



Recent Advances in Reactive Distillation

*AIChE Annual Meeting, Dallas
Paper 203c, November 3, 1999*

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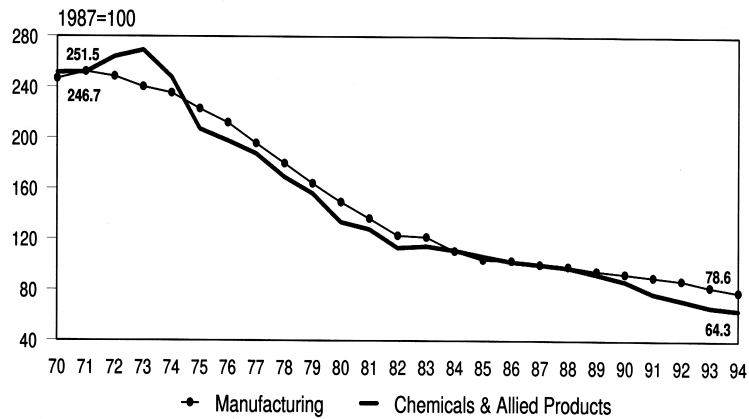
EPA/NSF Partnership. Grant NSF CTS-9613489
Additional Support from National Environmental Technology Institute

- Motivation and Background
- Feasibility & Alternatives for Fast Reactions
- Effects of Chemical Kinetics on Selectivity
- Sensitivity and Operability
- Research Needs



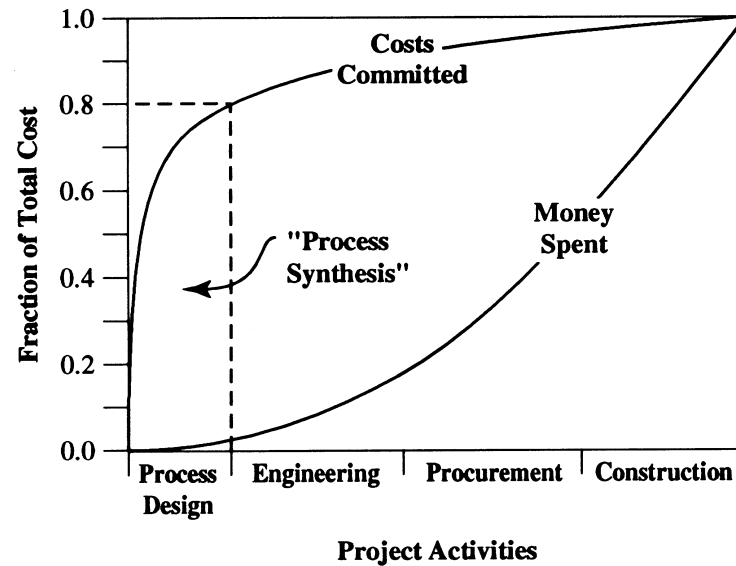
Motivation

Capital Productivity



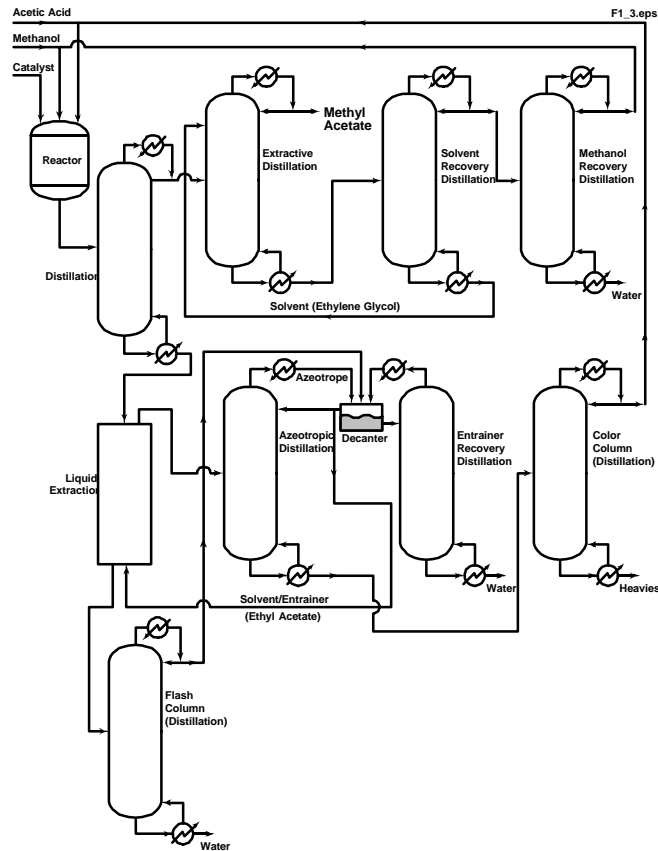
U.S. Chemical Industry Statistical Handbook, 1996, CMA, Arlington VA, p. 96

Conceptual Design



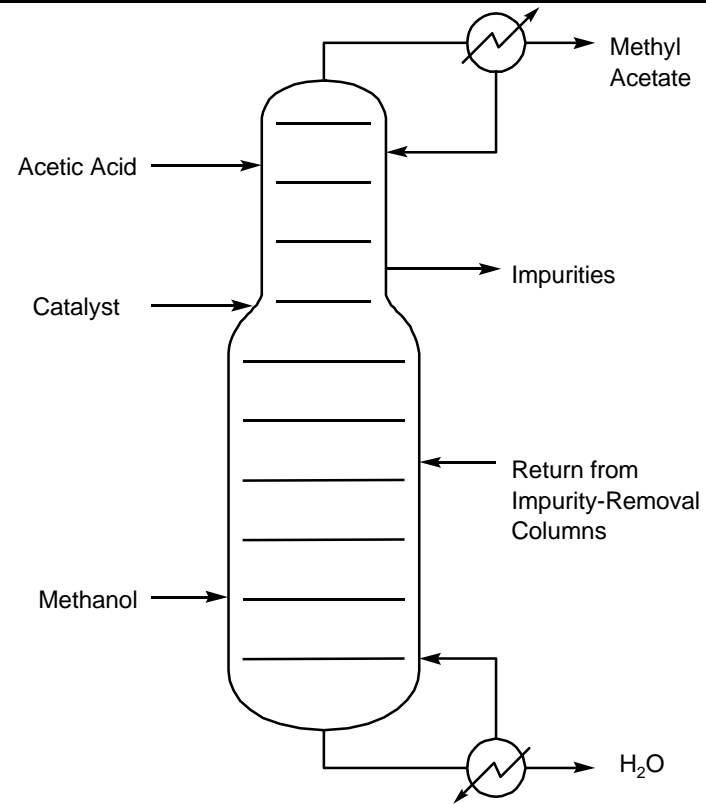


Example: Methyl Acetate



Traditional

AICHE Dallas, Nov., 1999



Reactive Distillation
(Agreda and Parten, 1984)

Doherty and Malone, UMass

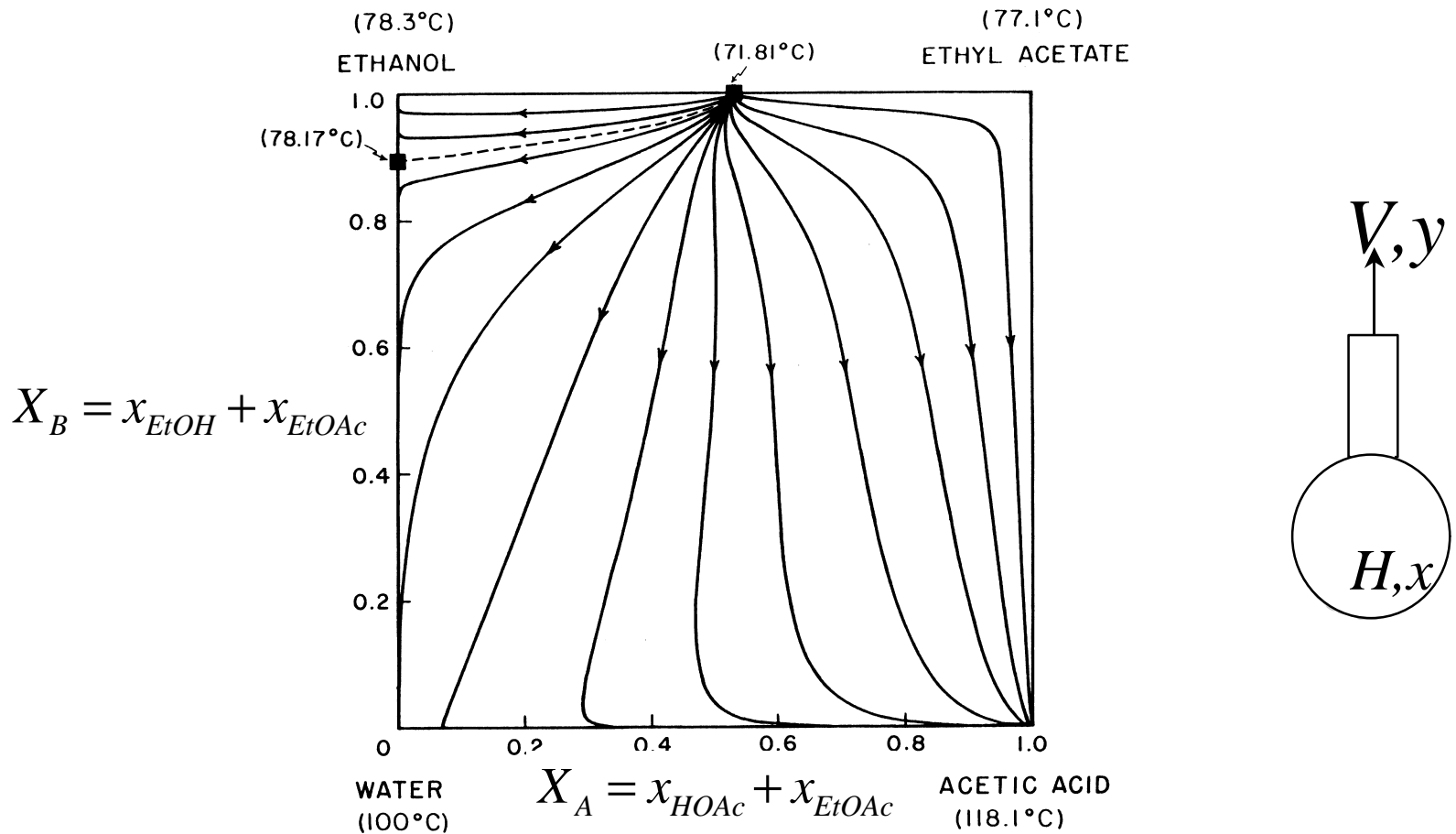


Reactive Distillation Potential

- Improve Selectivity
 - Reduce Raw Materials Usage
 - Reduce Byproducts Prevent Pollution
- Reduce Energy Use
- Handle Difficult Separations
 - Avoid Separating Reactants
 - Eliminate/Reduce Solvents
- Enhance Overall Rates
- “Beat” Low Equilibrium Constants

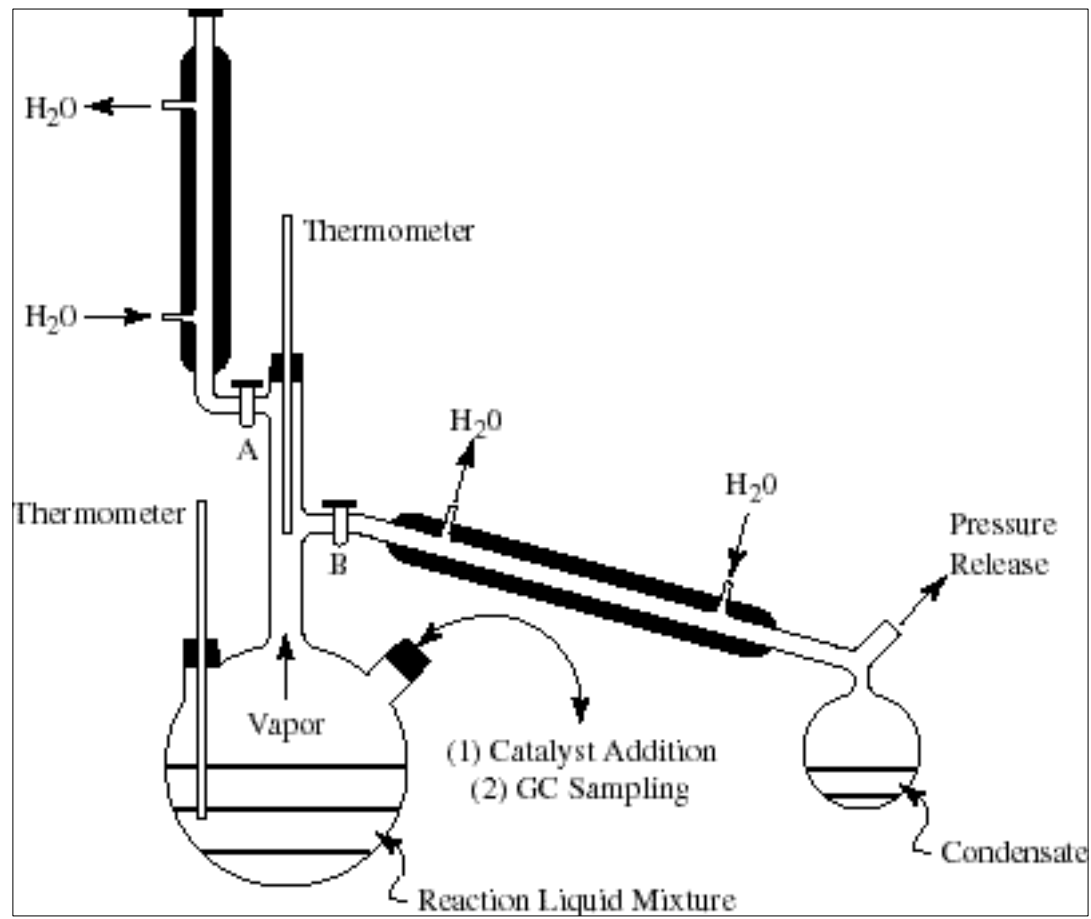


Residue Curves for Fast Reactions



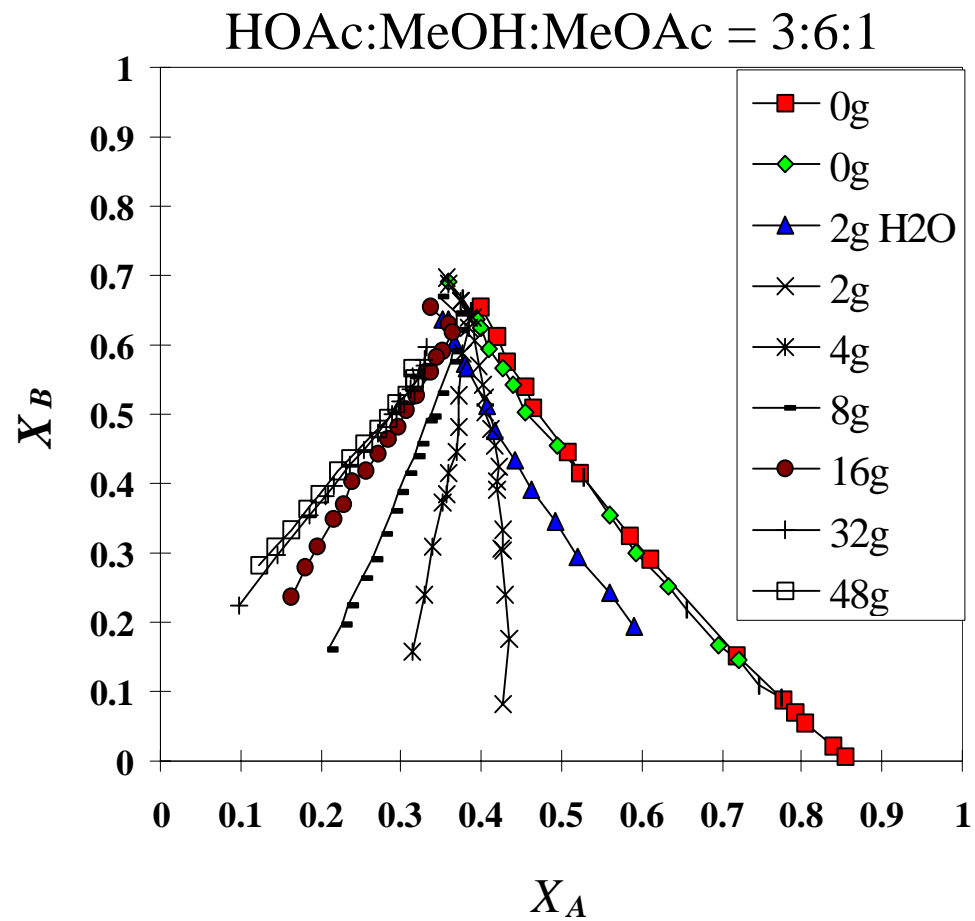


RCM Measurement





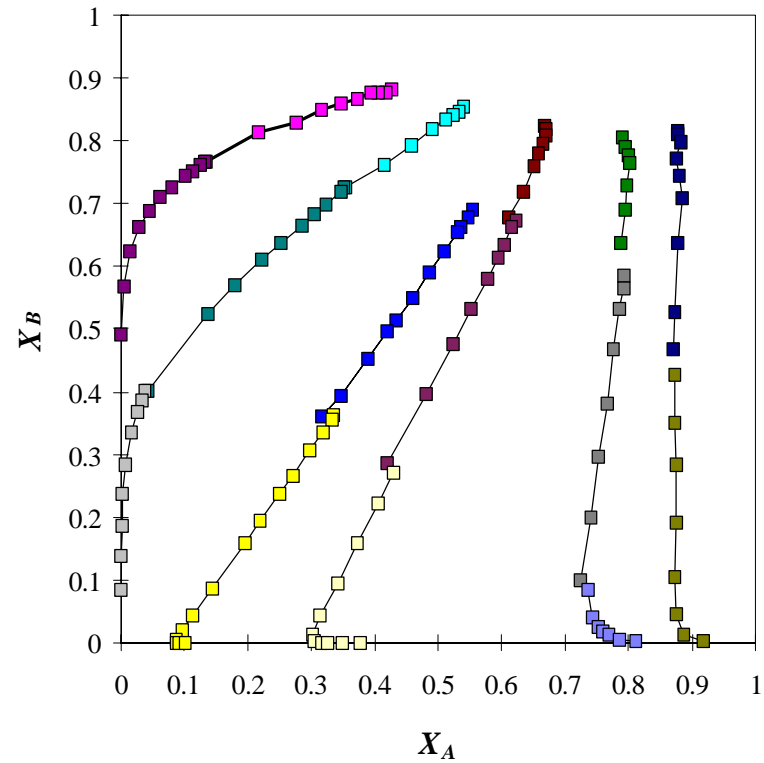
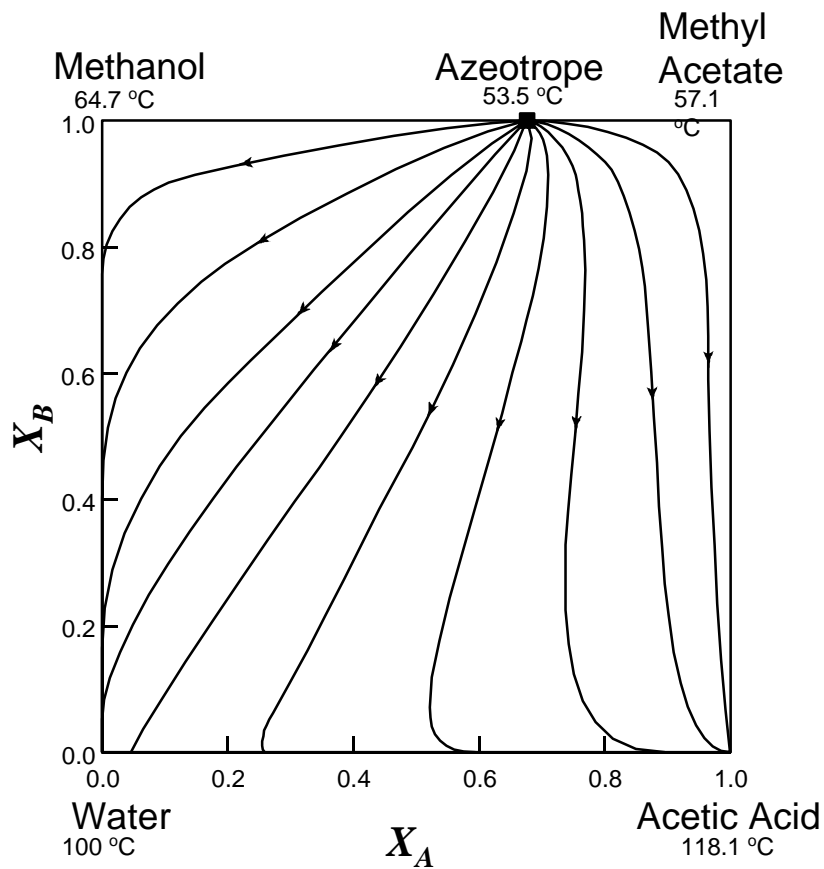
Effect of Catalyst Level





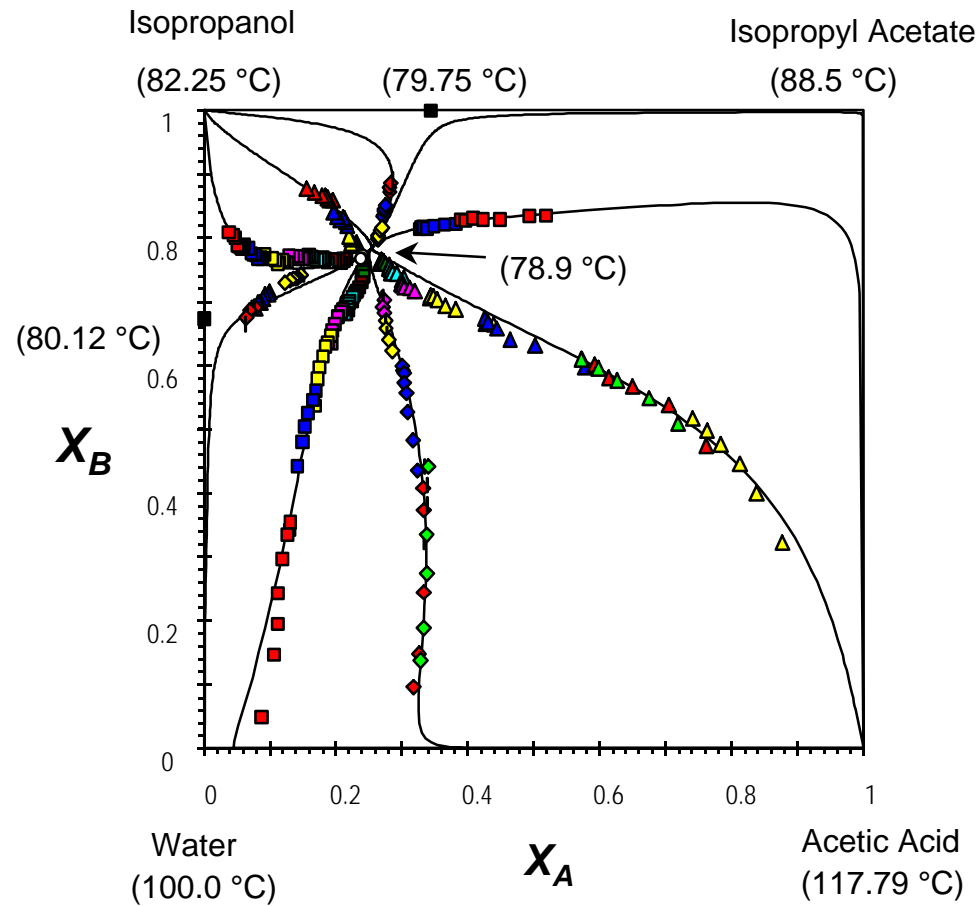
Residue Curve Map

W. Song, *et al.*, *I&EC Research*, 37, 1917-1928 (1998).





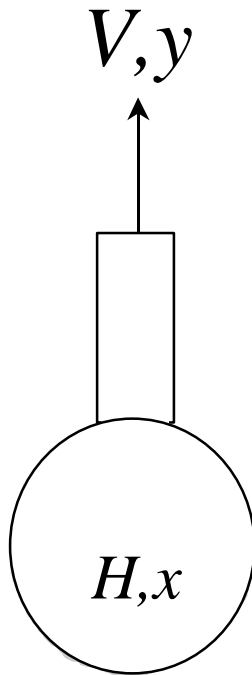
Isopropyl Acetate RCM



W. Song, et al., *Nature*, 388, August 7, 1997.



Reactive Distillation Kinetics



$$\frac{dx}{d\mathbf{x}} = x_i - y_i - Da' \times (\mathbf{n}_i - \mathbf{n}_T x_i) \times R$$

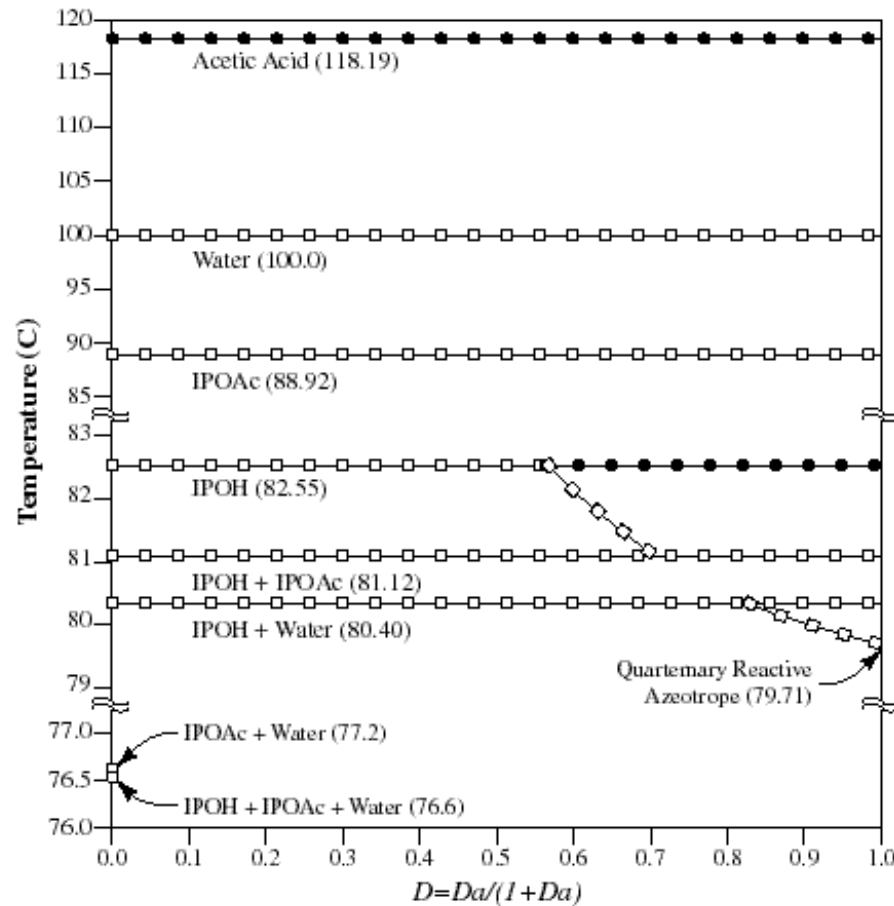
$$Da' = \frac{Hr_{ref}}{V}$$

$$Da = \frac{H_{ref} r_{ref}}{V_{ref}} = Da' \frac{H_{ref}}{H} \frac{V}{V_{ref}} \quad \text{and} \quad D = \frac{Da}{1 + Da}$$

G. Damköhler, "Strömungs und Wärmeübergangsprobleme in Chemische
Chem. Ing. Tech., 12, 469-480 (1939).



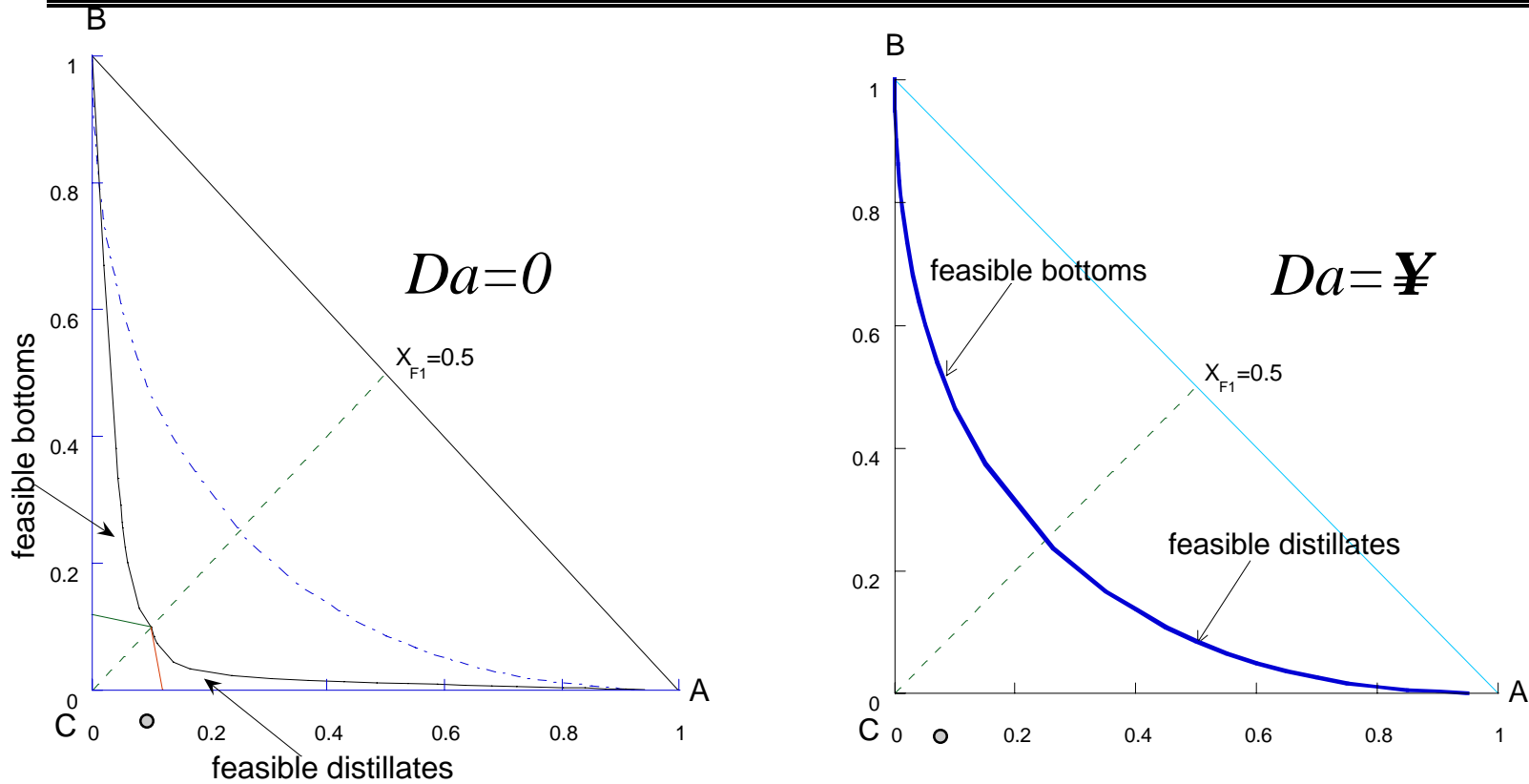
i-Propyl Acetate Bifurcations



Venimadhavan, G., Malone, M. F. and Doherty, M.F. "A Bifurcation Study of Kinetic Effects in Reactive Distillation," *AIChE Journal*, 45, 546-556 (1999).



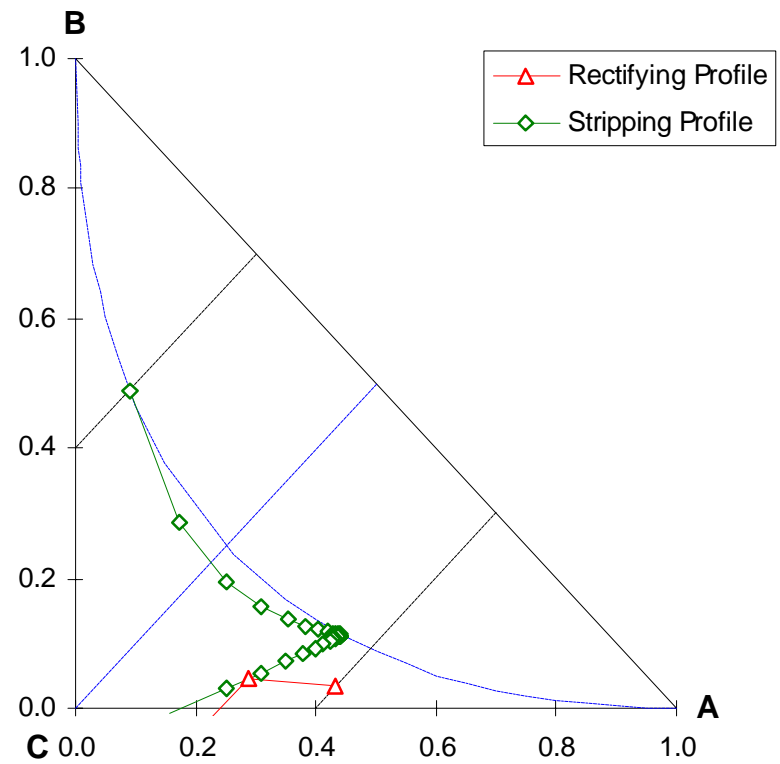
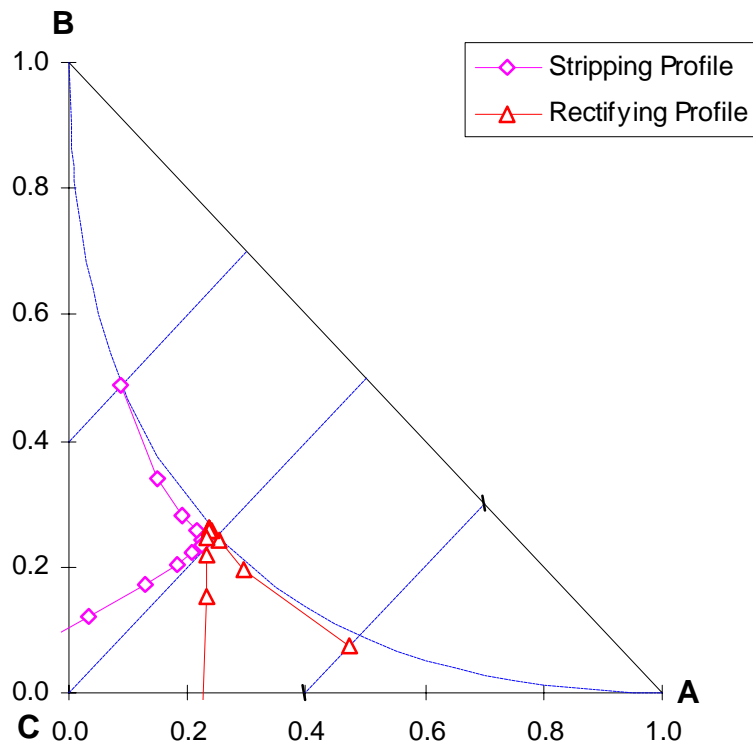
Feasible Products, $2C\hat{U}A+B$



N. Chadda, M. F. Doherty and M. F. Malone, paper 221f, *AIChE Annual Meeting*, Dallas, November (1999). Also: Chadda, N., Malone, M. F. Doherty, M. F. "Feasible Products for Kinetically Controlled Reactive Distillation," *AIChE J.*, 00, 000-000 (2000).

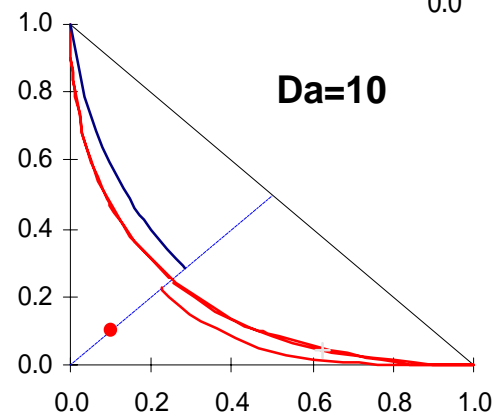
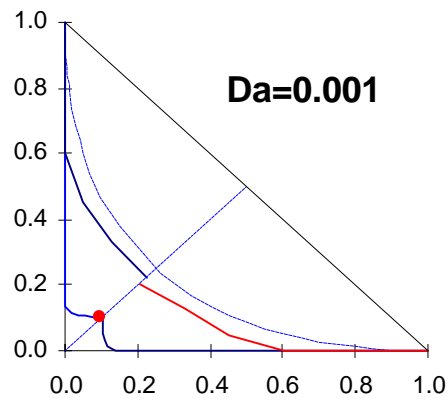
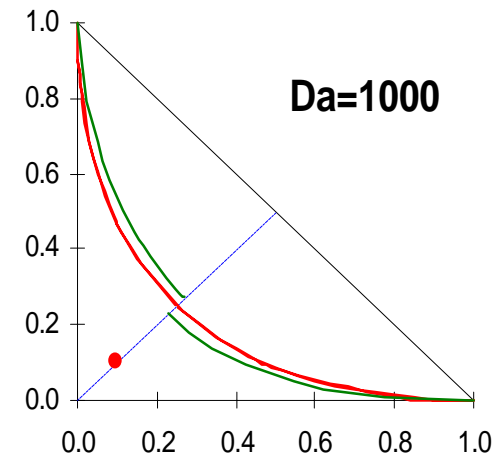
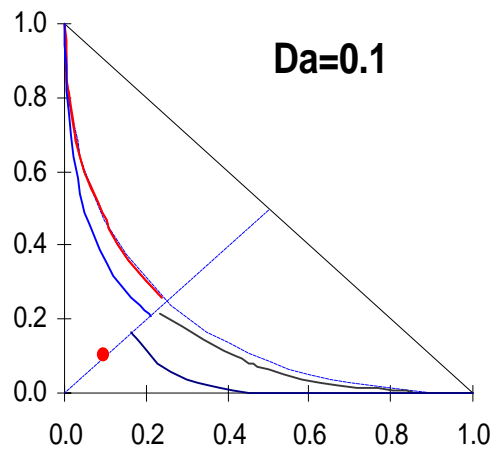


Limiting Feasible Designs





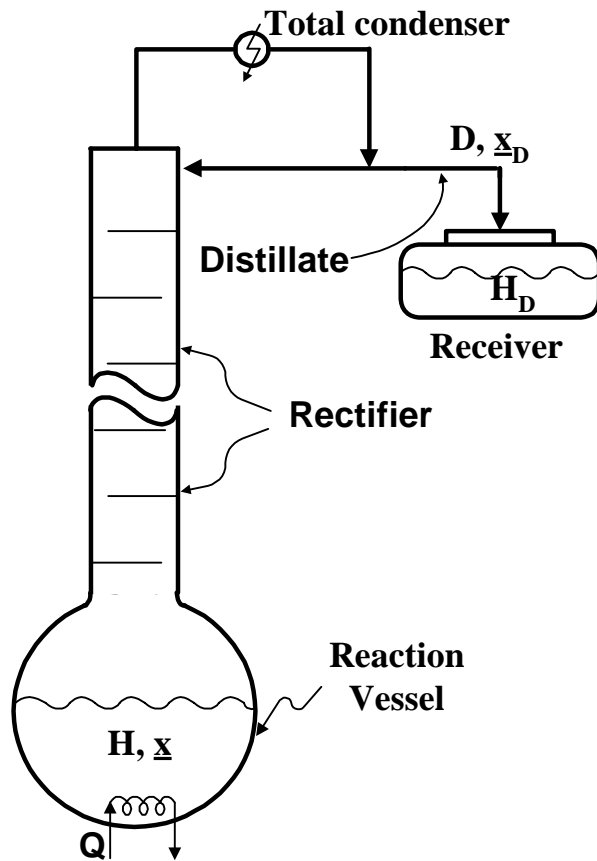
Feasible Product Regions





Batch Reactive Distillation

$A(l) \textcircled{R} B(i) \textcircled{R} C(h)$

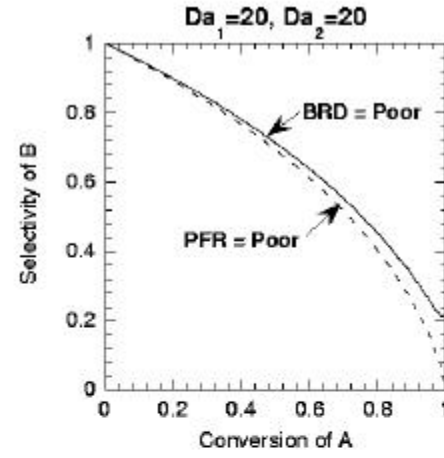
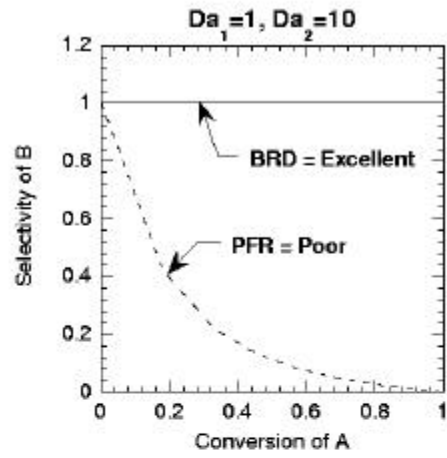


S. B. Gadewar, M. F. Doherty and M. F. Malone, paper 301d, *AIChE Annual Meeting*, Dallas, November (1999).

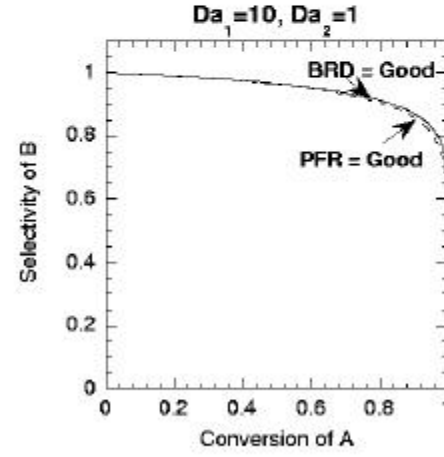
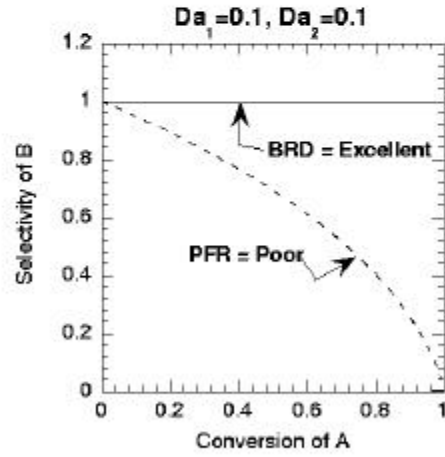
Also see:

- Venimadhavan, G., Malone, M. F. and Doherty, M. F. *Ind. Eng. Chem. Res.*, 38, 714-722 (1999).
- S. B. Gadewar, S. B., Malone, M. F. and Doherty, M. F. "Selectivity Targets for Batch Reactive Distillation," *Ind. Eng. Chem. Res.*, 00, 000-000 (2000).

High



Da_2



Low

Low

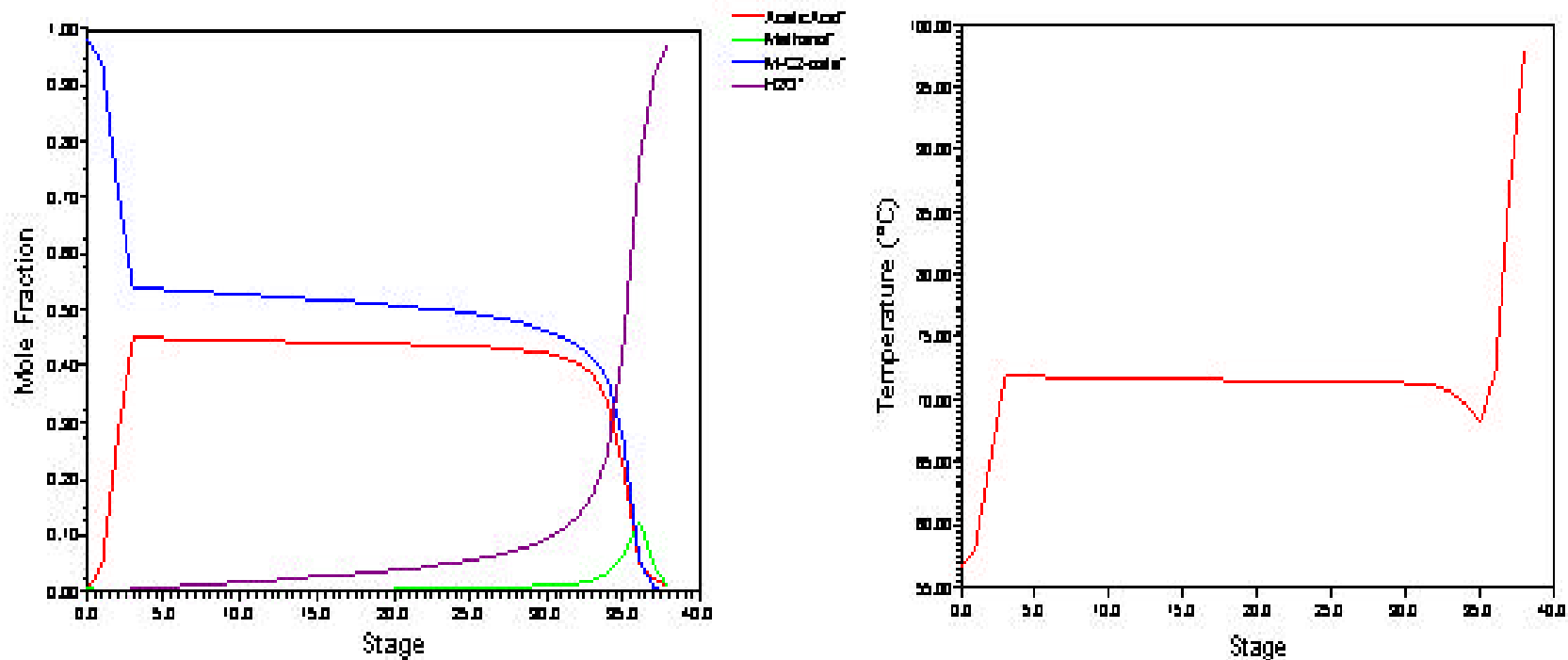
Da_1

High



MeOAc Equilibrium Design

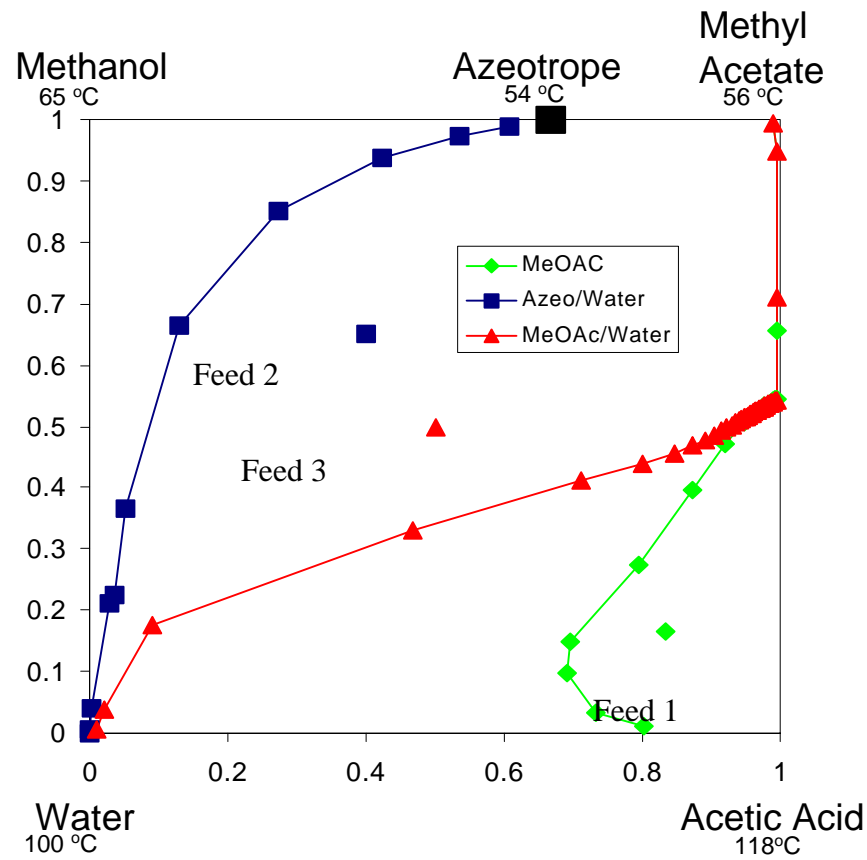
Huss, R.S., Chen, F., Malone, M. F. and Doherty, M. F. "Computer-Aided Tools for the Design of Reactive Distillation Systems," *Comput. chem. Engng., Suppl.*, S955-S962 (1999).



Distillate MeOAc: 98.54 mol% (99.20 wt%); Bottoms H₂O: 98.06 mol% (94.74 wt%).

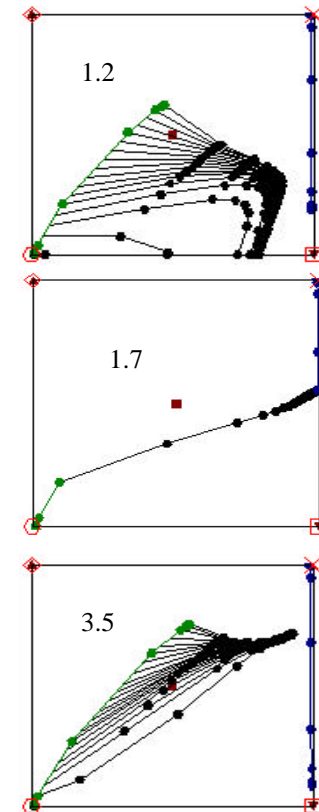
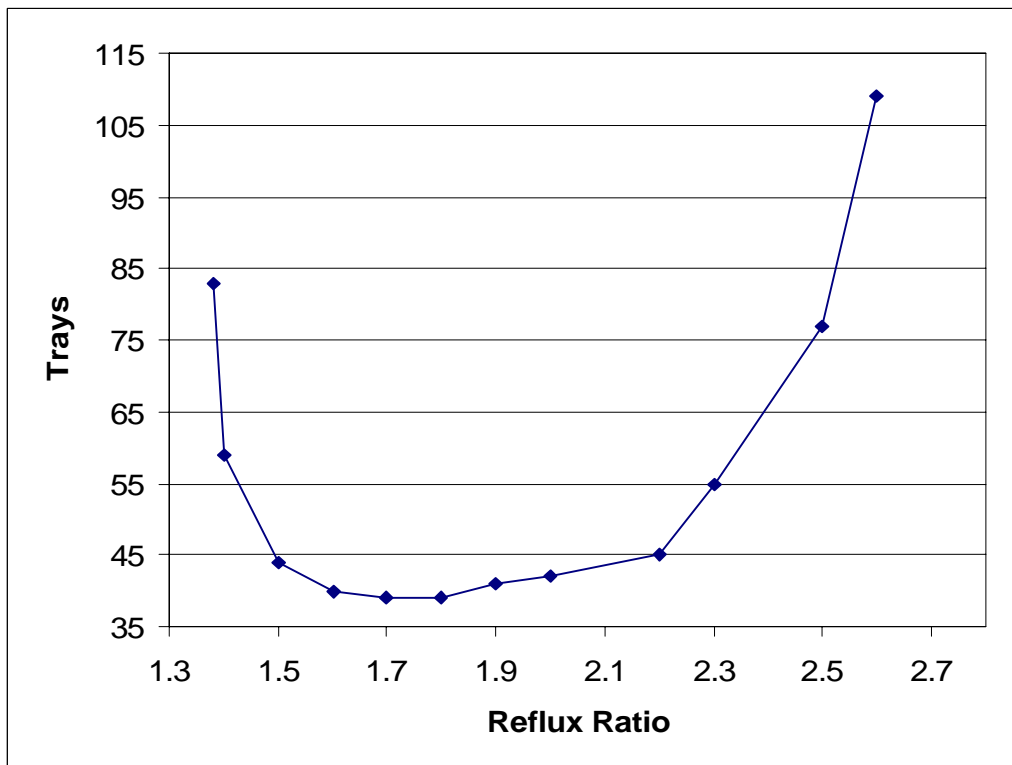


Equilibrium Designs



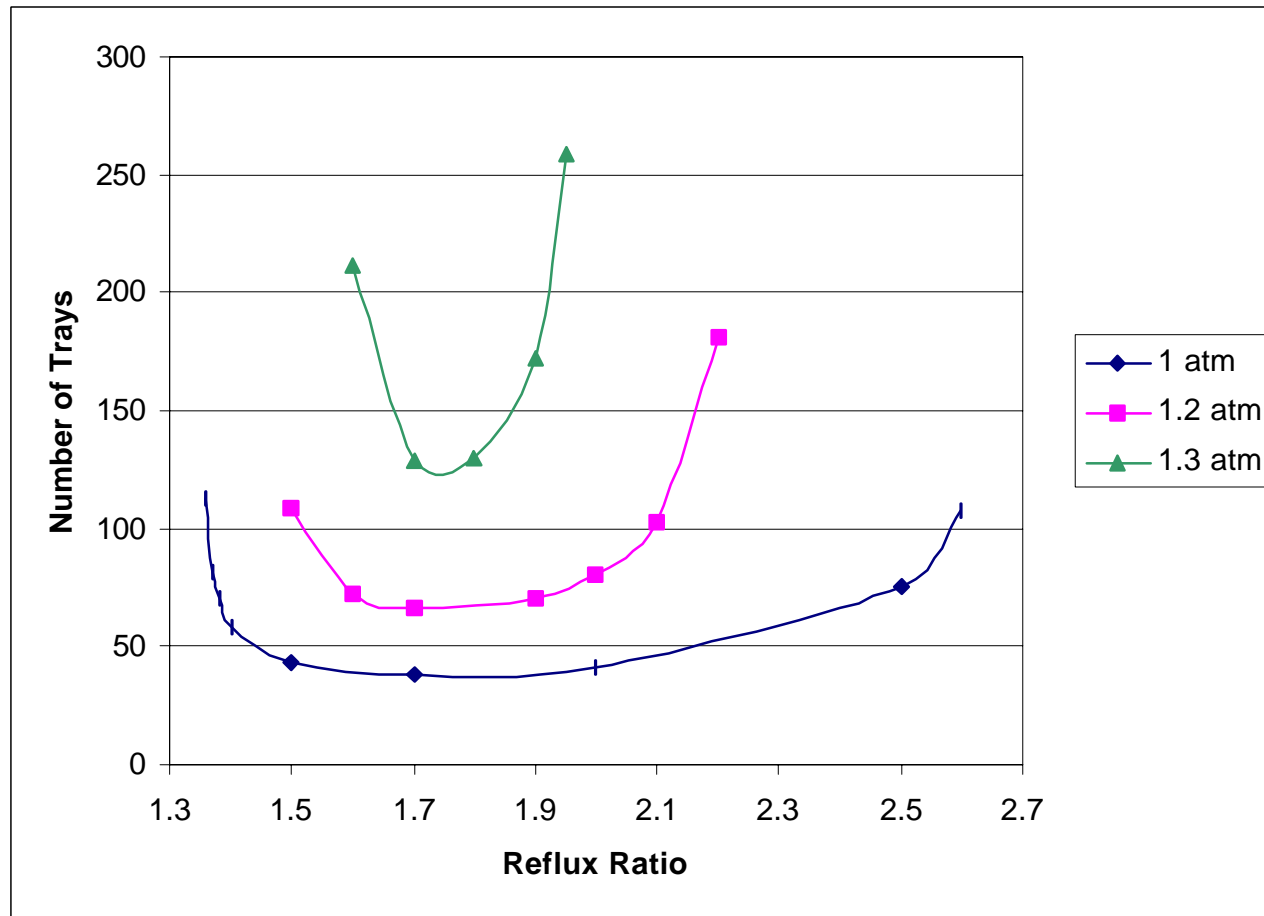


Effect of Reflux Ratio



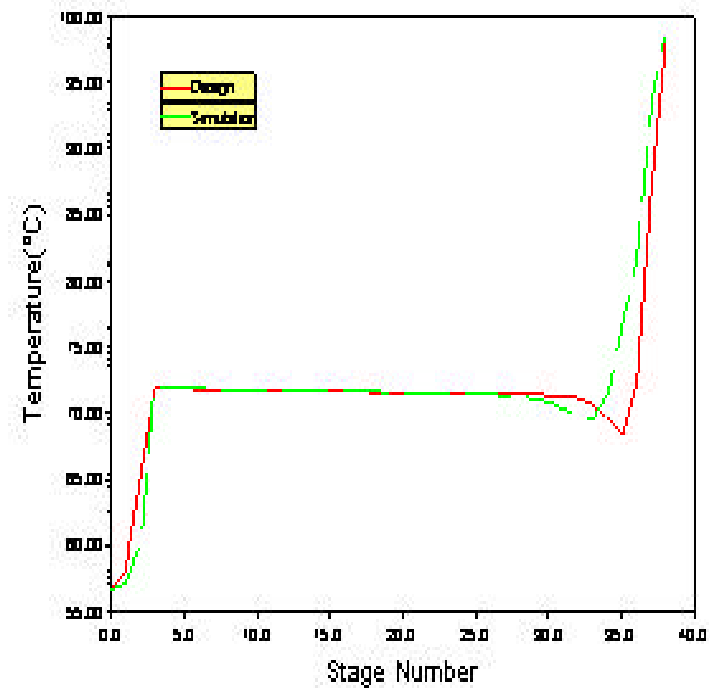
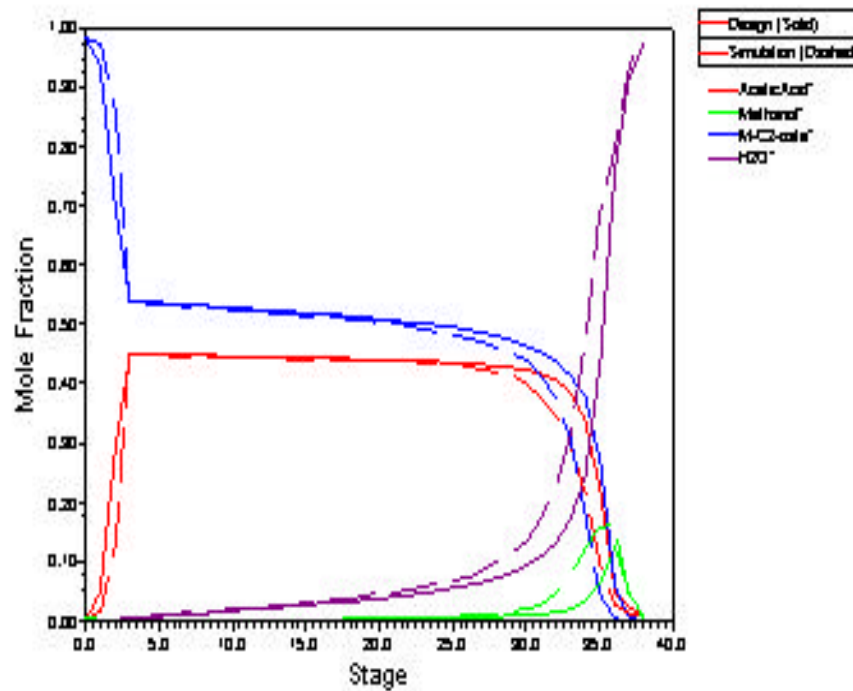


Effect of Pressure



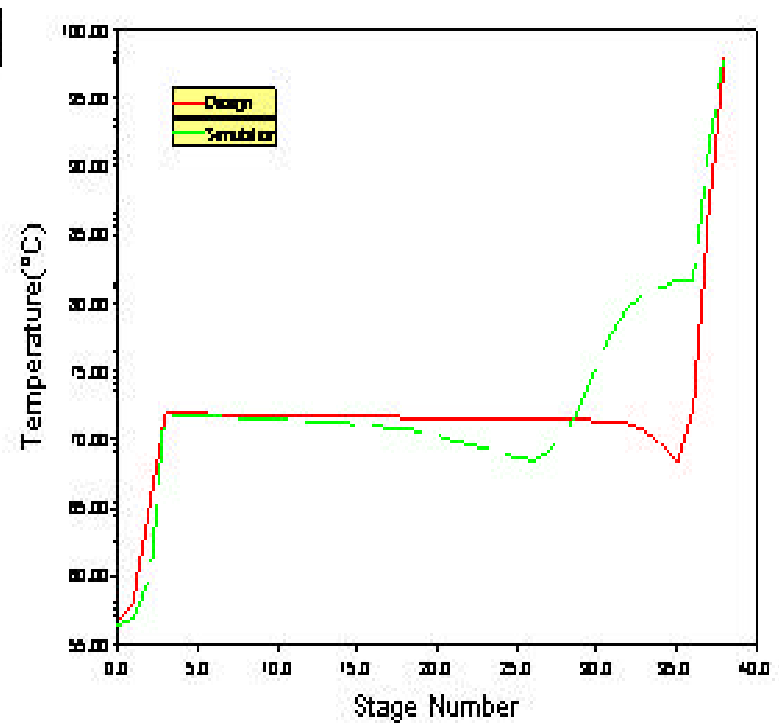
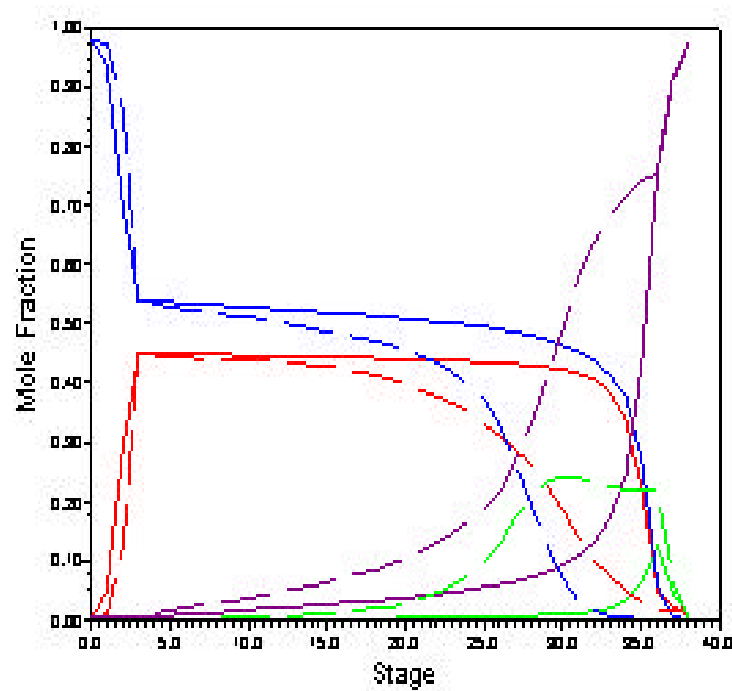


Design vs. Simulation ($Da=100$)





Design vs. Simulation (Da=15)





Summary

- Simultaneous Phase and Reaction Equilibrium can be closely approached experimentally
- Equilibrium theory agrees well with predictions for acetate systems
- Conclusive evidence for existence of a reactive azeotrope
- Bifurcation analysis gives foundation for systematic approach to feasibility/alternatives
- Initial approach for feasibility in kinetically-controlled systems



Research Needs

- Focus on kinetically controlled systems, e.g., general feasibility method, attainable regions, ...
- General method and experiments for complex chemistries
- System synthesis and design methods; geometric or optimization based?
- Simulation: catalysis and mass transfer effects, equipment constraints, distribution of residence times (effects on selectivity)
- Operability and control: multiple steady-states, oscillations and other sensitivities; significant heat effects; strategy for operability maxima