INTERPHASE TRANSPORT AND MULTISTAGE SEPARATIONS

Final Report
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Summary of Research Accomplished
September 1, 1984 through August 31, 1994

1. Collocation Analysis of Multistage Separation Systems

The large equation sets encountered in tray-by-tray modelling of distillation systems are a major obstacle in computer-aided process engineering. We have addressed this difficulty by approximating the multistage equations with much smaller sets, obtained by orthogonal polynomial interpolation over the stages. To get the full benefit of this approach, we have shown that polynomials orthogonal on the integers $1, \dots, M$ give optimal accuracy for an N -stage column section. That result was derived and demonstrated by Warren Stewart, Keith Levien and Manfred Morari in DOE-sponsored research just prior to the present project. Polynomials of this type were discovered by Tchebychef in 1975 and generalized by Hahn in 1949; thus our method has become known as Hahn polynomial collocation.

A new approach to column design was initiated in this project when we discovered how to extend our collocation formulas to modules containing non-integer numbers, N , of stages. The key to this extension is the continuity of the recursion formula for the n th-degree Hahn polynomial $Q_n(s-1, \alpha, \beta, N)$ with respect to N for all real values $N \geq n$. From this property and the continuity of Q_n with respect to s , it follows that the collocation points defined as the zeros of $Q_n(s-1, \alpha, \beta, N)$ are smooth functions of module length N , for any permitted values of α and β and thus for the preferred choice, $\alpha = \beta = 0$. Using this property, Chris Swartz and I devised a column design procedure which (unlike stage-by-stage computations) allows noninteger solutions for the numbers of rectification and stripping stages just as graphical procedures do. He thus reduced distillation design problems to continuous optimization problems, for which several efficient solution techniques are available. This work was presented at the AIChE Annual Meeting in 1985, and published in Paper 1 of this research.

The extension of our collocation formulas to noninteger module lengths proved equally useful for column simulations in the presence of more than one liquid phase. Chris Swartz and I developed a moving finite-element scheme, with element boundaries (breakpoints) located at positions of appearance or disappearance of a liquid phase, so that the states in each element could be interpolated as continuous polynomials. The location and adjoining states for each breakpoint were adaptively updated by Newton's method, along with the collocation grid and states. This interpolative treatment of the phase boundaries gave very efficient tracking of the solution, in contrast to the awkward iterations with variable-size equation sets which arise in tray-by-tray simulations of such systems. This work was presented at the AIChE Annual Meeting in 1986, and published in Paper 2 of this research.

We then investigated robust collocation strategies to handle locally steep concentration profiles and high-purity separations. For this purpose, Chris Swartz and I investigated the use of movable finite elements, with breakpoints adaptively chosen to minimize a global criterion of approximation error. A key discovery in this work was a quadrature formula for stagewise sums of squared residuals, which could be evaluated directly for finite elements of noninteger length. Using this approach, Chris simulated an 80-tray stripping column quite well with only six grid points, using two finite elements and also with three finite elements. Chris wished to reserve this research area for his faculty career, and I agreed to this, so publication of this work was left to him. So far, the work appears only in his doctoral thesis.

2. Heat and Mass Transport Fundamentals

As a basis for realistic modelling of fractionating trays, Tom Young and I did a comprehensive comparison of various computation methods for multicomponent mass transfer against detailed variable-property boundary-layer solutions. Detailed steady-state solutions were taken from Stewart & Prober, *Ind. Eng. Fund.*, **3**, 224–235 (1964), and detailed time-dependent solutions were computed in this project. Reference-state procedures for assignment of average physical properties to the mixtures were investigated and optimal weightings were established. The linearization method of Stewart, Prober and Toor proved most accurate among the approximate methods tested, and was accordingly used for our tray modelling research. This work was presented at the AIChE Annual Meeting in 1986, and published in Paper 3 of this project.

The Principal Investigator carried out a theoretical study of asymptotic forms for heat and mass transfer rates in boundary layers. Laminar and turbulent flows were treated explicitly for rigid and mobile interfaces. Slippery concepts such as surface renewal and eddy diffusivities were avoided, by working directly with the conservation equations at the microscopic level. Asymptotic expansions of the Nusselt or Sherwood number in terms of the corresponding Peclet number Pe and flux ratio R_T or R_ω were obtained for two important classes of contacting systems:

$$\langle Nu \rangle Pe^{-1/2} = a_{00} (1 - 0.636R) + a_{01} Pe^{1/2} + \dots \quad (1)$$

for short times or negligible drag on the interface, and

$$\langle \overline{Nu} \rangle Pe^{-1/3} = b_{00} (1 - 0.566R) + b_{01} Pe^{1/3} + \dots \quad (2)$$

for long-time averages on rigid interfaces when drag is present. These results were derived by simple dominant-balance arguments, with no integration and with minimal assumptions regarding the system geometry and velocity distribution. Extensive data confirm these relations for a variety of simple and complex flows, and show that the a_{01} and b_{01} terms are often unimportant. This work was presented at the AIChE Annual Meeting in 1985, and published in Paper 4 of this project.

Denis O'Sullivan and the Principal Investigator investigated mass transport in hydrodynamically developed wall turbulence, extending the Fourier analysis of this case which was begun in Paper 4. A more explicit treatment of the convection terms proved necessary to deal with the fluctuating near-wall vortices that cause the time-mean transfer coefficients to become spatially uniform after a short entrance region. Two spatial regions were studied: the thermal or diffusional entrance region, in which the convection is dominated by the downstream velocity component, and the far downstream region, in which the convection is dominated by transverse motions which draw fresh mainstream fluid into the boundary layer. The heat and mass transfer coefficients in each region were shown to satisfy Eq. (2), but with different coefficient functions b_{00} and b_{01} according to the region. These results were established by dominant-balance analysis; detailed integrations were attempted, but were discontinued for lack of sufficient information on the velocity fluctuations. A paper on this work is in preparation for *AIChE Journal*.

3. Fractionation Tray Modelling

Tom Young and the Principal Investigator developed a two-phase boundary-layer model for multicomponent heat and mass transfer on sieve trays, by extension of the methods of Papers 2 and 4. We imbedded this local model in a smoothed macroscopic model to describe the horizontal and vertical gradients in the froth on large-diameter distillation trays. To speed up computations with this model, we developed a special collocation scheme which gives accurate terminal states with only two grid points in the two considered dimensions of the tray. This scheme was presented in in Paper 5.

Tom Young performed a dimensional analysis of the conservation equations and boundary conditions for a tray, to obtain dimensionless groups for correlation forms of our tray model. He critically compiled distillation data from the literature, ultimately selecting 111 binary distillation experiments from three groups of investigators (Fractionation Research, Inc. and two university laboratories). He tested a large number of candidate model forms against these multiresponse data, first graphically and later by fitting each candidate model to the data by use of our nonlinear parameter estimation package GREG. Data reconciliation was included in these calculations, along with automatic estimation of the relative precisions of the three laboratories. The outputs from GREG were then used to select a preferred model, giving a good fit with not too many parameters. This work was presented at the AIChE Annual Meeting of 1990 and published in Paper 7, with the recommended dimensionless expression

$$a_{00} = (0.277 \pm 0.112) \left(\frac{\rho_G \langle v_G \rangle h_w}{\mu_L} \right)^{0.648 \pm 0.075} \times \left(\frac{A_{\text{act}}^2}{A_{\text{open}}^2} - 1 \right)^{0.344 \pm 0.139} \left(\frac{\mu_G \rho_L}{\mu_L \rho_G} \right)^{0.412 \pm 0.079} \quad (3)$$

for the interfacial hydrodynamic function a_{00} . The value ± 0.112 is a misprint, and was corrected later to ± 0.0112 . All intervals here are 95% posterior probability limits.

This model has two outstanding features: (1) its dimensional homogeneity and (2) its use of Eq. (1) [truncated to its leading term] to describe the transfer coefficients for both phases in terms of the relevant physical properties and a single adjustable function a_{00} . This model fitted the 111 binary experiments well, and also gave good predictions for four ternary experiments reported by Fractionation Research, Inc.

Later we noticed that the relative-area group in Eq. (3) would always be large enough so that the -1 term could be neglected. Doing so, one finds that this group is not needed if one bases the velocity in the Reynolds group on the open area of the tray, rather than on the nominal area as was done in Eq. (3). Making this change and fitting the resulting model to the data, we obtained a simpler correlation,

$$a_{00} = (0.2753 \pm 0.0097) \left(\frac{\rho_G V_o h_w}{\mu_G} \right)^{0.658 \pm 0.038} \left(\frac{\mu_G \rho_L}{\mu_L \rho_G} \right)^{0.420 \pm 0.046} \quad (4)$$

with more precise parameter estimates and an equally good fit of the data. This concise correlation is reported in Paper 11 of this research.

4. Computational and Statistical Methods

Newton's method is used in several of our computational algorithms for equation solving, parametric sensitivity analysis and nonlinear parameter estimation. Roderick Bain investigated modifications of the Newton method, designed to achieve convergence over a wider range of initial guesses. He produced a very robust algorithm, NNES, incorporating damped (shortened) Newton steps selected to satisfy either of two nonmonotonic line search criteria. By "nonmonotonic," one means that a damped step is accepted if it reduces either criterion function below the largest of its final values encountered in the preceding m accepted steps. This work is reported in Paper 8, and has been used to enhance the performance of our software packages DDASAC, PDASAC and GREG, described below.

Mike Caracotsios and the Principal Investigator have adapted Linda Petzold's package DDASSL (Double-precision Differential-Algebraic equation Solver from Sandia-Livermore) to simultaneous integration and parametric sensitivity computation. The resulting two packages are DDASAC (Double-Precision Differential-Algebraic Sensitivity Analysis Code) and PDASAC (Partial-Differential-Algebraic Sensitivity Analysis Code). Numerous enhancements have been made to these integrators since their creation in Mike Caracotsios' thesis of May 1985, including robust initialization; initial-step optimization; a stricter nonnegative solution option; stricter convergence testing; row scaling of each iteration matrix for more accurate Newton steps; optional stopping at a specified value of a function or derivative; and optional reconciliation of initial and boundary conditions in PDASAC. DDASAC is distributed by Sandia-Livermore with their package SENKIN. Paper 9 describes the current version of PDASAC.

The parameter estimation package GREG (Generalized REGression) has been important in this research. It has evolved over many years of research by Prof. Stewart and his students. Extensions of GREG under this grant include a nonmonotone line search algorithm (see Paper 6); a search algorithm for optimal selection of the next experiment from a set of simulated candidates; an improved objective function for multiresponse estimation, derived in Paper 8; and a detailed Jeffreys prior for multiresponse parameter estimation with unknown covariance matrix and gaps in the data table, to be reported in Paper 10. Paper 8 is based on an invited lecture by Prof. Stewart at the 1991 Joint Statistical Meetings in Atlanta.

Many investigations in engineering and science require the selection of a model from a set of candidates, by comparing their ability to fit a reference data collection. Stewart and Shon have recently derived and demonstrated (in Paper 12) a rigorous probability criterion for selection among multiresponse models, which generalizes the approach used by Young and Stewart in Paper 7. The method provides an objective penalty for each parameter estimated; thus, over-fitting of the data is avoided. This treatment parallels a single-response analysis begun some years ago by our colleague Prof. George Box; we are encouraging him to publish his results concurrently with ours.

Publications from Project DE-FG02-84ER-13291

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12. Stewart, W. E. and Y. Shon, Bayesian Discrimination of Multiresponse Models. Submitted to *Technometrics*, August 1994.