor Design

This module allows the student to examine nine reactor design problems, and investigate the effect of varying reactor parameters on process performance. The problems are organized as in a tic-tac-toe board (see Fig. 5). The reactors covered by these problems include PFRs, CSTRs, packed bed reactors and semi-batch reactors.

The student must master the concepts in enough squares (three adjacent squares horizontally, vertically, or diagonally) to successfully win the tic-tac-toe game. Each problem allows the student the opportunity to examine the effect of a specified operational parameter on reactor performance, using simulators:

After performing the “experiments,” the student proceeds to answer three questions that examine the effects observed. These effects can be explained through the Ergun, Arrhenius, and Van’t Hoff equations. In many cases, competing effects are highlighted. The square is “won” by answering two out of the three questions correctly.

ECOLOGY: Collection and Analysis of Rate Data - Ecological Engineering

The student, as an employee of a company trying to meet environmental regulatory agency standards, must sample concentration data for a toxic material found in a wetlands channel between a chemical plant upstream and a protected waterway downstream, and analyze the rate of decay of the toxic material.

The wetlands are modeled as a PFR. The student must first develop the necessary reactor



Figure 5. Frame from TICTAC module.

design equation for a PFR, then start to collect data. These concentration data, which include experimental error, are then analyzed in various ways (polynomial fit of the data followed by differentiation of the resulting equation, difference equations, etc.) to determine the rate law, the rate constants and the reaction order. Students must determine which points (if any) are to be excluded from the analysis and which points may be resampled.

The student then analyzes this information and submits a memo with the requested parameters. This information is reviewed by the boss, who evaluates the parameter values and makes recommendations.

HETCAT: Heterogeneous Catalysis

The review section of this module first covers the essential elements of heterogeneous catalysis. The student must derive the rate equation for a given reactive system by analyzing the rate data obtained in a differential reactor. The student then chooses which experiments to run, that is, the entering pressures of each species and total flow rate. In order to obtain the dependence of the rate equation on the pressure of a given species, the student selects which of the points are to be included in a plot of reaction rate vs. species partial pressure. Given the requested plot, the student must determine the form of the dependence of the rate law on the pressure of the given species.

Once all dependencies have been established, the student must decide which rate law parameters can be determined, through judicious plotting of the experimental data. The review section also outlines the derivation of the governing equations of heterogeneous catalysis.

HEATFX-1: Simulation - Mole and Energy Balances in a CSTR

This module allows students to investigate the effect of parameter variation on the operation of a non-isothermal CSTR. An extensive review section derives the energy balance for the CSTR, and also describes the terms in the mole balance that are temperature dependent.

A simulator is included in the review section. This allows the student to vary parameters and observe the effects on the conversion-temperature relationships (see Fig. 6) as described by both the mole balance and the energy balance. The parameters that may be varied include feed flow rate and temperature, the reversibility/irreversibility of the reaction, heat of reaction, heat exchanger area, and heat transfer fluid temperature. The operating conditions can be determined from the intersections of the mole balance and energy balance curves.

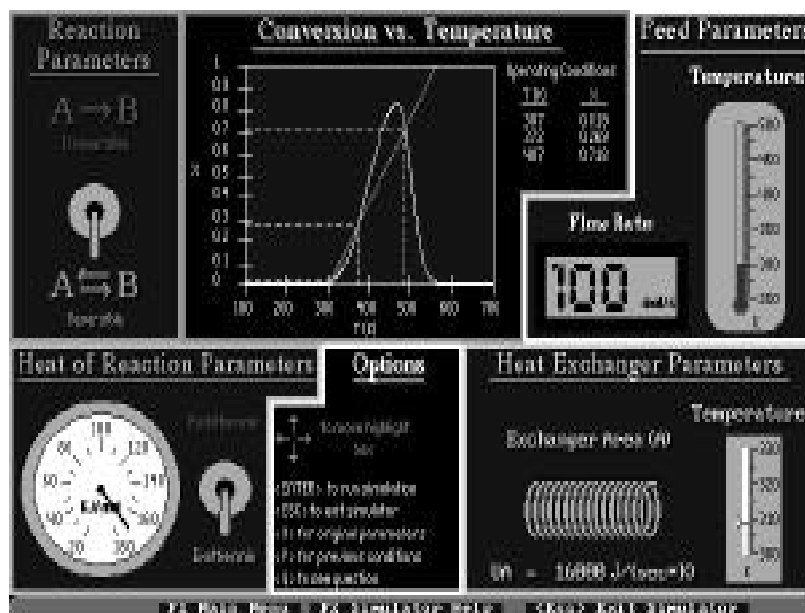


Figure 6. Frame from the HEATFX-1 module.

The module can also be run in the interactive mode, in which the scenario takes the student to a basketball tournament. The student has the choice of two-point and three-point questions. The simulator is available to help in answering the three-point questions.

HEATFX-2: Simulation - Mole and Energy Balances in a PFR

This simulation allows the student to explore the effects of various parameters on the performance of a non-isothermal plug flow reactor. The student may choose from eight simulations, that span all combinations of exothermic/endothermic, reversible/irreversible conditions, as well as one simulation that includes the effect of pressure drop. The parameters that may be varied include heat transfer coefficient, inlet reactant and diluent flow rate, inlet temperature, and ambient temperature.

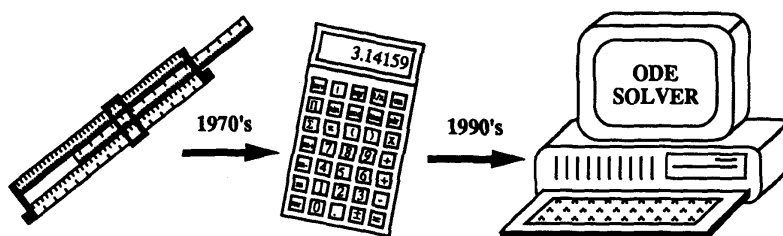


Figure 8. Paradigm shifts in chemical engineering education.

One of the most user friendly ODE solvers is POLYMATH, developed by Professors Michael Cutlip of the University of Connecticut and Mordechai Shacham of Ben Gurion University (Shacham and Cutlip, 1981a, 1981b, 1982, 1983). CACHE provided partial development support for the program and currently licenses POLYMATH to the industrial and university communities.

The numerical package developed by Cutlip and Shacham had its origins in a computer-based course on chemical reaction engineering using the PLATO (Programmed Logic for Automated Teaching Operations) System. This course, first offered in the late 1970s, was self-paced and had the following components:

- Self-Paced textbook (Fogler) 40%
- Homework assignments (on PLATO) 15%
- PLATO lessons 15%
- Videotape lectures 15%
- Reaction modeling and simulation (on PLATO) 7%
- Exams (on PLATO) 8%

This course was very successful when offered at both the University of Connecticut and the University of Michigan. As material on reaction engineering for the individual lessons became sufficiently developed, Professors Cutlip and Shacham focused their efforts on developing a numerical package that could be used with the course. Specifically, they began developing software to solve the non-linear ordinary differential equations typical of those found in chemical reaction engineering when heat effects are important. In addition to these ODE solvers, data analysis and polynomial fitting routines were developed for use in the course. These numerical packages were the origins of the current version of POLYMATH.

Unfortunately, the course that was developed for the PLATO system ceased to exist in the mid-1980s when support for it was withdrawn by its commercial supported. Fortunately, Professors Cutlip and Shacham were able to transport POLYMATH software from PLATO to IBM PCs. As a result, POLYMATH is now widely used throughout the US, Canada, Asia and

Europe. With POLYMATH, tedious and time consuming computer programming is eliminated, and the reaction engineering student can explore complex problems by varying the parameters and the operating conditions. Consequently, virtually every problem or homework assignment in chemical reaction engineering can be turned into an open-ended problem that will allow the students to practice their creative modeling and synthesis skills.

To illustrate this point, consider a gas phase exothermic reaction



carried out in a plug flow reactor with heat exchange.

For non-isothermal reaction in CRE we must choose which form of the energy balance to use (e.g., PFR, CSTR) and which terms to eliminate (e.g., $Q=0$ for adiabatic operation). The structure introduced to study these reactors builds on the isothermal algorithm by introducing the Arrhenius equation, and $k = A e^{-E/RT}$ in the *rate law* step, which results in *one* equation with *two* unknowns, X (conversion) and T (temperature), when we finish with the *combine* step (Reilly, 1972). For example, using the PFR mole balance and conditions, we have, for constant pressure:

$$\frac{dX}{dV} = \frac{A e^{-E/RT} (1-X)}{u_0 (1+eX)} \frac{T_0}{T} \quad (1)$$

We now recognize the necessity of performing an energy balance on the reactor to obtain a second equation relating X (conversion) and T (temperature). An energy balance on a PFR with heat exchange yields the second equation we need, relating the independent variables X and T:

$$\frac{dT}{dV} = \frac{[UA_c (T_a - T) + (r_A) (H_R)]}{F_{A0} C_{pA}} \quad (2)$$

These simultaneous differential equations can be solved readily with an ODE solver, as discussed below.

Obtaining the temperature and concentration profiles requires the solution of two coupled non-linear differential equations such as those given by Equations (1) and (2). In the past it would have been necessary to spend a significant amount of time choosing an integration scheme and then writing and developing a computer program before any results could be obtained. With the available software programs, especially POLYMATH, it rarely takes more than 10 minutes to type in the equations and obtain a solution (Sacham and Cutlip, 1982). As a result, the majority of the time for the exercise can be spent exploring the problem through parameter variation and analysis of the corresponding observations. For example, in the above exothermic reaction in a PFR with heat exchange the students can vary such parameters as the ambient and entering temperatures, the flow rates, and the heat transfer coefficient and look for conditions where the reaction will “ignite” and conditions for which it will “run away.” By trying their own different combinations and schemes, the students are able to carry out open-ended exercises that allow them to practice their creativity and better understand the physical characteristics of the system.

The following example, which was given as 50% of a 2 hour final exam at the University of Michigan, illustrates how significantly more complex problems can be rapidly solved with POLYMATH.

The elementary irreversible gas *exothermic* phase reaction



is carried out in a packed bed reactor. There is pressure drop in the reactor and the pressure drop coefficient is 0.007 kg^{-1} . Pure A enters the reactor at a flow rate of 5 mol/s , at a concentration of 0.25 mol/dm^3 , a temperature of 450 K and a pressure of 9.22 atm . Heat is removed by a heat exchanger jacketing the reactor. The coolant flow rate in the jacket is sufficient to maintain the ambient temperature of the heat exchanger at 27°C . The maximum weight of catalyst that can be packed in this reactor is 50 kg . The term giving the product of the heat transfer coefficient and area per unit volume divided by the bulk catalyst density is given by:

$$\frac{Ua}{\rho_B} = \frac{5 \text{ Joule}}{\text{kg cat s K}} \quad (3)$$

a) Plot the temperature, conversion X , and the pressure ratio ($y = P/P_0$) as a function of catalyst weight. b) At what catalyst weight down the reactor does the rate of reaction ($-r_A$) reach its maximum value? c) At what catalyst weight down the reactor does the temperature reach its maximum value? d) What happens when the heat transfer coefficient is doubled? e) What happens if the heat coefficient is halved? f) Discuss your observations of the effects on reactor performance (i.e., conversion, temperature and pressure drop).

Additional Information:

$H_R = -20,000 \text{ J/mol A}$ at 273 K , $C_{P_A} = 40 \text{ J/mol K}$, $C_{P_B} = 20 \text{ J/mol K}$, $E = 31.4 \text{ kJ/mol}$, and

$$k = 0.35 \exp \left[\frac{E}{R} \left(\frac{1}{450} - \frac{1}{T} \right) \right] \frac{\text{dm}^3}{\text{kg.cat.sec}} \quad (4)$$

The relevant equations are:

$$\frac{dX}{dW} = -r_A / F_{A0}$$

$$\frac{dP}{dW} = \frac{-T}{2} \frac{P_0}{T_0 (P/P_0)} (1+X) \quad \text{or} \quad \frac{dy}{dW} = \frac{-T}{2} \frac{(1+X)}{T_0 y}$$

$$\frac{dT}{dW} = \frac{\frac{U_a}{P_b}(T_a - T) + (-r_A)(-H_r)}{F_{A0} (C_{P_A} + X(2C_{P_B} - C_{P_A}))}$$

$$-r_A = k C_A$$

$$C_A = C_{A0} \frac{(1-X) T_0 P}{(1+X) T P_0}$$

$$k = 0.35 \exp(3776.76 \left(\frac{1}{450} - \frac{1}{T} \right))$$

The POLYMATH solutions for this problem are shown in Figs. 9-12.

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The equations:

$$d(x)/d(w) = -ra/fas$$

$$d(y)/d(w) = -alpha*(1+x)*(t1/450)/2/y$$

$$d(t1)/d(w) = ((2.5*(300-t1)+ra+dhr))/fas/cpa$$

$$k = .35 * \exp(3776.6 * ((1/450) - (1/t1)))$$

$$ca0 = .25$$

$$ca = ca0 * (1-x) * (450/t1) / (1+x) * y$$

$$ra = -k * ca$$

$$fas = 5.$$

$$dhr = -20000$$

$$cpa = 40$$

$$rate = -ra$$

$$alpha = .007$$

Initial values: $w_0 = 0.0$, $x_0 = 0.0$, $y_0 = 1.0000$, $t1_0 = 450.00$

Final value: $w_f = 50.0000$

CHANGE OPTIONS

e. Enter/Change/Delete equations. t. E/C/D the title.
 i. Change initial values. f. Change final value.
 r. Restart from the current conditions.
 F8 when done. F6 for helpful information.

Figure 9. POLYMATH equations.

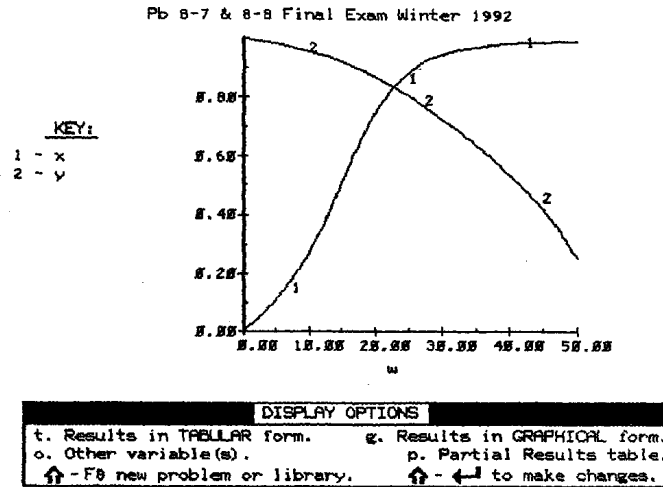


Figure 10. Conversion (x) and pressure ratio (y) as a function of catalyst weight.

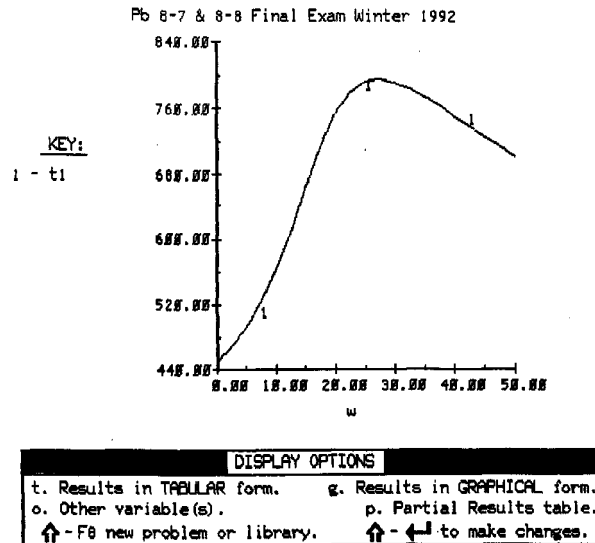


Figure 11. Temperature as a function of catalyst weight.

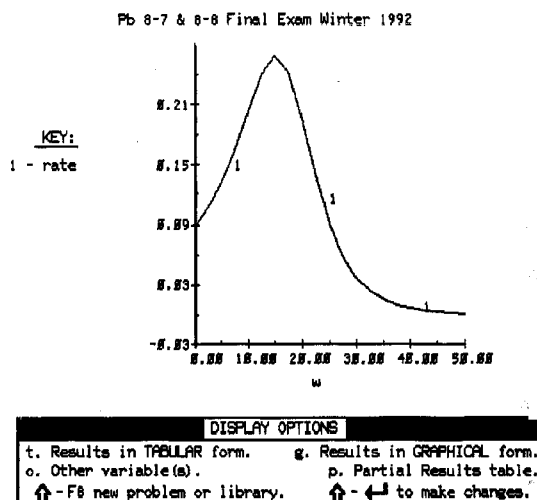


Figure 12. Reaction rate as a function of catalyst weight.

The Purdue-CACHE Modules

The Purdue-Industry Computer Simulation Modules are another educational innovation that CACHE fostered through Task Force support and distribution to virtually all chemical engineering departments in the US and Canada. Since 1986, a series of computer modules of state-of-the-art chemical engineering industrial processes have been and are being developed at Purdue University (Squire et al., 1992, Anderson et al., 1992). Each module has an industrial sponsor who furnishes data on a process on which the simulation is based and also produces a 20 minute videotaped "tour" of the real process. A number of these modules focus on chemical reaction engineering.

The modules are meant to supplement, not to replace, traditional laboratory experiments. Computer-simulated experiments have a number of advantages over traditional experiments:

- Processes that are too large, complex, or hazardous for the university laboratory can be simulated with ease on the computer.
- Realistic time and budget constraints can be built into the simulation, giving students a taste of "real world" engineering problems.
- The emphasis of the laboratory can be shifted from the details of operating a particular piece of laboratory equipment to more general considerations of proper experimental design and data analysis.
- Computer simulation is relatively inexpensive compared to the cost of building and maintaining complex experimental equipment.
- Simulated experiments take up no laboratory space and are able to serve large classes because the same computer can run many different simulations.

Each module is written as an industrial problem caused by a change of conditions in an existing process, requiring an experimental study to re-evaluate the characteristic constants of the process. These might include, for example, reaction rate constants, equilibrium constants, heat transfer and mass transfer coefficients, and phase equilibrium constants. The student teams are expected to design experiments that will enable them to evaluate the needed constants. This is referred to as the *measurements* section of the problem.

After the constants have been determined, the students must validate them by using them in an existing computer model of the process, and comparing the simulated and experimental results. When they are convinced that their constants are reliable, the students must use these constants to predict some other specific process performance characteristics. This is called the *applications* section.

Each process is made to seem realistic not just by the videotaped "tour" but also by the assigned financial budget and time constraints. The problems are open-ended in that the experimental conditions such as temperature, pressure, flow rates, and compositions are under the student's control. The cost and the associated duration of running experiments vary with the type of experiment and are also functions of operating conditions. Instructor-controlled statistical fluctuations are built into the simulations so that the results of duplicate experiments are not identical. The students must plan their experiments to obtain data from which, with proper analysis, the required constants may be determined without exceeding their budgetary and time constraints.

In the Purdue course, students work in teams of three and have eight 3-hour classes to complete the assignment. After an introductory 2-hour lecture, they are on their own. If they have queries, they are free to ask the consultant (the instructor, of course), but are charged a fee which is deducted from their budget. Written reports and a 20-minute oral presentation (video recorded for later analysis by the instructor and the student) are required.

Chemical kinetics has played a large role in most of the modules. The following section gives a brief outline of the chemical kinetics application of each of the Purdue modules.

Amoco Resid Hydrotreater (Squires et al., 1991)

This module requires the students to design a series of experiments (in a pilot plant, using one, two, or three CSTR's in series) to determine the rate constants of a series-parallel network of seven pseudo-first-order non-catalytic irreversible reactions. In addition, the rate constants must be determined for the catalytic desulfurization reaction, which follows Langmuir-Hinshelwood kinetics. This study is complicated by the fact that the catalytic activity deactivates with time.

Once the constants have been determined, the students are asked to start up the plant. This is complicated, since the reaction network is unstable with multiple steady-state solutions. Non-optimal control strategies may easily lead to temperature runaways.

Dow Styrene-butadiene Copolymerization (Jayakumar et al., 1995)

The students must determine the rate constants of the four propagation reactions and two chain transfer reactions, by designing experiments to be run in a two-gallon laboratory reactor.

Once the constants are determined, students are asked to predict the performance of a 10,000 gallon plant reactor. This is complicated, since the reactor has insufficient surface area for heat transfer. Students must determine:

- a. how much additional heat transfer surface area is needed, or
- b. the amount of feed pre-cooling required to achieve controllability.

Mobil Catalytic Reforming (Jayakumar et al., 1994)

In this study, the process is simplified by considering the catalytic reforming of only the C₆ range of hydrocarbons. The students must determine the catalyst deactivation parameter of a series of four coupled reforming reactions.

Once the parameters are known, students are asked to predict the hydrogen-to-hydrocarbon ratio in the feed that will optimize the annual profit of the process.

Eastman Chemical Reactive Distillation (Jayakumar et al., 1993)

One step in Eastman Chemicals acetic anhydride from coal process, involves the sulfuric acid catalyzed reaction:



This reaction is normally equilibrium limited. The key concept of the reactive distillation process relies on methylacetate being more volatile than the other reactants and products. The reaction occurs on a distillation tray, and a significant amount of methylacetate will vaporize, forcing the reaction to the right and increasing the yield beyond the normal equilibrium limitation.

Air Products Hydrogen Reactive Cooling Process

Hydrogen at room temperature is an equilibrium mixture of 25% para and 75% ortho. When cooled below 30°R the equilibrium mixture is almost 100% para-hydrogen. If the hydrogen is cooled in the absence of a catalyst, the ortho-para reaction will not take place and the resulting liquid hydrogen will still be 75% ortho. In the liquid hydrogen storage vessel the ortho-para reaction will occur, and the exothermic heat of this reaction will cause the vaporization of much of the liquid hydrogen.

In order to avoid the boil-off losses, it is necessary to catalyze the ortho-para hydrogen reaction during the cooling process rather than later in the storage vessel. The students must determine the rate constants for the ortho-para reaction.

Once the constants are determined, the students are asked to determine the optimum number of side reactors required for the reactive cooler design.

Concluding Comments

In July 1990, and again in July 1991, three-day workshops were held at Purdue University at which the chemical engineering faculty participants were given hands-on experience with all the modules. Faculty representatives from 56 chemical engineering departments in the United

States and Canada participated in these workshops. Many of these schools are now using some of the modules. It is particularly interesting to note that several of the other schools (notably Georgia Tech., Carnegie Mellon, West Virginia) are using the materials as problems in reactor design courses. The authors also presented a workshop on the project at the ASEE Chemical Engineering Faculty Summer School in August 1992. The modules are currently being used by 25 schools, including five schools in foreign countries.

The modules were originally created for execution on Sun (UNIX) workstations. NSF has recently funded a proposal to port the modules to other workstations (such as DEC, IBM, HP, and Silicon Graphics). Nine other schools have agreed to participate as beta-test sites in this work, bringing the total number of user schools to 34. Once the modules are available on these other computers, there should be a significant increase in the number of participating schools

The University Of Washington – CACHE Project

The Chemical Reactor Design Tool is a set of computer programs that permit a student to design chemical reactors, including the realistic transport effects that are frequently present. The interface is written in X-windows so that the student can include complications easily; the program automatically uses the correct, robust tools to solve the problem. Results are displayed graphically, which makes comparison studies especially easy. The programs were developed by Professor Bruce Finlayson under sponsorship of the National Science Foundation and the University of Washington, and are made available to universities through CACHE.

CRDT Educational Goals

Introductory textbooks concentrate on problems that can be solved analytically. Recent textbooks include material for problems that can be solved with an ordinary differential integrator. These include batch reactors and simple plug flow reactors; extensions from one reaction to several reactions are possible, but time-consuming. When attempting to solve real problems, students are faced with several difficulties, which are mostly difficulties in manipulation and book-keeping rather than conceptual. Phenomena that might be important include:

- Multiple reactions (lots of bookkeeping)
- Temperature of catalyst and fluid may be different
- There may be internal mass transfer (requires solving an effectiveness factor problem)
- There may be cooling at the wall (leads to radial dispersion)

Students and design engineers may not be able to make realistic estimates of which phenomena must be included. In some cases it is necessary to calculate with a suspected phenomenon included to see if it is important. That has been difficult to do, because each phenomenon creates problems that require special techniques to solve. Used in the CRDT are ordinary differential equation integrators, the orthogonal collocation method, the finite difference method, techniques to convert partial differential equations to sets of ordinary differential equations, iterative techniques to solve large sets on nonlinear equations, and linear programming methods to guide initial guesses for integrative techniques. All these methods are transparent to the user.

Key Aspects

The user can examine effects very easily and make their own deductions about the importance of physical phenomena. Phenomena that can be easily included are:

- Different reactors: CSTR, batch, plug flow
- Axial dispersion, radial dispersion
- Intraparticle heat and mass transfer
- Significant mole changes
- Significant pressure changes

The cases when it makes a difference are:

- Selectivity, especially in non-isothermal cases
- Non-isothermal problems

None of these complications is too complicated for the student to do, but there is not enough time to do so. In design problems, though, some of these complications are necessary.

Textbook Supplements

An important feature is the Textbook Supplement, which gives any new equations in the notation of that textbook. Since the programs are much more general than can be treated in most undergraduate books, it is necessary to explain the problems continuing the notation of the textbook being used by the student. In addition, a two-page handout provides hints on the best way to approach problems, summaries of the equations for easy reference, and standard correlations for some of the transport properties. This handout is designed for quick reference while using the program.

Design Decisions

Design decisions may revolve around conflicting constraints, none of which can be easily handled if one has to write the program:

- Use a small catalyst diameter to avoid diffusion resistance; but this increases the pressure drop.
- A recycle compressor may be an expensive component in a gas-phase reaction system.
- An adiabatic reactor avoids radial dispersion, but the temperatures may be too big; cooling at the wall usually makes radial dispersion important.

By using the Chemical Reactor Design Tool these realistic complications can be treated by the student-designer.

Output

Output is presented graphically in addition to printed form. The user can call for the following plots:

- line plots
- 3D perspective views
- 2D contour plots
- solution variables: concentration, molar flow rate, temperature wall flux
- each term in the equations: diffusion, reaction, convection terms

These plots are created automatically, but the user has some control over them either before they are created (contour and 3D views) or after they are created (line plots).

Conclusions

What will the next 25 years bring? We are already beginning to see the development of multimedia modules with the newest CACHE/NSF/University of Michigan initiative under the direction of Professor Susan Montgomery. Part of this project will involve development of kinetic and bioreactor modules which will incorporate video-clips showing growing bacteria as well as the transport of bacteria in porous media.

Another exciting area on the horizon is virtual reality (VR). CACHE has recently formed a Virtual Reality Task Force; within the next five years we will see a significant number of VR modules developed. One module currently under simultaneous development and testing at the University of Michigan is the prototype of a chemical plant that uses a straight-through transport reactor with a coking catalyst. Here the student uses VR to enter the plant lobby where he or she is given an overview of the process and is free to explore various parts of the room and video tapes at will, simply by moving a joy stick. After this introduction, the student enters the reactor room where he or she can change the operating parameters and see their effect on the reaction variables such as degree of coking, conversion, etc. The student can enter the reactor to observe the coking and catalyst transport, and, in addition, can enter the catalyst pellet to view the internal pore space and reactions occurring on the surface. This visualization of the process and reaction mechanisms will greatly enhance the students' understanding and appreciation of this reaction engineering process.

In addition to POLYMATH, the use of other software packages is on the rise in CRE courses. MATLAB, MAPLE, and Mathematica are becoming increasingly user friendly and also are now being introduced in the freshman calculus or required computing courses at many universities. These packages will provide greater flexibility and a higher level of sophistication in the type and degree of complexity of problems the students can solve. In addition to these ODE solvers, we can expect partial differential equation (PDE) solvers to be available in the not too distant future. The PDE solvers will allow the students to explore radial as well as longitudinal gradients in packed bed reactors.

Finally, we can expect our future textbooks to be on CD-ROMs, so that the student can interact with the book while reading it. Interactions will include video-clips, audio, animation of mechanisms and equations, and much more. The CACHE CD-ROM task force has already prepared and distributed two CD-ROMS containing many instructional modules, video-clips, POLYMATH, and early versions of some of the papers in this monograph. There are great excitements ahead in computing in chemical reaction engineering.

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TRANSPORT PHENOMENA

Bruce A. Finlayson
University of Washington
Seattle, Washington 98195

Andrew N. Hrymak
McMaster University
Hamilton, Ontario L8S 4L7 Canada

Abstract

This chapter describes computer software that is available for solving transport problems, including those with fluid flow. Included are programs that run on PCs, programs that need workstations, and commercial codes that run on large workstations. All programs described here were generated in the 1980s and 1990s.

Introduction

Chemical engineering education was revolutionized in the 1960s by the introduction of transport phenomena, as advanced originally by the seminal book *Transport Phenomena*, by Bird, Stewart and Lightfoot (1960). The subject requires more mathematics than other parts of the curriculum, and typical transport courses invoke heavy use of mathematics. Because mathematics in the 1960s was mostly done analytically, problems treated in transport courses have focused on problems that are simple enough to be solved analytically. Usually that means the problems are one-dimensional and linear, e.g., fully developed flow in a pipe. When flow occurs it is usually laminar. Situations involving two dimensional flows or turbulent flows are not handled except in extremely simple cases, e.g., flow past a sphere at zero Reynolds number, or with correlations, e.g., $Nu = f(Re, Pr)$.

With modern numerical tools it is possible to solve more realistic models. Thus the student must be able to formulate the problem in a reasonable way. In fact, industrially the problem may be solved by a packaged program, or a program written by a computer scientist. Thus the formulation of the problem, and the need to verify and understand assumptions, is especially important as we look into the future. Of all the areas in the curriculum, transport phenomena is probably the one that has been influenced least by the growth of computer power; it thus stands to gain the most by the introduction of computer tools.

In the 1980s CACHE established a task force to develop IBM PC lessons for chemical engineering courses other than design and control. This task force was under the chairmanship of Professor Warren Seider of the University of Pennsylvania and developed a number of modules

which were distributed to all Universities supporting CACHE. Only one of the lessons involved transport - design of a slurry pipeline, and it is described below. Throughout the 1980s the CACHE News ran a column announcing programs written by professors, edited by Professor Bruce Finlayson of the University of Washington. Only one of those programs falls into the class of a transport program - solving the convective diffusion equation in one-dimension and time, and it, too, is described below. A CACHE task force was formed to develop specific lessons for the IBM PC that could be used in transport courses. Most of these were eventually abandoned, it is very time-consuming to generate a decent computer lesson! However, Professor Scott Fogler at the University of Michigan persisted and developed several modules that are described below. Finally the use of spreadsheets can be advantageously applied to transport problems, and Professor Finlayson described those in a chapter in the second edition of a transport book by Professor Ray Fahien (1995) of the University of Florida. A brief summary of what can be done is provided here.

When looking to the future, an on-going project is described that makes available finite element tools to seniors to solve transport problems that are extensions of those in their texts. This is an advanced topic that may be most relevant to senior students and beginning graduate students. Described here is the philosophy of the Transport Module being prepared by Professor Finlayson, and then a review of commercial computational fluid dynamics codes is given for those that have access to them.

PC Programs

Design of a Slurry Pipeline

The slurry pipeline computer program was written by William Provine, Benny Feeman, Gregory Dow, and Professor Morton Denn at the University of California at Berkeley. The emphasis was to provide a design problem that students could solve using the theory and understanding they had achieved in their fluid mechanics course. The problem is to design a slurry pipeline for transporting material under specified conditions. The students can choose to dilute it, to reduce its viscosity, operate it in laminar or turbulent flow, and must avoid settling of the suspended solids. Simplifications are made - a maximum pressure is specified so that the cost factors involved in thicker pipe walls need not be included, the suspension exhibits no yield stress and no shear rate dependence - but the essential part of the problem remains. Economic data are supplied, along with a program to do some of the technical calculations.

The basic equations are

$$\eta = \frac{9}{8} \eta_{SF} \frac{(\phi / \phi_s)^{1/3}}{1 - (\phi / \phi_s)^{1/3}}$$

for the slurry viscosity,

$$\begin{aligned} \text{laminar: } f &= \frac{16}{\text{Re}} \\ \text{turbulent: } f &= \frac{0.046}{\text{Re}^{0.2}} \end{aligned}$$

for the friction factor, and

$$v_R = 1.3 \left[2gD \left(\frac{\rho_S}{\rho_{SF}} - 1 \right) \right]^{1/2}$$

for the minimum velocity for reentrainment of a sedimenting slurry. The problem statement then leads the student through exercises establishing the minimum power for turbulent flow, for laminar flow, and for any flow. The computer program runs on an IBM compatible computer under the DOS operating system.

CDEQN

This program was written by Professor Bruce Finlayson to solve the transient convective diffusion equation in one space dimension.

$$\frac{\partial c}{\partial t} + \text{Pe} \frac{\partial c}{\partial x} = \frac{\partial^2 c}{\partial x^2}$$

The methods used include the finite difference method and the Galerkin finite element method and the solution is plotted automatically at various times. A variety of numerical choices are available to the student, so that they can explore how those choices affect their solution. Such matters are very important when they turn to simulations of the flow of contaminants underground, for example; improper use of the packaged programs can lead to misleading results. Later this program was expanded into a commercial program, CONVECT, which has many more numerical methods. The program runs on a Macintosh computer with any operating system (although System 7 users must turn off the cache memory).

PC Lessons

A series of PC lessons has been developed at the University of Michigan under the direction of Professor Scott Fogler. The program "Shell: Shell Momentum and Energy Balances" leads the student through the exercise of making shell balances for three problems: water flowing down a vertical flat surface, water flowing through a vertical circular tube, and heat conduction in an electric wire. If the correct shell balance is achieved, the solution to the problem is displayed. The program "Simp: Simplification of the equations of motion and energy" works on the problem in the reverse order: the student chooses which terms to leave out of the equations to simplify them to model one-dimensional transport. This module uses the language of video games. It is called the "Equation Avenger," and the student 'shoots' the unnecessary terms. Since there seems to be a definite bias between boys and girls playing video games, and the type of game they prefer, this module may run afoul of the Politically-Correct Police and be inappropriate for the men and women in our classes! The program "Visc: Rheology - Identification of Liquids" helps the student review viscometer principles for identifying the type of non-Newtonian fluid. "Patch: Diffusion - Drug Patch Design" requires the student to design a drug patch that supplies a drug to astronauts in a space shuttle mission. The drug flow rate must fall within a specified range, and this flow rate must be maintained for a required amount of time. The student can use the simulator to experiment with different materials (diffusivities),

patch thicknesses, and different reservoir drug concentrations. Thus the student is exposed to open-ended design problems in the transport course, which is a trend of growing importance. "Thermowell: Conduction, Convection and Radiation" allows students to investigate the effects of various thermowell parameters on the temperatures measured by a thermocouple. Again the problem is open-ended and the computer allows students to try many choices easily and quickly.

Transport Using Spreadsheets

Professor Bruce Finlayson at the University of Washington has written a chapter entitled "Numerical Methods for Solving Transport Problems" for the second edition of the book *Fundamentals of Transport Phenomena*, by Ray W. Fahien, McGraw-Hill, New York (first edition: 1983). This chapter describes methods for solving typical and extended transport problems using the numerical tools that exist today.

The first section treats a heat transfer problem. First the problem is taken as a linear problem, so that the finite difference method can be described. Then complications are added to the problem: a thermal conductivity that depends on temperature and a heat generation rate that is not constant. The equations solved are

$$\frac{1}{r} \frac{d}{dr} \left(k r \frac{dT}{dr} \right) = - \frac{2 \Phi_0}{k} \left(1 - \frac{r^2}{R^2} \right)$$

$$k = k_0 [1 + a (T - T_R)]$$

Finally, the solution of these problems is described using a spreadsheet program with iteration capabilities, and detailed information is given about how to organize the calculations and check them. The next section considers transient heat transfer.

$$\frac{\partial T^*}{\partial t} = \alpha \frac{\partial^2 T^*}{\partial x^2}$$

The finite difference method is applied to reduce the problem to a set of ordinary differential equations (using the method of lines), and packages such as MATLAB are used to solve them. The final section considers the more complicated situation of heat conduction in both directions.

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0 \text{ in } 0 \leq x \leq 1, 0 \leq y \leq 1$$

Such problems can be solved using iterative methods as long as the domain has straight edges (either constant x or constant y , but there can be many of them). A problem is worked showing the effect of having a hole in the middle of the domain. The finite element method is also applied to the same problem so that students can see the limitations of using a spreadsheet program for such problems.

When solving differential equations numerically, though, there are still approximations made, and the possible error must be assessed. Throughout the chapter methods are given for organization of the calculations, often with solution of a simpler problem which is easily

checked, and with complications introduced one by one with checking at each step. Of even more importance, though, is the use of the truncation error to determine the error of the numerical solution. Since the error in the solution is proportional to some power of Δx , for example, the solution values should follow that behavior when the problem is resolved with a different Δx . By using this information, it is possible to assess the accuracy of the numerical solution, and improve it if necessary (it seldom is).

Workstation Programs

Brief Description of Transport Module

The Transport Module is being developed by Professor Bruce Finlayson at the University of Washington to allow students to solve fluid mechanics and transport problems in laminar two-dimensional flow situations. The program uses the finite element method to discretize the mesh. The user sketches the domain on the screen, identifies the fixed boundaries, flow boundaries, etc., sets the boundary conditions, and then instructs the program to solve the problem. The finite element mesh is constructed automatically, and the results are displayed graphically as contour plots. The user interface is constructed in X-windows for use on Unix machines.

Goals

With the Transport Module students will be able to investigate fluid flow phenomena, such as how vorticity is generated, convected and diffused, and how this influences the flow field, heat and mass transfer. They will be able to make quantitative estimates - such as: "Is it isothermal?", and "If not, how much error is introduced?" It is even possible that students can tackle design problems in their senior year that involve small-scale processes and transport limitations, including the interaction of flow, heat, and mass transport, such as might occur in chemical vapor deposition. As they solve problems under different assumptions, students will gain intuition rather than just make assumptions because the instructor says so, or because of mathematical convenience. Examples can be more exciting and can involve the newer technologies. A textbook supplement will provide problems that are tied to existing textbooks, making it easy to incorporate the new ideas in existing courses.

Detailed Description of the Transport Module

The three pillars on which the Transport Module is built are the user interface (to specify the problem), the finite element programs, and the graphics display of the results.

The user interface allows the user to sketch the domain as a series of lines or quadratic curves. Boundary conditions are specified for each of these lines in a natural way. Whereas most finite element codes allow you to specify each variable at each boundary node, this generality can also lead to gross modeling errors. Thus students are restricted to choosing boundary conditions that make sense: solid boundary, flow boundary, centerline (symmetric) boundary, etc. This restriction prevents gross errors, and it also makes the data entry considerably simpler. The fluid flow and heat transfer properties are easily entered in an X-windows interface.

The finite element codes allow a variety of problems to be solved, but are restricted to laminar flow in two dimensions, either Cartesian or cylindrical geometry. The Navier-Stokes

equations can be solved, including the possibility of the viscosity depending on shear rate, so that simple non-Newtonian fluids like power law and Bird-Carreau fluids can be modeled. The energy and transport equation can also be added, in which case the viscosity can depend on temperature as well. The user specifies a viscosity subroutine and a heat generation and rate of reaction term as well. The primary aim is to allow flow and heat transfer, rather than a complete inclusion of chemical reaction phenomena. Only one chemical species can be included, allowing for dilute systems or systems in which the number of moles does not change. Chemical reactor models are best handled with the Chemical Reactor Design Tool. The energy equation can be solved by itself for heat transfer problems, and the energy and mass transfer equation can be solved with a specified velocity for chemical reactor situations.

Following solution of the finite element problem, various post-processing programs are invoked to make the results more meaningful. First, vorticity and streamline are determined, if desired. Then various plotting options are chosen. The flow situation can be examined by plotting the streamlines and vorticity, but more detail is also available. The different terms in the equation can be plotted individually; thus the convective and the viscous terms can be compared for flow around a cylinder, and the student can explore the Stokes paradox. The stress components can be plotted, as can the viscosity throughout the domain. Both of these plots are useful for gaining insight to non-Newtonian flows. When the energy equation is solved, the viscous dissipation term can be plotted and compared with the diffusion or convection term; this helps the student see the validity of the constant temperature approximation. These pictures are especially meaningful when done in a 3D perspective view. In addition, certain properties can be viewed along boundaries: the drag forces and heat flux.

Because of the processing power needed to run the finite element codes, the actual calculations can best be done on a large computer, and the Unix environment makes this especially easy. With the X-windows display on a local computer screen, the graphics can be viewed locally (and printed locally), but the speed of the central processor is especially welcome. Of course, calculations can be done at the workstation, too, but with more delay. When computer power increases it will be possible to do the processing locally, too.

Of course it is necessary for educational purposes that the student be able to solve many problems they have seen before. Most of the problems they solved in transport are one-dimensional, but these can be solved in the Transport Module as well (with some loss of efficiency). Couette flow, Poiseuille flow, and combined Couette-Poiseuille flows are all solvable. The Graetz problem can be solved with fully developed flow, with developing flow, with Newtonian and non-Newtonian fluids, and with temperature-dependent viscosity. Laminar boundary layer problems can be solved, as can flow past spheres and cylinders. The effect of walls around the spheres and cylinders can be explored, provided the geometry still retains a two-dimensional character.

In the time since the project was defined the power and availability of commercial codes has increased (see below) to the point that this program may never be made available. However, the method of using them in class and interacting with the existing curriculum have value that is not provided by commercial codes. Such interactions are described below.

Sample Questions which can be Explored

Consider any flow problem, e.g., flow past a sphere. What is the effect of Reynolds number? How small is small, so the inertial effects can be ignored? How large is large, so the inertial effects must definitely be included? How big are the inertial terms (which one would like to ignore) compared with the diffusion terms? These are questions which can be answered by students using the Transport Module. Once their intuition has been developed, the Transport Module can be used in more design-type situations. They can compare the effect of different shapes (at least cylindrical shapes with different cross sections).

In the heat transfer problems the students can see the effect of Prandtl number, in that it effects the boundary layer thickness, which they will see in the plots. They can allow the thermal conductivity to depend on temperature if they think that is important, and compare results to simulations in which the thermal conductivity is constant. The heat transfer module can also be used to solve Laplace's equation, making it suitable for some problems in electronic materials processing. There the effect of different geometries can be easily explored.

Sample Extension Problems

Listed below are several problems of the kind that can extend those in current textbooks. The examples are some of those related to Denn's book (1980), but textbook supplements can easily be prepared for all major textbooks. For the Chemical Reactor Design Tool only two textbooks supplements were prepared, because there are only two major books used by universities, but the added work to prepare a second supplement is small compared to the work necessary to prepare the first one.

Flow of a sphere in a tube, p. 61. How far away does the outer boundary have to be for less than 5% effect? Check the correlation in Figure 4-6. Extend that correlation as a function of Reynolds number.

Flow past objects that are not regular, p. 66. Compare the drag of a sphere with that of a disk oriented with the flat edge forward. Consider other shapes. Prepare a universal graph (and test it) by using the surface to volume ratio to obtain an effective diameter.

Calculate pressure drops in a reaction injection molding device, p. 136.

Flow in a manifold, p. 125. With one inlet and several outlets, how much flow goes out each?

Determine the errors incurred when measuring the pressure at the bottom of a hole or slit.

Entrance pressure loss in contracting flows, p. 336. Correlate it, design a shape that will minimize it, do for power law fluids, too.

Flow Distribution in a single screw extruder, p. 197. Do a two dimensional analysis and determine the errors in the one dimensional analysis.

Boundary layer flow, p. 286. Do an complete analysis for flow past a flat plate and examine the terms that have been neglected in the boundary layer analysis. Are they really small? How small? How large a region is affected?

Examples

Examples of the problems that can be solved are given here.

The problem of heat transfer to flow past a sphere is commonly treated in textbooks. For slow flow ($Re < 0$) the asymptotic formulas have been derived for large and small Peclet number.

$$Nu = 2 + \frac{Pe}{2} + \frac{1}{4} Pe^2 \ln Pe + 0.03404 Pe^2 + \frac{1}{16} Pe^3 \ln Pe, Pe < 1, Re \text{ small}$$

$$Nu = 0.991 Pe^{1/3}, Pe \text{ large, } Re \text{ small}$$

An undergraduate and Professor Finlayson used the finite element code to generate solutions for Peclet numbers between 1 and 1000, as well as Reynolds numbers between 1 and 50. That data was then correlated in the following form

$$\frac{1}{Nu - 2} = \frac{1}{Pe/2} + \frac{1}{0.9 Pe^{1/3} Re^{0.11}}$$

This correlation agrees with the asymptotic formulas in their region of validity. Interestingly, it is an even better correlation of the heat transfer experimental data than the usual formulas derived from the data in the form

$$Nu = 2 + [0.4 Re^{1/2} + 0.06 Re^{2/3}] Pr^{0.4}$$

See Finlayson and Olson (1987). Westerberg and Finlayson (1990) showed that for very small Reynolds number the term $0.9Pe^{1/3}Re^{0.11}$ should be replaced by $0.89Pe^{1/3}$. The temperature profiles in different regimes clearly show the meaning of the Peclet number as a ratio of convection to conduction of energy. Figure 1 and 2 show temperature contours for cases with small and large Pe.

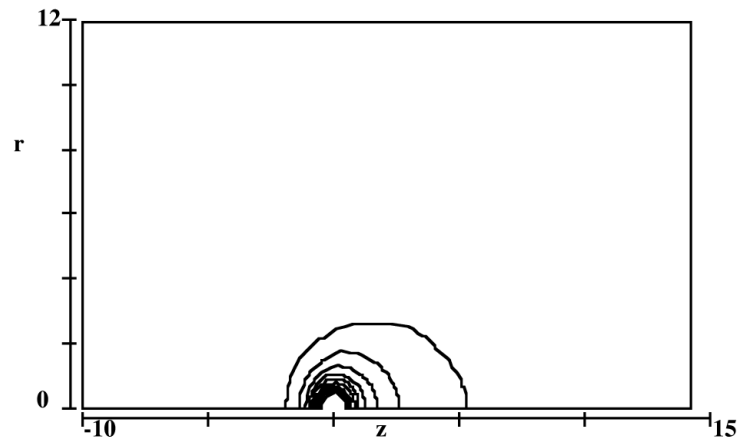


Figure 1. Temperature contours for $Re = 1, Pe = 1$.

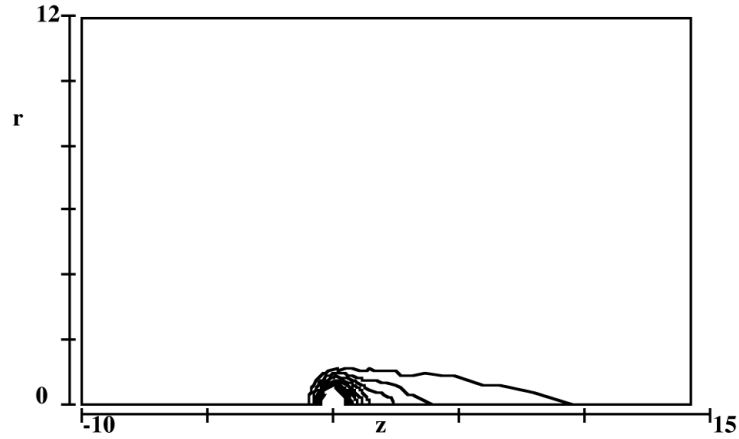


Figure 2. Temperature contours for $Re=1$, $Pe=20$.

Another example is the study of concentration distribution of adenosine diphosphate which is released from a platelet membrane during thrombus growth (Folie and McIntire 1989). The goal was to model thrombi of various shapes and dimensions. Because the finite element method can easily model changes in shape it is possible to study the effect of geometry.

Another example of a problem involving complicated geometry is the design of a thermal conductivity cell, as shown in Fig. 3. Calculations can determine the errors caused by conduction through the plexiglass and the heat losses to the surroundings. One dimensional calculations should be done first to give an estimate, and the estimate can be checked with the more detailed calculations.

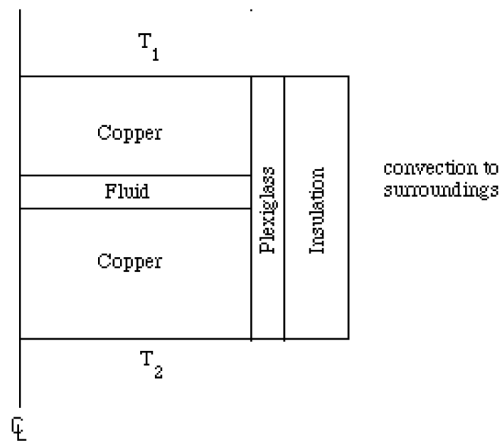


Figure 3. Thermal conductivity cell.

The last example is a problem to design a slotted-electrode electrochemical cell, as described by Orazem and Newman (1984). The problem can be reduced to that shown in Fig. 4, which is easily solved using the code for heat conduction. The student can then consider other designs (geometries) to insure that the current is uniform along the face.

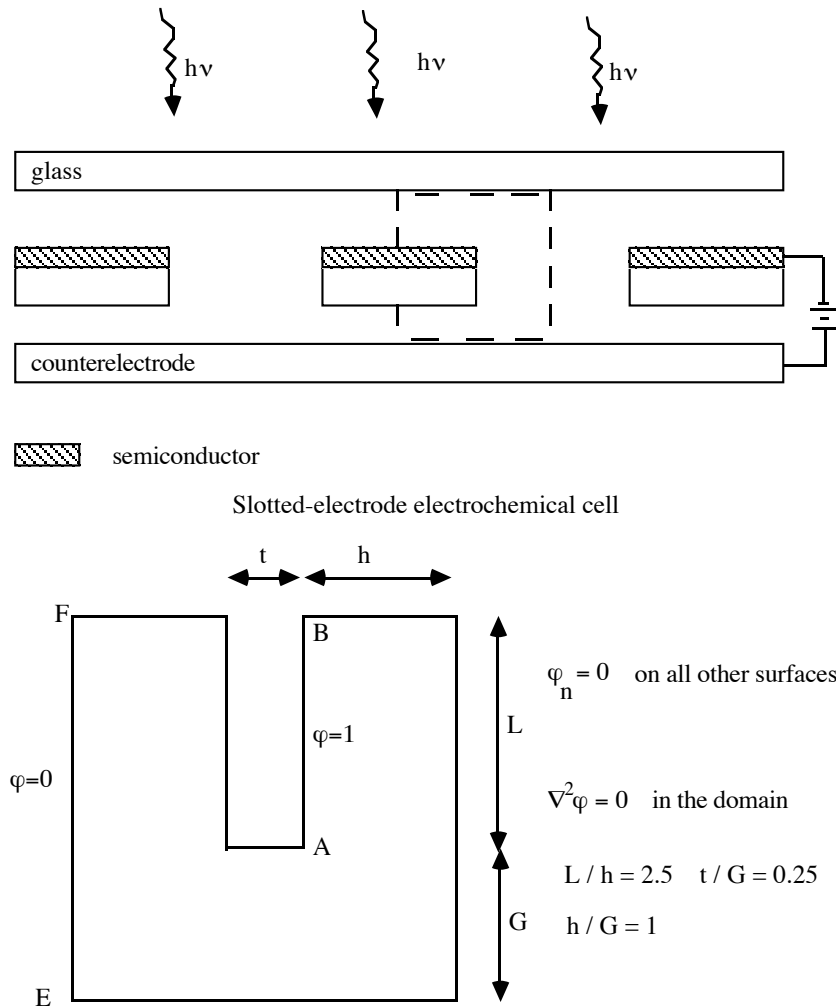


Figure 4. Problem description for slotted-electrode electrochemical cell.

Computational Fluid Dynamics

At the advanced undergraduate and graduate levels, the equations needed for the study of transport phenomena become more difficult. Two-dimensional transient, three spatial dimensions, nonlinear physical properties and convective model components are a few of the com-

plications that arise with more realistic problem specifications. The first method of attack is to simplify the problem so that perturbation methods, Green's functions or transforms can be used (Finlayson, 1980; Denn, 1980; Leal, 1992).

In general, numerical methods will be needed to solve problems with complicated geometry or nonlinear effects. Computational fluid dynamics (CFD) is the name commonly applied to the study of fluid flows using computer simulation methods. Other transport processes, such as heat and mass transfer, are also included in CFD since many problems involve the solution of coupled transport processes. The use of numerical methods to solve transport process problems, with either coupled or uncoupled phenomena, has a long history that precedes the use of computers. The current availability of powerful computers and the development of sophisticated discretization algorithms for the solution of the partial differential equation (PDE) sets found in transport problems has led to the wide use of CFD in industry and academe.

The conservation equations for mass, momentum and energy require constitutive relations to form a closed set of equations. In general, the exact solution cannot be found and we seek an approximate solution to the state variables which will be defined at discrete points, or nodes, within the domain. There may be local approximating polynomials which interpolate the state variables between sets of neighboring nodes. The discretization method replaces the PDE set by an algebraic or differential equation set. For steady state problems, the PDE would be converted to a set of algebraic equations, the discrete equation set, with an equation for each state variable at each node. In transient problems, algorithms exist to generate algebraic equations for each state variable at each node for a given point in time. The method of lines, as applied to transient PDE sets, generates a set of differential equations which define the value of each state variable at each node as a function of time.

We can write a general steady state differential equation for the state variables as follows, which applies to the conserved species:

$$\nabla \cdot (\rho u \phi + (-\Gamma \nabla \phi)) - S = 0 \quad (1)$$

Given an approximation to ϕ called θ , which is inserted into the governing PDE,

$$\nabla \cdot (\rho u \theta + (-\Gamma \nabla \theta)) - S = R \quad (2)$$

The magnitude of R , the residual error, varies locally and measures how well the conservation equation is being satisfied at a particular point in space. The Method of Weighted Residuals (MWR) defines a set of algebraic relationships between the values θ_i (which are the approximated values of the state variables at each node) and its neighboring nodal values. The weighted integral of R is forced to zero through

$$\int_V W R dV = 0 \quad (3)$$

The choice of W , the weighting function, determines the type of method. The numerical schemes that are most often used include: finite differences, finite volumes, finite elements and collocation methods. The *finite difference* method has a value of $W=1$ at node i , zero elsewhere, and thus the residual is forced to zero at each node. The derivatives of the state variables are approximated using Taylor Series expansions. If the approximation to θ is given by a polyno-

mial and the weighting function is $W=1$ at specified sampling points, the method is called *collocation* (Finlayson, 1980). *Finite element* methods use a definition of a polynomial for θ over a small region within the domain with the values of the state variables at defined nodes such that

$$\theta(x,y,z) = \sum_i^{(e)} N_i(x,y,z) \theta_i^{(e)} \quad (4)$$

The terms N_i are known as shape functions and are defined within each element such that their value is 1 at the node i , a value between 0 and 1 within the element and zero outside the element. The choice of W defines the particular type of finite element method. For example, $W = N_i$ defines the widely used Galerkin finite element method.

$$\int_{V^{(e)}} N_i \left[\nabla \cdot \left(\rho u \left(\sum_i^{(e)} N_i^{(e)} \theta_i \right) + (-\Gamma \nabla \left(\sum_i^{(e)} N_i^{(e)} \theta_i \right)) \right) - S \right] dV = 0 \quad (5)$$

Finally, *finite or control volume* methods can be derived by starting with $W=1$ within a control volume around the node i and zero outside of this subdomain (Patankar, 1980). The integral can then be broken into a volume integral and a surface integral which satisfies the integral form of the conservation equations

$$\int_{A^i} (\rho u \theta + (-\Gamma \Delta \theta)) \cdot n dA - \int_{V^i} S dV = 0 \quad (6)$$

Variations on the finite volume methods depend on how the control volume is chosen around the nodal points and the manner in which gradient terms are approximated using neighboring nodes and their respective control volumes. Thus, from a basic definition, one can derive the basic versions of all the popular methods used in solving advanced CFD problems. The methods share the common feature of gridding where the network of nodes, which will define the points at which the state variables will be determined, is chosen and some methods require the definitions for the elements or subdomains. The basic steps for all the methods are the same: choose the conservation equations and terms within the equations appropriate to the problem, divide the domain into an appropriate set of nodes and subdomains/elements, assemble the discretized forms of the PDEs as (non)linear algebraic equations and solve the equation set.

Graduate courses which use the concepts described above vary widely in content depending on the objectives for the student. One approach is to do an overview of the different discretization methods and then provide a series of problems which require a numerical analysis. Commercial CFD simulators are widely used both in industry and academe, for example: FLUENT/BFC which uses the finite volume method (Fluent Inc., 1990), FIDAP which uses the finite element method (FDI, 1993) and NEKTON which uses the spectral element method (Fluent Inc., 1992). Readers are referred to the annual Software Directory published by *Chemical Engineering Progress* for current listings of available software applicable to chemical engineering problems and the article by Wolfe (1991). Commercial simulators have a variety of tutorial problems based on practical problems taken from the literature. It is common to ask students to modify existing meshes or modify boundary conditions to simulate another prob-

lem. It is important to recognize the amount of time it takes to generate a good mesh for the solution of realistic problems. The general rule-of-thumb is that 80% of the user's time will be in the development of the mesh. In posing problems for students it is important to keep the time requirements in mind when dealing with complicated geometry when an existing mesh is not available to the student. The problems that are currently available in commercial CFD package libraries span a wide spectrum of applications and include: crystal growth, polymer flows, porous media flows, electronic packaging cooling and particle-laden fluid flows. All the packages have an interface to develop the mesh and post-processing capabilities to visualize the resulting flow velocities and other state variables in the domain. Though implementations exist for the personal computer platform (PC-DOS and Macintosh), most realistic problems require a workstation.

It is very important to build up the expertise of the student by encouraging the solution of problems for which experimental data are available. The amount of data produced by a CFD code can be overwhelming, particularly in 3-D problems, and so a thorough grounding in the expected flows and fluxes of well-characterized problems provides a good basis for analysis of more complicated problems. The effects on the calculated state variable values of mesh density, coupling of transport processes and sensitivity of the solution to physical property parameters requires skills gained through experience. It is too easy to determine a steady-state solution to a problem for which no steady-state exists!

Another approach for teaching CFD courses is to develop a particular method in the classroom and have the students implement subroutines as they learn the important concepts of the method. For example, students may implement a basic meshing algorithm, the formulation of the discretized equations and the linear equation solver. Visualization software should be used to simplify analysis of the results. This type of course gives the student a better perspective on the development of the equations and the problems in solving the final set of equations, but limits their exposure to more complicated problem formulations. Sample reference textbooks for each of the methods as applied to CFD include: Anderson et al. (1984) for finite differences, Baker (1983) and Dhatt and Touzot (1984) for finite elements and Patankar (1980) for control volumes. Minkowycz et al. (1988) and Fletcher (1988) provide chapters dedicated to the use of different numerical schemes common in CFD applications.

In summary, CFD and the numerical solution of the transport equations are important fields which are widely taught at the graduate level and are beginning to be exposed in the undergraduate curriculum. The wider use of CFD has been accelerated by the combined availability of faster computers, more sophisticated numerical solution techniques and graphic tools to visualize the results.

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SEPARATIONS PROCESSES

Ross Taylor
Clarkson University
Potsdam, NY 13699

Abstract

The equilibrium stage has been used for modeling separations process problems for nearly 100 years. The model equations are particularly amenable to computer solution, and teachers of separations courses were among the first to introduce computers into undergraduate chemical engineering curricula. CACHE has supported development and use of interactive instructional modules for the separations area, and has promoted distribution of the powerful *ChemSep* multicomponent distillation design tool for use in separations courses.

In recent years, it has become possible to model separations processes using mass-transfer, rate-based *nonequilibrium* models. These nonequilibrium models are likely to see increased use in the future, particularly for simulating nonideal systems, systems with reaction, and/or processes with multiple feeds and products. This trend toward introduction of nonequilibrium (and also dynamic) models should act as a spur for closer integration of separations and mass-transport courses.

Introduction

A recent advertisement for a journal claims that there are 40,000 distillation columns and that operating these columns requires 7% of all of the energy consumed in the United States alone. When we consider all of the distillation columns elsewhere in the world, as well as all the closely related operations of absorption, stripping and extraction, it is clear that, even if these figures are significantly in error (other published figures put the energy consumption at about 3%), the classical separation processes are unusually important unit operations.

Chemical engineers (whether they are professionals in industry or university students) have been solving separation process problems using the *equilibrium stage model* for about 100 years (since Sorel first used the model for the distillation of alcohol). The key assumption in the equilibrium stage model is that the vapor and liquid streams leaving a stage are in equilibrium with each other. The equations that model equilibrium stages are known as the *MESH* equations. The *M* equations are the Material balance equations, the *E* equations are the equilibrium relations, the *S* equations are the mole fraction summation equations, and the *H* equations are the enthalpy balance equations. The unknown variables determined by solving these equations are the mole fractions of both phases, the stage temperatures, and the flow rate of each phase.

There can be few other mathematical models in any branch of engineering which are so well suited to computer solution and that have prompted the development of so many truly different algorithms as have the *MESH* equations of the equilibrium stage model. Indeed, it would not be too far from the truth to claim that it is equilibrium stage calculations that brought computing into chemical engineering (or should that be chemical engineers to computers?). Since computers became available in the late 1950s hardly a year has passed without the publication of at least one new algorithm for solving the equilibrium stage model equations and, in many years, several new algorithms have appeared. Most of the better numerical methods (and some of the not so good ones) have been used in the solution of equilibrium stage problems. Indeed, a good test of a numerical method might therefore be to see if it can be used to solve distillation problems.

It is not our intention to provide a complete review of computer-based methods for separation process calculations; readers can consult one of several textbooks that includes some discussion on computer-based methods (Smith, 1964; King, 1980; Henley and Seader, 1981). Other books have focused almost entirely on the computational aspects (Holland, 1963, 1975, 1981) and Seader (1985) gives an interesting history of equilibrium stage separations calculation methods with more detail than is appropriate this brief article.

CACHE Contributions

Nowadays, even chemical engineering students solve their distillation problems using computer software. In this section we review the part that CACHE has played in making this possible.

While not a CACHE product, it would be remiss of us not to mention the collection of programs for separation process simulation by Hanson, Duffin, and Somerville (1962). Their book included several programs in Fortran for solving a wide variety of multistage separation process problems including distillation, absorption, stripping and liquid-liquid extraction. A chapter at the end of the book discusses the peculiar difficulties associated with interlinked columns. Several introductory chapters serve to introduce the reader to "a sufficient number of techniques... to make possible convergent solutions to *any* problem" (emphasis added). The optimism expressed in the above quotation is interesting for, despite many developments that have taken place over the past 30 years, we still have not reached that happy (for some) situation where all of our equilibrium stage separation process problems can be solved the first time they are attempted. We are, however, a great deal closer to that goal.

Included in the CACHE series *Computer Programs for Chemical Engineering Education* published in 1972 (and mentioned elsewhere in this volume as well) was a volume entitled *Stagewise Computations* (Christensen, 1972). The paperback edition included descriptions, examples of usage, and listings of 17 Fortran programs for modeling such operations as counter-current leaching, liquid-liquid extraction, batch distillation, and multicomponent distillation, stripping and absorption. The programs in this book represented a cross-section of computerized implementations of old-fashioned calculation methods, originally devised for solving separations process problems by hand, and programs that implemented methods that better represented the state of the art as it was at the time. These programs were used at many universities around the world.

Among the programs in the CACHE collection are two by N.S. Berman and O.C. Sandall that implement the stage-to-stage calculation method developed by Lewis and Matheson (1932) (and refined by others). D.M. Watt provided a program that used another algorithm from the same era, the method of Thiele and Geddes (1933). L.L. Hovey provided an implementation of the Amundsen - Pontinen (1957) method. This was one of the first methods to exploit matrix algebra in the solution of counter-current separations problems.

WHENDI by P.J. Johansen and J.D. Seader implements the Wang and Henke (1966) bubble point method for distillation, which is a modification of the Amundsen - Pontinen (1957) method. STAB, by the same authors plus T. Shinohara, solves absorption and stripping problems using the sum-rates method (Sujata, 1961; Burningham and Otto, 1967). Bubble point and sum-rates methods belong to a class of algorithm known as equation-tearing methods and have been used in industry for several decades. These methods pair model equations and variables in two loops and alternately solve the equations in each loop until convergence is reached. Bubble point methods use temperatures as inner loop variables and the total vapor flow profile is adjusted in an outer loop by solving the energy balances. Sum-rates methods fix the temperature and pressure profile for the column and the mass balance and phase equilibrium equations are solved simultaneously for the component flow rates in an inner loop. The energy balance equations are solved in an outer loop in order to adjust the temperature profile.

J.W. Tierney contributed a program that could handle interlinked columns. The program employed an algorithm that falls into the class of 2N Newton methods that Tierney and his co-workers helped to develop in the late 1960s and early 1970s (Tierney and Bruno, 1967; Tierney and Yanosik, 1969). In these methods the temperatures and flows are adjusted simultaneously using Newton's method.

Newton's method now is widely used in commercial simulation programs (although it has taken many years longer than it should to have gained the measure of acceptance it now enjoys). To the best of our knowledge, a method to solve *all* the MESH equations for all stages at once using Newton's method was first described by Whitehouse (1964). Among other things, Whitehouse's code could solve problems involving purity specifications or of T , V , L or Q on any stage. Interlinked systems of columns and nonideal solutions also could be handled. Unfortunately, Whitehouse's work was published in a rather obscure proceedings volume (Stainthorp and Whitehouse, 1967) and had essentially no influence on the development of computer-based simulation methods. The credit for showing us how to use Newton's method for separation process calculations, therefore, goes to Naphtali and Sandholm, (1971) and to Goldstein and Stanfield (1970) for distillation and to E.C. Roche (1971), who applied the method to liquid-liquid extraction and who contributed the program LIQLIQ that is included in the CACHE collection.

In 1987 CACHE distributed to supporting departments a collection of computer-based lessons containing "open-ended" design type problems for use in courses other than the capstone design course (Seider, 1987). Among the six lessons were three for separations courses: Supercritical fluid extraction (by J. Kellow, M.L. Cygnarowicz, and W.D. Seider, Pennsylvania), Gas Absorption with Chemical Reaction (by K. Nordstrom and J.H. Seinfeld, Cal Tech), and Design of Flash Vessels and Distillation Towers (by B.A. Finlayson, E.W. Kaler, and W.J. Heideger, Washington) based on short-cut methods of column design. The major change in

computing practices brought about by the personal computer in the decade of the 1980s is evident in this release; the material was provided on floppy disks for use with IBM PC compatible computers.

In 1992 CACHE made available *ChemSep*, a computer software system developed by R. Taylor and H.A. Kooijman (1992). As a piece of software *ChemSep* is much more closely related to flowsheet simulation programs than to the computer-based lessons and modules discussed above. The program was created for use in university separations courses (but may also be useful in thermodynamics and design) but also can be (and is) used by professionals in industry. *ChemSep* features a menu-driven user interface and simulation programs that can handle flash, and single distillation, absorption and liquid-liquid extraction columns with multiple feeds and sidestreams. Many of the most widely used thermodynamic models are available in *ChemSep* and Newton's method is used to solve the large, sparse system of nonlinear equations. The CACHE version of the package includes a database for 189 different chemicals and can handle up to 10 components and 100 stages.

H.S. Fogler and S. M. Montgomery (1993) have created a collection of interactive (personal) computer modules for chemical engineering instruction. There are five of these modules for separations courses including: BASIS - An introduction to Separation Processes, CASCADES - Liquid-liquid Extraction, MCCABE - Binary Distillation (via the McCabe-Thiele method), ABSORP - Packed absorber design, and MEMBRANES - Spiral membrane process optimization. These modules feature animations within a graphical user interface that allow students to interactively review material and to carry out simulated experiments (see Figs. 1 and 2).

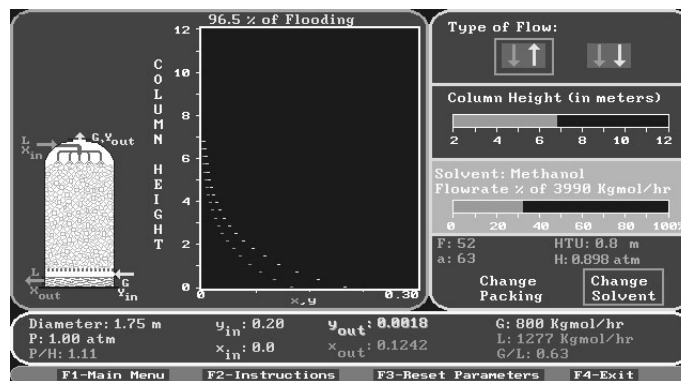


Figure 1. Screen image from CACHE module ABSORP for absorption column design.

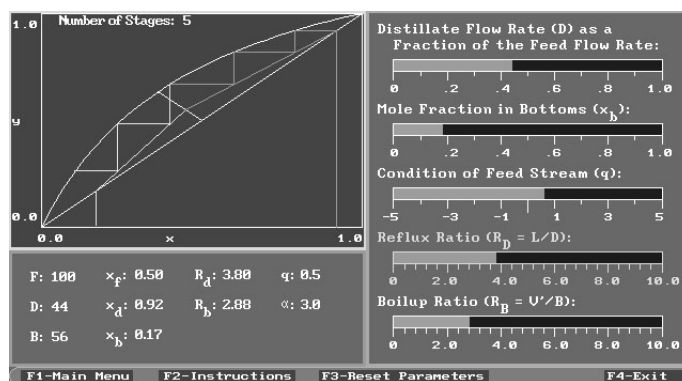


Figure 2. Screen image from CACHE module MCCABE for binary distillation.

It is interesting to contrast the first CACHE programs with their more recent offerings. WHENDI, for example, is just 635 lines of Fortran. Contrast this with *ChemSep* which consists of about 100,000 lines of Fortran (of which about 10,000 is just the part that computes physical properties) and Turbo Pascal. The comparison is, of course, not entirely fair since WHENDI was never intended to be able to handle the range of problems that can be tackled with *ChemSep*. Nevertheless, it serves to illustrate one of the negative aspects of modern software, a trend to ever larger software systems; a trend that, fortunately, is countered by the ever increasing speed and capacity of computer hardware.

The Impact of Computer-Based Tools on Separations Courses

Perhaps nowhere else in the chemical engineering curriculum has the impact of computers been greater than in the teaching of separations. The availability of computer-based tools such as *ChemSep* make it possible to include realistic multicomponent distillation design problems in the first undergraduate course on separations. In spite of these developments, the graphical McCabe-Thiele method, devised in the 1920s, combines simplicity and elegance and remains a useful method for the analysis of distillation type operations, even for multicomponent systems, as shown in Fig. 3. Indeed, graphical techniques (McCabe-Thiele diagrams and column profiles such as those in Figs. 4 and 5) for the visualization of numerical simulation results are extremely valuable instructional tools. (With the exception of Figs. 1 and 2, all of the illustrations in this article were created by *ChemSep*, printed to a file using one of several graphic image formats supported by the program, and imported into the word processor used to create this article.)

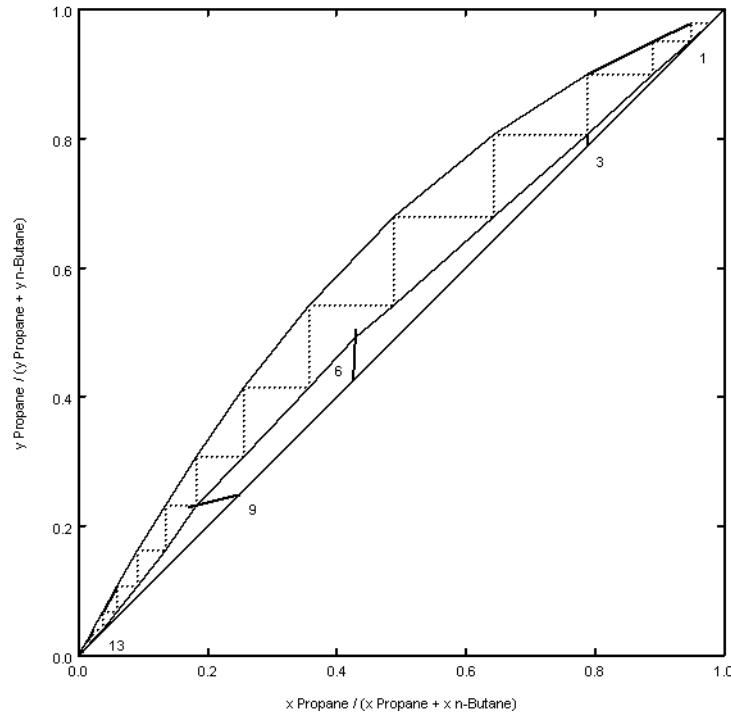


Figure 3. Modified McCabe-Thiele diagram for an example involving a five component system. This particular example accompanies the CACHE program WHENDI (see Christensen, 1972, p. 384; Henley and Seader, 1981, p 568) although, in this case, the results were obtained with the CACHE program Chem-Sep.

Several topics that are covered at length in some separations texts no longer need to be covered in the first course on separations. Once-popular graphical methods (Ponchon diagrams, for example) are being dropped from undergraduate courses as computer-based methods are used more frequently. It is no longer necessary to teach undergraduate students all (or even any) of the gory details behind the algorithms used to solve multicomponent distillation problems; computer software has become sufficiently reliable that our students no longer need to know *how* the model equations are solved. It is, however, useful to provide some sort of instruction on how to use computer tools to solve open-ended separation process engineering problems. For example, students need to know what specifications are most likely to allow computer-based algorithms to find converged solutions (and what specifications may lead them into trouble). What can we do in the event that convergence is not obtained? What process variables can be changed in order to improve the operation and/or design? Short-cut methods, based on several more or less limiting assumptions, remain useful for preliminary design.

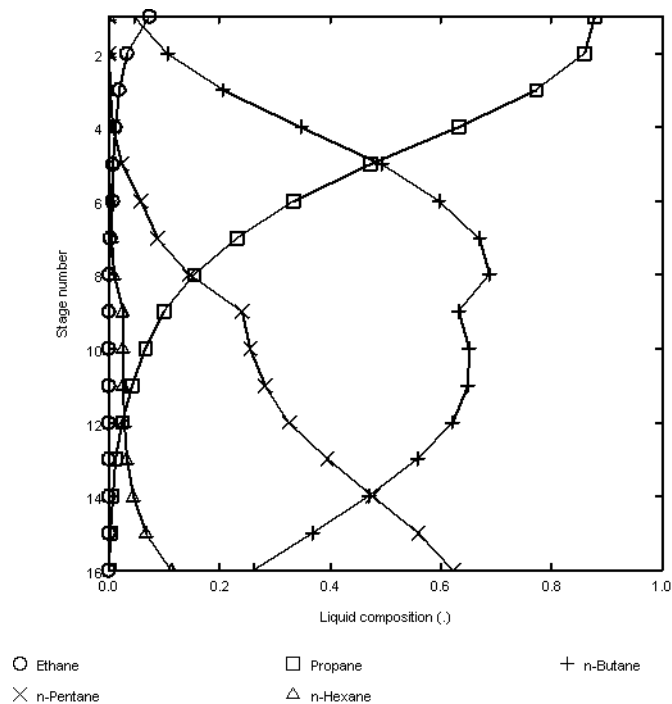


Figure 4. Composition profiles for the column in Fig. 3.

Material that can be relegated to a second (elective) course on separation process modeling and simulation includes details of the algorithms that are used to solve the *MESH* equations, methods for the solution of large sparse linear systems of equations, Newton's method for solving systems of nonlinear equations (although, in view of the versatility and power of this approach, a case could be made for covering the method elsewhere in the curriculum), problems associated with Newton's method such as its sensitivity to the initial estimates, and homotopy-continuation methods for solving difficult problems.

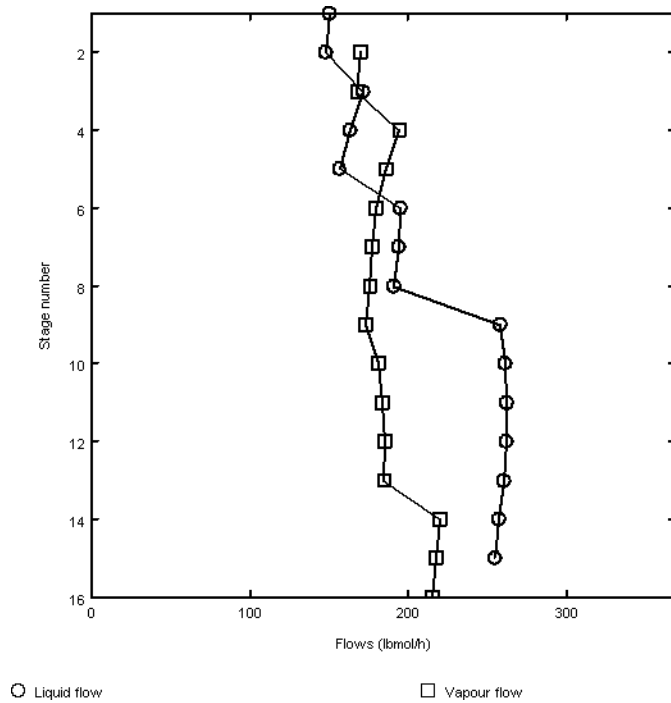


Figure 5. Flow profiles for the column in Fig. 3.

Future Trends

As noted above, the equilibrium stage model has been part of chemical engineering - and of a chemical engineer's education - for over a century. It is, of course, well known that the trays in multicomponent distillation columns do not operate at equilibrium. The usual way around this problem is to use an efficiency factor of some kind and separations texts discuss the evaluation of efficiencies at some length. Using efficiencies introduces new problems and the drawbacks of these quantities also are well known (see, for example, Seader, 1989).

In recent years it has become possible to model separation processes as the mass transfer rate-based operations they really are (Krishnamurthy and Taylor, 1985; Taylor and Krishna, 1993). Efficiencies are not used in these *nonequilibrium* (or *mass transfer rate-based*) models (although they may be calculated *after* a simulation has been completed, Fig. 6). The building blocks of these models include the mass and energy balances, equilibrium and summation equations that are familiar to us from the equilibrium stage model. There is, however, a fundamental difference in the way these equations are used. In a nonequilibrium model the balance equations are written for each phase rather than for the stage as a whole. The K-values are eval-

uated at the temperature, pressure, and composition of the interface, which is assumed to be an equilibrium surface, offering no resistance to mass transfer. Equations that model the mass and energy transfer across the phase boundary are included in the model and solved simultaneously with the other equations. Mass and energy are transferred across the interface at rates that depend on the extent to which the phases are *not* in equilibrium with each other. These rates are calculated from models of mass transfer in multicomponent systems (see Taylor and Krishna (1993) for an extended discussion of such models). Mass and heat transfer coefficients and interfacial areas must be computed from empirical correlations or theoretical models. These coefficients depend on the column design as well as on its method of operation. Nonequilibrium models can be used to simulate packed columns just as easily as they can tray columns, thereby avoiding the use of HETPs (Height Equivalent to a Theoretical Plate). A nonequilibrium column model was included in Version 3 of the CACHE product ChemSep.

It is very likely that nonequilibrium models will see increased use in the future; they will be particularly useful for simulating nonideal systems, systems with chemical reaction, and low-efficiency systems (this includes some nonideal separations and many gas absorption processes), and columns with multiple feeds and products. A thorough understanding of mass transfer (with or without simultaneous chemical reaction) in multicomponent systems will be essential for the engineer (and student) working with nonequilibrium models. It is pertinent to point out that mass transfer in binary systems constitutes a very special case in that none of the interesting phenomena that can take place in systems with more than two components can occur. Multicomponent mass transfer effects can manifest themselves in interesting ways, including causing distillation point efficiencies of different components to *not* be equal from component to component or from tray to tray (as they are so often assumed to be) as is clearly evident in Fig. 6 and, to a lesser degree, Fig. 7. Any emphasis on mass transfer rate based models in the future should act as a spur to educators to more tightly integrate courses on separations and mass transport; the latter will need to be modified in order to cover the elements of multicomponent mass transfer (see Taylor and Krishna, 1993).

The equations that describe multicomponent mass transport (the Maxwell-Stefan equations) have, in fact, been with us even longer than has the equilibrium stage model although their application to modeling stagewise separations is a relatively recent development. However, not only do the Maxwell-Stefan equations allow us to model mass transfer in conventional operations such as distillation, absorption, and liquid-liquid extraction, they also describe mass transfer in all of the less common separation operations such as membrane processes, the ultracentrifuge, thermal diffusion columns, and many more. Indeed, the Maxwell-Stefan formulation of mass transfer can provide a basis for unifying the treatment of separation processes (Krishna, 1987).

Models of the dynamic behavior of column performance are being used more frequently in industry. Improvements in hardware and software will mean that ten years from now there will be no excuse for not using a dynamic model to explore the operation of a real distillation column. Dynamic models will become available that are based on fundamental mass and energy transfer processes. These models will also be used in undergraduate courses and will make it possible to provide more convincing software demonstrations of how real columns behave.

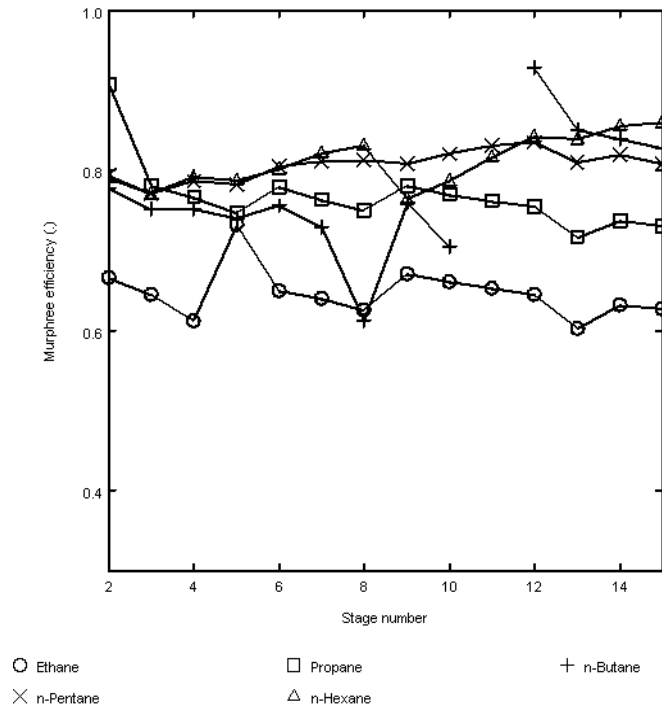


Figure 6. Efficiency profiles calculated following a nonequilibrium simulation of the column in Figs. 3 to 5. The usual assumption of equal component efficiencies is clearly inappropriate.

Of course, models based on equilibrium stage concepts will not be abandoned, nor is there any need to do so. New approaches to process visualization (see Fig. 8), and design and analysis of separation processes using equilibrium stage models have been pioneered by M.F. Doherty, M.F. Malone and their coworkers at the University of Massachusetts (see, for example, Fidkowski *et al.*, 1991; Doherty and Buzad, 1992; Julka and Doherty, 1993). At the time of writing, however, there is no software product that implements their methods that is available from CACHE.

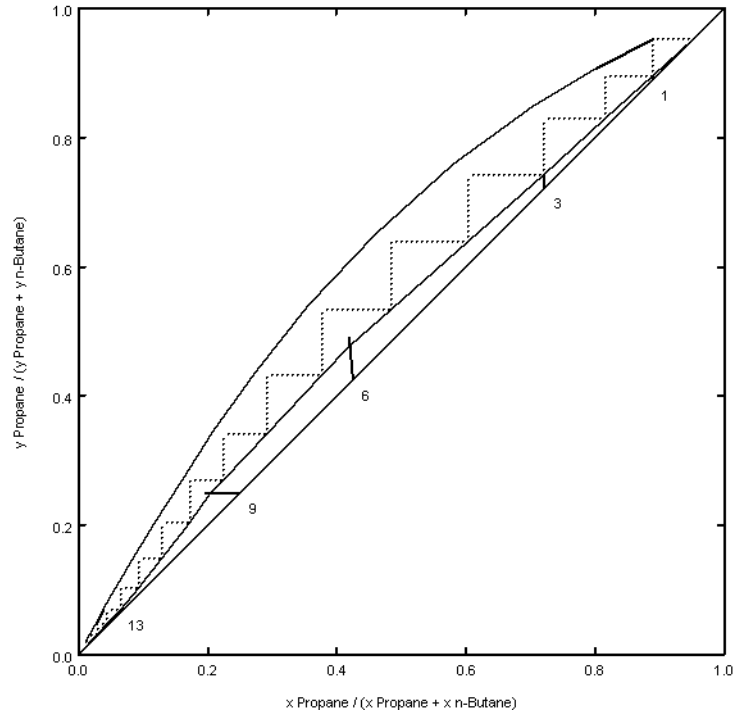


Figure 7. Modified McCabe-Thiele diagram provides an interesting view of the effects of mass transfer in stagewise separations. Note how the triangles representing the trays do not reach the equilibrium line, demonstrating that they are not equilibrium stages.

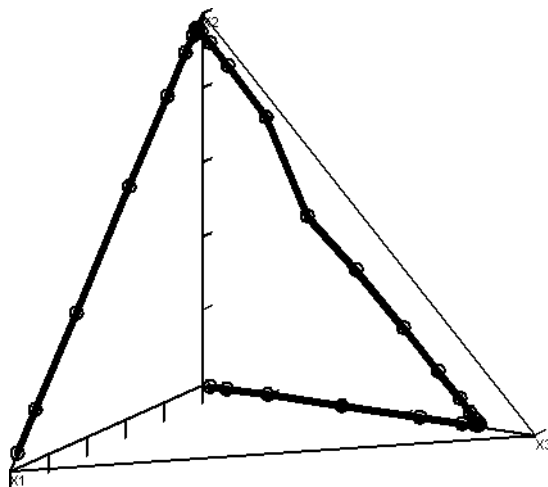


Figure 8. Composition profiles in a distillation column processing a four component system. This illustration is based on an exercise in Henley and Seader (1981). Graphics inspired by, for example, Julka and Doherty (1993).

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