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A Parametric Reactive Distillation Study: Economic Feasibility and Design Heuristics

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To the Graduate Council:

I am submitting herewith a dissertation written by Craig Alan Hoyme entitled "A Parametric Reactive Distillation Study: Economic Feasibility and Design Heuristics." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Paul Bienkowski, Major Professor

We have read this dissertation and recommend its acceptance:

Jeff J. Siirola, Robert M. Counce, W. Alexander Vanhook

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Vice Chancellor and Dean of Graduate
Studies

A Parametric Reactive Distillation Study:
Economic Feasibility and Design Heuristics

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Craig Alan Hoyme
May 2004

DEDICATION

This dissertation is dedicated to my wife, Debra Hoyme, for her love and patience during my many years of graduate study and to my parents, Larry and Colleen Hoyme, who instilled in me a desire to work hard and do the best I can in everything I do.

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I would like to thank the members of my family for their continued support throughout my life. I extend my deepest love and gratitude to my wife, Debra P. Hoyme, who was the original inspiration for me to start my graduate studies. Finally, I would like to thank my parents, Larry and Colleen Hoyme, who have helped give me moral as well as financial support throughout my entire educational experience.

Most importantly, I would like to acknowledge my Lord Jesus Christ to whom I am grateful for giving me the intelligence, strength, courage, and wisdom necessary to complete the requirements for this degree.

ABSTRACT

The integration of reaction and distillation into a single column is called reactive distillation or catalytic distillation. Reactive distillation provides many benefits such as reduced capital and operating costs, circumventing non-reactive azeotropes, and overcoming equilibrium limited reactions. Industry has been successful in applying reactive distillation; however the integration of reaction and distillation is not applicable for all reaction/separation systems and it is not always clear when reactive distillation is a feasible design alternative.

Heuristics or rules-of-thumb are an integral part of process systems engineering and are used to provide initial guidance and insight for the analysis of process feasibility and conceptual design. Heuristics are developed from experience, computer simulations, and process data and usually are simple rules that greatly reduce the effort required to determine initial process feasibility and design. Due to the complex interactions that occur when combining reaction with distillation, heuristics for reactive distillation have been slow to develop.

In order to generate a set of heuristics for single column reactive distillation, a parametric study was conducted for ideal chemical reactive systems involving one or two reactants and one or two products. Each reactive system was divided into regions of similar component boiling point ordering which were expected to exhibit similar reactive distillation characteristics. The parametric study focused on the affects that changing relative volatility and chemical reaction equilibrium have on reactive distillation. Simulation results were used to develop a set of heuristics which outline the initial reactive distillation column design required to produce a desired product as well as the limits of economic feasibility. The generation of these heuristics was facilitated by a graphical representation which relates economic feasibility to reaction equilibrium constant, volatility ordering, relative volatility, and reflux ratio. The graphical representations are a useful screening tool which can be used to identify systems likely to benefit from single column reactive distillation. These heuristics were verified using real chemical reactive systems that are available in the reactive distillation literature.

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NOMENCLATURE

A = generic first reactant, always the most volatile reactant
B = generic second reactant
C = generic first product, always the desired product
D = generic second product, always the by-product
K_{eq} = chemical equilibrium constant
Π = product operator
x_i = liquid phase mole fraction for species i
$x_{D,i}$ = distillate mole fraction for species i
$x_{B,i}$ = bottoms mole fraction for species i
$x_{F,i}$ = feed mole fraction for species i
X_i = Transformed coordinate for species i
γ_i = liquid phase activity coefficient for species i
ν_i = stoichiometric coefficient for species i
α_{ij} = relative volatility for species i and j.
P_i^{sat} = vapor pressure (mmHg) for species i.
$T_{bp,i}$ = boiling point for species I (K)
T = liquid phase temperature (K)
A1 = Antoine coefficient
A2 = Antoine coefficient (K)
A3 = Antoine coefficient (K)
M_w = species molecular weight (g/mol)
T_c = critical temperature (K)
P_c = critical pressure (atm)
V_c = critical volume (cc/mol)
Z_c = critical compressibility factor
H_{vap} = heat of vaporization (kJ/kmol)
R = the gas constant
RR = reflux ratio
F_F = total column feed (lbmol/hr)
F_D = total column distillate flow (lbmol/hr)
F_B = total column underflow (lbmol/hr)
ξ = extent of reaction (lbmol/hr)
y_i = vapor phase mole fraction of species i
P = Pressure (mmHg)
$C_P^{*,ig}$ = ideal gas heat capacity (kJ/kmol· K)
V^l_m = molar volume (m^3/mol)
T_r = reduced temperature
Da_j = Damköhler number for stage j
H_j = molar liquid holdup for stage j
L_{j-1} = liquid vapor flow on stage j-1
$k_{f,ref}$ = forward rate constant
$\O_j$= fraction of feed vaporized on stage j

I. INTRODUCTION

Process systems engineering is traditionally defined as understanding and developing systematic procedures for the design and operation of chemical processes. This definition has recently been expanded to also include the improvement of decision-making processes for the creation and operation of the chemical supply chains (Grossman and Westerberg, 2000). Process systems research involves the creation of representations, models, and procedures to generate feasible design alternatives and to select a solution from these designs that best meets the process design objectives. This research adds to the tools available for process intensification (Stankiewicz and Moulijn, 2000), specifically the integration of reaction and distillation processing units. This integration of reaction and distillation into a single countercurrent column is called reactive distillation or sometimes catalytic distillation.

A general reactive distillation column is shown in Figure 1. The column has a reactive zone and can have a non-reactive rectifying section and/or a non-reactive stripping section. The rectifying section and/or the stripping section may not be needed depending on the reaction and desired separation. In the reactive zone, chemical reaction and distillation occur simultaneously. The catalyst, if necessary, can be a solid catalyst fixed in the reactive zone (Degarmo et al., 1992) or a homogeneous catalyst that is fed into the reactive zone and recycled back to the reactive zone after catalyzing the reaction (Agreda, 1984). In the non-reactive rectifying and stripping sections, the reaction products and unconverted reactants may be purified further by distillation.

Reactive distillation provides many benefits. (1) Reduction in capital costs because of the combination of reaction and distillation into one column eliminates the need for separate process units. (2) The reaction temperature is usually fixed at the boiling point of the liquid, thereby eliminating hot spots or run away reactions. (3) An exothermic heat of

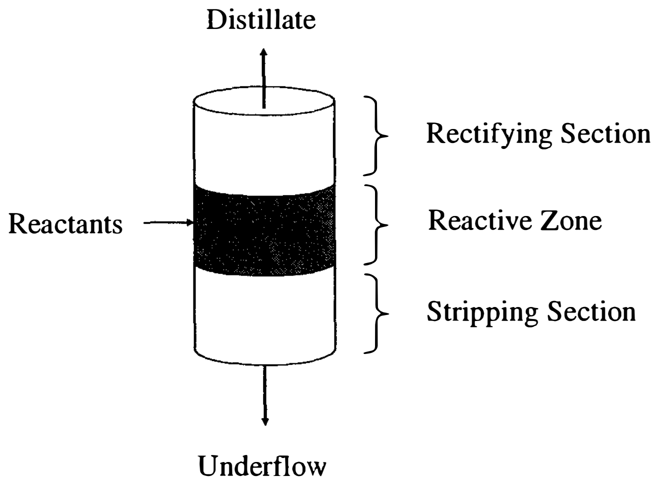


Figure 1. Reactive Distillation Column

reaction helps to drive the vaporization of the liquid thereby reducing the energy requirements for distillation. (4) The removal of product(s) from the column's reactive zone can help to drive equilibrium limited reactions to completion following LeChatelier's principle. (5) Removal of the desired product(s) from the reactive zone can minimize the affect of consecutive reactions, which may improve selectivity. (6) The presence of reaction can improve separation performance by "reacting away" undesirable chemical species. (7) Azeotropes sometimes can be circumvented using the unique thermodynamic properties arising from the combination of reaction and distillation (Lee et al., 2000a).

Reactive distillation has been applied to many different types of reactions such as isomerization, dimerization, etherification, hydration of olefins, alkylations, esterification and hydrolysis, and reactions involving the separation of closely boiling isomers (Podrebarac et al., 1997). Some commercial applications of reactive distillation are highly successful such as the production of methyl *tert*-butyl ether (MTBE) (Smith, 1981) and methyl acetate (Agreda, 1984).

Although reactive distillation can be very beneficial, it is not applicable to all chemical reaction and distillation systems. (1) The reaction components must be able to be separated by distillation. (2) The reaction must occur to an appreciable extent at the reactive zone temperature. (3) The reaction should be neutral to exothermic because strongly endothermic reactions will cause the vapor to condense and could severely limit the separation of the product components.

Since incorporation of reactive distillation into a process design is highly desirable because of the expected economic and operating advantages. How does one know when reactive distillation will work and when it will not? What combinations of reactant and product boiling points and chemical reaction equilibrium constants lead to favorable reactive distillation column designs and which combinations do not? For example:

- If the products are more volatile than the reactants, and if the difference in boiling points between the products and reactants is large, and if the chemical reaction equilibrium constant is favorable, then reactive distillation is probably feasible and economically advantageous.
- If the reactants are the intermediate boiling components in a reactive chemical system, and if the differences in boiling points between the products and reactants are large, and if the chemical reaction equilibrium constant is favorable, then reactive distillation is probably feasible and economically advantageous.

These are two generally accepted heuristics for reactive distillation, however they are quite vague. In fact, they are so vague that if the engineer thinks a chemical reaction system meets the criteria for one of these heuristics, does the engineer really know that the system will work? How far apart do the reactant and product boiling points have to be? How favorable does the equilibrium constant have to be? How is the minimum necessary boiling point difference correlated with the minimum favorable chemical reaction equilibrium constant for reactive distillation to still be economically feasible? Is it really necessary for the reactant to be intermediate boiling? It is important to not only be able to answer these questions, but do so quickly in order to screen systems of interest. These questions provide the motivation for this research project.

Research Objective

The objective of this research is to develop initial process economic feasibility and design heuristics for single column reactive distillation based on reactant stoichiometry, actual reactant and product relative volatilities, and chemical equilibrium constants. These heuristics are developed from the evaluation of extensive computer simulations and are compared to actual chemical systems available in the reactive distillation literature in order to validate the heuristics.

Methodology

A parametric study of generic reactive distillation systems was undertaken using Aspen Technology Aspen Plus® simulation software to generate data for evaluation. This study focused on the effects that relative volatility, volatility ordering, and chemical reaction equilibrium have on reactive distillation economic feasibility and design. The following reaction systems were studied in detail:

- $A \leftrightarrow C$
- $A \leftrightarrow C+D$
- $A+B \leftrightarrow C$

Generic reactant and product relative volatilities were generated from correlations developed from a small set of real chemicals. The reactant and product relative volatility parameters were selected such that all unique combinations of reactant and product relative volatility orderings are studied. A broad range of chemical equilibrium constants were studied in conjunction with these relative volatility orderings.

Simulation results from this parametric study were evaluated and heuristics indicating initial economic feasibility and design of reactive distillation were developed. The proposed heuristics were compared to reactive distillation systems currently available in the literature in order to verify that the simulations and heuristics are applicable and correct.

Results from the reaction systems studied in detail were extended to illustrative examples of the $A+B \leftrightarrow C+D$ reaction system. However, an exhaustive study of the $A+B \leftrightarrow C+D$ system for all possible combinations of relative volatilities amongst the four components was beyond the scope of this project.

II. LITERATURE REVIEW

Reactive distillation has been an area of interest industrially for many years with Backhaus (1921) first proposing a route to esters from alcohols and acids via reactive distillation eighty years ago. Interest in reactive distillation has continued to grow as the demand for improved financial earnings coupled with market maturity drives the chemical processing industry to improve product margins and maintain competitive advantage (Barnicki and Siirola, 2004; Stankiewicz, 2003; Schoenmakers and Bessling, 2003). Academia has also shown a long interest in reactive distillation (Keyes, 1932) with a significant increase in research shown over the past fifteen years. Recent review articles summarize recent advancements in reactive distillation and areas requiring future research (Malone and Doherty, 2000; Taylor and Krisha, 2000).

Physical Feasibility of Reactive Distillation

The physical feasibility of reactive distillation is typically determined from the given feed composition, process pressure/temperature, chemical reaction kinetics, and desired products. Feasibility determination must incorporate all of the thermodynamic features for ideal and non-ideal (i.e. azeotropic phase behavior), and new phenomena caused by the introduction of chemical reactions (i.e. multiple reactions, reactive azeotropes, etc). Analysis of reactive distillation feasibility has been done along three lines: residue curve maps/bifurcation theoretic methods, reaction difference-point methods, and attainable region methods.

Reactive Residue Curve Maps/Bifurcation Theoretic Feasibility Methods

In non-reactive simple distillation, the liquid composition will change as the more volatile components evaporate from the liquid phase. A non-reactive residue curve is the locus of the liquid compositions remaining in an isobaric open evaporation from some initial starting composition. The collection of all of these residue curves from different starting compositions for a given system is called a residue curve map (Doherty and Malone, 2001). In the presence of a liquid phase chemical reaction, the simple distillation proceeds as the reaction simultaneously approaches (or reaches) chemical equilibrium. A reactive residue curve is the locus of liquid compositions in an isobaric open evaporation in the presence of a liquid phase chemical reaction for some initial starting composition with a collection of these reactive residue curves being defined as a reactive residue curve map. These reactive residue curve maps indicate the composition profiles in continuous reactive distillation columns at infinite reflux and thus give feasibility information for continuous reactive columns. Barbosa and Doherty (1998a) developed reactive residue curve maps using transformed variables with a single chemical reaction. Transformed variables are a combination of the system mole fractions and reaction stoichiometry and take on the same value before and after chemical reaction. This unique property allows distillation design techniques based on non-reactive residue curve theory to be extended to reactive distillation design. Reactive residue curve maps in transformed variables have been developed for systems with multiple equilibrium chemical reactions and inerts (Ung and Doherty, 1995a,b; Espinosa et al., 1995) and chemical reactions that are kinetically controlled (Venimadhaven et al., 1994). In order to determine if reactive distillation is feasible or infeasible for a given distillate or bottoms composition, the reactive residue curve map is studied in order to determine the singular points from which potential distillate and bottoms products are selected from the unstable (lowest boiling) and stable (highest boiling) nodes for each residue curve. The feasible product regions from reactive residue curves can be estimated using "bow-tie" regions that have previously been used for product feasibility evaluation of conventional non-reactive distillation processes (Van Dongen and Doherty, 1985; Fien and Liu, 1994). However, the use of transformed variables makes it difficult to completely understand the interaction between separation and reaction since the transformed variables project the original composition into a reaction invariant composition. Therefore, one loses the ability to understand or visualize graphically how reaction and separation interact inside the reactive zone within a reactive distillation column.

Bessling et al. (1997) combined the transformed composition variables from Barbosa and Doherty (1998a) with distillation lines to evaluate reactive distillation feasibility. Distillation lines are the locus of vapor compositions that are in equilibrium with the residue curve liquid phase compositions. The evaluation of reactive distillation feasibility using reactive distillation lines is the same as that described for reactive residue curves, except reactive distillation line maps are used in place of reactive residue curve maps. The differences between residue curves and distillation curves are not normally significant (Fien and Liu, 1994).

Bifurcation theoretic methods are an extension of residue curve map analysis and have been applied to reactive distillation which do not reach chemical equilibrium (Okasinski and Doherty, 1997; Venimadhaven et al., 1999a; Okasinski and Doherty, 2000). This mathematical analysis method allows the evaluation of the affects of chemical reaction kinetics and column hold up on the feasible distillate and bottoms compositions. The term bifurcate is defined as "to cause to divide into two branches or parts" and in this case, the bifurcation is a splitting of a phase behavior stationary point, such as a pure component, non-reactive azeotrope, or reactive azeotrope. One of the primary advantages of this bifurcation analysis is that the initial evaluation of feasible product compositions does not depend on accurate development of reaction kinetics or column hold up. By varying a couple of dimensionless quantities, Damköhler number (Da) and feed fraction vaporized (Ø) (see Equations (2.1) and (2.2)), it is possible to visually assess the potential changes in the unstable (lowest boiling) and stable (highest boiling) nodes of the system and therefore the potential distillate and bottoms products for kinetically limited, as opposed to equilibrium limited, systems (Chadda et al. 2001; Chadda et al., 2002).

The feasible distillate product is the unstable (lowest boiling) node in the rectifying section bifurcation diagram and the bottoms product is the stable (highest boiling) node in the stripping section bifurcation diagram.

$$Da_j = \frac{\left(H_j \middle/ L_{j-1} \right)}{\left(1 \middle/ k_{f,ref} \right)} = \frac{\text{characteristic liquid residence time}}{\text{characteristic reaction time}} \tag{2.1}$$

$$\phi_j = \frac{V_j}{L_{j-1}} \tag{2.2}$$

Reaction Difference-point Feasibility Methods

Difference-point methods have been used to study non-reactive and extractive processes for many years (Hoffman, 1964). A reaction vector was proposed by Hauan and Lien (1996) and has been included in what they call a phenomena-based method consisting of a mixing vector, a separation vector, and a reaction vector. The feasibility of a particular process is indicated by the direction of the combined vectors. A more detailed analysis of the combination of non-reactive and reactive difference points has been presented by Hauan et al. (2000a). The feasibility of reactive distillation columns has been studied by Lee et al. using a reactive difference point method (Lee et al., 2001; Lee, 2002). The proposed reactive distillation system is feasible if: (1) the feed composition, the reactive difference point, and the pseudo-feed composition are on the same straight line (material balance constraint) and if given the top product liquid composition: (2) the liquid composition vectors must lie within or move towards the forward reaction region and the reachable region from the bottoms product of the non-reactive stripping section or if given the bottom product liquid composition: (3) the liquid composition vectors must lie within or move towards the forward reaction region and the reachable region from the bottoms product of the non-reactive rectifying section. The pseudo-feed composition is conceptually the reaction conversion of the feed within the reactive distillation column which allows the visualization of the extent of reaction, but this method can quickly become visually difficult to understand for higher order systems involving more than two components.

Attainable Region Feasibility Methods

The attainable region method is a very powerful geometric approach and identifies all feasible compositions, but not necessarily the optimal process configuration. The attainable region approach to reactor network feasibility has been studied primarily by Glasser et al. (1987) who identified the feasible concentration space from a given feed for any reaction and mixing combination. Nisoli et al. (1997) combined this geometric approach to reactor synthesis with a geometric approach to separation feasibility and the combination was demonstrated using MTBE production by reactive distillation as an example.

Giessler has studied reactive distillation feasibility by using the method of static analysis (Giessler et al., 1998, 1999, 2001). The static analysis method was originally developed by Serifimov's group and has the advantage of requiring minimal knowledge of the physiochemical properties of the system. The primary assumption in this method is that the vapor and liquid flow rates are very large, which means the composition change caused by the reaction on each tray can be neglected. Essentially, this assumption allows the separation of the reactive distillation column into 2 process units, a reactor and distillation unit and allows the use of distillation lines for the description of the column trajectories. According to this method, a steady state is feasible if the corresponding trajectory (1) fits to the mass balance line and (2) some of its points lie outside the reverse reaction region (must have some forward reaction). The assumption of large vapor and liquid flow rates does not allow the evaluation of the extent of reaction on each stage. Therefore, pinch situations such as reactive azeotropes and reactive fixed points cannot be shown.

Conceptual Design of Reactive Distillation

Conceptual design methods estimate process specifications such as: equipment sizes (number of reactive stages, number of non-reactive stages, and column diameter), feed flows and locations, heating and cooling loads, catalyst concentrations, and liquid holdups. Reactive distillation design methods have recently begun to emerge and are currently an active area of research within process systems engineering. Several different approaches to conceptual reactive distillation design have been used and can be categorized as: geometric methods, difference-point methods, and mathematical programming methods.

Geometric Design Methods

Barbosa and Doherty developed a "boundary value" method using transformed variables for the determination of reactive distillation design feasibility, minimum reflux ratio, and number of stages for a column with a single chemical reaction with either a single feed (Barbosa and Doherty, 1988b) or double feed (Barbosa and Doherty, 1988c). The boundary value method consists of specifying the feed, distillate, and bottoms compositions in transformed compositions and integrating the design equations from both ends of the column toward the center until the stripping and rectifying profiles intersect (and middle-section profile for a double-feed column) by varying the reflux ratio. This approach has been extended to systems with multiple chemical reactions and systems containing inerts (Ung, 1994). Buzad and Doherty developed a similar design method for kinetically controlled reactive distillation columns using the analysis of fixed-points (Buzad and Doherty, 1994, 1995). Applications of this design approach have also been extended to reactive distillation design for packed-bed columns (Mahajani and Kolah, 1996) and determining feasible product regions for kinetically controlled reactive distillation (Chadda et al., 2000). The original design method has been generalized by relaxing some of the original method assumptions (Okasinski and Doherty, 1998; Melles et al., 2000) and has been applied to many different examples (Chen et al., 2000).

Difference-point Design Methods

Reactive difference points can be used to evaluate and generate design alternatives for reactive distillation processes. Lee et al. (2000b) develop design alternatives by evaluating a lever rule consisting of linear combinations of reaction difference points, stoichiometric coefficient vectors of reactants and products, and composition vectors. Stage by stage calculations using reactive difference points have been used to determine the total number of stages and the distribution of reaction zones inside a column (Lee and Westerberg, 2000c). Extension of the Ponchon-Savarit and McCabe-Thiele diagrams for the design of reactive systems has been presented (Lee et al., 2000d,e) and shown to be effective in evaluating design alternatives for reactive distillation systems with complicating azeotropes (Lee et al., 2000a,f) and in distributing reaction zones within the column (Lee et al., 2000g).

Mathematical Programming Design Methods

Mathematical optimization methods have been applied to reactive distillation design in a few studies (Jackson and Grossman, 2001). A mixed integer nonlinear programming model (MINLP) has been formulated for the optimization of ethylene glycol production via reactive distillation (Ciric and Gu, 1994a). An objective function, the total annualized cost, is minimized subject to constraints such as the material and energy balances at each tray, material balances at the top and bottom of the column, and thermodynamic relationships. This MINLP method has also been applied using phenomena-based representations for the cost optimization of ethyl acetate production via reactive distillation (Ismail et al., 1999).

Heuristics Design Methods

Heuristics, or rules-of-thumb, are used to provide guidance and insight for initial analysis of process feasibility and conceptual design. Heuristics for the analysis of conventional distillation feasibility and design have been developed from experience, experimental data, computer simulations, and industrial process data and can be found in most texts on conventional distillation design (Douglas, 1988; Kister, 1992). For example, as a general rule-of-thumb, the optimum reflux ratio for a conventional distillation column usually falls in the range of 1.1 to 1.3 times the minimum reflux ratio.

Literature specific to reactive distillation heuristics is limited. Some initial reactive distillation design heuristics have been proposed by Fair (1998) and give general guidance to the application and conceptual design of reactive distillation. Once a process has been deemed feasible and advantageous with respect to a solid-catalyzed reactive distillation, Subawalla and Fair (1999) have developed extensive guidelines for column design based on applying the Fenske-Underwood method to the column's non-reactive stripping and rectifying sections with the required catalyst volume determining the length of the catalytic section of the column. Feasibility and selectivity heuristics for reactive distillation with competing side reactions have recently been developed from computer simulations for specific cases of system relative volatilities (Gadewar et al., 2000; Blagov et al., 2000).

Of the heuristics currently available in the literature for initial reactive distillation feasibility and design, these are the rules that relate to this research project:

1. Bessling et al. (1997)
   a. Reactive distillation is a feasible and probably an economic operation if both products are connected by a reactive distillation line, the products are nodes in a reactive distillation line diagram, and the boiling point difference between the products is large.
   b. If it is necessary to separate a product that is not in the reaction space, a section with non-reactive distillation trays must be added.
   c. If one or both products are saddles (intermediate boiling), a high conversion is required at a stoichiometric ratio of reactants, the separation between the saddles and nodes is difficult, the boiling point difference between the products is large, no distillation border must be crossed, and the chemical equilibrium is on the side of the desired products, then the reactive distillation is a feasible and probably and economic operation.
2. Fair (1998)
   a. There needs to be an advantage in shifting the equilibrium of the chemical reaction. If the equilibrium conversion is already high, for instance 90% or more, there is little incentive for using reactive distillation.
   b. The reaction products must boil in an appropriate range and be separable by distillation. If the boiling point of the desired product instead falls within a range of other products, more distillation columns will be needed.
   c. The pressure and temperature conditions for separation must be compatible with the reaction conditions since both operations are carried out together.
   d. Only one liquid phase should be present.
   e. Determine feed location based on volatilities of reactants.
   f. Recognize that reacting reflux ratios will be higher than non-reacting reflux ratios. Use a factor of 1.2-1.4 x minimum ratio.
3. Okasinski (1999)
   a. The practical limit for reactive distillation with systems with extremely small reaction equilibrium constants is a K_{eq} of approximately 10^{-4} to 10^{-5}.
4. Subawalla and Fair (1999) post feasibility analysis:
   a. The reactive section should be located toward the top of a column when the limiting reactant is the most volatile component and the product is the least volatile component in the system. When the product is the more volatile component, the procedure is reversed.
   b. For a 4 component system where the reactants are the 2 intermediate boiling components, the reactive zone should be located in the middle of the column. The less volatile product is removed in the bottoms, while the more volatile product is removed in the distillate.

    c. If reactants are the most volatile components in the system, then the feed should be introduced at the bottom of the reactive zone. When products are more volatile than reactants, the reactants should be fed at the top of the reactive section. If the volatilities of the reactants are very different, a subsidiary feed location may be required to ensure stoichiometric quantities of reactants in the reactive zone.
    d. For low-boiling reactants, and increase in reflux increases the reactant recycle across the reactive zone.
5. Lee et al. (2000g) for binary isomerization and dimerization reactions:
    a. If the reaction has a heavy reactant and a light product, the reaction zone should be in the rectifying section (i.e. above the feed stage) to enhance the separation efficiency and avoid possible pinch points.
    b. If the reaction has a light reactant and a heavy product, we should construct the reaction zone in the stripping section (i.e. below the feed stage).
6. Kaymak and Luyben (in press)
    a. Reactive distillation is 2.5 – 3.0 times more cost effective than a traditional reactor/separation/recycle process configuration for a four component chemical reactive system where the products are the lowest and highest boiling components and the relative volatility ratios are 4:2:8:1 (α_A: α_B: α_C: α_D)

It should be noted that most of these heuristics are very general and although they do provide good basic guidance, they do not help to answer specific questions such as: How small can the chemical reaction equilibrium constant be before reactive distillation is not economically feasible? How close or far apart do the reactant and product relative volatilities have to be in order for reactive distillation to be feasible? How does the interaction of the chemical reaction equilibrium constant and the reactant and product relative volatilities help or hinder reactive distillation? This research project was designed to answer these questions.

Reactive Distillation Processes (Academic and Industrial)

Reactive distillation has proven to be effective for several types of chemical reactions including etherifications, alkylations, and esterifications. Some of the more important examples of industrial and academic reactive distillation processes are the production of cumene, ethylene glycol, methyl acetate, and methyl tert-butyl ether.

Etherifications

Methyl tert-Butyl Ether (MTBE) is currently produced commercially via reactive distillation and is a popular system of study in the academic community (Ung, 1995a,b; Espinosa et al., 1999). MTBE and other oxygenates, such tert-Amyl Methyl Ether (TAME) (Sundmacher et al., 1999; Mohl et al., 1998), and Ethyl tert-Butyl Ether (ETBE) (Sneesby et al., 1998; Quitain et al., 1999), and 2-methoxy-2,4,4-trimethylpentane

(Rhiko-Struckmann et al., 2004) have been studied because of the large increase in demand for oxygenates for gasoline reformulation driven by the Clean Air Act as was initially indicated by Degarmo et al. (1992). MTBE can be produced from methanol and isobutylene using a single stage conventional process using two series-flow reactors followed by a separation and external recycle of excess methanol. Conversions of 90-97% of isobutylene were achieved with this conventional process. Degarmo suggested that an isobutylene conversion greater than 99% could be achieved using a reactive distillation column. This increase in yield would quickly compensate the capital costs of changing to the reactive distillation process (Lander et al., 1983). The industrially practiced MTBE reactive distillation column configuration would be similar to that shown in Figure 2.

If a completely reactive column were used to generate MTBE, MTBE could only be produced at a purity of approximately 92% because of the presence of the MTBE-methanol azeotrope that limits the attainable bottoms product purity. If a hybrid reactive distillation column like Figure 2 is used with an appropriate feed composition, the bottom's product will be essentially pure MTBE because the non-reactive stripping section returns the unreacted reactants (and azeotrope) to the reactive zone, thereby generating pure MTBE as the bottom's product.

Alkylations

Cumene and ethylbenzene can also be successfully manufactured by a reactive distillation configuration similar to Figure 2 (Shoemaker and Jones, 1987; Smith, 1989).

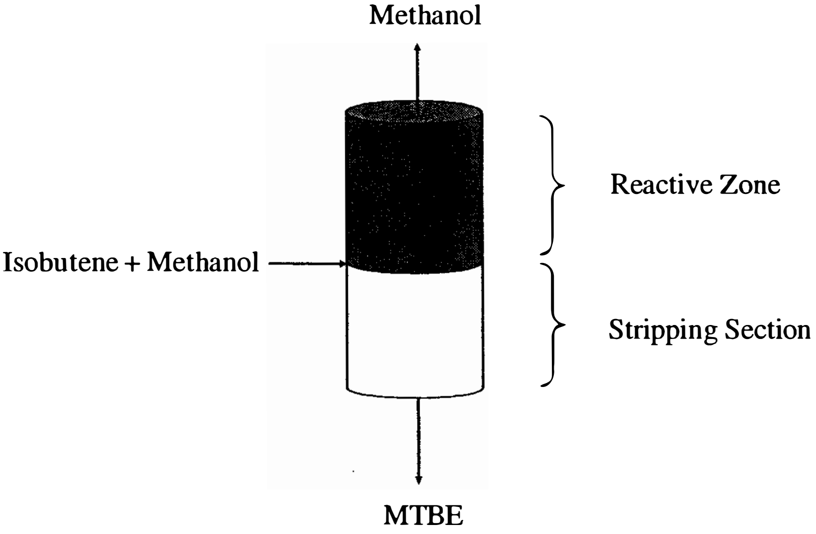


Figure 2. MTBE Reactive Distillation Column

For the cumene production from benzene and propylene, the distillate product is returned to the reactive zone in order to enhance the overall propylene conversion for this reaction system. The reactive distillation bottoms product will be primarily cumene. The propylene concentration in the liquid phase of the reactive distillation column is kept low to minimize propylene oligomerization and to restrict the production of diisopropylbenzene and triisopropylbenzene byproducts. Propylene conversions are 98%, while benzene is essentially completely converted. Although the alkylation of benzene is extremely exothermic, the process catalyst life is prolonged in reactive distillation because the reaction temperature is limited by the liquid phase boiling point. This prevents hot spots from being formed in the catalyst zone, which will decrease the catalyst activity. This heat of reaction is used effectively in reactive distillation to provide the energy required for vaporization. Energy requirements are 800-850 Btu/lb. cumene for reactive distillation vs. 1200 Btu/lb. cumene in the conventional process. Reactive distillation production for other alkylbenzenes have been studied as well (Knifton et al., 2003; Lei et al., 2003).

Esterification/Hydrolysis of Esters

Interest in esterification reactions using reactive distillation has been of interest for many years. Keyes (1932) reviewed the early status of esterification processes. These reactions have been a popular area of study for reactive distillation because of the limitations that the chemical reaction equilibrium places on producing pure product. Reactions studied for application to reactive distillation include: methyl acetate (Agreda, 1984; Agreda et al., 1990; Huss et al., 2003), ethyl acetate (Bock et al., 1997; Vora and Daoutidis, 2001; Kloker et al., in press), isopropyl acetate (Okasinski and Doherty, 1997, 2000), butyl acetate (Zhicai et al., 1998; Venimadhavan et al., 1999b; Steinigeweg and Gmehling, 2002), methyl decanoate (Steinigeweg and Gmehling, 2003), n-hexyl acetate (Schmitt et al., 2004), methyl dodecanoate and 2-ethylhexyl dodecanoate (Omota et al., 2003a,b) as well as the reverse reaction (i.e. hydrolysis of esters) for methyl acetate (Fuchigami, 1990; Hoyme and Holcome, 2003). Transesterifications have also been studied (Fang an Xiao, in press; Jimenez et al., 2002; Jimenez and Costa-Lopez, 2002; Oyevaar et al., 2000).

Esterification reactions are prime candidates for reactive distillation because the formation of esters is equilibrium limited and reversible. This problem limits conversion in a fixed bed or stirred tank reactor. Eastman Chemical Company currently produces methyl acetate (99 wt %) using a reactive distillation configuration similar to that shown in Figure 3.

In the actual industrial design, a double feed column is used with methanol fed near the bottom of the column and acetic acid fed near the top of the column, which results in counter-current flow between the reactants with the high concentrations of reactants at opposite ends ensuring a high conversion of both reactants at the opposite ends of the reactive zone. The catalyst is sulfuric acid which is fed at the top of the reactive zone. Since the catalyst is homogenous, the entire bottom section of the reactive distillation

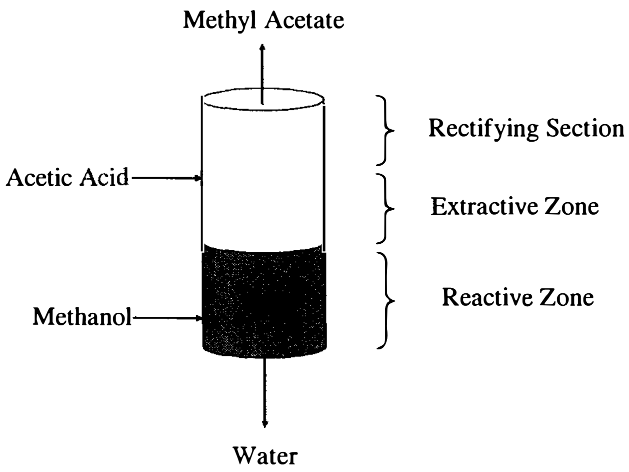


Figure 3. Methyl Acetate Homogeneous Reactive Distillation Column

column is reactive and there is no non-reactive stripping section of the column. In the non-reactive rectifying section, the unreacted methanol is removed from the water by-product, while the distillate product should be pure methyl acetate since it is the low boiling pure component. However, two minimum boiling methyl acetate azeotropes complicate this situation. Methyl acetate forms non-reactive azeotropes with water and with methanol both of which have lower boiling points than the methyl acetate product.

In order to improve the methyl acetate distillate product purity, acetic acid is used as a solvent by adding the acetic acid above the reactive zone. This results in an extractive section in the column, which helps to break the methyl acetate azeotropes by removing the water and to a lesser extent the unreacted methanol. The acetic acid is removed from the methyl acetate product in the rectifying section resulting in essentially pure methyl acetate in the distillate product. The reduction in capital and operating costs for producing methyl acetate in this reactive distillation column design is just one-fifth of that for a more conventional design for the production of methyl acetate (Siirola, 1995).

Methyl Acetate has also been experimentally produced using a configuration similar to that shown in Figure 4. Instead of using a homogeneous catalyst, a heterogeneous catalyst was used to produce methyl acetate, which results in a non-reactive stripping section at the bottom of the reactive distillation column (Gorak and Hoffmann, 2001; Popken et al., 2001; Bessling et al., 1998; Adbulla, 1997).

The change from a homogeneous catalyst to a heterogeneous catalyst has no real affect on the products from the reactive distillation column as long as an extractive zone is maintained as part of the column itself. The non-reactive stripping section does not change water from being the product underflow as long as all of the acetic acid fed to the reactive distillation column is converted to methyl acetate before the start of the non-reactive stripping section. The only significant change that is required is in the reactive

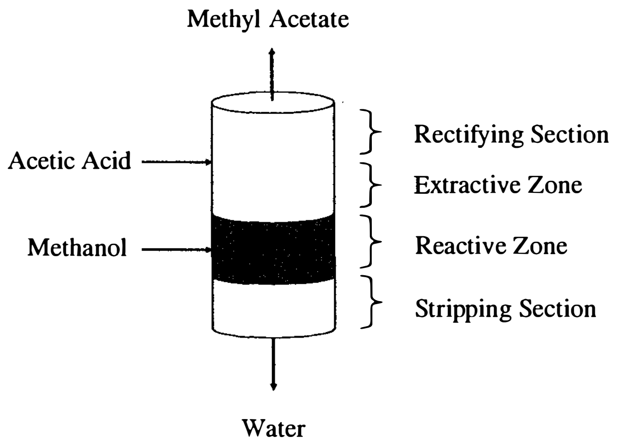


Figure 4. Methyl Acetate Heterogeneous Reactive Distillation Column

zone staging to compensate for the change in reaction kinetics from the use of a heterogeneous catalyst.

Other Reactions

Ethylene glycol production from ethylene oxide and water using reactive distillation has been proposed by Circ and Gu (1994a) and has undergone further study more recently (Kumar and Daoutidis, 1999; Monroy-Loperena et al., 2000; Cardoso et al., 2000). The conventional process for ethylene glycol formation requires an excess water feed to minimize the formation of diethylene glycol and triethylene glycol byproducts. The proposed reactive distillation process should improve the selectivity of ethylene glycol by minimizing the amount of ethylene oxide present for reaction and fast removal of products in the reactive zone as well as improving the water/ethylene oxide feed ratio. A complicating factor in the process is there are possible steady state multiplicities (Ciric and Miao, 1994b; Monroy-Loperena and Alvarez-Ramirez, 1999). One of these steady states results in ethylene oxide accumulating in the top of the column, which is undesirable because ethylene oxide at this concentration is a potential safety hazard because of the possibility of rapid uncontrolled polymerization. Enantiomerically-pure propylene glycol production from propylene oxide has also been studied (Okasinski and Doherty, 2003).

Many other reaction types have been studied and proposed in addition to those already described: amines (Hayes, 2001), the production and decomposition of alcohols (Xu et al., 2002; Gonzalez et al., 1997), olefin metathesis (Jackson and Grossman, 2001), aldol condensations (Nicol, 2003), and others (Podrebarac et al., 1997).

Reactive Azeotropes

Reactive distillation has been extremely effective in producing chemicals that may be hindered by non-reactive azeotropes in more traditional reactor/separator designs (see the previous sections on methyl acetate and MTBE). However, the combination of reaction and distillation can create mathematical stationary points that are not present without chemical reaction. These stationary points are called reactive azeotropes and can impact the expected distillate and bottoms products. Reactive azeotropes can be defined as a liquid mixture where one or more chemical reactions are taking place that boils at a constant temperature where the composition of the vapor phase is identical to the composition of the boiling liquid. For this situation to occur, the liquid phase chemical reaction must compensate equally for the change in liquid phase composition because of distillation. The conditions for reactive azeotropes have been proposed for both single liquid phase chemical reactions (Barbosa and Doherty, 1987) and for multiple liquid phase chemical reactions (Ung and Doherty, 1995c) and have been shown to exist experimentally (Song et al., 1997; Teodorescu et al., 2001). Reactive azeotropes have been extensively studied (Okasinski and Doherty, 2000; Frey and Stichlmair, 1999a,b; Hauan et al., 2000b; Maier et al.; 2000; Harding and Floudas, 2000) and have been extended to include heterogeneous reactive azeotropes (Okasinski and Doherty, 2000).

III. METHODOLOGY

As evidenced in the literature review, significant improvements have been made in graphical and computational methods for reactive distillation. Even with these advances, it is still difficult to determine whether a given reaction/separation process can be accomplished using reactive distillation because of the highly complicated system that results from the combination of reaction and distillation. This complexity hinders the initial evaluation of process feasibility and design and can be extremely time consuming, as the current evaluation process still consists of extensive simulation and experimentation. A set of heuristics for the initial feasibility and design assessment of reactive distillation for a given reaction/separation combination would be extremely beneficial to the design engineer.

This objective of this research project was to generate such heuristics for a variety of chemical reaction systems. Primary emphasis was placed on studying the effects that relative volatility ordering and chemical reaction equilibrium have on the economic feasibility of reactive distillation for the chemical reaction system of interest. For each chemical reaction system studied, the potential boiling points for the generic chemical components were broken into regions of similar volatility ordering. For each of these volatility order regions, the range of potential relative volatilities was divided into a workable number of combinations. For each relative volatility combination, several reactive distillation column configurations with and without non-reactive stripping and rectifying sections with a given chemical equilibrium constant were simulated using Aspen Technology Aspen Plus® software. For each successive simulation, the chemical equilibrium constant was decreased by a factor of 10 until the reactive distillation column was not able to meet the criteria for economic feasibility. Another relative volatility combination was chosen and the process was repeated.

Reactive Distillation Economic Feasibility Criteria

A combination of relative volatility and chemical equilibrium constant was considered economically feasible if the reactant conversion was greater than 95.0%, the desired product purity was greater than 99.0%, and the reactive distillation column design was practical (total stages ≤ 100, etc).

Conversion of reactant A was defined as:

$$\text{Conversion} = \frac{(\text{moles of A in distillate} + \text{moles of A in underflow})}{\text{moles of A in feed}} \qquad (3.1)$$

Product purity of desired product C was defined as:

$$\text{Purity} = \frac{\text{Moles of C in product stream}}{\text{Total moles in product stream}} \qquad (3.2)$$

Reactive Distillation Column Design

In addition to the chemical equilibrium constant and generic compound physical properties previously described, the following are inputs for the reactive distillation column design used in the Aspen Plus simulations: reflux ratio, distillate/feed ratio, number of stages (reactive, rectifying, stripping), feed ratio, and single or double feed stage location(s).

Reflux Ratio

The minimum reflux ratio (RR) for a reactive distillation column cannot be accurately calculated using traditional methods, such as the Underwood method, because the reflux ratio effects both the reaction and separation (Subawalla and Fair, 1999). Minimum reflux ratio estimation procedures for reactive distillation have been proposed, but are complex. Barbosa and Doherty have proposed a calculation procedure for minimum reflux ratio for both single feed (Barbosa and Doherty, 1988b) and double feed (Barbosa and Doherty, 1988c) columns using transformed compositions. Bessling has recently proposed a simplified reflux ratio calculation for the "preferred separation" (Bessling, 2000).

Because of the complexity of determining a minimum reflux ratio, a predetermined range of reflux ratios (1, 2.5, 5, 10, and 100) was used in this reflux project. Unless the system produces essentially no or very little distillate, reflux ratios larger than 100 result in very large vapor/feed flow ratios within a reactive distillation column. These large reflux ratios may or may not be economically feasible for a reactive distillation column with the column requiring a very valuable product to offset the large energy costs from the large reflux ratios. The simulation results for the reflux ratios analyzed in this research project are reported as "economically feasible" with the understanding that the economics for all reflux ratios actually depend on the product value.

Distillate to Feed Ratio

The molar distillate to feed ratio (F_D/F_F) was determined using the mass balance equations for the reactive distillation system, the expected product location, and expected flow for the reactive chemical system product. The desired product C could accumulate in either the distillate or bottoms stream of the reactive distillation column depending on the relative volatilities of the chemical species in the system under study. If product C was the lowest boiling component, the column was designed to generate product C in the distillate stream. If product C was the highest boiling component, the column was designed to generate product C in the bottoms stream. If product C was an intermediate boiling component in the $A \leftrightarrow C+D$ system, the column was designed to generate product C opposite from the by-product D. This design was chosen because if the reactive distillation column was designed so that both product C and D were to come out in the same stream, it would not be possible to generate product C at 99% purity (of course a reactive distillation column for such a system could be designed to generate both products C and D in the same stream for subsequent separation in a second non-reactive column). If product C was an intermediate boiling component in the A+B↔C system, then the reactive distillation column design was evaluated with product C as both the distillate or bottoms product as it was not possible to predetermine the best design prior to simulation.

Additionally, the molar distillate to feed ratio was chosen such that the desired flow for the product was maximized and the other flow was primarily unreacted reactants and/or by-products. For example, for the A↔C system when the boiling point temperature for A is less than C, the following equations were solved.

$$
\begin{aligned}
&F_F x_{F,A} = F_D x_{D,A} + F_B x_{B,A} - \xi \\
&F_F x_{F,C} = F_D x_{D,C} + F_B x_{B,C} + \xi \\
&1 = x_{D,A} + x_{D,C} \\
&1 = x_{B.A} + x_{B,C} \\
&1 = x_{F,A} + x_{F,C} \\
&\xi = 0.95(F_F x_{F,A}) \\
&x_{F,A} = 1.0 \\
&x_{B,C} = 0.99 \\
&F_F = 100
\end{aligned}
\tag{3.3}
$$

These equations do not explicitly solve for the F_D/F_F, therefore an analysis of the resulting F_D/F_F ratio for a given distillate composition was calculated with the results shown in Table 1. For this case, a molar distillate to feed ratio of 0.05 was chosen as the best ratio for the reactive distillation column design because this molar distillate to feed ratio results in a column that meets the economic feasibility criteria (a product purity of > 99.0% and a reactant conversion of > 95.0%) with maximum product flow. Calculations similar to this were completed for all of the cases within the chemical reactive systems in this study.

Reactive Distillation Configurations

Reactive distillation columns can be categorized into four general configurations (Figure 5). They are a reactive distillation column with: (1) a reactive section and a non-reactive stripping section (Configuration I), (2) a reactive section with a non-reactive rectifying section and a non-reactive stripping section (Configuration II), (3) a reactive section and a non-reactive rectifying section (Configuration III), and (4) all stages being reactive (Configuration IV). All configurations except for the completely reactive column, Configuration IV, were evaluated for economic feasibility in this research project. Different configurations can result in different results for both product purity and reactant conversion. This will be discussed further in later sections of this dissertation.

Table 1. Molar Distillate to Feed Ratio Mass Balance Calculations

$x_{D,A}$	$x_{D,C}$	F_D/F_F	Dist Flow (F_D) (lbmol/hr)	Distillate Flow for A (lbmol/hr)	Bottoms Flow (F_B) (lbmol/hr)	Bottoms Flow for C (lbmol/hr)
0.05	0.95	1.000	100.0	5.00	0.0	0.0
0.10	0.90	0.444	44.4	4.44	55.6	55.0
0.20	0.80	0.211	21.1	4.21	78.9	78.2
0.30	0.70	0.138	13.8	4.14	86.2	85.3
0.40	0.60	0.103	10.3	4.10	89.7	88.8
0.50	0.50	0.082	8.2	4.08	91.8	90.9
0.60	0.40	0.068	6.8	4.07	93.2	92.3
0.70	0.30	0.058	5.8	4.06	94.2	93.3
0.80	0.20	0.051	5.1	4.05	94.9	93.3
0.81	0.19	0.050	5.0	4.05	95.0	94.1
0.90	0.10	0.045	4.5	4.04	95.5	94.6
0.95	0.05	0.043	4.3	4.04	95.7	94.8
0.99	0.01	0.041	4.1	4.04	95.9	95.0

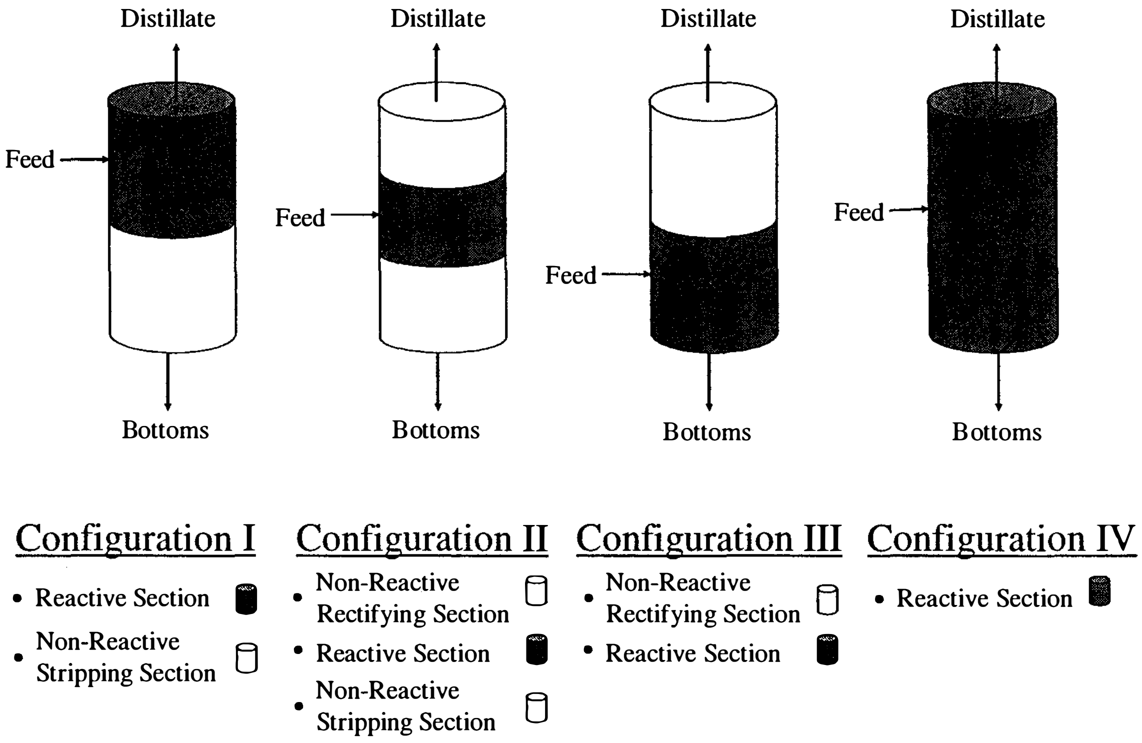


Figure 5. Reactive Distillation Column Configurations

Number of Stages (Reactive, Rectifying, Stripping)

Because of the complexity of the simulation calculations, it was not possible to fix the total number of reactive and non-reactive stages for the reactive distillation column at some predetermined value. The combination of reaction and distillation inhibits the simulation software from converging and generating useable results for a fixed column staging. Therefore, the reactive and non-reactive stages for the reactive distillation column were varied in a deliberate, stepwise manner using a Microsoft® Excel/Visual Basic driver program. The steps were chosen to be large enough to move as quickly as possible through the required relative volatility and chemical equilibrium constant combinations without inhibiting the simulation software's ability to converge and generate accurate results.

As part of the economic feasibility criteria, the total number of stages for each reactive distillation column was held to a maximum of 100 stages. By definition, each reactive distillation column has at least one reactive stage. The reactive and non-reactive stripping and/or rectifying sections of the column were varied from 1-99 stages depending on the reactive distillation column configuration.

Feed Ratio

The feed ratio has important implications for the reactive distillation column design. In order to limit the scope of this research project, only reactants were present in the feed. For the $A \leftrightarrow C$ and $A \leftrightarrow C+D$ chemical reaction systems, only pure A was fed to the reactive distillation column. For the $A+B \leftrightarrow C$ chemical reaction system, only a stoichiometric feed of A and B was evaluated.

Single Feed or Double Feed Locations

Reactive distillation columns can have a single feed or multiple feeds. The $A \leftrightarrow C$ and $A \leftrightarrow C+D$ systems were only evaluated using single feeds. Both single and double feeds systems were evaluated for $A+B \leftrightarrow C$. The double feeds were 2 feeds consisting of pure component A and pure component B, each fed at the outside stages of the reactive zone. The feeds to all reactive distillation columns in this research project were saturated liquid feeds at atmospheric pressure and temperature.

The feed location was confined to the reactive zone for both single feed and double feed columns. For the $A \leftrightarrow C$ chemical reaction system, there was only one reactive stage and, thus, only one location for the feed because additional reactive stages do not improve the formation of product C. For the $A \leftrightarrow C+D$ chemical reaction system, only a single feed was evaluated and the feed location was the top, middle, or bottom reactive stage. For the $A+B \leftrightarrow C$ chemical reaction systems, the feed was allowed to be placed on any stage within the reactive zone for the single feed reactive distillation column. For the double feed reactive distillation column, feed locations were allowed to be placed on any reactive stage but the component B feed was always above the feed for component A because component A was always the lower boiling reactant. Barbosa and Doherty (1988c) evaluated the possibility of inverting the feeds so that the lower boiling reactant was the upper feed and the higher boiling reactant was the lower feed, but discovered that this reactive distillation column design always generated poorer results than the conventional design.

Parametric Study

Chemical Reaction Systems and Chemical Equilibrium

The following reactive chemical systems were studied in order to generate data for the development of reactive distillation heuristics:

- $A \leftrightarrow C$
- $A \leftrightarrow C+D$
- $A+B \leftrightarrow C$
- $A+B \leftrightarrow C+D$

The chemical equilibrium constant for each reaction and relative volatility combination was varied starting with a chemical equilibrium constant of 10,000. After that simulation was completed, the chemical equilibrium constant was decreased by a factor of 10 for each successive simulation until the chemical system under study no longer met the economic feasibility criteria.

The chemical equilibrium constant was defined as:

$$K_{eq} = \prod (x_i \gamma_i)^{\nu_i} \tag{3.4}$$

Since the systems studied in this research project were ideal, the activity coefficients were all equal to 1 and the equilibrium constant reduces to:

$$K_{eq} = \prod (x_i)^{\nu_i} \tag{3.5}$$

For all reactive generic chemical systems used in this research project, the equilibrium constant was assumed to be constant, temperature independent, and occurred only in the liquid phase.

Relative Volatilities

The combinations of reactant and product relative volatilities were varied from 0.01 to 100, but were occasionally limited by the generic compound correlations described in greater detail in the Modeling and Simulation section of this dissertation. For the given reactive systems, all relative volatilities were calculated using component A as the reference component. For all chemical reactive systems studied, component A was always a reactant and if there was another reactant in the chemical reaction, component A always was the lower boiling reactant. This eliminated redundant combinations of reactant relative volatilities.

The relative volatilities for this research project were calculated as follows:

- From a chosen boiling point for each generic component, the component vapor pressure was calculated from the Antoine coefficient correlations (see later section on Modeling and Simulation for details).
- The vapor pressure for each reactant and product in the chemical system was calculated at the average boiling point temperature for the individual components in the reactive chemical system.
- The relative volatility for each pair was calculated from the individual generic component vapor pressures using the following equation.

$$\alpha_{Ai} = \frac{P_A^{sat}}{P_i^{sat}} \qquad (3.6)$$

Not all reactant and product boiling point combinations were simulated because different combinations of boiling points would result in essentially same relativity volatility combinations. This assumption helped to limit the required number of simulations for this study, but does not limit the applicability for the resulting heuristic rules as was shown by the real chemical systems available in the reactive distillation literature.

To achieve the primary objective of this research project, all unique relative volatility orderings for each chemical system in conjunction with a given chemical equilibrium constant were studied. Table 2 outlines the various volatility order regions that were studied for the A↔C, A↔C+D, and A+B↔C+D systems. Each of these regions have a common relative volatility ordering for the reactants and products and are expected to share similarities for successful reactive distillation designs, distillate to feed ratios, potential reactive azeotropes, and potential success in meeting the economic feasibility criteria.

Predetermined relative volatility combinations within each region were chosen to cover the entire range of reactant and product boiling points for most real chemical systems. Although not all reactant and product relative volatilities within each region were studied, it is expected that the heuristics generated from the evaluation of the data can be applied to all relative volatility combinations within that region.

Reactive Azeotropes

Since the generic compounds within this research study are ideal, non-reactive azeotropes are not present. However, reactive azeotropes may exist even in "ideal" reactive systems

Table 2. Volatility Order Regions

Region	Chemical Systems		Molar Distillate/ Feed ratio
$A \leftrightarrow C$			
1	$\alpha_{AC} > 1.0$ ($T_{bp,A} < T_{bp,B}$)	Reactive Azeotropes may exist	0.05
2	$\alpha_{AC} < 1.0$ ($T_{bp,A} > T_{bp,B}$)	Reactive Azeotropes may exist	0.95
$A \leftrightarrow C+D$			
1	($T_{bp,A} < T_{bp,D} < T_{bp,C}$) $\alpha_{AD} > 1.0$, $\alpha_{AD} < \alpha_{AC}$, $\alpha_{AC} > 1.0$	Reactive Azeotropes may exist	1.0
2	($T_{bp,A} < T_{bp,C} < T_{bp,D}$) $\alpha_{AD} > 1.0$, $\alpha_{AD} > \alpha_{AC}$, $\alpha_{AC} > 1.0$	Reactive Azeotropes may exist	0.95
3	($T_{bp,C} < T_{bp,A} < T_{bp,D}$) $\alpha_{AD} > 1.0$, $\alpha_{AD} > \alpha_{AC}$, $\alpha_{AC} < 1.0$		0.95
4	($T_{bp,D} < T_{bp,A} < T_{bp,C}$) $\alpha_{AD} < 1.0$, $\alpha_{AD} < \alpha_{AC}$, $\alpha_{AC} > 1.0$		1.0
5	($T_{bp,D} < T_{bp,C} < T_{bp,A}$) $\alpha_{AD} < 1.0$, $\alpha_{AD} < \alpha_{AC}$, $\alpha_{AC} < 1.0$	Reactive Azeotropes may exist	1.0
6	($T_{bp,C} < T_{bp,D} < T_{bp,A}$) $\alpha_{AD} < 1.0$, $\alpha_{AD} > \alpha_{AC}$, $\alpha_{AC} < 1.0$	Reactive Azeotropes may exist	0.95
$A+B \leftrightarrow C$			
1	($T_{bp,A} < T_{bp,B} < T_{bp,C}$) $\alpha_{AB} > 1.0$, $\alpha_{AB} < \alpha_{AC}$, $\alpha_{AC} > 1.0$	Reactive Azeotropes may exist	0.05
2	($T_{bp,A} < T_{bp,C} < T_{bp,B}$) $\alpha_{AB} > 1.0$, $\alpha_{AB} > \alpha_{AC}$, $\alpha_{AC} > 1.0$		0.475 or 0.05
3	($T_{bp,C} < T_{bp,A} < T_{bp,B}$) $\alpha_{AB} > 1.0$, $\alpha_{AB} > \alpha_{AC}$, $\alpha_{AC} < 1.0$	Reactive Azeotropes may exist	0.475

and so must be recognized. If a reactive azeotrope exists, it could impact the product purity and/or reactant conversion depending on the reactive azeotrope composition and boiling point, just like non-reactive azeotropes impact conventional distillation columns.

The volatility order regions where reactive azeotropes may exist are indicated in Table 2. In these regions, reactive azeotropes may or may not exist depending on the chemical equilibrium constant and the magnitude of the product and reactant relative volatilities. The conditions for a reactive chemical system to potentially have a reactive azeotrope have been determined by Barbosa and Doherty (1988d). As a general rule, for chemical reactive systems of constant relative volatility, reactive azeotropes can only occur if the volatility of all the reactants is either higher or lower than the volatility of all the products. A commercial version of the University of Massachusetts Fortune reactive distillation analysis software contained within Hyprotech Distil 2.0.1 was used to evaluate the relative volatility and chemical equilibrium combinations within these regions to identify any existing reactive azeotropes. The presence of a reactive azeotrope for a given combination within a region was included in the data evaluation and was noted if the reactive azeotrope had any impact on the final product purity or reactant conversion.

Reactive Distillation Systems for Heuristic Verification

The heuristics generated from this research project were compared to chemical systems currently available in the reactive distillation literature in order to verify that the heuristic rules and diagrams were applicable and correct. A list of reactive distillation systems for use in verification of the heuristics derived from the research is shown in Table 3.

Table 3. Reactive Distillation Literature Examples

Reactive Distillation System	Boiling Points (°C)	Relative Volatilities (α_{AC})	K_{eq}
A↔C			
1,4-dichloro-2-butene (A) ↔ 1,2-dichloro-3-butene (C)	A=156 C=115	α_{AC}=0.33	0.66
2-methyl-1-butene (A) ↔ 2-methyl-2-butene (C)	A=31 C=39	α_{AC}=1.32	12.0
2,4,4-trimethyl-1-pentene (A) ↔ 2,4,4-trimethyl-2-pentene (C)	A=102 C=105	α_{AC}=1.10	0.30
α-isophorone (A) ↔ β-isophorone (C)	A=203 C=174	α_{AC}=1.9	0.02
A+B↔C			
iso-Propylene (A) + Benzene (B) ↔ Cumene (C)	A= -48 B= 80 C=152	α_{AB} = 50 α_{AC} = 500	5.0
A↔C+D			
Cumene (A) ↔ iso-Propylene (C) + Benzene (D)	A=152 B=-48 C=80	α_{AC} = 0.002 α_{AD} = 0.1	0.2
A+B↔C+D			
2-Pentene (A) + 2-Pentene (B) ↔ 2-Butene (C) + 3-Hexene (D)	A = 37 B = 37 C = 3.7 D = 66	α_{AB} = 1.00 α_{AC} = 0.33 α_{AD} = 2.84	0.25
Methanol (A) + Acetic Acid (B) ↔ Methyl Acetate (C) + Water (D)	A = 64 B = 118 C = 56 D = 100	α_{AB} = 6.5 α_{AC} = 0.87 α_{AD} = 3.7	20
Acetic Acid (A) + Butanol (B) ↔ Butyl Acetate (C) + Water (D)	A = 118 B = 118 C = 126 D = 100	α_{AB} = 1.01 α_{AC} = 1.28 α_{AD} = 0.54	12.5
iso-Propanol (A) + Acetic Acid (B) ↔ iso-Propyl Acetate (C) + Water (D)	A = 82.6 B = 118 C = 88.9 D = 100	α_{AB} = 3.6 α_{AC} = 1.28 α_{AD} = 1.97	8.7

IV. MODELING AND SIMULATION

Simulations of the various reactive systems were conducted to generate a database with which to develop the desired heuristic rules and diagrams. These simulations of the generic reactive systems were performed using Aspen Technology Aspen Plus® simulation software driven by a Microsoft® Excel/Visual Basic program. The Excel/Visual Basic program was used to step the Aspen Plus simulator through the changing column stages, physical properties, reflux ratios, distillate to feed ratios, and column designs. The Excel/Visual Basic program was also used to collect the simulation results for further analysis.

Assumptions

This research project assumed the following: (1) the vapor and liquid phases were ideal, (2) chemical equilibrium was attained on every reactive stage, (3) chemical reaction occurred only in the liquid phase, and (4) vapor-liquid equilibrium was attained on every stage. Although one of the great benefits of reactive distillation is the ability to overcome non-reactive azeotropes that limit the more traditional design of separate reaction and distillation units, this initial project focused on simple systems and provides an initial set of heuristics based on the research assumptions. The results from this research project can be used as a stepping stone for future research with more complicated reactive distillation systems such as those containing non-reactive azeotropes, kinetically controlled reactions, and mass transfer limited designs.

Mass Transfer Affects and Kinetically Controlled Reactions

Understanding the affects of mass transfer and kinetically controlled reactions are an integral part to an effective evaluation of feasibility and design for reactive distillation processes. Mass transfer (Subawalla et al, 1997;Akbarnejad et al., 2000; Higler et al., 2000; Baur et al., 2000a,b; Van Baten et al., 2001) and kinetically controlled reactions (Chadda et al., 2001; Buzad and Doherty, 1994, 1995; Lee et al., 2003) are currently an area of active research for reactive distillation. Although mass transfer and kinetically controlled reactions are very important in the rigorous analysis of reactive distillation feasibility and design, adjustments can initially be made by assuming a reaction or mass transfer efficiency for the initial reactive distillation column. Later on in the process design, increasing liquid hold up or other unique adjustments may be made to overcome the process mass transfer or reaction kinetic limitations. This research project focused on the problems that exist from the vapor-liquid equilibrium and chemical equilibrium when combining reaction and distillation and not the unique problems that occur with mass transfer or kinetically controlled reactions.

Heat Effects

In the initial feasibility and design assessment of traditional distillation columns, it is standard practice to initially ignore heat affects and assume a constant molar overflow model. Constant molar overflow exists if the liquid and vapor rates within the distillation column are constant and can be assumed when the column is adiabatic and the heat of vaporization is constant. This is usually a good starting point as the heats of vaporization are usually much larger than the heat of mixing and also larger than the differences in pure component heats of vaporization. However, when a chemical reaction is added to the distillation mixture, an additional release or consumption of heat occurs that is not normally present within a traditional distillation column.

A study on heat effects within a reactive distillation column was conducted by Pohjola and Tanskanen (2000). The conclusion of this study was that heat effects within a reactive distillation with a heterogeneous catalyst cancel out and can be ignored when computing composition profiles within the column except for the case when mass transfer is very poor. Since one of the assumptions within this study is that chemical reaction and vapor-liquid equilibrium is attained on every stage, heat effects can be safely ignored for the composition profiles in this research project. However, this study did point out that heat effects within a reactive distillation column may have an effect on molar flows within the column.

In this research project, heat effects from the heat of reaction were ignored with the heat of reaction fixed to be athermal irregardless of the value of the chemical reaction equilibrium constant. This assumption should have negligible consequences on the results from this research project except for very large or very small values of the chemical reaction equilibrium constant where the heats of reaction may be large. For these values, the effects of ignoring the heat of reaction has not been reported in the reactive distillation literature in great detail, although it has been suggested that ignoring the heat effects from heat of reaction can result in non-equimolar liquid and vapor flows within the reactive distillation column (Pohjola and Tanskanen, 2000). Okasinski and Doherty (1998) reported the effects of varying heats of reaction for an individual reactive distillation example. For a given reboil ratio, their results indicate that only a small number of additional stages were required to produce the same distillate and bottoms streams for an athermal and an endothermic reaction when compared to an exothermic reaction. Future research studies should be undertaken to further evaluate the consequences of ignoring heat effects for the design and feasibility of reactive distillation.

Generic Compound Physical Properties

The physical properties for the generic compounds in this research project were estimated from the actual physical properties from a small list of real chemicals. These real chemicals were chosen because of their use in reactive distillation processes, but a few of the compounds were chosen at random. Table 4 lists the chosen real chemicals along with their physical properties (Dean, 1992).

Table 4. Data for Generic Component Physical Property Development

Compound	$T_{bp,i}$ (K)	A1	A2	A3	M_w	T_c (K)	P_c (atm)	V_c (cc/mol)
Acetic Acid	391	7.388	1533	222	60.1	594.4	57.1	171
Acetic Anhydride	413	7.150	1444	200	102.1	569.0	46.2	290
Benzene	353	6.906	1211	221	78.1	562.1	48.3	259
Dimethyl Ether	248	6.976	889	242	46.1	400.0	53.0	178
Ethylbenzene	409	6.957	1424	213	106.2	617.1	35.6	374
Methanol	338	7.898	1474	229	32.0	512.6	79.9	118
Methyl acetate	330	7.065	1157	220	74.1	506.8	46.3	228
n-Hexane	342	6.876	1171	224	86.2	507.4	29.3	370
n-Pentane	309	6.853	1064	233	72.2	469.6	33.3	304
Propylene	225	6.778	770	246	42.1	365.0	45.6	181
Water	373				18.0	647.3		56

A linear regression was used to correlate each variable with the boiling point or molecular weight of the real compound. These linear equations were then used to calculate the following required physical properties for each generic compound used in the Aspen Plus simulations.

Antoine Equation

The Antoine equation is used to calculate the vapor pressure of each compound. The Antoine equation is widely applied for the description of vapor-liquid equilibria and values for the equation constants for a wide number of chemical compounds have been tabulated. The Antoine equation is

$$\log\left(P_i^{sat}\right) = A1 - \left(\frac{A2}{T + A3}\right) \tag{4.1}$$

where T = °C. The Antoine coefficients (A1, A2, and A3) for each real compound from Table 4 were plotted vs. their boiling point at atmospheric pressure except for water. A linear regression of this data resulted in the following linear equations that were used for the calculation of the generic compound Antoine coefficients. The linear regression used for the development of these equations was a feature within Excel and was used for all linear regressions in this research study.

The generic Antoine coefficients calculated using Equation 4.2 are applicable in the boiling point temperature range of -40°C to 125°C. Outside of these limits, the correlations do not generate a vapor pressure that is acceptable to Aspen Plus (i.e. the

$$
\begin{aligned}
A1 &= 0.0017\left(T_{bp,i}\right)+6.5216 \\
A2 &= 3.7543\left(T_{bp,i}\right)-47.168 \\
A3 &= -0.1969\left(T_{bp,i}\right)+291.13
\end{aligned}
\qquad (4.2)
$$

normal boiling point vapor pressure must be within ±10% of 1 atm). It should be noted that the vapor pressure correlations were developed only to provide a calculated reaction component relative volatility. The proposed heuristics reported in this research project are dependent on the relative volatilities only and not the actual calculated vapor pressures from Equations 4.1 and 4.2.

Critical Temperature

The generic component critical temperature (T_c) was required for the calculation of the heat of vaporization, critical compressibility factor, enthalpy, entropy, and density calculations within Aspen Plus. The compounds from Table 4 were plotted vs. their boiling points at atmospheric temperature. A linear regression of this data resulted in the following equation that was used for the calculation of the generic compound critical temperature.

$$T_c = 1.3475\left(T_{bp,i}\right)+65.6 \qquad (4.3)$$

Critical Pressure

The generic component critical pressure (P_c) was required for the calculation of the heat of vaporization, critical compressibility factor, and density calculations within Aspen Plus. The compounds from Table 4 were plotted vs. their molecular weights. A linear regression of this data resulted in the following equation that was used for the calculation of the generic compound critical pressure.

$$\mathrm{P_c} = -0.3943(\mathrm{M_w})+75.02 \qquad (4.4)$$

Critical Volume

The generic component critical volume (V_c) was required for the calculation of the critical compressibility factor and the generic component density calculation within Aspen Plus. The compounds from Table 4 were plotted vs. their molecular weights. A linear regression of this data resulted in the following equation that was used for the calculation of the generic compound critical volume.

$$\mathrm{V_c} = 3.2736(\mathrm{M_w})+16.547 \qquad (4.5)$$

Critical Compressibility Factor

The critical compressibility factor (Z_c) for each generic component was calculated from the individual correlations for the component critical pressure, temperature, and volume as shown below and was required for calculating the liquid molar volume in Aspen Plus.

$$Z_c = \frac{P_c V_c}{RT_c} \tag{4.6}$$

Heat of Vaporization (Riedel Equation (Smith and Van Ness, 1987))

The Riedel equation was used for the calculation of the heat of vaporization and is shown below:

$$H_{vap} = 1.092 RT_{bp.i} \frac{\ln(1.01325 P_c) - 1.013}{0.93 - \left(\frac{T_{bp,i}}{T_c}\right)} \tag{4.7}$$

The individual component heat of vaporization calculated from this equation is assumed to be constant in all simulations for this research project.

Simulations

Aspen Plus simulation software has been used extensively in industry and academia to evaluate and design reactive distillation columns for a wide variety of reactive chemical systems (Lee et al., 2000a; Smejkal and Soos, 2002; Venkataraman et al., 1990; Abufares and Douglas, 1995; Hanika et al., 2001). The reactive chemical systems for this research project were simulated using Aspen Plus software to evaluate the economic feasibility for each chemical reaction system. All reactive distillation columns were operated at a column pressure of 1 atm.

The IDEAL property method within Aspen Plus was used for all simulations (Aspen Physical Property Methods and Models, 2001).This property method accommodates Raoult's Law and uses the ideal activity coefficient model for the liquid phase (γ_i=1), the ideal gas equation of state PV^1_m=RT for the vapor phase, and the Rackett model for liquid molar volume (V^1_m).

Raoult's Law

Raoult's Law is used to compute vapor-liquid equilibrium for multicomponent systems and is given by:

$$y_i P = x_i P_i^{sat} \tag{4.8}$$

Molar Volume (Rackett Equation)(Aspen Physical Property Methods and Models, 2001)

The Rackett equation was used by Aspen Plus to calculate the liquid molar volume for the liquid phase mixture.

$$V_m^l = \frac{RT_c\left(Z_m^{RA}\right)^{\left[1+(1-T_r)^{2/7}\right]}}{P_c} \qquad (4.9)$$

Heat Capacity

$$C_p^{*,ig} = 29.1\frac{\text{kJ}}{\text{kmol}\cdot\text{K}} \qquad (4.10)$$

Excel/Visual Basic Program

Aspen Plus simulation software does not have the capability to complete all of the simulations proposed in this research project without significant intervention. In order to reduce the time required to complete this research, a Visual Basic program within Excel was written to drive the Aspen Plus simulator for each reactive chemical system studied in this research project. This program:

1. sets the generic physical properties for each simulation
2. sets the initial reactive distillation column design parameters (F_D/F_F ratio, etc)
3. varies the chemical equilibrium constant
4. varies the reflux ratio
5. varies the number of reactive, rectifying, and stripping stages
6. varies the feed stage location
7. calculates the reactant conversion, product purity, relative volatility, etc.
8. collects the feasible reactive distillation column results in an Excel worksheet

The Visual Basic program was adjusted based upon the desired column design, stage stepping rate, and simulation conversion time.

V. SYSTEMS WITH ONE REACTANT AND ONE PRODUCT

Introduction

The first generic system studied was the A↔C system, which is the simplest example for reactive distillation. Potential boiling points and corresponding relative volatilities for this particular chemical reactive system can be split into two distinct volatility order regions (Table 2). The first region (Region 1) is where the reactant (A) boiling point is lower than the product (C) boiling point ($\alpha_{AC} > 1.0$). With this boiling point ordering, the product is expected to accumulate in the bottom section of the reactive distillation column because it is the highest boiling component in the chemical reactive system. All reactive distillation columns in this region were structured to produce the product in the underflow and with a molar distillate to feed ratio (F_D/F_F) of 0.05.

The second region (Region 2) is where the reactant boiling point is higher than the product boiling point ($\alpha_{AC} < 1.0$). In this region, the product is expected to concentrate in the vapor flow going up the distillation column because it is the lowest boiling component in the chemical reactive system. Therefore, all reactive distillation columns in this region were structured to generate the product in the distillate and were designed with a molar distillate to feed ratio (F_D/F_F) of 0.95, which was selected from mass balance calculations for this region.

It is noted that the distillate flow is small for systems in Region 1 and consists almost entirely of reactant A. Therefore, the distillate stream could be returned completely to the column (deadhead configuration) potentially resulting in further improvement in reactant conversion and product generation. Similarly, the bottoms flow is small for systems in Region 2 and consists almost entirely of reactant A, which could be returned entirely to the column as well. However, this complete return of distillate or bottoms flow was not studied in this research project.

For each region, the component boiling points were broken into a fixed set of relative volatilities covering the studied range of boiling points. For Region 2, the relative volatilities (α_{AC}) selected for study were 0.01, 0.1, 0.25, 0.5, 0.68, 0.83, 0.91, 0.97, and 0.99. For Region 1, they were 1.01, 1.03, 1.10, 1.20, 1.50, 2.0, 4.0, 10.0, and 100. The equilibrium constant (K_{eq}) for the chemical reaction started with 10,000 and was sequentially reduced by a factor of 10 until the economic feasibility criteria was no longer met for a given relative volatility. As was stated in the prior section on feasibility, the acceptance criteria for an economically feasible reactive distillation column was that total column stages were less than 100, the reactant conversion was greater than 95.0%, and the product purity was greater than 99.0%.

A↔C Economic Feasibility: Configuration II

We will start with Configuration II (Figure 6), which is defined as a reactive distillation column with a reactive section, a non-reactive stripping section, and a non-reactive

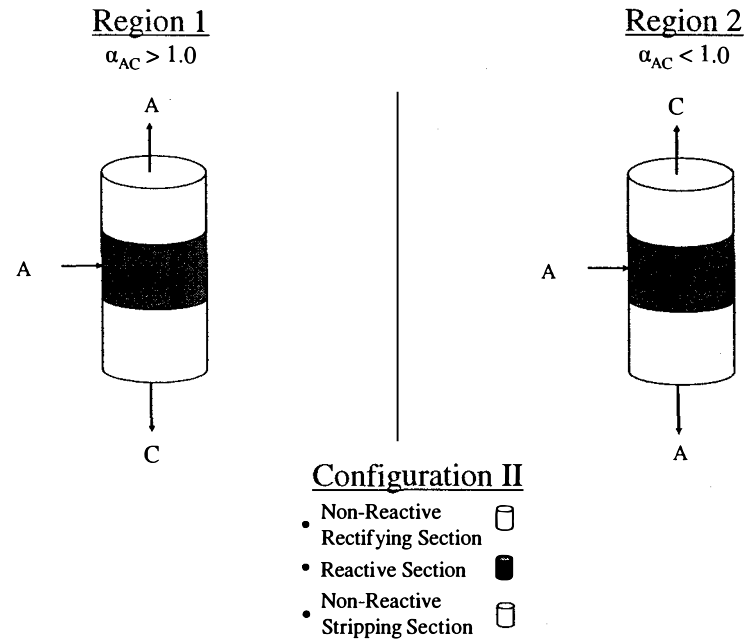


Figure 6. A↔C Configuration II

rectifying section. As shown in Figure 6, when the reactant (A) is the lowest boiling component ($\alpha_{AC} > 1.0$), the product (C) is designed to be the primary bottoms constituent. When the reactant is the highest boiling component in the binary system ($\alpha_{AC} < 1.0$), the product is designed to be the primary distillate constituent.

There was just one reactive stage in all simulated reactive distillation columns for the A↔C system because additional reactive stages did not improve the overall reactant conversion. Any concentration enhancement provided by distillation on the initial reactive stage will be countered back to the chemical reaction equilibrium composition on the next reactive stage since chemical reaction equilibrium was assumed on every reactive stage. Therefore, additional reactive stages do not provide any benefit for the A↔C system and actually hinders the ability of the column to meet the economic feasibility criteria by adding unnecessary stages to the reactive distillation column. This is only true for a binary reactive system. This configuration also requires at least one non-reactive stripping and one non-reactive rectifying stage, with additional stripping and/or rectifying stages added to the column if necessary to further separate the reactant from the product.

Figure 7 shows feasibility boundaries (reactant conversion > 95.0%, product purity > 99.0%, total column stages < 100) for the combinations of relative volatility and chemical reaction equilibrium for A↔C for a reactive distillation column of Configuration II and a reflux ratio of 100. Figure 7 is an example of an Economic Feasibility Diagram which plots the chemical reaction equilibrium constant (K_{eq}) on the x-axis, the relative volatility

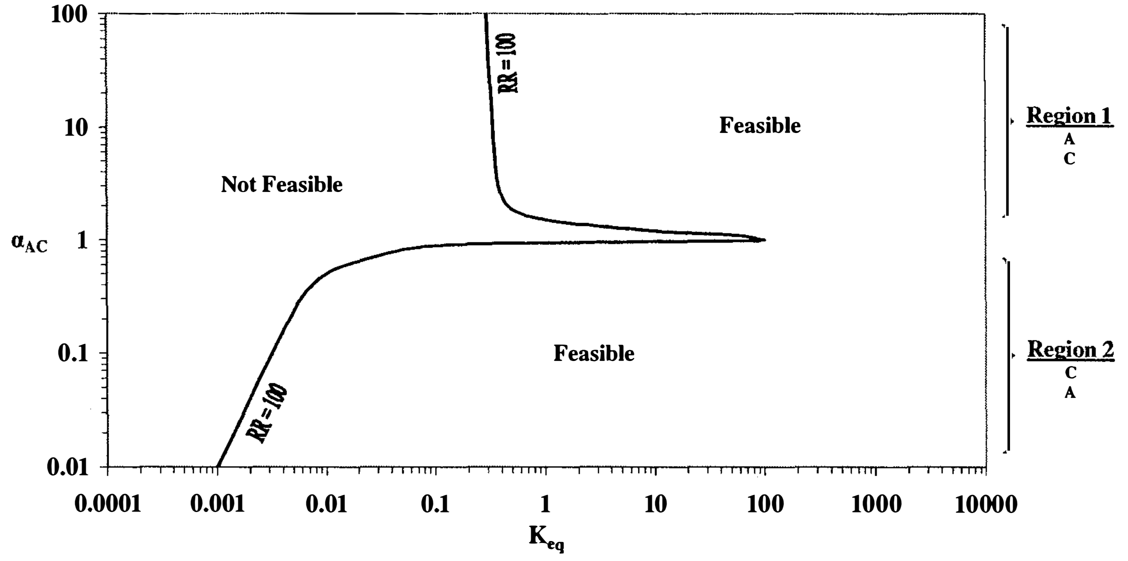


Figure 7. A↔C Economic Feasibility Diagram RR=100 Configuration II

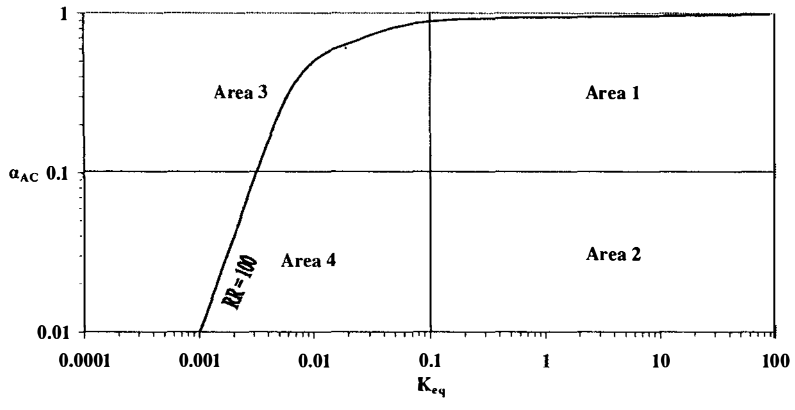
(α_{AC}) on the y-axis, and the economic feasibility boundary for a chosen reflux ratio (or reflux ratios). The boiling point orderings for each region are shown in each Economic Feasibility Diagram and are located below the region label. For example, for Region 1 in Figure 7, the reactant is the lowest boiling component and is located on top of the list and the product is the highest boiling component and is located on the bottom of the list. For $\alpha_{AC} < 1.0$ (C is the distillate product), the economically feasible combinations of relative volatility and chemical reaction equilibrium are below the boundary, while the economically feasible combinations for $\alpha_{AC} > 1.0$ (C is the bottoms product) are above the boundary. For example, a combination of $\alpha_{AC} = 0.1$ and $K_{eq} = 1$ is feasible, whereas a combination of $\alpha_{AC} = 10$ and $K_{eq} = 0.01$ is not economically feasible.

The dissymmetry of the chart above and below $\alpha_{AC} = 1.0$ occurs because the chemical reaction takes place only in the liquid phase of the reactive distillation column. When the reactant is the high boiling component (i.e. $\alpha_{AC} < 1.0$), the product is removed from the liquid phase because it is the lighter of the two components and will preferentially boil into the vapor phase away from the reacting liquid mixture. This improves the binary reactive system's ability to overcome the limitations set by chemical reaction equilibrium because the product is continually removed from the reacting liquid phase while the reactant stays in the liquid phase. This continual concentration of the reactant in the reacting liquid phase enhances the range of feasibility for this region. When the reactant is the low boiling component (i.e. $\alpha_{AC} > 1.0$), the product can be removed from the reacting stage because it is the heavier of the two components and will drop away from the reactive zone if the reactive zone is placed high in the column. This removal of the product from the reactive zone will enhance the conversion of the reactant. However, the reactant will preferentially boil into the vapor phase and will not concentrate in the reacting liquid phase. This phenomenon hinders reactant conversion and is a situation when distillation may actually hinder the ability of the reacting mixture to meet the economic feasibility criteria. When $\alpha_{AC} > 1.0$, reactive distillation may still have advantages over separate reaction and distillation processing units, but the economic feasibility will not extend to as small values of the chemical reaction equilibrium constant because the reactant is the low boiling component.

A qualitative review of Figure 7 indicates that certain areas of the Economic Feasibility Diagram share certain characteristics. When $\alpha_{AC} < 1.0$ and $K_{eq} > 0.1$, the diagram indicates that almost all relative volatilities for binary chemical reactions meet the economic feasibility criteria. In this area, the chemical reaction equilibrium constant is large enough to overcome almost all separation limitations caused by relative volatility. For smaller chemical reaction equilibrium constants, less reactant is converted into product and it becomes harder to meet the economic feasibility criteria. Where $\alpha_{AC} < 1.0$ and $K_{eq} < 0.01$, the chemical reaction equilibrium constant is actually so small that it is now the limiting factor for reactive distillation to meet the economic feasibility criteria and not the relative volatility.

When the relative volatility of the binary reactive system is close to 1.0, the reactant and product are more difficult to separate by distillation and the relative volatility of the components is the limiting factor for reactive distillation. Figure 7 indicates that if $\alpha_{AC} > 0.5$, the relative volatility becomes the limiting factor for reactive distillation to meet the economic feasibility criteria. Where $\alpha_{AC} < 0.5$, the reactant and product separation actually helps to overcome chemical equilibrium because the product is preferentially removed from the reacting liquid phase which helps to drive the chemical reaction conversion of the reactant. In this area of Figure 7, the relative volatility is actually helping reactive distillation meet the economic feasibility criteria.

Further analysis of these qualitative assessments indicates that one can divide the $\alpha_{AC} < 1.0$ area of the diagram into four distinct areas (Figure 8). In the first area (Area 1), the chemical reaction equilibrium constant is large, but the boiling points of the reactant and product are close so the separation is the limiting factor in meeting the economic feasibility criteria. In the second area (Area 2), both the chemical reaction and separation contribute positively to the reactive distillation design because the chemical reaction equilibrium constant is large and the reactant and product boiling points are not close. In the third area (Area 3), the chemical reaction equilibrium constant is small and so the chemical reaction is not generating much product. Additionally, the reactant and product boiling points are close and they are more difficult to separate by distillation. Therefore, both the chemical reaction and the separation are hindering the ability of the binary reactive system to meet the economic feasibility criteria. In the fourth area (Area 4), the separation of the reactant and product contributes positively to reactant conversion and product purity because the product can be easily separated from the reactant and the reacting liquid phase. However, the chemical reaction equilibrium constant is small and so the chemical reaction limits the ability of the chemical system to meet the economic feasibility criteria.



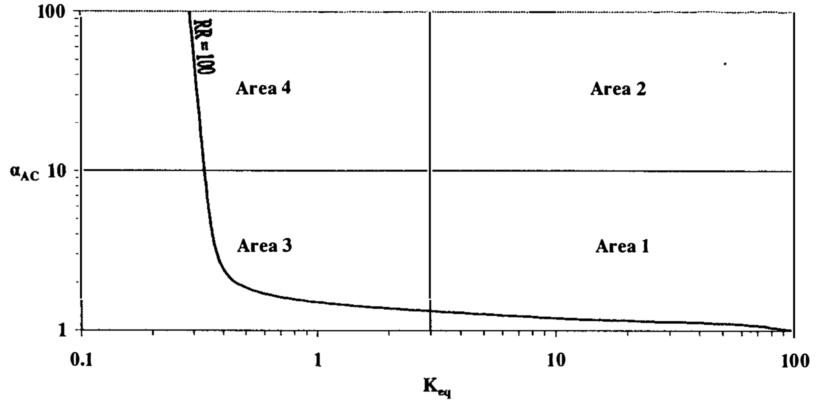
(3) K_{eq} is limiting α_{AC} is limiting	(1) K_{eq} is not limiting α_{AC} is limiting
(4) K_{eq} is limiting α_{AC} is not limiting	(2) K_{eq} is not limiting α_{AC} is not limiting

Figure 8. A↔C Economic Feasibility Diagram $\alpha_{AC} < 1.0$ Limiting Areas

This qualitative assessment can be made for $\alpha_{AC} > 1.0$ as well (Figure 9). For each area described in the case where $\alpha_{AC} < 1.0$, there is an area that has the identical limitations for the $\alpha_{AC} > 1.0$ section of the diagram. In Area 1, the chemical reaction equilibrium constant is large, but the separation is limiting the economic feasibility. In Area 2, both the chemical reaction and separation contribute positively to the reactive distillation column design. In Area 3, both the chemical reaction and the separation are limiting. In Area 4, the separation of product from the reactant contributes positively but the chemical reaction is limiting the ability of the binary reactive system to meet the economic feasibility criteria for reactive distillation.

For each of the economic feasibility boundaries shown in Figures 8 and 9, it is interesting to note that the boundary is essentially a straight line within Areas 1 and 4. It is only in Area 3 where the feasibility boundary is not a straight line. This can be explained because in this area both the separation and chemical reaction are similar in contribution when it comes to the ability of the binary reactive system to meet the economic feasibility criteria. This transition from limiting cases (Areas 1 and 4) produces in an area (Area 3) where it is difficult to meet the economic feasibility criteria for reactive distillation because both separation (i.e. distillation) and chemical reaction are not helping overcome any limitations inherent in the binary reactive system.

Further data were collected for reflux ratios from 100 down to 1.0 for the A↔C system with the economic feasibility boundaries for each reflux ratio (Figure 10). Figure 10



(4) K_{eq} is limiting α_{AC} is not limiting	(2) K_{eq} is not limiting α_{AC} is not limiting
(3) K_{eq} is limiting α_{AC} is limiting	(1) K_{eq} is not limiting α_{AC} is limiting

Figure 9. A↔C Economic Feasibility Diagram $\alpha_{AC} > 1.0$ Limiting Areas

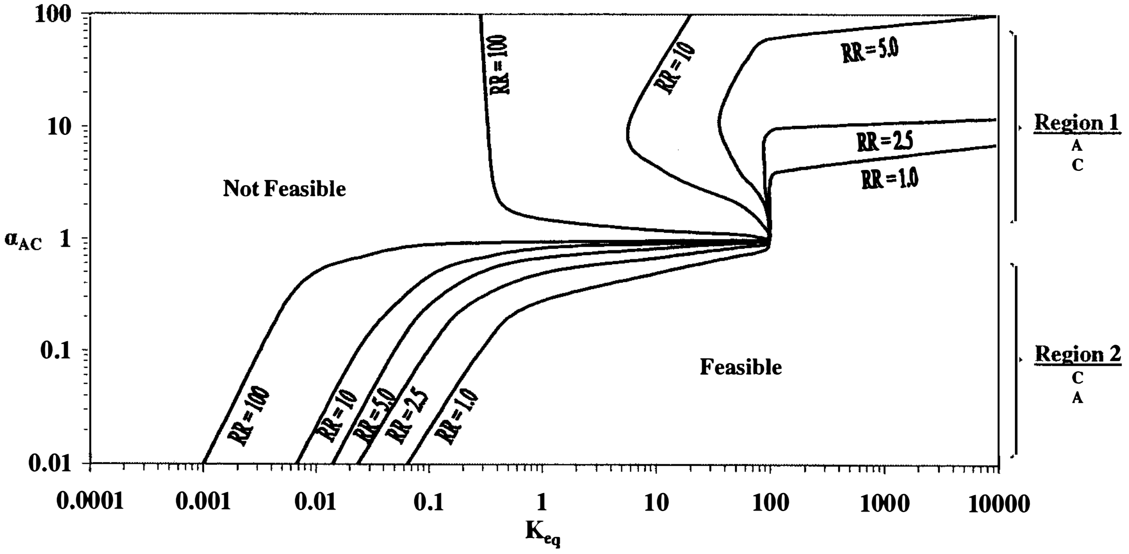


Figure 10. A↔C Economic Feasibility Diagram Configuration II

shows the continuum of feasibility boundaries for the A↔C system for the reflux ratios studied in this research project. Since a fixed set of reflux ratios were used, the feasibility boundaries provide an initial indication of the reflux ratio required to meet the economic feasibility criteria. For example, if the chemical system of interest has a $K_{eq} = 1.0$ and a $\alpha_{AC} = 0.4$, a reactive distillation column with Configuration II should require a reflux ratio between 1.0 and 2.5 to meet the economic feasibility criteria.

Economically acceptable reflux ratios and hence, energy consumption and operating cost, depend upon the situation. Considerations include such factors as the distillate to feed ratio and the value of the desired product. For example, in cases where only reactants appear in the distillate and the distillate to feed ratio is very small, a very large (or even infinite) reflux ratio may be economically acceptable, while in other cases where the distillate contains principally product, a reflux ratio even as large as 5 may be economically prohibitive.

A review of Figure 10 shows that the area of economic feasibility increases with increasing reflux ratio for all combinations of relative volatility and chemical reaction equilibrium constant. The need for larger reflux ratios with smaller chemical reaction equilibrium constants is a function of reactant conversion. With larger reflux ratios, the reactant spends more time in the reactive distillation column and hence, more time in contact with the catalyst. If the product can be preferentially separated from the reactant at these larger reflux ratios, then more reactant will be converted to product following Le Chatelier's principle. This allows systems with smaller chemical reaction equilibrium constants to meet the economic feasibility criteria for a given relative volatility.

All economic feasibility boundaries shown in Figure 10 have the same general shape except for the boundaries in the upper right hand corner of the diagram, specifically where K_{eq}'s > 1 and $\alpha_{AC} > 3$. One may initially anticipate that with a positive chemical reaction equilibrium constant, a binary reactive system with a relative volatility of 100 would be better than a system with a relative volatility of 10 due to the better separation of reactant and product. However, that is not the case for reflux ratios less than approximately 100. The reason that a large positive relative volatility does not enhance the economic feasibility of a reactive distillation column is due to the large concentration of reactant in the non-reactive vapor phase. For large positive relative volatilities, the reactant is removed from the reacting liquid phase to a much greater extent than with smaller relative volatilities, which results in the reactant not "seeing" the catalyst and concentrating in the top of the reactive distillation column. For reflux ratios less than 100, the reactant accumulated in the top of the reactive distillation column is not returned back to the column reactive zone for further conversion to product and the reactant is allowed to leave the reactive distillation column in the distillate stream without being converted to product. Therefore, larger than expected reflux ratios are required to meet the economic feasibility criteria for chemical reactive systems with a $\alpha_{AC} > 1.0$ and a given chemical reaction equilibrium constant.

The upper right portion of Figure 10 is shown in greater detail in Figure 11. This portion of the Economic Feasibility Diagram can be broken into sections where certain phenomena are controlling economic feasibility. The first section is where the chemical reaction equilibrium constant is large enough to overcome any difficulties in separating the product from the reactant. The second section of economic feasibility is where the reactant boiling point approaches the product boiling point. This causes the separation of the product from the reactant to become difficult and larger chemical reaction equilibrium constants are required to meet the economic feasibility criteria. The next section of the boundary is controlled by the chemical reaction. Here the reactant volatility is small enough so the reactant "sees" the catalyst in the reacting liquid phase without being so close to the product volatility that the separation of the product from the reactant is now limiting, but the chemical reaction equilibrium is now small and limits the economic feasibility of the reactive chemical system. For reflux ratios < 100, an additional section of economic feasibility is found. Within this section, the feasibility of reactive distillation is controlled by the reactant volatility. The reactant is so volatile and the reflux ratio is so small that the volatile reactant is not in sufficient concentration in the reacting liquid phase to generate enough product to meet the economic feasibility criteria. The different areas described within Figure 11 show the complexity of reactive distillation and how process intensification can result in unique and very distinct areas of operation.

It is important to recognize that for A↔C reactive systems, the reactant rich distillate or bottoms streams could actually be returned entirely back to the reactive distillation column, which could help drive the complete conversion of the reactant to product. For example, if the component boiling points fall within Region 1, the reactant will

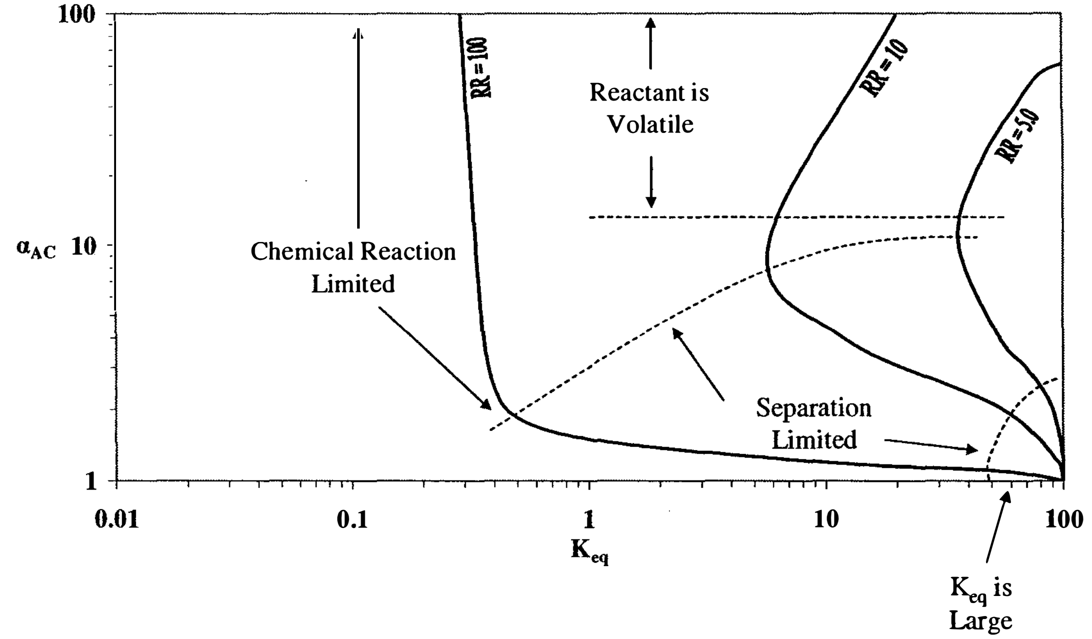


Figure 11. A↔C Economic Feasibility Diagram: Config. II, RR≤100, α_{AC}>1.0

concentrate in the top of the reactive distillation column because it is the lowest boiling component in the system. The distillate stream from the reactive distillation column can be returned entirely to the column with the product leaving the reactive distillation column in the bottoms stream. For systems in Region 2, a similar design with the complete return of the bottoms stream to the column is expected to provide the same advantages in reactant conversion and product generation. This deadheading of the reactive distillation could be another economically acceptable design than the designs included in this research project.

A↔C Reactive Azeotropes

It is extremely important to be aware of reactive azeotropes when assessing the feasibility of reactive distillation. Their presence can inhibit the effectiveness of reactive distillation(Okasinski and Doherty, 2000; Song et al., 1997) and need to be included in the initial assessment of reactive distillation feasibility and design.

For the reactive A↔C generic system, the presence of reactive azeotropes was determined with the results shown in Figure 12. A detailed review of this data shows that all binary reactive systems have reactive azeotropes and that the composition of these binary reactive azeotropes is independent of relative volatility. This independence is true only for binary reactive systems because any liquid phase composition difference caused by the separation of the reactant and product (i.e. relative volatility) will be corrected back to the chemical reaction equilibrium composition when the mixture reaches a reactive stage. For example, if the product is preferentially separated from the reacting liquid mixture, the product rich vapor will react back to the chemical reaction equilibrium

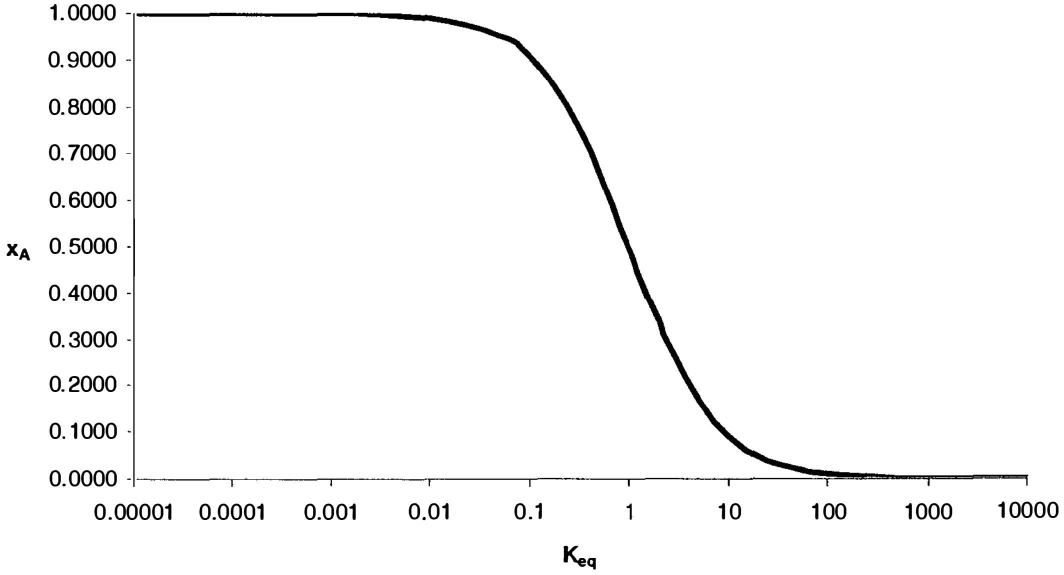


Figure 12. A↔C Reactive Azeotropes

composition when it reaches a reactive stage. This singularity results in a reactive residue curve map that is a single point. So for a binary reactive system, the distillate and/or bottoms composition will be the reactive azeotrope composition if the top and/or bottom stage of the column is a reactive stage and this composition is only dependent on the chemical reaction equilibrium constant.

For chemical reactive systems with more than two components, the reactive azeotrope composition is dependent on the relative volatilities of the individual components and the chemical reaction equilibrium constant, if a reactive azeotrope exists. The component composition of the reactive azeotrope will be at chemical reaction equilibrium, but the reactive azeotrope composition will also be dependant on the relative volatility of the system because of the additional degree of freedom provided by the presence of more than two components.

A↔C Economic Feasibility: Configurations I and III

Configuration II, with both non-reactive stripping and rectifying stages, is able to overcome any limitations caused by the presence of reactive azeotropes because the reactive azeotropes are destroyed by the non-reactive stages of the column. However, there are other reactive distillation configurations beside Configuration II. A reactive distillation column with a reactive section and a non-reactive rectifying section was designated as Configuration III in this study (Figure 13).

Figure 13 outlines the expected distillate and bottoms products for the two different

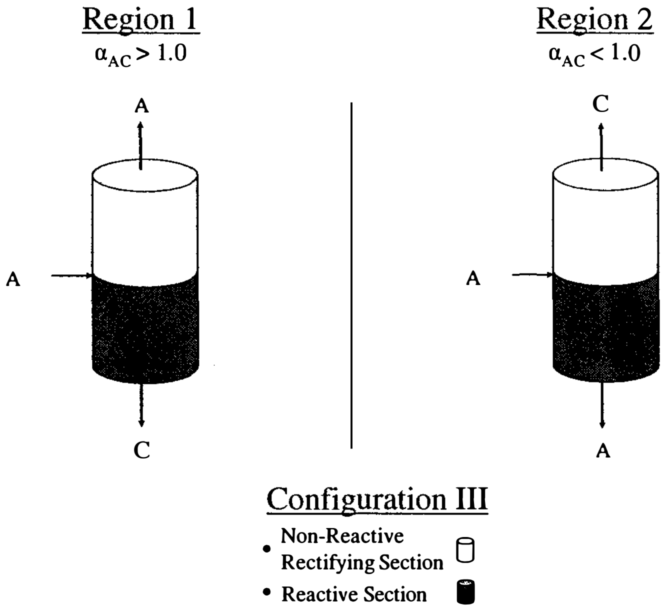


Figure 13. A↔C Configuration III

regions within the A↔C system for a reactive distillation column of Configuration III. In Region 2, the product is lighter than the reactant and so is expected to concentrate in the distillate product. The presence of reactive azeotropes does not hinder Configuration III in this region because the product has to pass through at least one non-reactive stage before leaving the reactive distillation column. However, in Region 1 the product is the heavier component and is expected to be the primary bottoms product. Since the product is designed to leave the reactive distillation column through a reactive stage, the composition of the column underflow will be limited to the reactive azeotrope composition. This limitation on the underflow composition for Region 1 was verified by the simulations and can be seen in the A↔C Economic Feasibility Diagram for Configuration III in Figure 14.

If one compares Figure 10 for Configuration II with Figure 14 for Configuration III, one can see a striking difference along with similarities. In Region 2 where $\alpha_{AC} < 1.0$, the feasibility boundaries for Configurations II and III are essentially the same for all studied reflux ratios. The results for $\alpha_{AC} < 1.0$ are similar for both Configurations II and III because the advantage gained by purifying the low boiling product with non-reactive rectifying stages is maintained in both configurations. The expected disadvantage that Configuration II would have when compared to Configuration III is that Configuration II has to have at least one non-reactive stripping stage. The presence of this non-reactive section allows the liquid phase with the higher boiling reactant to move down the column and leave the reactive section which could hinder the conversion of reactant to product to some degree. However, this limitation must not be large for the A↔C system and probably is due to the requirement that only one non-reactive stage needs to be present for Configuration II. Therefore, the advantage of extending the reactive section to the

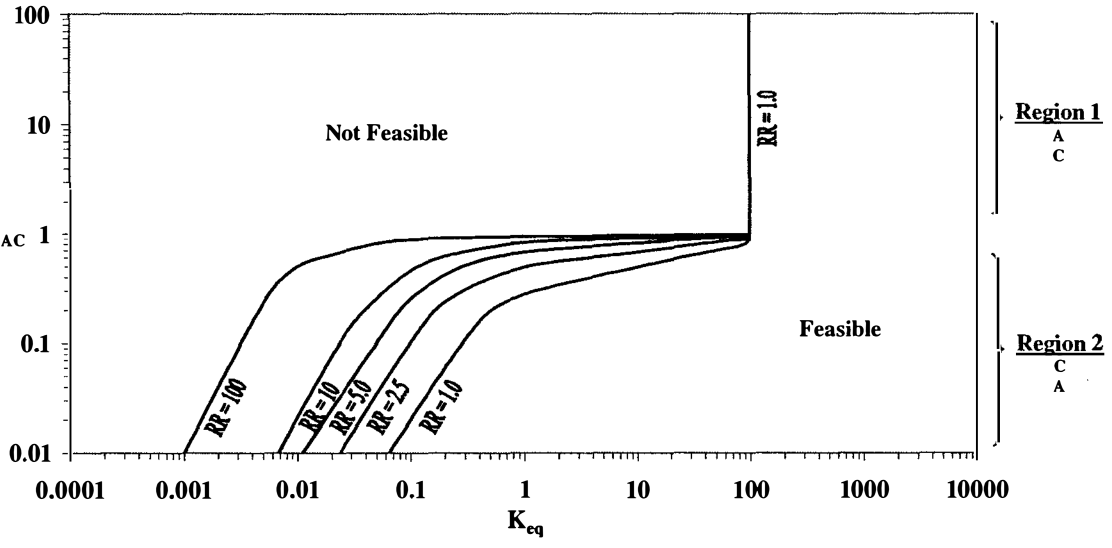


Figure 14. A↔C Economic Feasibility Diagram Configuration III

very bottom of the column is a small one and not significant in this study for the A↔C system.

The four limiting areas described in the discussion of Configuration II (Figure 8) can still be seen in the feasibility boundaries for $\alpha_{AC} < 1.0$ in Configuration III (Figure 14). The feasibility boundaries for Configuration III have the same areas where the relative volatility is limiting, where the chemical reaction equilibrium constant is limiting, where both are limiting, and an area where neither are limiting the ability of the chemical system to meet the economic feasibility criteria.

In Region 1 where $\alpha_{AC} > 1.0$, there are no Configuration III feasibility boundaries for any studied reflux ratios whereas there are feasibility boundaries for Configuration II (compare Figures 14 and 10). This is because of the presence of reactive azeotropes which limit the underflow product composition. As was previously discussed in the section on reactive azeotropes, the underflow composition from the reactive distillation column will always be the reactive azeotrope composition since there are no non-reactive stripping stages in Configuration III. The only chemical reactive systems for $\alpha_{AC} > 1.0$ that are economically feasible for this configuration are for systems with a $K_{eq} > 100$. Reactive azeotropes for these systems still exist, but the product composition has a mole fraction that is greater than 0.99, which meets the economic feasibility criteria for this research project. The limited economic feasibility of Configuration III for Region 1 demonstrates that for binary chemical reactive systems with $\alpha_{AC} > 1.0$, there is no advantage to having non-reactive rectifying stages and the high boiling product gains no advantage from purification by non-reactive stages above the reactive zone.

Another possible configuration for a reactive distillation column is shown in Figure 15. Reactive distillation Configuration I has a reactive section and non-reactive stripping section. The difference between this configuration and Configuration II is that there are no non-reactive rectifying stages above the reactive zone. Once again, the low boiling product in Region 2 is expected to be the primary distillate component for Configuration I while in Region 1 the high boiling product is expected to be the primary underflow component.

As shown in Figure 16, there are no reflux ratios or column stagings that meet the economic feasibility criteria for a reactive distillation column of Configuration I and a $\alpha_{AC} < 1.0$ except for chemical reactive systems with a $K_{eq} \geq 100$, which is once again due to the presence of reactive azeotropes. For a $\alpha_{AC} < 1.0$, the low boiling product is expected to be the primary distillate component (Figure 15). However, the Configuration I feasibility for a $\alpha_{AC} < 1.0$ is limited by the lack of non-reactive rectifying stages and therefore cannot break the reactive azeotropes present in the reaction zone. The only chemical reactive systems that meet the economic feasibility criteria are the systems where the reactive azeotropes have a product mole fraction that is greater than 0.99. Because of these reactive azeotropes, Configuration I was not able to meet the economic feasibility criteria for a $\alpha_{AC} < 1.0$, except for systems with a $K_{eq} \geq 100$.

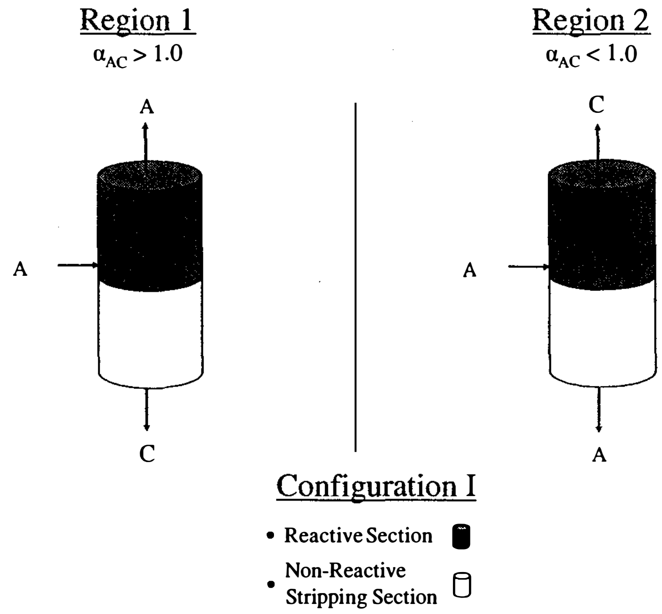


Figure 15. A↔C Configuration I

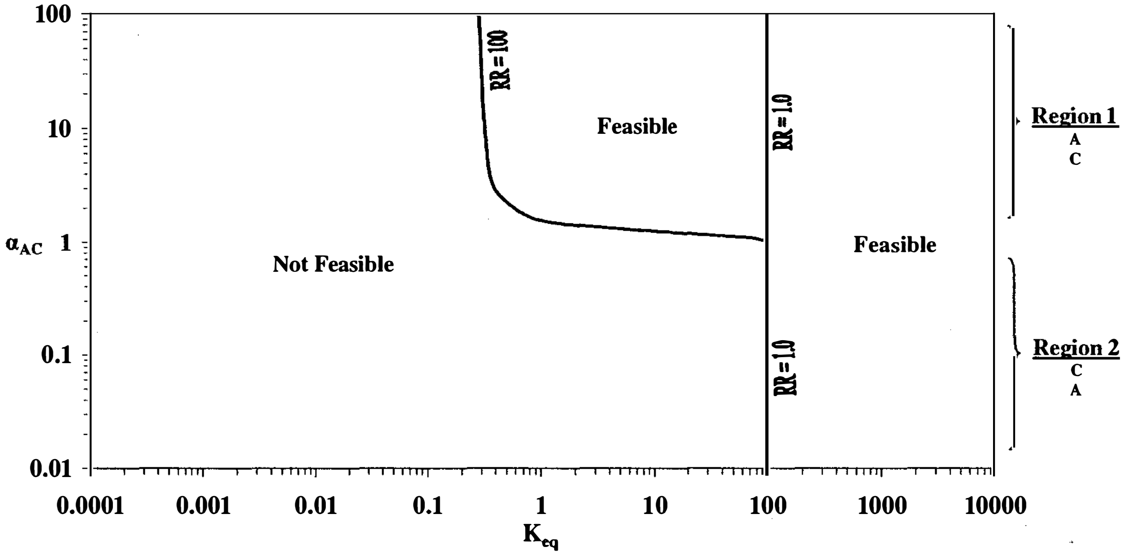


Figure 16. A↔C Economic Feasibility Diagram Configuration I

Given a chemical reactive system with $\alpha_{AC} > 1.0$, the feasibility boundaries for Configuration I are essentially the same as Configuration II for a reflux ratio of 100. For reflux ratios less than 100, the simulations did not converge for any relative volatility combination with a $K_{eq} < 100$. For reactive systems with a $K_{eq} \geq 100$, the reactive distillation column needed a molar F_D/F_F ratio of 0.95 to generate an economically feasible reactive distillation design. Surprisingly, a reactive distillation column with a molar F_D/F_F ratio of 0.05 had difficulty converging and therefore did not meet the economic feasibility criteria. For a molar F_D/F_F ratio of 0.95, the reactive distillation column is essentially operating like a reactor with distillation not playing a significant role in the production or purification of the product. It is expected that for chemical reactive systems with $K_{eq} > 100$, a more traditional reactor and non-reactive distillation column would be the process design of choice over a single reactive distillation column.

By definition, a traditional reactor would meet the economic feasibility criteria for reactant conversion and product purity for all $A \leftrightarrow C$ systems with $K_{eq} \geq 100$. A reactive distillation column might be expected to generate the same results and this was found to be true for Configurations I and III, but not for Configuration II. For chemical reactive systems with a $\alpha_{AC} < 1.0$ and $K_{eq} \geq 100$, reactive distillation columns of Configurations I, II, and III were found to meet the economic feasibility criteria for all relative volatilities and reflux ratios ≥ 1.0 and therefore were able meet the economic feasibility criteria just like the traditional reactor. However, for chemical reactive systems with a $\alpha_{AC} > 1.0$ and $K_{eq} > 100$, only Configurations I and III met the economic feasibility criteria for all relative volatilities and reflux ratios ≥ 1.0. Reactive distillation columns of Configuration III met the criteria with an expected molar F_D/F_F ratio of 0.05. However, Configuration I did not converge with a F_D/F_F ratio of 0.05, but required a F_D/F_F ratio of 0.95 to meet the economic feasibility criteria. With this F_D/F_F ratio, the reactive distillation column of Configuration I was essentially operating like a traditional reactor with distillation not playing a significant role in purifying or producing the desired product.

Reactive distillation columns of Configuration II had mixed results for chemical systems with a $\alpha_{AC} > 1.0$ and $K_{eq} > 100$ (Figure 10). The reason for these mixed results is that reactive distillation columns of Configuration II have two non-reactive sections. These non-reactive sections limit the reactant contact in the liquid phase of the reactive zone, which inhibits reactant conversion to the desired product. If the reactive distillation column of Configuration II is designed with a F_D/F_F ratio of 0.05, the column will meet the economic feasibility criteria for all relative volatilities, but will require larger reflux ratios for those reactive systems where the reactant boiling point is significantly lower than the product boiling point. This is necessary to increase the reactant concentration in the reactive zone of the reactive distillation column. A F_D/F_F ratio of 0.95 is not a viable design because this ratio allows all of the reactant to leave the distillation column without having sufficient concentration with the liquid phase in the reactive zone. Figure 17 summarizes the economic feasibility results for $A \leftrightarrow C$ systems with a $K_{eq} > 100$. These unexpected results highlight the importance of designing the reactive distillation column so that the reactant has sufficient concentration in the liquid phase of the reactive zone.

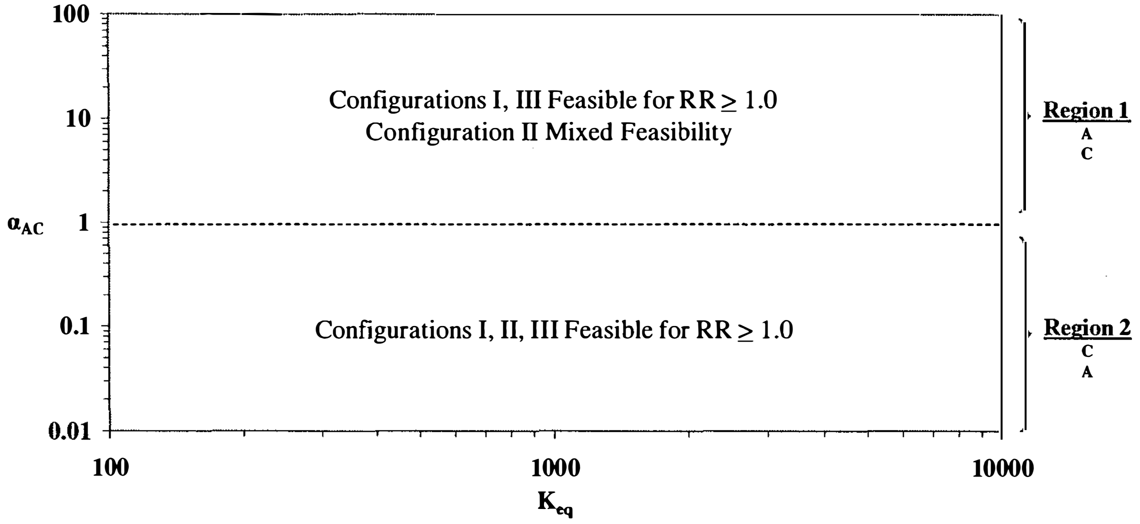


Figure 17. A↔C Economic Feasibility Diagram $K_{eq} \geq 100$

Where the reactant and product have the same boiling points, reactive distillation is not expected to be an economically feasible choice as a processing unit because distillation cannot separate the product from the reactant. However, following the criteria in this research project, reactive distillation is an economically feasible choice if $K_{eq} \geq 100$.

Literature Examples

The reactive distillation literature was reviewed with the intent of finding real chemical reactive systems that could be used to verify the heuristics and diagrams generated from this research. Four real examples for the A↔C system (Table 5) were simulated in both the forward and the reverse directions with Aspen Technology Aspen Plus® using the economic feasibility criteria defined in this research project.

For the examples shown above, all three reactive distillation column configurations were simulated using the same reflux ratios as the A↔C generic system (i.e. 1, 2.5, 5, 10, and 100) and a column pressure of one atm.

Literature Examples: Configuration II

The examples from the reactive distillation literature were first evaluated using reactive distillation column Configuration II (Figure 6). The first reaction studied was 1,4-dichloro-2-butene (156°C) ↔ 1,2-dichloro-3-butene (115°C) which was used by Lee et al. (2000f,g) as an example for the study of reactive difference points. At equilibrium for the chemical reaction, the mol fraction of 1,2-dichloro-3-butene was reported to be 0.397, which provides a chemical reaction equilibrium constant of 0.66 for the reaction of 1,4-dichloro-2-butene going to 1,2-dichloro-3-butene (Table 5). This chemical reaction

Table 5. A↔C Literature Examples

Reactive Distillation System A↔C	Boiling Points (°C)	Relative Volatilities (α_{AC})	K_{eq}
1,4-Dichloro-2-butene (A) ↔ 1,2-Dichloro-3-butene (C)	A=156 C=115	α_{AC}=0.33	0.66
1,2-Dichloro-3-butene (A) ↔ 1,4-Dichloro-2-butene (C)	A=115 C=156	α_{AC}=3.0	1.52
2-methyl-1-butene (A) ↔ 2-methyl-2-butene (C)	A=31 C=39	α_{AC}=1.32	12.0
2-methyl-2-butene (A) ↔ 2-methyl-1-butene (C)	A=39 C=31	α_{AC}=0.76	0.08
2,4,4-trimethyl-1-pentene (A) ↔ 2,4,4-trimethyl-2-pentene (C)	A=102 C=105	α_{AC}=1.10	0.30
2,4,4-trimethyl-2-pentene (A) ↔ 2,4,4-trimethyl-1-pentene (C)	A=105 C=102	α_{AC}=0.91	3.33
α-isophorone (A) ↔ β-isophorone (C)	A=203 C=174	α_{AC}=1.9	0.02
β-isophorone (A) ↔ α-isophorone (C)	A=174 C=203	α_{AC}=0.53	50.0

equilibrium constant was assumed to be independent of temperature for the temperature range within the reactive distillation column. There are no non-reactive azeotropes present for this mixture at a pressure of one atmosphere based on the results from the Peng-Robinson equation in Aspen Plus, which was used to model the vapor-liquid equilibrium for this example. The forward reaction has a relative volatility of 0.33 and is plotted in Figure 18 using a '▲' symbol. The reverse reaction of 1,2-dichloro-3-butene going to 1,4-dichloro-2-butene was also studied as an example for the A↔C heuristics. The reverse reaction was plotted using a '▲' symbol as well, but the reverse reaction has a chemical reaction equilibrium constant of 1.52 and a relative volatility of 3.33.

Figure 6 indicates that the forward reaction should require a reflux ratio of 2.5 to meet the economic feasibility criteria, while the reverse reaction will require a reflux ratio of 100 (Figure 18). The reflux ratios expected from Figure 6 for this example reaction were verified using Aspen Plus as a reflux ratio of 1.0 did not meet the economic feasibility criteria for the forward reaction and reflux ratios of 1.0, 2.5, 5, and 10 did not meet the economic feasibility criteria for the reverse reaction. Therefore, the heuristic reflux ratios from Figure 6 accurately indicated the actual reflux ratios required in Aspen Plus for the 1,4-dichloro-2-butene/1,2-dichloro-3-butene forward and reverse chemical reactions. The expected reflux ratios for a reactive distillation column of Configuration II (Figure 6 and 18) and the actual Aspen Plus simulation reflux ratios for each literature example are shown in Table 6.

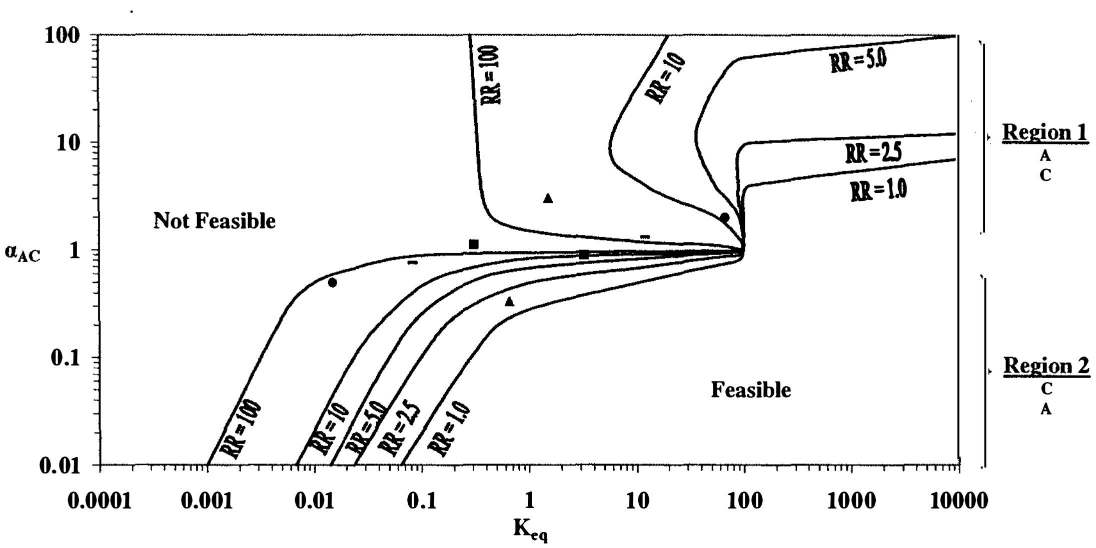


Figure 18. A↔C Reactive Distillation Literature Examples: Configuration II

Table 6. A↔C Literature Example Economic Feasibility Reflux Ratios: Configuration II

Chemical Reaction A↔C	Reflux Ratio	
	Heuristic	Actual
1,4-Dichloro-2-butene ↔ 1,2-Dichloro-3-butene	2.5	2.5
1,2-Dichloro-3-butene ↔ 1,4-Dichloro-2-butene	100	100
2-methyl-1-butene ↔ 2-methyl-2-butene	100	100
2-methyl-2-butene ↔ 2-methyl-1-butene	100	100
2,4,4-trimethyl-1-pentene ↔ 2,4,4-trimethyl-2-pentene	Not Feasible	
2,4,4-trimethyl-2-pentene ↔ 2,4,4-trimethyl-1-pentene	100	100
α-isophorone ↔ β-isophorone	100	100
β-isophorone ↔ α-isophorone	5	1

The next isomerization reaction studied was the 2-methyl-1-butene (31°C) ↔ 2-methyl-2-butene (39°C) reaction which has been documented in reactive distillation studies on *tert*-amyl-methyl ether (TAME) (Subawalla and Fair, 1999; Chen et al, 2002; Kiviranta-Paakkonen and Krause, 2003; Higler et al., 2000). The 2-methyl-1-butene/2-methyl-2-butene chemical system does not contain any non-reactive azeotropes at atmospheric pressure according to the literature or the WILSON property method physical properties in Aspen Plus. The reported chemical reaction equilibrium constant for the forward reaction is dependent on temperature and is approximately 12.0 for the range of temperatures within an atmospheric reactive distillation column. The reverse reaction was also studied with Table 5 detailing the boiling points, relative volatilities, and chemical reaction equilibrium constants for both the forward and reverse reactions. According to Figures 6, the forward and reverse reaction for 2-methyl-1-butene, indicated with a '—' symbol in Figure 18, should require a reflux ratio of 100 to meet the economic feasibility criteria for Configuration II with the Aspen Plus simulations verifying these required reflux ratios (Table 6).

The isomerization of 2,4,4-trimethyl-1-pentene (102°C) to 2,4,4-trimethyl-2-pentene (105°C) has been studied as part of the reactive distillation production of 2-methoxy-2,4,4-trimethylpentane (Rihko-Struckmann et al, 2004; Karinen et al., 2001, Karinen and Krause, 2001). This chemical system does not contain any non-reactive azeotropes according to the literature or the WILSON property method physical properties in Aspen Plus. The chemical reaction equilibrium constant for the forward reaction is 0.30 and for the reverse reaction is 3.33 for the temperature range within an atmospheric reactive distillation column (Table 5). In Figure 18, a '■' symbol is used to indicate the positions of the forward and reverse reactions for 2,4,4-trimethyl-1-pentene and a review of Figure 18 shows that the forward reaction will not be economically feasible and a reflux ratio of 100 is required for the reverse reaction. These results were verified in Aspen Plus.

The last binary reaction used to verify the heuristic diagrams was α-isophorone (203°C) ↔ β-isophorone (174°C). This reaction has been granted a patent for production via reactive distillation (Krill et al., 1999) with the vapor-liquid equilibria and reaction kinetics serving as a topic for a recent Ph.D. dissertation (Roederer, 1999). This chemical system also does not contain any non-reactive azeotropes based on the study by Roederer. A '●' symbol was used in Figure 18 to designate the forward and reverse reactions for this binary system with Figure 6 indicating that the forward reaction should require a reflux ratio of 100 with the reverse reaction requiring a reflux ratio of 10. The simulation of the forward reaction did require a reflux ratio of 100 to meet the economic feasibility criteria, but the reverse reaction simulation only required a reflux ratio of 1.0 instead of the expected reflux ratio of 10.

Where the reverse reaction data point is located in Figure 6, the feasibility boundaries have a distinctive shape to them (Figure 11). The reverse reaction is in the area where the chemical equilibrium constant is large and is starting to overcome the difficulty in separating the reactant and product. The difference in required reflux ratio for this real binary reactive system is probably be due to a slight difference in vapor-liquid equilibria between the generic A↔C example and the isophorone example. Given a relative volatility of 1.9, the difference in chemical reaction equilibrium constant is 67 vs. 86 for the 10 and 1.0 feasibility boundaries. This difference is not very large and so a small difference in vapor-liquid equilibria may provide enough difference to throw off the expected reflux ratio indicated in Figure 6.

Literature Examples: Configurations I and III

The literature examples were also studied using Configurations I (Figure 15) and III (Figure 13). Both of these configurations have areas where the economic feasibility boundaries existed for Configuration II but are missing for Configurations I and III. It is expected from Figure 16 that Configuration I will not be able to meet the economic feasibility criteria for any binary reaction with a $\alpha_{AC} < 1.0$ and $K_{eq} < 100$. For $\alpha_{AC} > 1.0$, Configuration I could meet the economic feasibility criteria depending on the chemical reaction equilibrium constant, relative volatility, and reflux ratio. The simulation results and expected reflux ratios for the literature examples are shown in Figure 19 and Table 7 for a reactive distillation column with Configuration I. Table 7 and Figure 19 show that the heuristic diagram in Figures 16 was able to accurately predict the reflux ratio required to meet the economic feasibility criteria for all of the studied literature examples.

It is expected from Figure 14 that Configuration III will not be able to meet the economic feasibility criteria for any binary reaction with a $\alpha_{AC} > 1.0$ and $K_{eq} < 100$. Configuration III could meet the economic feasibility criteria for binary reactions with $\alpha_{AC} < 1.0$, depending on the chemical reaction equilibrium constant, relative volatility, and reflux ratio.

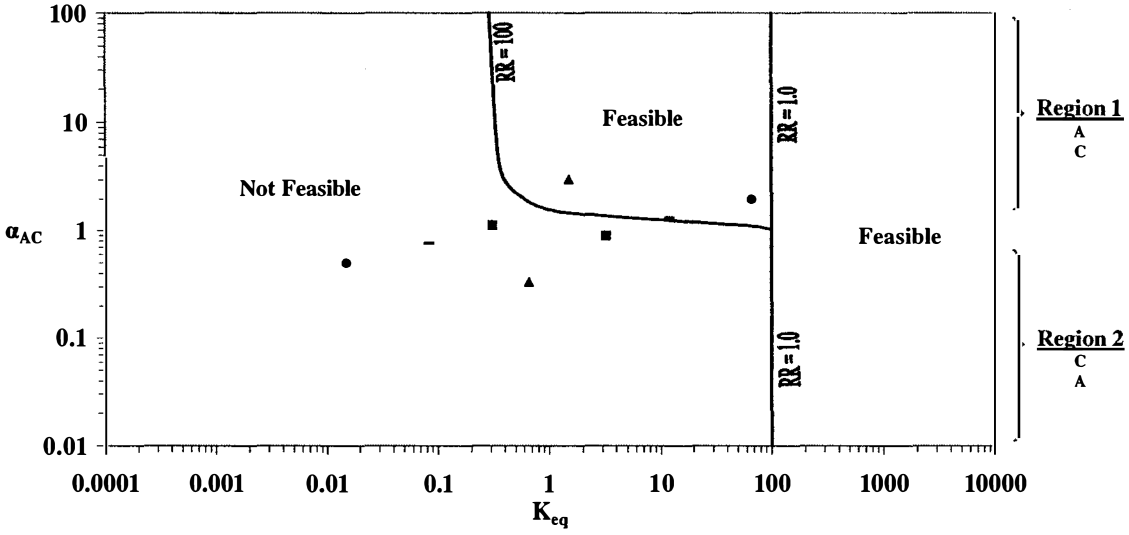


Figure 19. A↔C Reactive Distillation Literature Examples: Configuration I

Table 7. Literature Example Economic Feasibility Reflux Ratios: Configuration I

Chemical Reaction A↔C	Reflux Ratio	
	Heuristic	Actual
1,4-Dichloro-2-butene ↔ 1,2-Dichloro-3-butene	Not Feasible	
1,2-Dichloro-3-butene ↔ 1,4-Dichloro-2-butene	100	100
2-methyl-1-butene ↔ 2-methyl-2-butene	100	100
2-methyl-2-butene ↔ 2-methyl-1-butene	Not Feasible	
2,4,4-trimethyl-1-pentene ↔ 2,4,4-trimethyl-2-pentene	Not Feasible	
2,4,4-trimethyl-2-pentene ↔ 2,4,4-trimethyl-1-pentene	Not Feasible	
α-isophorone ↔ β-isophorone	Not Feasible	
β-isophorone ↔ α-isophorone	100	100

Figure 20 and Table 8 show the expected reflux ratios and simulation results for the literature examples for a reactive distillation column with Configuration III. These results show that the heuristic diagram for Configuration III (Figures 14) was able to accurately predict the expected reflux ratios for all of the literature examples.

As expected, both Configurations I and III were unable to meet the economic feasibility criteria for all of the literature reactions depending on whether the reaction relative volatilities fell into the 'Not Feasible' region of the diagram or not. These 'Not Feasible' results for Configurations I and III are caused by the presence of reactive azeotropes. As was shown previously, every binary reactive system has one and only one reactive azeotrope and the composition of which depends only on the chemical reaction equilibrium constant.

A reactive azeotrope was expected to be present in the distillate flow for Configuration I and also to be present in the underflow for Configuration III. If a reactive azeotrope was actually present, the composition of the distillate flow for Configuration I and underflow for Configuration III should not change with additional reactive stages or changes in reflux ratio. Therefore, the number of reactive stages and reflux ratio was varied in the Aspen Plus simulations for reactive distillation columns of Configurations I and III in

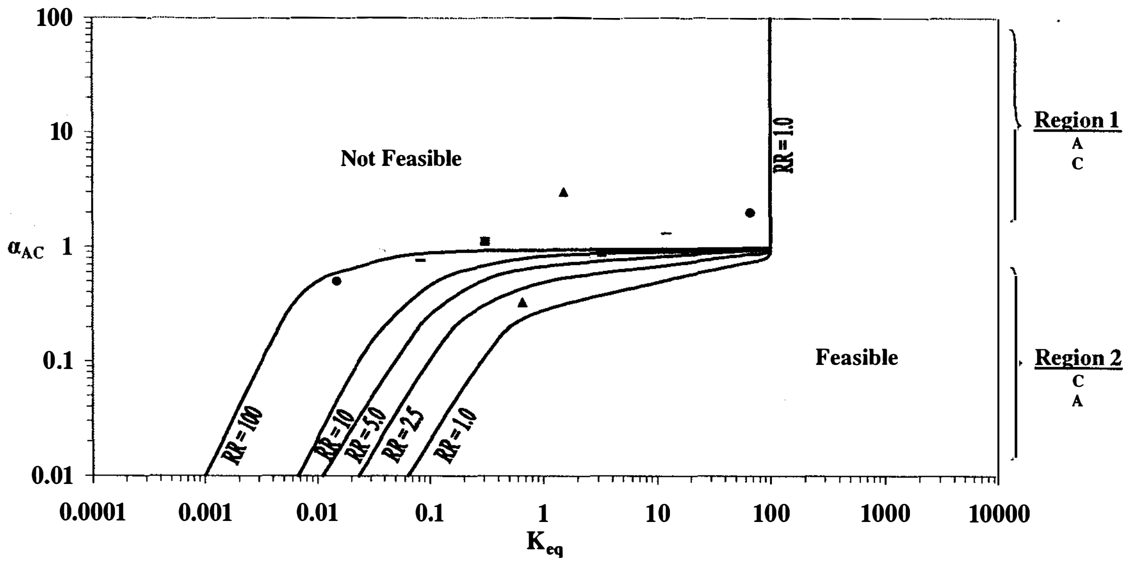


Figure 20. A↔C Reactive Distillation Literature Examples: Configuration III

Table 8. Literature Example Economic Feasibility Reflux Ratios: Configuration III

Chemical Reaction A↔C	Reflux Ratio	
	Heuristic	Actual
1,4-Dichloro-2-butene↔ 1,2-Dichloro-3-butene	2.5	2.5
1,2-Dichloro-3-butene ↔ 1,4-Dichloro-2-butene	Not Feasible	
2-methyl-1-butene ↔ 2-methyl-2-butene	Not Feasible	
2-methyl-2-butene ↔ 2-methyl-1-butene	100	100
2,4,4-trimethyl-1-pentene ↔2,4,4-trimethyl-2-pentene	Not Feasible	
2,4,4-trimethyl-2-pentene ↔ 2,4,4-trimethyl-1-pentene	100	100
α-isophorone ↔ β-isophorone	100	100
β-isophorone ↔ α-isophorone	Not Feasible	

order to verify the presence of reactive azeotropes within these real chemical reactive systems.

All literature examples were found to have reactive azeotropes and the composition of these azeotropes correspond to the composition predicted by the generic A↔C system (Table 9). In fact, the reactive azeotrope composition from the literature examples is exactly what was predicted except for the 2-methyl-1-butene example. This difference in the expected reactive azeotrope concentration and the actual reactive azeotrope concentration for this system is probably due to the difference in the estimated chemical reaction equilibrium constant of 12.0 and the actual temperature dependent reaction equilibrium constant value. If a better initial estimate were made for the equilibrium constant (i.e. a value of 11.7), the expected and actual reactive azeotrope composition would have been exactly the same.

It is important to note that the overall reactive azeotrope composition is the same for the forward and backward reaction for every binary system. The reaction changes the reactant and product composition of reactive azeotrope, but the reaction does not change the overall chemical composition of the reactive azeotrope. Additionally, the Configuration I distillate and Configuration III underflow compositions are exactly the same. These results verify that the reactive azeotrope is the only composition present within the reactive zone for a reactive binary chemical system and that the reactive azeotrope composition is independent of the relative volatility for the binary system.

This is true only for a binary reactive chemical system as the reactive azeotropes for chemical systems with more than two compounds are dependent on the relative volatility of the constituents as well as the chemical reaction equilibrium constant.

Reactive azeotropes only affect the distillate for Configuration I and the underflow for Configuration III because Configuration I does not have a non-reactive rectifying section and Configuration III does not have a non-reactive stripping section. The presence of reactive azeotropes does not affect the results for Configuration II because this configuration has both a non-reactive rectifying and a non-reactive stripping section, which break the reactive azeotrope.

Observations and Heuristics

For the binary reactive systems and reactive distillation column configurations studied in this chapter, certain similarities were found for related combinations of relative volatilities and chemical reaction equilibrium constants. These similarities were analyzed and condensed into a set of observations and proposed heuristics for the initial feasibility assessment and conceptual design of binary reactive distillation columns. The proposed set of observations and heuristics are as follows:

Table 9. Literature Example Reactive Azeotropes

Chemical Reaction A↔C	Configuration	Reactive Azeotrope			
		Expected		Actual	
		x_A	x_C	x_A	x_C
1,4-dichloro-2-butene ↔ 1,2-dichloro-3-butene	I	0.603	0.397	0.603	0.397
	II	-		-	
	III	0.603	0.397	0.603	0.397
1,2-dichloro-3-butene ↔ 1,4-dichloro-2-butene	I	0.397	0.603	0.397	0.603
	II	-		-	
	III	0.397	0.603	0.397	0.603
2-methyl-1-butene ↔ 2-methyl-2-butene	I	0.077	0.923	0.079	0.921
	II	-		-	
	III	0.077	0.923	0.079	0.921
2-methyl-2-butene ↔ 2-methyl-1-butene	I	0.923	0.077	0.921	0.079
	II	-		-	
	III	0.923	0.077	0.921	0.079
2,4,4-trimethyl-1-pentene ↔ 2,4,4-trimethyl-2-pentene	I	0.765	0.235	0.765	0.235
	II	-		-	
	III	0.765	0.235	0.765	0.235
2,4,4-trimethyl-2-pentene ↔ 2,4,4-trimethyl-1-pentene	I	0.235	0.765	0.235	0.765
	II	-		-	
	III	0.235	0.765	0.235	0.765
α-isophorone ↔ β-isophorone	I	0.985	0.015	0.985	0.015
	II	-		-	
	III	0.985	0.015	0.985	0.015
β-isophorone ↔ α-isophorone	I	0.015	0.985	0.015	0.985
	II	-		-	
	III	0.015	0.985	0.015	0.985

Observations

1. Every binary reactive system has one and only one reactive azeotrope.
2. The reactive azeotrope composition is independent of the relative volatility of the reactant and product for all binary reactive systems.
3. For all binary reactive systems, the reactive azeotrope has a unique composition and that composition is determined by the chemical reaction equilibrium constant and is independent of the direction of the reaction (i.e. forwards or reverse).
4. The reactive azeotrope is the only composition within the reactive zone for a reactive binary system.

Heuristics

1. A reactive distillation column must have at least one non-reactive rectifying stage to produce a product in the column distillate with a composition other than the reactive azeotrope composition for a binary reactive system.
2. A reactive distillation column must have at least one non-reactive stripping stage to produce a product in the column underflow with a composition other than the reactive azeotrope composition for a binary reactive system.
3. If chemical reaction equilibrium is attained on every stage for a binary reactive system, only one reactive stage is necessary for any reactive distillation column design because additional reactive stages do not improve the reactant conversion.
4. If chemical reaction equilibrium is attained on the reactive stage, there is no advantage to removing the non-reactive rectifying zone for binary systems where the reactant is the low boiler or removing the non-reactive stripping zone for binary systems where the reactant is the high boiler.
5. For a reactive distillation column without any non-reactive rectifying stages (Configuration I), there are no binary reactive systems that are economically feasible* for a binary reactive system with a $\alpha_{AC} < 1.0$ and a $K_{eq} < 100$.
6. For a reactive distillation column without any non-reactive stripping stages (Configuration III), there are no binary reactive systems that are economically feasible for a binary reactive system with a $\alpha_{AC} > 1.0$ and a $K_{eq} < 100$.
7. For any given reflux ratio, the chemical reaction equilibrium constant can be over 100 times smaller for a binary reactive system with a $\alpha_{AC} < 1.0$ then system with a $\alpha_{AC} > 1.0$ for an economically feasible reactive distillation column with a non-reactive rectifying zone, a reactive zone, and non-reactive stripping zone. In other words, reactive distillation is more effective for binary reactive systems where the reactant is the highest boiling component and the product can be preferentially vaporized and removed from the reactive liquid phase.
8. Reactive distillation is economically feasible for all binary reactive systems with a $K_{eq} > 30$ and with $\alpha_{AC} \geq 1.01$ or $\alpha_{AC} \leq 0.99$.
9. For a binary reactive system where $\alpha_{AC} > 1.0$, reactive distillation is not economically feasible for $K_{eq} < 0.1$.
10. For a binary reactive system where $\alpha_{AC} < 1.0$, reactive distillation is not economically feasible for $K_{eq} < 10^{-3}$.

* Economic feasibility criteria:

1. reactant conversion $\geq$ 95.0%
2. product purity $\geq$ 99.0%
3. total column stages $\leq$ 100.
4. reflux ratio $\leq$ 100 (economic reflux ratios depend on product value).

These heuristics are based on data collected with the following assumptions:

1. The reactant is a single feed and is fed directly on the reactive stage.
2. Chemical reaction equilibrium is attained on every reactive stage.
3. Vapor-liquid equilibrium is attained on every stage.
4. Vapor and liquid phases are ideal.
5. The feed is 100% reactant.
6. Any heat effects cancel within the reactive distillation column.
7. The reactive distillation column has a total condenser.

Summary

In this chapter, a set of heuristics was proposed for the initial feasibility assessment and conceptual design of binary reactive distillation columns involving the reaction $A \leftrightarrow C$. These heuristics were developed from a data set collected from Aspen Plus simulations using a generic binary reactive system. For this generic system, a range of relative volatilities and chemical reaction equilibrium constants were chosen to cover the expected range of potential binary reactive systems. Three different reactive distillation column configurations were evaluated. The first configuration had a reactive section and non-reactive stripping section. The second configuration had a non-reactive rectifying section, a reactive section, and a non-reactive stripping section. The third configuration had a non-reactive rectifying section and a reactive zone. Diagrams were created indicating economic feasibility for each reactive distillation column configuration. One and only one reactive azeotrope was found to be present in every binary reactive system and was determined to be independent of the reactant and product relative volatility. The reactive azeotrope composition is dependent only upon the chemical reaction equilibrium constant and is the only composition in the reactive zone. This requires that a non-reactive section must be placed above (for low boiling products) or below (for high boiling products) the reactive zone to produce pure product. The heuristics and simulation results for the generic binary reactive system were verified using several real binary reactive chemical systems available in the reactive distillation literature.

VI. SYSTEMS WITH ONE REACTANT AND TWO PRODUCTS

Introduction

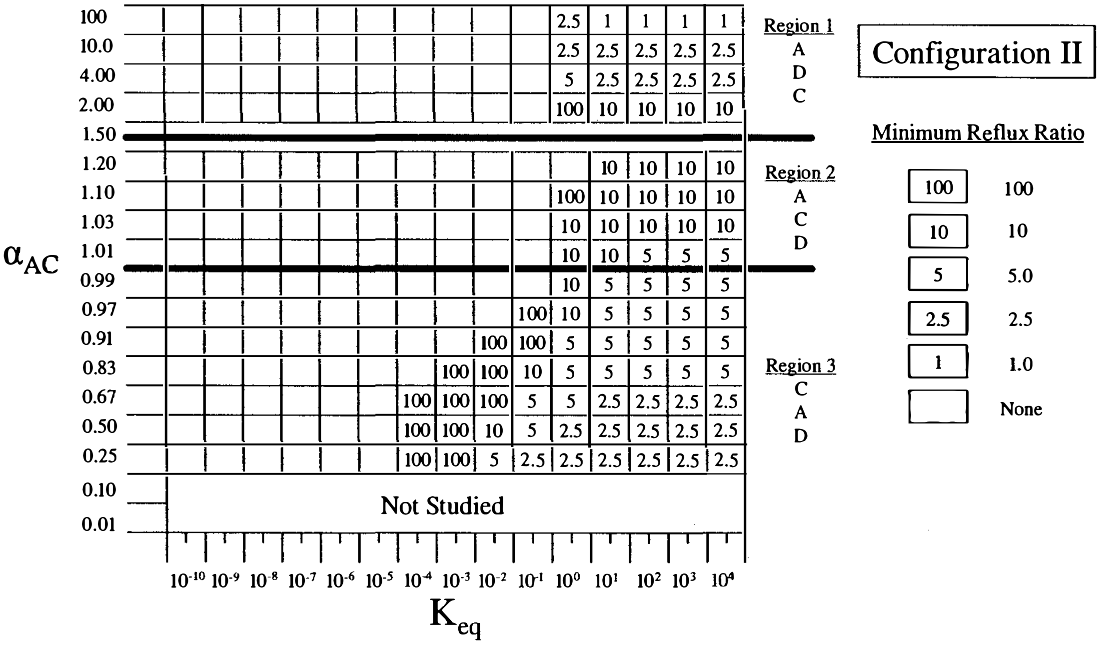
The reactant and product boiling points for the A↔C+D system were divided into six volatility order regions, which are defined in Table 2. For the A↔C+D system, component C will always be the desired product and component D will always be the by-product. Relative volatility combinations within each region share similar characteristics for reactive distillation feasibility and design. Therefore each region for the A↔C+D system will be evaluated individually with the commonalities within each region condensed into a final set of observations and heuristics for this ternary reactive system.

The component boiling points within each region were broken into a fixed set of relative volatilities covering the potential range of component boiling points. In general, the relative volatilities for the reactant and desired product (α_{AC}) and the reactant and by-product (α_{AD}) were 0.01, 0.10, 0.25, 0.50, 0.67, 0.83, 0.91, 0.97, 0.99, 1.01, 1.03, 1.10, 1.20, 1.50, 2.0, 4.0, 10.0, and 100 with each combination of α_{AC} and α_{AD} fitting into one of the six regions. Simulations for each relative volatility combination were run with the chemical reaction equilibrium constant (K_{eq}) sequentially reduced from 10,000 by a factor of 10 until the reactive distillation column no longer met the economic feasibility criteria. The acceptance criteria for an economically feasible reactive distillation column was set so that the total column stages must be less than 100, the reactant conversion greater than 95.0%, and the product purity greater than 99.0%.

Rough Economic Feasibility Diagrams

The initial simulation results for all regions within the A↔C+D system were organized into Rough Economic Feasibility Diagrams, which can be found in Appendix A (Figures 37-54). These Rough Economic Feasibility Diagrams serve as the foundation for the development of the final observations and heuristics for this chemical reactive system. Figure 21 shows an example of a Rough Economic Feasibility Diagram.

A unique Economic Feasibility Diagram was created for each studied combination of reactant and by-product relative volatility (α_{AD}) and reactive distillation configuration. For the Rough Economic Feasibility Diagram shown in Figure 21, the reactive distillation column was of Configuration II and the reactant and by-product relative volatility was $\alpha_{AD} = 1.50$. A Rough Economic Feasibility Diagram consists of the chemical reaction equilibrium constant (K_{eq}) plotted on the x-axis, the relative volatility of the reactant and desired product (α_{AC}) on the y-axis, a region boundary where $\alpha_{AC} = \alpha_{AD}$, and another region boundary where $\alpha_{AC} = 1.0$. The K_{eq} is plotted on the x-axis on a logarithmic scale while the α_{AC} is not plotted to scale. The regions between the boundaries are identified on the diagram and have the boiling point orderings described in Table 2. The component boiling point ordering list for the region is shown below the region title with the lowest boiling component on top of the list and the highest boiling component on the



α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100											2.5	1	1	1	1
10.0											2.5	2.5	2.5	2.5	2.5
4.00											5	2.5	2.5	2.5	2.5
2.00											100	10	10	10	10
1.50															
1.20												10	10	10	10
1.10											100	10	10	10	10
1.03											10	10	10	10	10
1.01											10	10	5	5	5
0.99											10	5	5	5	5
0.97										100	10	5	5	5	5
0.91									100	100	5	5	5	5	5
0.83								100	100	10	5	5	5	5	5
0.67							100	100	100	5	5	2.5	2.5	2.5	2.5
0.50							100	100	10	5	2.5	2.5	2.5	2.5	2.5
0.25							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
0.10	Not Studied														
0.01															

Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
☐	None

Figure 21. A↔C+D Rough Economic Feasibility Diagram α_{AD}=1.50: Configuration II

bottom. For example, Region 1 in Figure 21 is where the reactant (A) is the lowest boiling component and is on the top, the by-product (D) is the intermediate boiling component shown in the middle, and the desired product (C) is the highest boiling component and is on the bottom. Each block within the Rough Economic Feasibility Diagram consists of a α_{AD}, α_{AC}, and K_{eq} combination and within this block is written the minimum reflux ratio required for the reactive distillation column to meet the economic feasibility criteria. For example, Figure 21 shows an A↔C+D system with $\alpha_{AD} = 1.50$, $\alpha_{AC} = 0.83$, and a $K_{eq} = 10^{-1}$ requires a reactive distillation column of Configuration II to have a minimum reflux ratio of 10 to meet the economic feasibility criteria.

Most A↔C+D systems have a combination of relative volatility and chemical reaction equilibrium constant that fall in between the blocks shown in the Rough Economic Feasibility Digrams. The blocks within the Rough Economic Feasibility Diagrams are not intended to provide detailed boundaries, but can be used to provide initial guidance for economic feasibility with the understanding that the actual minimum reflux ratio for a particular A↔C+D system falls within the range of reflux ratios indicated by adjacent blocks. For example, an A↔C+D system with $\alpha_{AD} = 1.50$, $\alpha_{AC} = 0.25$, and a $K_{eq} = 0.0022$ will require a reflux ratio between 5.0 and 100 as indicated in Figure 21. A more detailed study of this particular system shows that the actual minimum reflux ratio required to meet the economic feasibility criteria is 10 for a reactive distillation column of Configuration II, which is in between the minimum reflux ratios shown in adjacent blocks.

One of the region boundaries within the Economic Feasibility Diagram truly is a boundary for economic feasibility. For A↔C+D systems where $\alpha_{AC} = \alpha_{AD}$ or when α_{AC} is close to α_{AD}, there are no economically feasible reactive distillation columns because it is not possible to separate the desired product from the by-product by distillation. When $\alpha_{AC} = \alpha_{AD}$ or when α_{AC} is close to α_{AD}, the desired product and by-product boiling points are the same or very close to the same and distillation cannot separate them which creates a barrier for the economic feasibility of reactive distillation. All Economic Feasibility Diagrams have this region boundary and this boundary cannot be crossed by any reactive distillation column for A↔C+D systems.

The other region boundary is where $\alpha_{AC} = 1.0$ and is an arbitrary boundary set to define regions where the boiling point orderings change from one reactant, product, and by-product ordering to another ordering. This region boundary is not a true boundary to economic feasibility for reactive distillation because chemical reaction can convert enough of the reactant to products so that the separation between the reactant and product is no longer necessary. This phenomenon will be described in greater detail in the later sections.

Refined Economic Feasibility Diagrams

A few of the Rough Economic Feasibility Diagrams were studied in much greater detail to show what the actual economic feasibility boundaries look like for given a combination of relative volatility and chemical reaction equilibrium constant. Figure 22 shows the Refined Economic Feasibility Diagrams for $\alpha_{AD} = 1.50$ and Figure 23 shows the Refined Economic Feasibility Diagrams for $\alpha_{AD} = 0.67$. There are three Refined Economic Feasibility Diagrams for every reactant and by-product relative volatility combination, one diagram for each reactive distillation configuration.

The regions shown in the Refined Economic Feasibility Diagrams are labeled and have the component boiling point ordering list for the region shown below the region title with the lowest boiling component on top of the list and the highest boiling component on the bottom. These Refined Economic Feasibility Diagrams along with the Rough Economic Feasibility Diagrams in Appendix A (Figures 37-54) will serve as the basis for the development of observations, heuristics, and trends for the A↔C+D system.

Economic Feasibility Qualitative Areas

The Refined Economic Feasibility Diagram boundaries shown in Figures 22 and 23 indicate that the same qualitative limiting areas found in the A↔C system (Figures 8 and 9) are present for the A↔C+D system (Figure 24). Area 1 is where the separation of the product and reactant is limiting the economic feasibility of reactive distillation. Area 2 is where the chemical reaction equilibrium constant and the separation of the product and reactant are both enhancing the feasibility of reactive distillation. Area 3 is where both the chemical reaction equilibrium constant and the separation of the product and reactant are limiting the feasibility of reactive distillation. Area 4 is where the chemical reaction

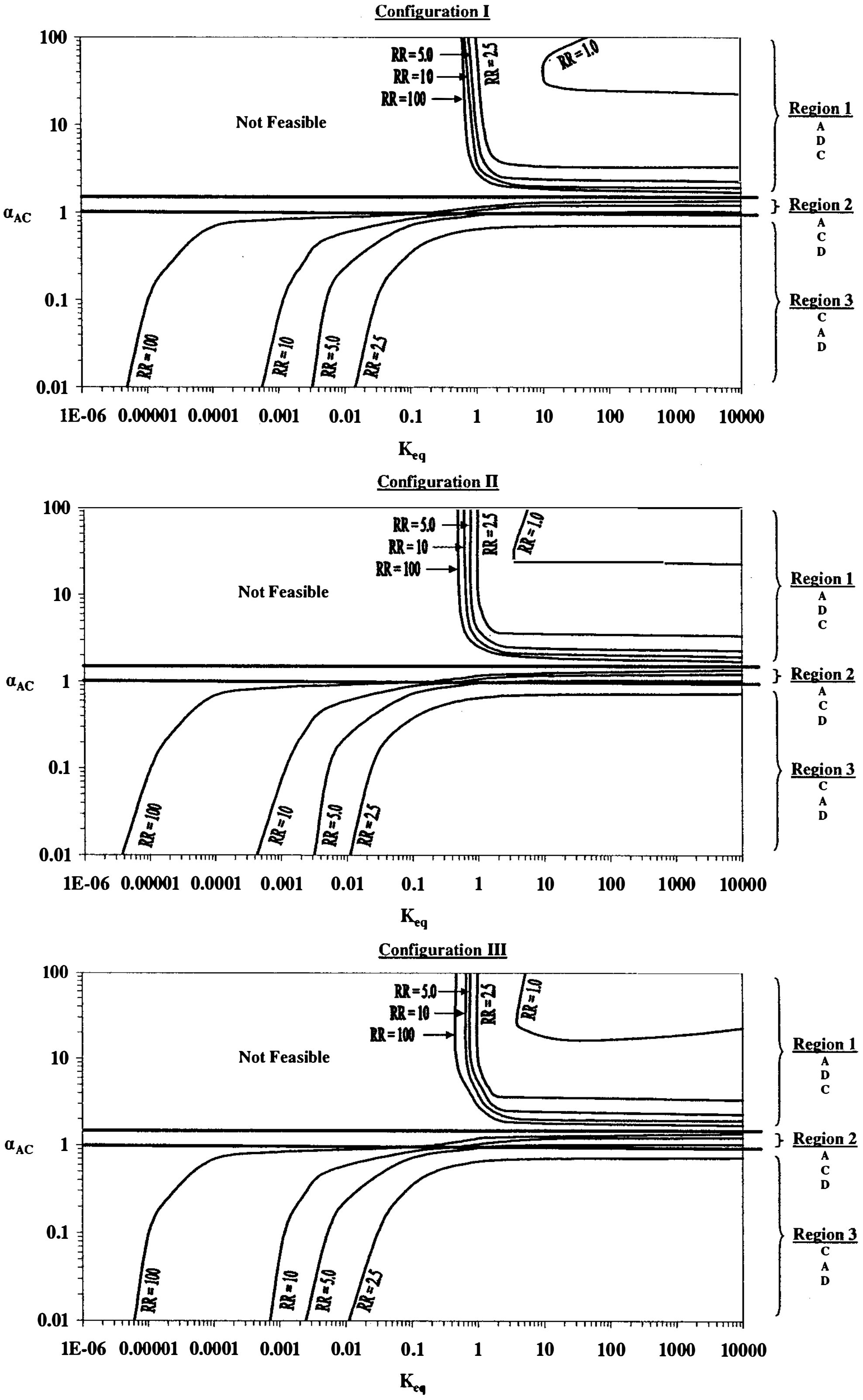
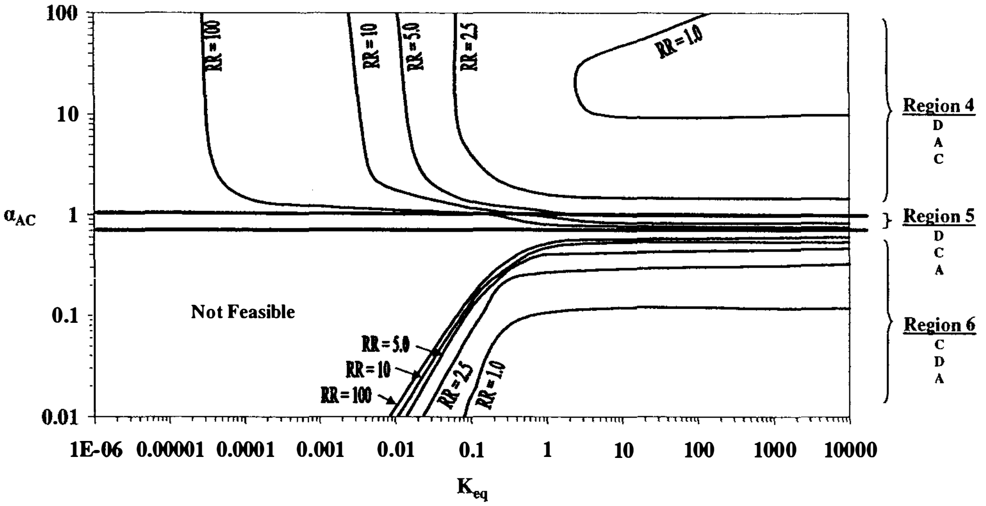
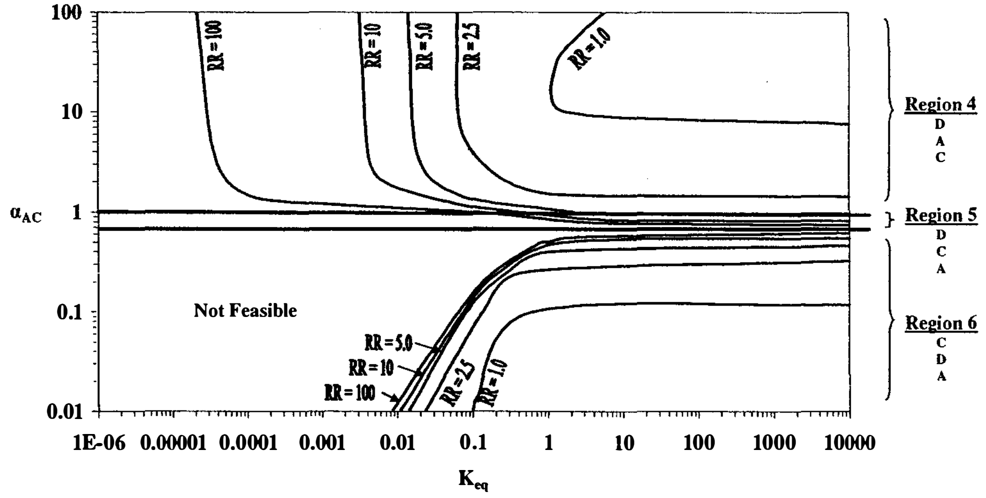


Figure 22. A↔C+D Refined Economic Feasibility Diagrams α_{AD}=1.50

Configuration I



Configuration II



Configuration III

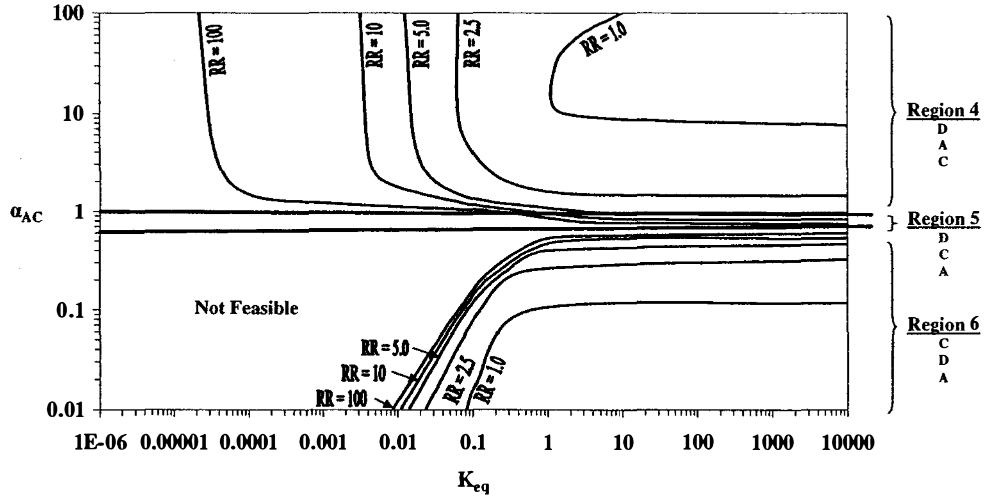
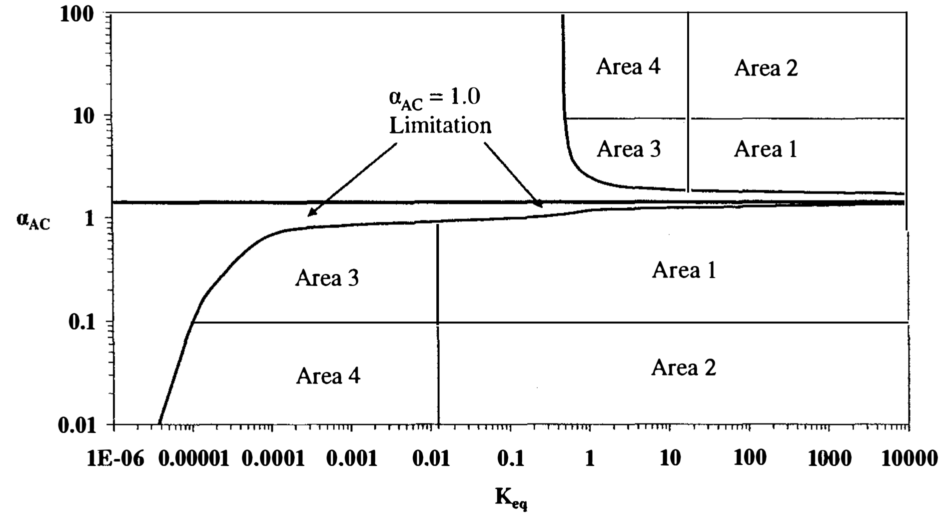


Figure 23. A↔C+D Refined Economic Feasibility Diagrams α_{AD}=0.67



Area 1: K_{eq} not limiting, α_{AC} is limiting
Area 2: K_{eq} not limiting, α_{AC} not limiting
Area 3: K_{eq} is limiting, α_{AC} is limiting
Area 4: K_{eq} is limiting, α_{AC} is not limiting

Figure 24. A↔C+D Economic Feasibility Diagram α_{AD}=1.50, RR=100: Limiting Areas

equilibrium constant is limiting the feasibility of reactive distillation.

One difference in the qualitative area assessment for the A↔C+D system vs. the A↔C system is that the separation boundary occurs when $\alpha_{AC} = \alpha_{AD}$ for the A↔C+D system, whereas the separation boundary occurs when $\alpha_{AC} = 1.0$ for the A↔C system. This is because the primary separation difficulty for the A↔C+D system is between the desired product and by-product, while the primary separation difficulty for the A↔C system is between the reactant and desired product.

Initially, it may be anticipated that reactive distillation would not be feasible for A↔C+D systems where the desired product and reactant have the same or similar boiling points because of the difficulties in separating the close boiling components by distillation. But if the by-product boiling point is not close to the reactant and product boiling points, the limitation caused by separation may be overcome by reactive distillation.

In a more traditional process design, a separate reactor and distillation column(s) would be used to produce the desired product. The chemical reaction would take place in the reactor with the reactor effluent being sent to a distillation column(s) to recover the unconverted reactant and purify the desired product from the by-product. However, in A↔C+D systems where the chemical reaction equilibrium constant is small, distillation will not be able to purify the product from the unconverted reactant if the desired product boiling point is close to the reactant boiling point. In these cases, reactive distillation may be able to overcome the chemical reaction equilibrium and separation limitations of the more traditional process design. Reactive distillation can overcome the chemical reaction equilibrium limitation by preferentially removing the by-product from the reactive zone and thereby driving the complete conversion of the reactant to desired product. If the reactant can be completely converted to product, the difficulty in separating the reactant from the desired product disappears because the reactant is no longer present and the only separation that is necessary is to separate the product from the by-product. This ability of reaction distillation to overcome separation and chemical reaction limitations is one of the significant advantages of this process design when compared to the more traditional reactor/distillation column design.

The separation of the desired product and reactant still has a slight affect on the shape of the economic feasibility boundaries for the A↔C+D system. When the reactant and product boiling points are close, there is a slight change in curvature of the economic feasibility boundaries (Figure 24). This indicates that the economic feasibility of reactive distillation is limited somewhat when the desired product boiling point is equal or close to the boiling point of the reactant, but this limitation is not insurmountable.

Reactant, By-Product, Desired Product Splits

Since this study focused the feasibility of a single reactive distillation column, a sharp split between the product (C) and the by-product (D) was required in order to meet the economic feasibility criteria of a product purity that was greater than 99.0%. However, for certain A↔C+D systems it may be economically beneficial to design the reactive distillation column so that the sharp split occurs between the reactant and the product (or by-product) and then separate the product and by-product using a non-reactive distillation column. This is conceptually a strong possibility for Regions 1, 2, 5, and 6 since the reactant is either the lowest boiling or highest boiling component in these chemical reactive systems. Figure 25 shows the potential process designs for a single reactive distillation column and a non-reactive distillation column for Regions 1, 2, 5, and 6.

For these reactive distillation/non-reactive distillation process designs, the reactant rich distillate or bottoms flow can be returned entirely back to the reactive zone of the distillation column, which helps to drive the complete conversion of the reactant to product. For example, if the A↔C+D system component boiling points fall within Region 1, the reactant will concentrate in the top of the reactive distillation column because it is the lowest boiling component in the system. The distillate stream from the reactive distillation column can be returned entirely to the reactive zone of the reactive distillation column with the products leaving the reactive distillation column in the bottoms stream. This removal of the products from the reactive distillation column, the complete return of the reactant to the reactive zone, and the separation of the products in a non-reactive distillation column is expected to provide a more economical design than a single reactive distillation column.

The results from the A↔C system can be used to provide some initial guidance for the A↔C+D systems within Regions 1, 2, 5, and 6 because the sharp split between the

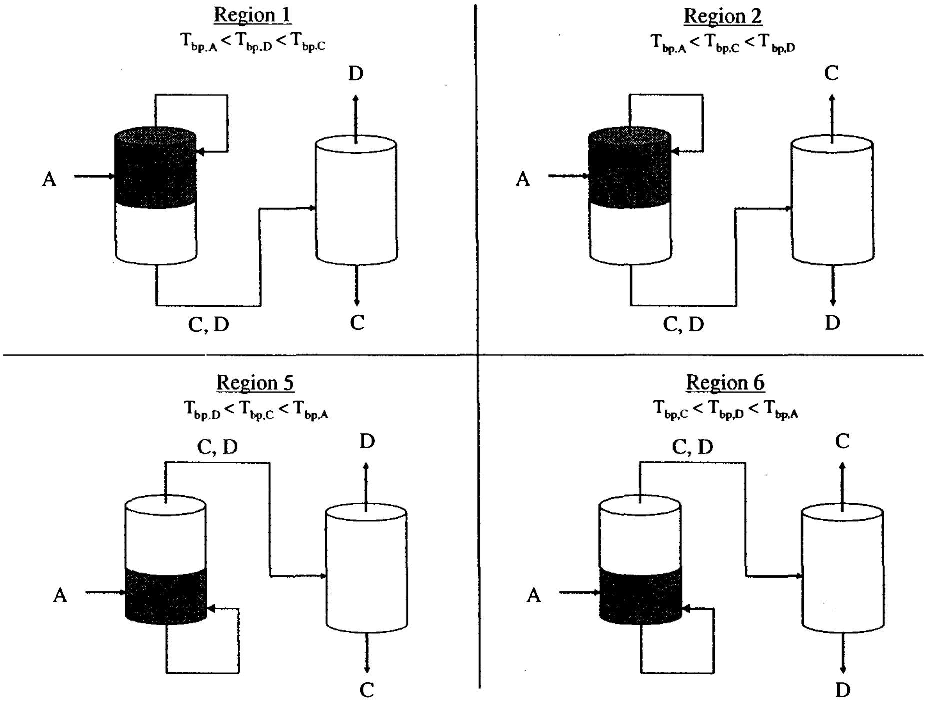


Figure 25. A↔C+D Alternate Process Designs: Regions 1, 2, 5, and 6

reactant and product for the A↔C systems are just like the proposed reactant and product split for the A↔C+D systems. However, a complete feasibility analysis for the A↔C+D systems must contain an assessment of the separation of the product and by-product. If the product and by-product boiling points are sufficiently different and there are not any non-reactive azeotropes present, the non-reactive distillation column should be able to separate them. When the product and by-product boiling points are close together or non-reactive azeotropes interfere with separation, distillation will not be able to separate the product and by-product and a different overall process design will be required to produce a pure desired product.

Reactive Azeotropes

Reactive azeotropes are not present for all A↔C+D systems, just like non-reactive azeotropes for non-reactive systems. The affects of reactive azeotropes on reactive distillation feasibility and design is the same as non-reactive azeotropes for non-reactive distillation, except reactive azeotropes are only present in the reactive zone of the reactive distillation column.

For chemical reactive systems with more than two components, the reactive azeotrope composition is dependent on the relative volatilities of the individual components and the chemical reaction equilibrium constant, if a reactive azeotrope exists. Barbosa and Doherty (1988d) have shown that for constant volatility systems, reactive azeotropes can only occur if the volatility of all the reactants is either higher or lower than the volatility of all the products. Assuming that the relative volatilities are constant for the A↔C+D systems in this study, only those systems that fall within Regions 1,2, 5, and 6 can have reactive azeotropes. For the A↔C+D systems within Regions 3 and 4, the reactant is the middle boiling component and these systems will not have reactive azeotropes.

The presence of reactive azeotropes was determined for each studied combination of relative volatility and chemical reaction equilibrium constant. The results were organized by α_{AD} and contain a diagram showing the combinations of relative volatilities and chemical reaction equilibrium constant that have a reactive azeotrope indicated by a reference number(s) if a reactive azeotrope was found to be present. The reference number ties the relative volatility and chemical reaction equilibrium constant combination to the raw data found below the diagram, which contains the composition, boiling point, and type of node for the reactive azeotrope. The reactive azeotrope diagrams for the A↔C+D systems are located in Appendix A (Figures 55-72) with the component boiling point ordering for each region shown below the region title with the lowest boiling component on top and the highest boiling component on the bottom, just like the region boiling points orderings are for the Economic Feasibility Diagrams. Chadda et al. (2002) provide a detailed explanation of the associated node nomenclature found with the raw data in the reactive azeotrope figures.

Reactive distillation columns of Configuration II are not directly limited by reactive azeotropes because this configuration has both a non-reactive stripping section and a non-reactive rectifying section which break any reactive azeotrope composition leaving the reactive zone. Reactive distillation columns of Configuration I may be limited by minimum boiling reactive azeotropes (unstable nodes) and columns of Configuration III may be limited by maximum boiling reactive azeotropes (stable nodes), which is because of the absence of a non-reactive rectifying section for Configuration I and the absence of a non-reactive stripping section for Configuration III.

Reactive azeotropes do not have the same impact on economic feasibility for A↔C+D systems as for the A↔C systems. For the A↔C systems, whole regions are not economically feasible for Configurations I and III because of limitations from reactive azeotropes. For the A↔C+D systems, the economic feasibility limitations caused by the presence of reactive azeotropes are more subtle because every region has at least some area of economic feasibility.

In order to visually evaluate the specific consequences caused by reactive azeotropes for each A↔C+D region, the reactive azeotrope mole fractions were transformed into the transformed coordinates proposed by Doherty et al. (Barbosa and Doherty,1988a; Ung and Doherty, 1995a,b). Transformed variables are a combination of the system mole fractions and reaction stoichiometry and take on the same value before and after chemical reaction. This unique property allows certain traditional distillation design techniques to be extended to reactive distillation design. For A↔C+D systems, the equations for the transformed variables are shown in Equations 6.1 and 6.2 when the reactant A is selected as the reference component.

$$X_B = \frac{(x_B - \nu_A x_A)}{(1 - \nu_A x_A)} \tag{6.1}$$

$$X_C = \frac{(x_C - \nu_A x_A)}{(1 - \nu_A x_A)} \tag{6.2}$$

Using these transformed variables, a reactive residue curve map can be constructed, which for the A↔C+D system results in a straight line (Figure 26). The pure reactant feed used in this research project has the transformed composition of $X_B=X_C=0.5$ and is shown in Figure 26. The transformed composition for a pure desired product is $X_C=1.0$ and a pure by-product is $X_B=1.0$. For an A↔C+D system with no reactive azeotrope, a completely reactive distillation column will conceptually be able to produce pure product and pure by-product as indicated by the reactive residue curve map. However, if an A↔C+D system has a reactive azeotrope, a completely reactive distillation column will only be able to produce either a pure product or a pure by-product depending on the feed composition fed to the reactive distillation column.

An analysis of the reactive azeotropes present in the A↔C+D systems shows that reactive azeotropes are present in Regions 1, 2, 5, and 6. The reactive azeotropes for

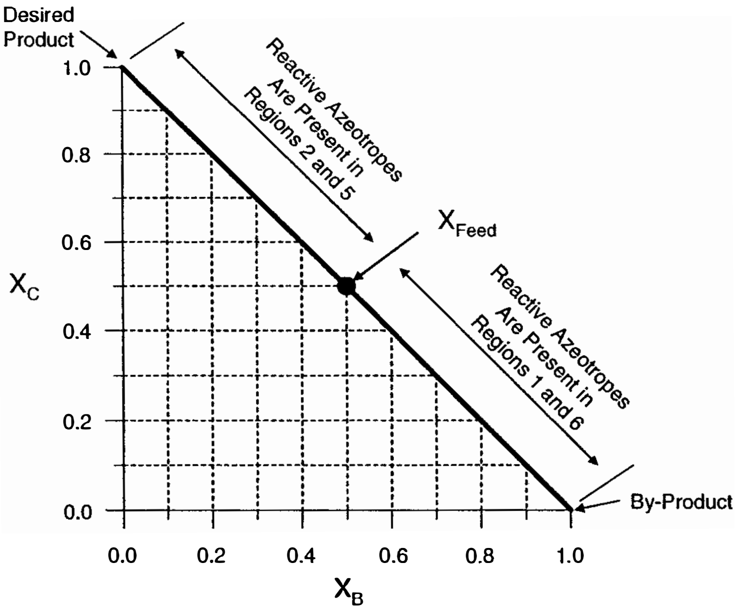


Figure 26. A↔C+D Reactive Azeotropes: Basic Reactive Residue Curve Map

Regions 1 and 6 fall into an area where the transformed compositions are $X_C < 0.5$, while Regions 2 and 5 fall into an area where the transformed compositions are $X_C > 0.5$ (Figure 26). Since the transformed feed composition for a stoichiometric feed is $X_C = 0.5$, any reactive azeotrope with a transformed composition $X_C > 0.5$ will result in a reactive distillation column that is limited by a reactive azeotrope because the reactive azeotrope transformed composition is between the feed composition and the desired product composition. This reactive azeotrope composition will limit the economic feasibility of the reactive distillation column unless the reactive azeotrope composition is $x_C \geq 0.99$ or the reactive azeotrope is destroyed by a non-reactive rectifying section in the reactive distillation column.

This result indicates that the economic feasibility of reactive distillation columns for $A \leftrightarrow C+D$ systems within Regions 2 and 5 can be directly limited by reactive azeotropes while $A \leftrightarrow C+D$ systems within Regions 1 and 6 are not directly limited by reactive azeotropes for a reactive distillation column with a stoichiometric feed (Figure 26). More specifically, reactive distillation columns of Configuration I are limited by reactive azeotropes in Region 2 because the product and reactive azeotrope are both low boiling and the reactive zone extends to the very top of the reactive distillation column. Similarly, reactive distillation columns of Configuration III are limited in Region 5 because the product and reactive azeotrope are both high boiling and the reactive zone extends to the very bottom of the reactive distillation column.

For example, in Region 1 where $\alpha_{AD} = 1.2$, $\alpha_{AC} = 2.0$, and $K_{eq} = 0.1$, a reactive azeotrope was found to exist and has a transformed composition of $X_C = 0.361$, which falls in between the feed composition and the by-product composition (Figure 27). This reactive azeotrope does not limit the economic feasibility for a pure reactant feed to a reactive distillation column because the reactive azeotrope composition falls between the feed and by-product composition.

An example of a system that is limited by the presence of a reactive azeotrope can be found within Region 5, where $\alpha_{AD} = 0.67$, $\alpha_{AC} = 0.83$, and $K_{eq} = 0.1$. For this $A \leftrightarrow C+D$ system, the reactive azeotrope transformed composition is $X_C = 0.607$, which falls in between the feed composition and the desired product composition (Figure 28). In this case, a pure reactant feed will not allow a completely reactive distillation column or a column of Configuration III to produce pure product. However, if the feed had a transformed composition where $X_{C,feed} > X_{C,azeo}$, then a reactive distillation column of Configuration III or a completely reactive column would be able to produce pure desired product as the distillate because there would be no reactive azeotrope between the reactant and desired product composition.

These examples highlight the limitation that reactive azeotropes may or may not present for the economic feasibility of reactive distillation. Specific findings for the $A \leftrightarrow C+D$ systems studied are (1) reactive azeotropes may only be present in Regions 1, 2, 5, and 6 if $K_{eq} \leq 1.0$, (2) reactive azeotropes are not present in these regions if $K_{eq} > 1.0$ or if the $A \leftrightarrow C+D$ system boiling point ordering falls within Regions 3 or 4, (3) the economic

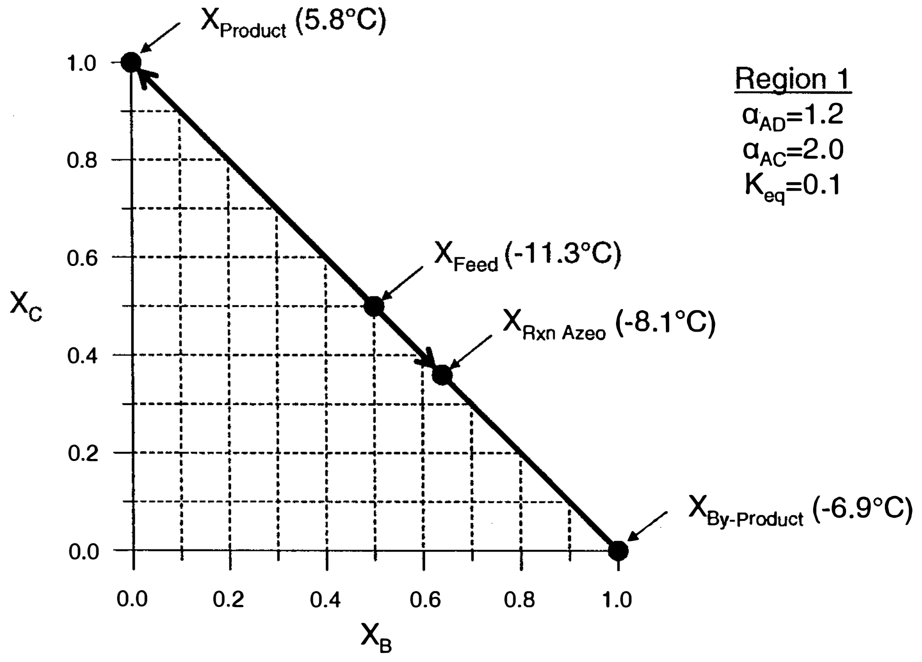


Figure 27. A↔C+D Reactive Azeotropes: Region 1 Reactive Residue Curve Map

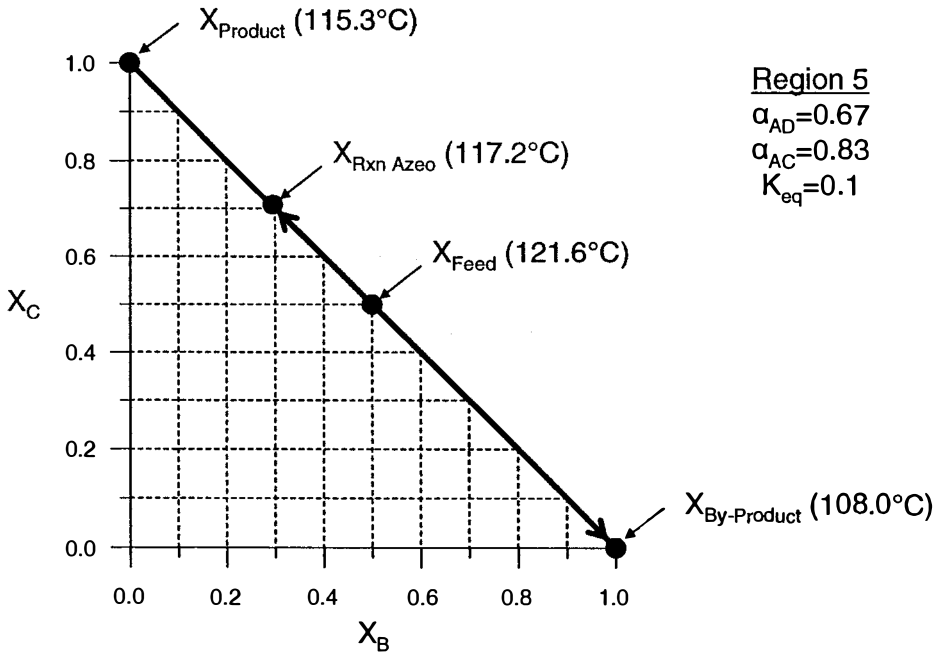


Figure 28. A↔C+D Reactive Azeotropes: Region 5 Reactive Residue Curve Map

feasibility boundaries for Regions 1,2, 5, and 6 will continue to at least $K_{eq} \approx 1.0$ unless the by-product and desired product boiling points are so close together that distillation cannot separate them, (4) that only A↔C+D systems within Regions 2 and 5 are directly limited by reactive azeotropes from meeting the economic feasibility criteria.

A↔C+D Economic Feasibility: Region 1

Volatility order Region 1 is defined as where boiling points for the reactant ($T_{bp,A}$), the desired product ($T_{bp,C}$), and the by-product ($T_{bp,D}$) are of the order $T_{bp,A} < T_{bp,D} < T_{bp,C}$. In all regions for the A↔C+D system, a sharp split was required between the product and the by-product so that the product purity can be greater than 99.0% and meet the economic feasibility criteria. If this sharp split was not obtained, the by-product "contaminated" the product and limited the final product purity. Therefore the by-product must be the primary component in the distillate stream and the desired product must be the primary component in the bottoms stream for this region since the by-product is lower boiling than the desired product. Since the reactant is the lowest boiling component in this region, all reactive distillation columns for this region were designed with a molar distillate to feed ratio of 1.0 to allow the unconverted reactant to leave with the by-product in the distillate stream and maximize the product purity in the bottoms stream. This reactive distillation design is shown in Figure 29 for the three different reactive distillation configurations studied in this research project.

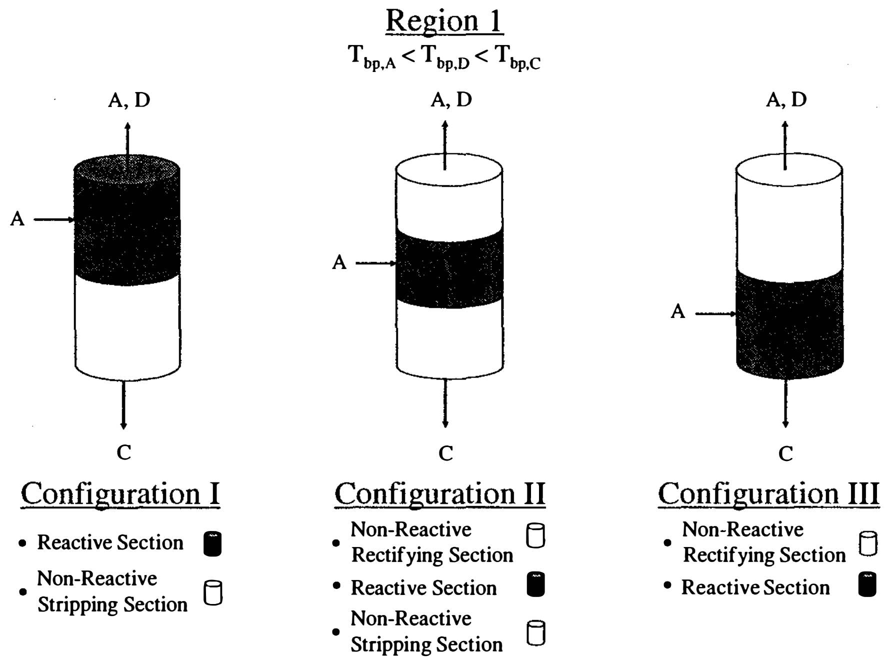


Figure 29. A↔C+D Region 1: Configurations I, II, III

The top sections of the Rough Economic Feasibility Diagrams for $\alpha_{AD} > 1.0$ (Figures 37-45) and the Refined Economic Feasibility Diagrams in Figure 22 contain the simulation results for Region 1. An initial review of the three Refined Economic Feasibility Diagrams for each reactive distillation configuration indicates that there is not a significant difference between the configurations for any studied reflux ratio, except for a reflux ratio of 1.0. For this reflux ratio, the economic feasibility boundaries for reactive distillation columns of Configuration II or III are essentially the same, but for Configuration I, the economic feasibility boundary does not extend to the same K_{eq} for $A \leftrightarrow C+D$ systems with $\alpha_{AC} \geq 25$.

This difference appears to go against what may initially be expected for this set of relative volatilities. Since the reactant is lowest boiling component in this system, one would initially expect the best design to be with the reactive zone placed at the very top of the column where the reactant is most concentrated (i.e. Configuration I). However, this anticipated advantage in configuration is actually a disadvantage at low reflux ratios when $\alpha_{AC} \geq 25$ and $\alpha_{AD} \leq 10$. Since chemical reaction is occurring at the very top stage of the reactive distillation column for Configuration I, some product will be generated at the top of the column. At low reflux ratios (i.e. approximately 1.0), this product is allowed to leave the reactive distillation column and is not returned back to the column for further separation from the reactant and by-product, thus limiting product production and reactant conversion. Configurations II and III have a non-reactive section at the top of the reactive distillation column, which allows the separation of the desired product from the other two components and limits any product lost for columns with low reflux ratios. This difference is most noticeable when the product boiling point is very different from the other two components (i.e. $\alpha_{AC} = 100$ and $\alpha_{AD} < 10$). The advantage of Configurations II and III at low reflux ratios disappears when the by-product boiling point approaches the product boiling point and the non-reactive rectifying section cannot separate the desired product from the by-product (i.e. $\alpha_{AC} = 100$ and $\alpha_{AD} \geq 10$). This Configuration I disadvantage at low reflux ratios can found in the Rough Economic Feasibility Diagrams for the other studied relative volatility combinations within Region 1 as well.

All $A \leftrightarrow C+D$ systems within this region must have a $K_{eq} > 0.1$ to be economically feasible regardless of reflux ratio or column staging. Reactive azeotropes are present in this region and are present for $A \leftrightarrow C+D$ systems with $K_{eq} \leq 0.01 - 1.0$, but the reactive azeotropes are not a direct limitation on the economic feasibility for this region because the reactive azeotropes are unstable (lowest boiling) nodes which will not limit the purification of the desired product because it is a high boiler. The reactive azeotropes may be limiting for feeds where the feed transformed coordinate is $X_C < 0.5$, but the exact point of limitation changes based on the $A \leftrightarrow C+D$ system relative volatility and chemical reaction equilibrium constant.

The primary feature of Region 1 is the region boundary that exists when the by-product boiling point is the same as the desired product boiling point (i.e. $\alpha_{AC} = \alpha_{AD}$). Reactive distillation is not economically feasible for $A \leftrightarrow C+D$ systems when $\alpha_{AC} = \alpha_{AD}$ no matter what the chemical reaction equilibrium constant is because distillation cannot separate the desired product from the reaction by-product. For A↔C+D systems where $\alpha_{AC} \rightarrow \alpha_{AD}$ and $K_{eq} > 1.0$, the by-product and desired product separation is limiting economic feasibility and a larger reflux ratio does improve the economic feasibility for these systems. This additional reflux ratio allows the distillation column to overcome the difficult product and by-product separation and improve the economic feasibility for these particular A↔C+D systems. Chemical systems within this region where the desired product and by-product relative volatility is $0.92 \leq \alpha_{DC} \leq 1.0$ are not economically feasible regardless of the chemical reaction equilibrium constant because of the separation difficulties between the product and by-product.

It is interesting to compare the A↔C+D systems within this region with the results from the A↔C systems where $\alpha_{AC} \geq 1.0$. For α_{AC} in this A↔C+D region that are significantly different than the α_{AD}, the minimum reflux ratios are comparable for a given chemical reaction equilibrium constant. However, when α_{AC} is close to α_{AD} in the A↔C+D system, the reflux ratios required for economic feasibility are significantly larger than in the A↔C system with the same α_{AC}. This is because of the difficulty in separating the by-product from the product in the A↔C+D system, which the A↔C system does not have to overcome.

As was discussed in the earlier section on reactant, by-product, and desired product splits, it is clearly recognized that a reactive distillation column is not the most economical process design for all chemical reactive systems. For A↔C+D systems within this region, it may be economically beneficial to use other process designs such as a single reactive distillation column followed by a non-reactive distillation column with the design split occurring between the reactant and products (Figure 25). The results for this region should be used to evaluate the feasibility of a single reactive distillation column in conjunction with the evaluation of other potential process designs.

A↔C+D Economic Feasibility: Region 2

Volatility order Region 2 is defined as where the reactant, desired product, and by-product boiling points are of the order $T_{bp,A} < T_{bp,C} < T_{bp,D}$. With the required sharp split between the desired product and by-product, the desired product must be the primary distillate product and the by-product must be the primary bottoms product for this region since the desired product is lower boiling than the by-product. All reactive distillation columns for this region were designed with a molar distillate to feed ratio of 0.95 to allow the product purity to meet the criteria set for economic feasibility. Since the reactant is the lowest boiling component in this region, the reactant will accumulate at the top of the reactive distillation column and leave with the desired product in the distillate stream. This reactant and product boiling point ordering will require that the reactant be almost totally converted to product so that the unconverted reactant does not limit the desired product purity and inhibit the economic feasibility of the reactive distillation column. The distillate and bottoms product design for this region is shown in Figure 30 for the three different reactive distillation configurations.

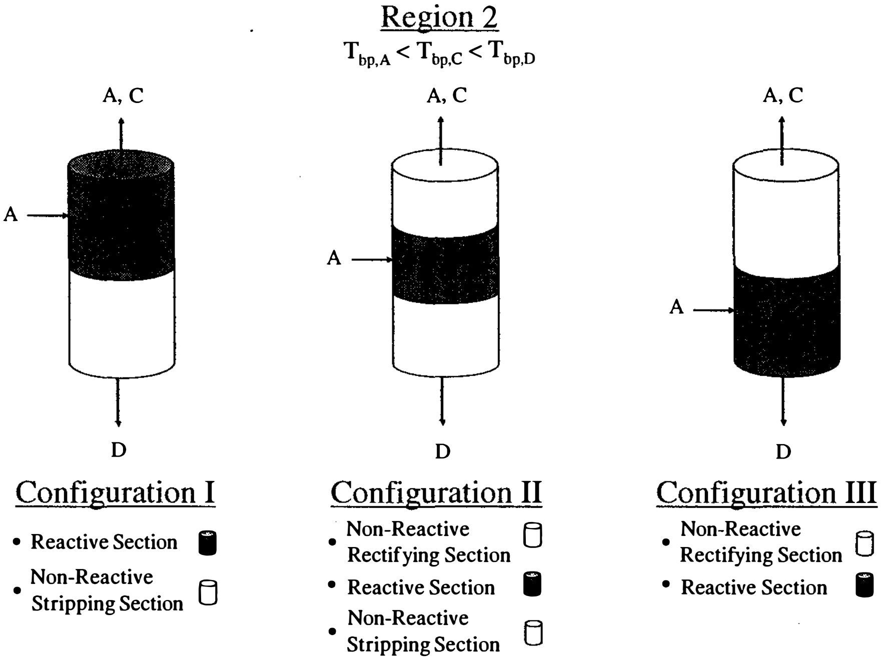


Figure 30. A↔C+D Region 2: Configurations I, II, III

The middle sections of the three diagrams in Figure 22 and the Rough Economic Feasibility Diagrams for $\alpha_{AD} > 1.0$ (Figures 37-45) contain the simulation results for Region 2. One may initially expect that only a few economically feasible A↔C+D systems would exist within this region because the product is the intermediate boiling component and distillation would not be able to produce product with 99.0% purity except for systems with very high chemical reaction equilibrium constants. However, the data compiled in the Rough Economic Feasibility Diagrams show that there are A↔C+D systems that have chemical reaction equilibrium constants as low as 1.0 that are economically feasible for reactive distillation columns with reasonable reflux ratios (i.e. less than 10). For example, the Refined Economic Feasibility Diagram in Figure 22 shows that a reactive distillation column of Configuration II and with a reflux ratio of 10 is still economically feasible for a A↔C+D system with a $\alpha_{AC} = 1.10$, $\alpha_{AD} = 1.50$, and $K_{eq} = 1.7$.

In some cases, the combination of reaction and distillation allows a reactive distillation column to overcome certain separation limitations by reacting away the component limiting the separation. For A↔C+D systems in this region, a non-reactive distillation column with a feed containing all three components would not be able to separate the desired product from the by-product and generate a desired product purity of 99.0%. This level of product purity would not be possible with a non-reactive distillation column because the reactant is the lowest boiling component in the system and would leave the column with the desired product in the distillate stream. However, the combination of reaction and distillation for $A \leftrightarrow C+D$ systems in this region allows the by-product to be preferentially removed from the reacting liquid phase, which helps to drive the complete conversion of the reactant to product for chemical reaction equilibrium limited systems. The complete conversion of reactant removes the need to separate the product from the reactant and effectively reduces the distillation separation to only the product and by-product separation. In fact, the $\alpha_{AC} = 1.0$ region boundary in the Economic Feasibility Diagrams is not an actual physical boundary for economic feasibility for this very reason. This is a significant advantage for reactive distillation when compared to more traditional reactor/distillation train separations for $A \leftrightarrow C+D$ systems that are within this region.

All $A \leftrightarrow C+D$ systems within this region must have a $K_{eq} \geq 0.1$ to be economically feasible and the boiling point of the desired product should not be close to the by-product (i.e. α_{AC} must not be close to α_{AD}). Larger reflux ratios are required to meet the economic feasibility criteria for systems where the by-product boiling point is close to the desired product boiling point than for systems where the boiling point of the product is close or equal to the reactant. For example, an $A \leftrightarrow C+D$ system with $\alpha_{AD} = 2.0$, $\alpha_{AC} = 1.2$, and $K_{eq} = 1.0$ requires a minimum reflux ratio of 10 to meet the economic feasibility criteria while a system with $\alpha_{AD} = 2.0$, $\alpha_{AC} = 1.1$, and $K_{eq} = 1.0$ only requires a reflux ratio of 5. Chemical systems within this region where $1.0 < \alpha_{DC} < 1.07$ are not economically feasible for any chemical reaction equilibrium constant because the desired product cannot be sufficiently separated from the by-product.

Reactive azeotropes are present in this region for $A \leftrightarrow C+D$ systems with $K_{eq} < 0.01 - 1.0$ and are a direct limitation on the economic feasibility for reactive distillation columns of Configuration I. However, the economic feasibility for Configurations II and III are not significantly better than Configuration I as can be seen in a review of the Rough Economic Feasibility Diagrams in Appendix A (Figures 37-45). Configurations II and III have a non-reactive rectifying section at the top of the reactive distillation column which will break the reactive azeotrope composition. Since the economic feasibility boundaries are not significantly better for these configurations when compared to reactive distillation columns of Configuration I, the reactive azeotropes must not be the primary cause for limiting the economic feasibility of $A \leftrightarrow C+D$ systems in this region.

The primary feature of this region is the actual physical boundary for economic feasibility that exists when $\alpha_{AC} = \alpha_{AD}$ and when α_{AC} is close to α_{AD}. For $A \leftrightarrow C+D$ systems near the $\alpha_{AC} = \alpha_{AD}$ boundary, the separation of the by-product and the desired product limits economic feasibility. Larger reflux ratios do help improve the economic feasibility, but for systems where α_{AC} is very close to α_{AD}, there actually are no economically feasible reflux ratios or reactive distillation column designs for any chemical reaction equilibrium constant. The separation of the product and by-product is the primary factor limiting economic feasibility for $A \leftrightarrow C+D$ systems within this region.

It is interesting to compare $A \leftrightarrow C+D$ systems within this region with the results from the $A \leftrightarrow C$ systems where $\alpha_{AC} \geq 1.0$. For α_{AC} in this $A \leftrightarrow C+D$ region that are significantly different than the α_{AD}, the minimum reflux ratios are comparable to the $A \leftrightarrow C$ systems for a given chemical reaction equilibrium constant. However, when α_{AC} is close to α_{AD} in the A↔C+D system, the reflux ratios are significantly larger for the A↔C+D system than the A↔C system for the same α_{AC}. This is because of the difficulty in separating the by-product from the product in the A↔C+D system.

As was discussed in the earlier section on reactant, by-product, and desired product splits, it is clearly recognized that a reactive distillation column is not the most economical process design for all cases. For A↔C+D systems within this region, it may be economically beneficial to use other process designs such as a single reactive distillation column followed by a non-reactive distillation column with the design split occurring between the reactant and products (Figure 25). The results for this region should be used to evaluate the feasibility of a single reactive distillation column in conjunction with the evaluations of other potential process designs.

A↔C+D Economic Feasibility: Region 3

Volatility order Region 3 is defined as where the reactant, desired product, and by-product boiling points are of the order $T_{bp,C} < T_{bp,A} < T_{bp,D}$. The sharp split for this region will occur between the unconverted reactant and the desired product with the product leaving the reactive distillation column in the distillate stream because it is the lowest boiling component in the system. All reactive distillation columns for this region were designed with a molar distillate to feed ratio of 0.95 to allow any unconverted reactant to leave the column in the bottoms stream with the high boiling by-product and maximize the desired product purity in the distillate stream. This distillate and bottoms product design is shown in Figure 31 for the three different reactive distillation configurations.

The bottom section of the three Refined Economic Feasibility Diagrams in Figure 22 and the corresponding Rough Economic Feasibility Diagrams in Appendix A (Figures 37-45) for $\alpha_{AD} > 1.0$ contain the simulation results for Region 3. A↔C+D systems within this region are particularly amenable to reactive distillation because the reactant is the middle boiler and the products are the extreme boilers. This boiling point ordering of reactant and products is desirable for reactive distillation because distillation removes the products from the reactive zone and forces the reactant back to the liquid phase in the reactive zone, which helps drive the equilibrium limited reaction to completion. A review of the Refined Economic Feasibility Diagrams in Figure 22 and the Rough Economic Feasibility Diagrams (Figures 37-45) show that A↔C+D systems within Region 3 usually require a much smaller reflux ratio to meet the economic feasibility criteria than the A↔C+D systems in Regions 1 and 2.

As the Rough Economic Feasibility Diagrams show, Configuration II is the most advantageous reactive distillation column configuration for A↔C+D systems within this region. Reactive distillation columns of Configuration II have both a non-reactive rectifying section and a non-reactive stripping section which can improve reactant conversion and product purification for chemical reactive systems in Region 3. The non-reactive sections of this configuration allow the low boiling product and high boiling by-

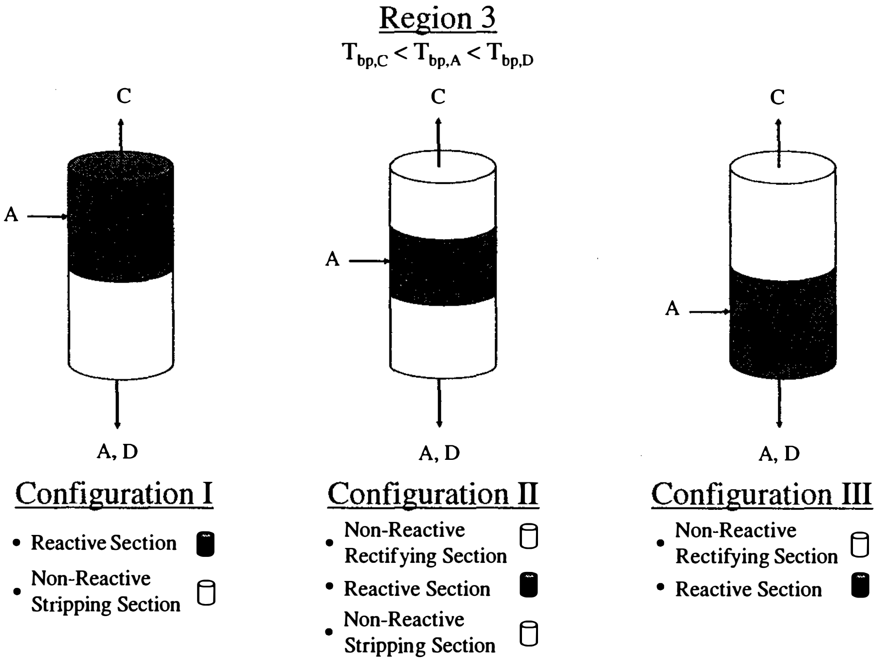


Figure 31. A↔C+D Region 3: Configurations I, II, III

product to be purified and separated by distillation away from the reactive zone, which is in the middle of the column. The low boiling product boils up and away from the reactive zone and is separated from the reactant and by-product in the non-reactive rectifying section of the reactive distillation column. The high boiling by-product drops away from the reactive zone into the non-reactive stripping section and is separated from the reactant and desired product. The intermediate boiling, unconverted reactant is constantly returned to the middle of the reactive distillation column where it is converted to more product and by-product. This continual separation of products from the reactant and product removal from the reactive zone drives the chemical equilibrium reaction to completion following Le Chatelier's principle. Only when the by-product is very heavy, $\alpha_{AD} = 100$, and $K_{eq} \geq 10$ does a reactive distillation column of Configuration III have an apparent slight advantage over Configuration II for a reflux ratio of 1.0 (Appendix A).

Even with this advantageous boiling point ordering, chemical systems within this region where $1.0 \leq \alpha_{DC} \leq 1.07$ are not economically feasible for all chemical reaction equilibrium constants. As is always the case with the A↔C+D system, if the product and by-product boiling points are close together, distillation cannot sufficiently separate the product from the by-product and a process configuration other than reactive distillation will have to be selected.

It is interesting to compare the A↔C+D systems within this region with the results from the A↔C systems where $\alpha_{AC} \leq 1.0$. For $\alpha_{AC} < 0.5$ and a given reflux ratio, an A↔C+D system can have a chemical reaction equilibrium constant that is much smaller than a A↔C systems with the same α_{AC}. For example, when $\alpha_{AC} = 0.83$ the A↔C system can have a $K_{eq} = 15$ and still be economically feasible for a reactive distillation column with a reflux ratio of 5.0. An A↔C+D system with $\alpha_{AC} = 0.83$ and $\alpha_{AD} = 1.5$ can have a $K_{eq} = 0.2$ and still be economically feasible for the same reflux ratio and column configuration. However, for A↔C+D systems where the boiling point of the desired product is close to the by-product (i.e. $\alpha_{DC} \rightarrow 1.0$), the corresponding A↔C system with the same α_{AC} will be economically feasible for systems with smaller K_{eq} and the A↔C+D systems actually may not be economically feasible at all. This is because of the required separation between the product and the by-product which the A↔C systems do not have to overcome. For example, for A↔C+D systems with $\alpha_{AC} = 0.83$ and $\alpha_{AD} < 1.2$, there are no economically feasible reactive distillation columns with a reflux ratio of 5.0 or less and Configuration II. These results emphasize the importance that the separation of the by-product from the desired product has on reactive distillation for A↔C+D systems.

A↔C+D Economic Feasibility: Region 4

Volatility order Region 4 is defined as where the reactant, desired product, and by-product boiling points are of the order $T_{bp,D} < T_{bp,A} < T_{bp,C}$. The sharp split for this region will occur between the unconverted reactant and product with the product leaving the reactive distillation column in the bottoms stream because the product is the highest boiling component in the system. All reactive distillation columns for this region were designed with a molar distillate to feed ratio of 1.0 to allow any unconverted reactant to leave the column in the distillate stream with the by-product and maximize the desired product purity in the bottoms stream. This distillate and bottoms product design is shown in Figure 32 for the three different reactive distillation configurations.

The top section of the three diagrams in Figure 23 and the corresponding Rough Economic Feasibility Diagrams in Appendix A (Figure 46-54), where $\alpha_{AD} < 1.0$, contain the simulation results for Region 4. A↔C+D systems within this region are particularly amenable to reactive distillation because the reactant is the middle boiler and the products are the extreme boilers. As was discussed in for the A↔C+D systems in Region 3, this boiling point ordering is the most desirable situation for reactive distillation because the distillation removes the products from the reactive zone, returns the reactant to the liquid phase of the reactive zone, which drives the chemical equilibrium limited reaction to completion.

The corresponding Rough Economic Feasibility Diagrams for Region 4 in Appendix A (Figures 46-54) show that a reactive distillation column of Configuration II is the best configuration for this region. The non-reactive sections of Configuration II allow the product and by-product to be purified from the reactant before leaving the reactive distillation column, just like the A↔C+D systems that fall within Region 3. This purification separates the products from the unconverted reactant and returns the reactant

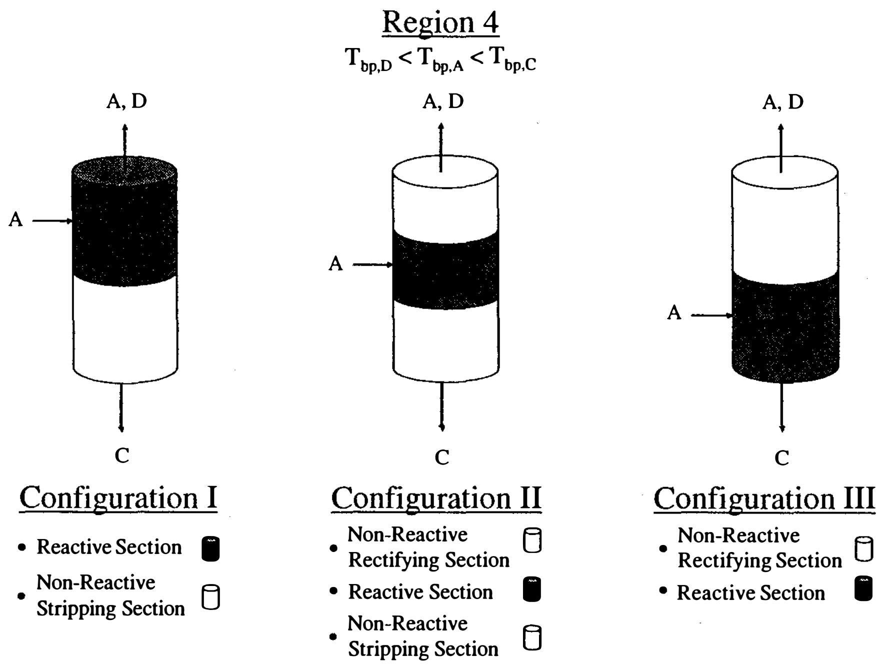


Figure 32. $A \leftrightarrow C+D$ Region 4: Configurations I, II, III

back to the reactive zone in the reactive distillation column for further reaction. This purification allows the reactive distillation column to overcome very low chemical reaction equilibrium constants and deliver a very pure product from the process.

Chemical systems within this region where the desired product and by-product relative volatility is $0.94 \leq \alpha_{DC} \leq 1.0$ are not economically feasible for any chemical reaction equilibrium constant. This limitation is once again caused by the inability of distillation to separate the product and by-product when their boiling points are close together.

When comparing the $A \leftrightarrow C+D$ systems within this region with the results from the $A \leftrightarrow C$ systems where $\alpha_{AC} \geq 1.0$, the $A \leftrightarrow C+D$ systems can have a much smaller K_{eq} for a given reflux ratio than a $A \leftrightarrow C$ system with the same α_{AC} and remain economically feasible. The reason is the same as that for $A \leftrightarrow C+D$ systems in Region 3, the low boiling by-product and high boiling desired product are removed from the reactive zone by distillation and the reactant is retained in the reactive zone for further conversion. This allows reactive distillation to overcome the economic feasibility limitations caused by much smaller chemical reaction equilibrium constants. This improvement is shown when comparing the $A \leftrightarrow C$ system in Figure 10 with the $A \leftrightarrow C+D$ system in Figure 23 for a reactive distillation column of Configuration II. For a $\alpha_{AC} = 10$ the economic feasibility boundary for a reflux ratio of 10 is at a $K_{eq} = 6$ for the $A \leftrightarrow C$ system and is at a $K_{eq} = 0.005$ for the $A \leftrightarrow C+D$ system.

A↔C systems are more economically feasible than A↔C+D systems when the product and by-product have similar boiling points because the reactive distillation column does not have to separate the by-product from the product the A↔C systems, while this separation is the limiting factor for A↔C+D systems, especially for systems with large K_{eq}.

For A↔C+D systems with $\alpha_{AC} \geq 25$, the economic feasibility of reactive distillation is not enhanced by the large boiling point difference between the reactant and product for columns with reflux ratios < 2.5. This difference appears to go against what may initially be expected for A↔C+D systems with this set of product and reactant relative volatilities. Since the reactant boiling point is much lower than the desired product boiling point, one would initially expect reactive distillation to be enhanced because the product could be easily separated from the unconverted reactant. However, this anticipated advantage is actually a disadvantage at low reflux ratios for these A↔C+D systems. Since the reactant boiling point is significantly lower than the product, any unconverted reactant will concentrate at the top of reactive distillation column. For small reflux ratios, the unconverted reactant will not be returned to reactive distillation column for further conversion and so the economic feasibility of these particular A↔C+D systems is limited by reactant losses. This phenomenon is not dependent on the boiling point of the by-product.

A↔C+D Economic Feasibility: Region 5

Volatility order Region 5 is defined as where the reactant, desired product, and by-product boiling points are of the order $T_{bp,D} < T_{bp,C} < T_{bp,A}$. The sharp split for this region will occur between the by-product and desired product with the by-product leaving the reactive distillation column in the distillate stream because it is the lowest boiling component in the system. All reactive distillation columns for this region were designed with a molar distillate to feed ratio of 1.0 to allow the by-product to leave the reactive distillation column in the distillate stream and maximize the desired product purity in the bottoms stream. Since the reactant is the highest boiling component in this region, the reactant will accumulate at the bottom of the reactive distillation column and leave with the desired product in the bottoms stream. This will require that the reactant be almost totally converted to product so that any unconverted reactant does not limit the desired product purity and inhibit the economic feasibility of the reactive distillation column. This distillate and bottoms product design is shown in Figure 33 for the three different reactive distillation configurations.

The middle section of the three diagrams in Figure 23 and the Rough Economic Feasibility Diagrams in Appendix A (Figures 46-54), where $\alpha_{AD} < 1.0$, contain the simulation results for Region 5. One may initially expect that the economic feasibility for A↔C+D systems in this region would be severely limited because the product is the intermediate boiling component, which limits product purification by distillation. However, the data compiled in the Rough Economic Feasibility Diagrams show that there are A↔C+D systems that are chemical reaction equilibrium limited and are still

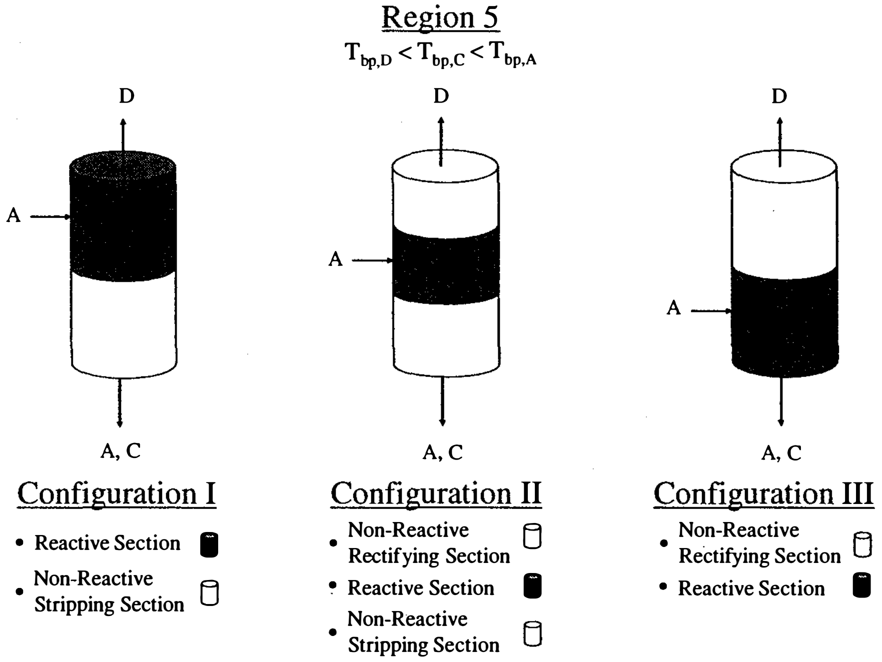


Figure 33. A↔C+D Region 5: Configurations I, II, III

economically feasible for reactive distillation columns with reasonable reflux ratios. For example, the Refined Economic Feasibility Diagram in Figure 23 shows that a reactive distillation column of Configuration II and with a reflux ratio of 10 is economically feasible for a A↔C+D system with a $\alpha_{AC} = 0.97$, $\alpha_{AD} = 0.67$, and $K_{eq} = 0.8$.

The economic feasibility within this region is possible for the same reason that the region boundary between Regions 4 and 5 and Regions 2 and 3 are not real physical boundaries. As was previously discussed, the combination of reaction and distillation allows reactive distillation columns to overcome certain distillation limitations by reacting away the component that is limiting the distillation separation. This is a significant advantage for reactive distillation when compared to more traditional reactor/distillation train separations for A↔C+D systems that are within this region.

A more detailed review of the Economic Feasibility Diagrams in this region indicates that there is a difference between the three configurations for A↔C+D systems. Reactive distillation columns of Configuration II have the advantage over Configurations I and III, especially for A↔C+D systems where $K_{eq} \approx 0.1$. For example, the Rough Economic Feasibility Diagrams for $\alpha_{AD} = 0.67$ show that Configuration II would be the preferred configuration over Configurations I and III for A↔C+D systems where $\alpha_{AC} < 0.50$ and $K_{eq} = 0.01$ to 1.0.

Reactive azeotropes are present in this region for A↔C+D systems with $K_{eq} < 0.0001 - 1.0$ and are a direct limitation on the economic feasibility for reactive distillation columns of Configuration III. However, the economic feasibility for Configurations I and II are not significantly better than Configuration III as can be seen in a review of the Rough Economic Feasibility Diagrams in Appendix A (Figures 46-54). Configurations I and II have a non-reactive stripping section at the bottom of the reactive distillation column which will break the reactive azeotrope composition. Since the economic feasibility boundaries are not significantly better for these configurations when compared to reactive distillation columns of Configuration III, the reactive azeotropes must not be the primary cause for limiting the economic feasibility of A↔C+D systems in this region.

All A↔C+D systems within this region must have a $K_{eq} \geq 0.01$ to be economically feasible and the boiling point of the desired product must not be close to the by-product (i.e. α_{AC} must not be close to α_{AD}). Larger reflux ratios are required for systems within this region where the by-product boiling point is closer to the desired product boiling point than for systems where the boiling point of the product is close or equal to the reactant. Chemical systems within this region where the desired product and by-product relative volatilities are $0.91 \leq \alpha_{DC} \leq 1.0$ are not economically feasible for any chemical reaction equilibrium constants. This is because of the difficulties that distillation has in separating the close boiling by-product and desired product. The separation of the product and by-product is the primary factor limiting economic feasibility for A↔C+D systems within this region.

The primary feature of this region is the actual physical boundary for economic feasibility that exists when $\alpha_{AC} = \alpha_{AD}$ and when α_{AC} is close to α_{AD}. For A↔C+D systems near the $\alpha_{AC} = \alpha_{AD}$ boundary, the separation of the by-product and the desired product limits economic feasibility. Larger reflux ratios do help improve the economic feasibility, but for systems where α_{AC} is very close to α_{AD}, there actually are no economically feasible reflux ratios or reactive distillation column designs for any chemical reaction equilibrium constant.

It is interesting to compare the A↔C+D systems in this region with the results from the A↔C systems where $\alpha_{AC} < 1.0$. For A↔C+D systems where α_{AC} is significantly different than the α_{AD}, the minimum reflux ratios are comparable to the A↔C systems for a given chemical reaction equilibrium constant. However, when α_{AC} is close to α_{AD} in the A↔C+D system, the minimum reflux ratios are significantly larger than in the A↔C system with the same α_{AC}. This is because of the difficulty in separating the by-product from the product in the A↔C+D system, whereas the A↔C system only has to separate any unconverted reactant from the desired product.

As was discussed in the earlier section on reactant, by-product, and desired product splits, it is clearly recognized that a reactive distillation column is not the most economical process design for all cases. For A↔C+D systems within this region, it may be economically beneficial to use other process designs such as a single reactive distillation column followed by a non-reactive distillation column with the design split occurring between the reactant and products (Figure 25). The results for this region should be used to evaluate the feasibility of a single reactive distillation column in conjunction with the evaluations of other potential process designs.

A↔C+D Economic Feasibility: Region 6

Volatility order Region 6 is defined as where the reactant, desired product, and by-product boiling points are of the order $T_{bp,C} < T_{bp,D} < T_{bp,A}$. The sharp split for this region will occur between the by-product and product with the product leaving the reactive distillation column in the distillate stream because it is the lowest boiling component in the system. All reactive distillation columns for this region were designed with a molar distillate to feed ratio of 0.95 to allow the unconverted reactant and by-product to leave the reactive distillation column in the bottoms stream and maximize the desired product purity in the distillate stream. This distillate and bottoms product design is shown in Figure 34 for the three different reactive distillation configurations.

The bottom section for each of the three diagrams in Figure 23 and the Rough Economic Feasibility Diagrams in Appendix A (Figures 44-52), where $\alpha_{AD} < 1.0$, contain the simulation results for Region 6. Reactive distillation columns of Configuration II have the advantage over other configurations in this region, except for A↔C+D systems where $\alpha_{AD} = 0.10$, $\alpha_{AC} = 0.01$, and $K_{eq} > 1.0$. For systems with this boiling point ordering, reactive distillation columns of Configuration III are preferred.

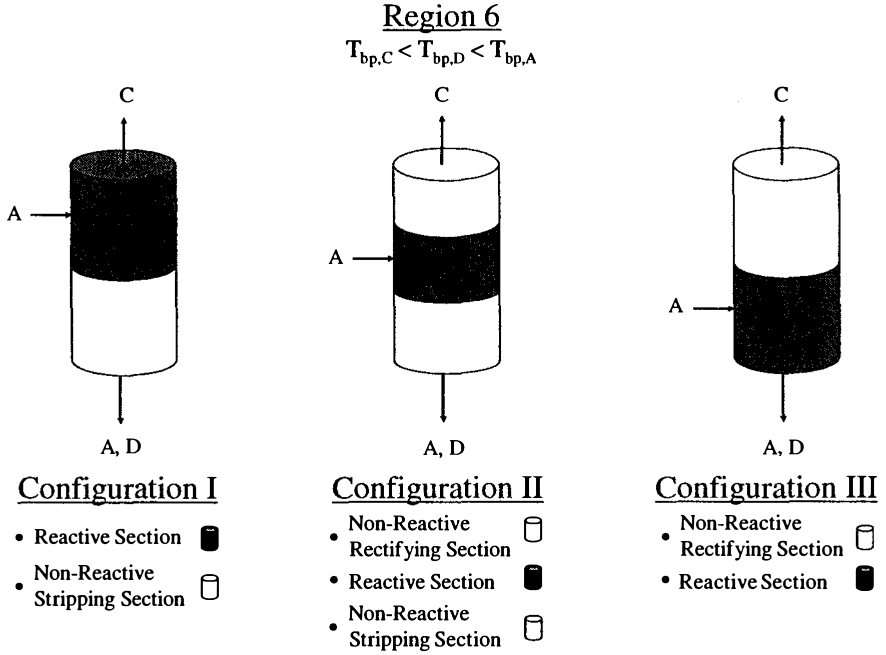


Figure 34. A↔C+D Region 6: Configurations I, II, III

All A↔C+D systems within this region must have a $K_{eq} \geq 0.01$ to be economically feasible and the boiling point of the desired product must not be close to the by-product . (i.e. α_{AC} must not be close to α_{AD}). Reactive azeotropes are present in this region and are present for A↔C+D systems with $K_{eq} \leq 0.001 - 1.0$, but the reactive azeotropes are not a direct limitation on the economic feasibility for this region because the reactive azeotropes are stable (highest boiling) nodes which will not limit the purification of the desired product because it is the lowest boiling component. The reactive azeotropes may be limiting for feeds where the feed transformed coordinate is $X_C < 0.5$, but the exact point of limitation changes based on the A↔C+D system relative volatility and chemical reaction equilibrium constant.

The primary feature of this region is the actual physical boundary for economic feasibility that exists when $\alpha_{AC} = \alpha_{AD}$ and when α_{AC} is close to α_{AD}. For A↔C+D systems near the $\alpha_{AC} = \alpha_{AD}$ boundary, the separation of the by-product and the desired product limits economic feasibility, just like the other regions bounded by the $\alpha_{AC} = \alpha_{AD}$ boundary. Larger reflux ratios do help improve the economic feasibility, but for systems where α_{AC} is very close to α_{AD}, there actually are no economically feasible reflux ratios or reactive distillation column designs for any chemical reaction equilibrium constant. Chemical systems within this region where the desired product and by-product relative volatilities are $1.0 \leq \alpha_{DC} \leq 1.07$ are not economically feasible for any chemical reaction equilibrium constants. This is because of the difficulties that distillation has in separating the close boiling by-product and desired product. Just like all of the other A↔C+D reactive systems, the separation of the product and by-product is the primary factor limiting economic feasibility for A↔C+D systems within this region.

It is interesting to compare the A↔C+D systems in this region with the results from the A↔C systems where $\alpha_{AC} < 1.0$. For A↔C+D systems where α_{AC} is significantly different than the α_{AD}, the minimum reflux ratios are comparable to the A↔C systems for a given chemical reaction equilibrium constant for reflux ratios ≤ 10. However, when α_{AC} is close to α_{AD} in the A↔C+D system, the minimum reflux ratios are significantly larger for the A↔C+D system than A↔C systems with the same α_{AC}. This is because of the difficulty in separating the by-product from the desired product in the A↔C+D system.

As was discussed in the earlier section on reactant, by-product, and desired product splits, it is clearly recognized that a reactive distillation column is not the most economical process design for all cases. For A↔C+D systems within this region, it may be economically beneficial to use other process designs such as a single reactive distillation column followed by a non-reactive distillation column with the design split occurring between the reactant and products (Figure 25). The results for this region should be used to evaluate the feasibility of a single reactive distillation column in conjunction with the evaluations of other potential process designs.

Literature Example

The reactive distillation literature was reviewed with the intent of finding real chemical reactive systems that could be used to verify the heuristics and observations proposed in this research project. The production of cumene (isopropylbenzene) is present in the reactive distillation literature (Shoemaker and Jones, 1987; Stadig, 1987) and can be used as an example of an A↔C+D system if the reaction is reversed and the production goal is the decomposition of cumene. For the purpose of this study, it was assumed that cumene will not react with the isopropylene product to form di-alkyl or tri-alkyl substituted cumene compounds and isopropylene does not oligomerize with itself. The system boiling points, relative volatilities, and chemical reaction equilibrium constant for this particular reactive system is shown in Table 10.

Cumene Reactive Azeotropes

A review of the reactive azeotrope diagrams for the production of benzene (Figure 71) and the production of isopropylene (Figure 72) from cumene indicate that reactive azeotropes may or may not be present because the cumene reactive system falls on the border between the studied A↔C+D combinations that have reactive azeotropes and combinations that do not have reactive azeotropes. A reactive feasibility assessment of the cumene decomposition using Hyprotech Distil 2.0.1 indicates that reactive azeotropes are not present for this particular reactive system and therefore, will not be a direct limitation on the economic feasibility of any reactive distillation configuration for the production of benzene or isopropylene from cumene.

Economic Feasibility: Cumene Decomposition

The economic feasibility of the decomposition of cumene was evaluated using reactive distillation columns of Configurations I, II, and III (Figures 53 and 54) at an operating pressure of one atm. The cumene reactive system has a boiling point ordering that falls within Region 5 for the production of pure benzene and within Region 6 for the

Table 10. A↔C+D Literature Examples

Reactive Distillation System A↔C+D	Boiling Points (°C)	Relative Volatilities (α_{Ai})	K_{eq}
cumene (A) ↔ benzene (C) + isopropylene (D)	A = 152 C = 80 D = -48	$\alpha_{AC} = 0.1$ $\alpha_{AD} = 0.002$	0.2
cumene (A) ↔ isopropylene (C) + benzene (D)	A = 152 C = -48 D = 80	$\alpha_{AC} = 0.002$ $\alpha_{AD} = 0.1$	0.2

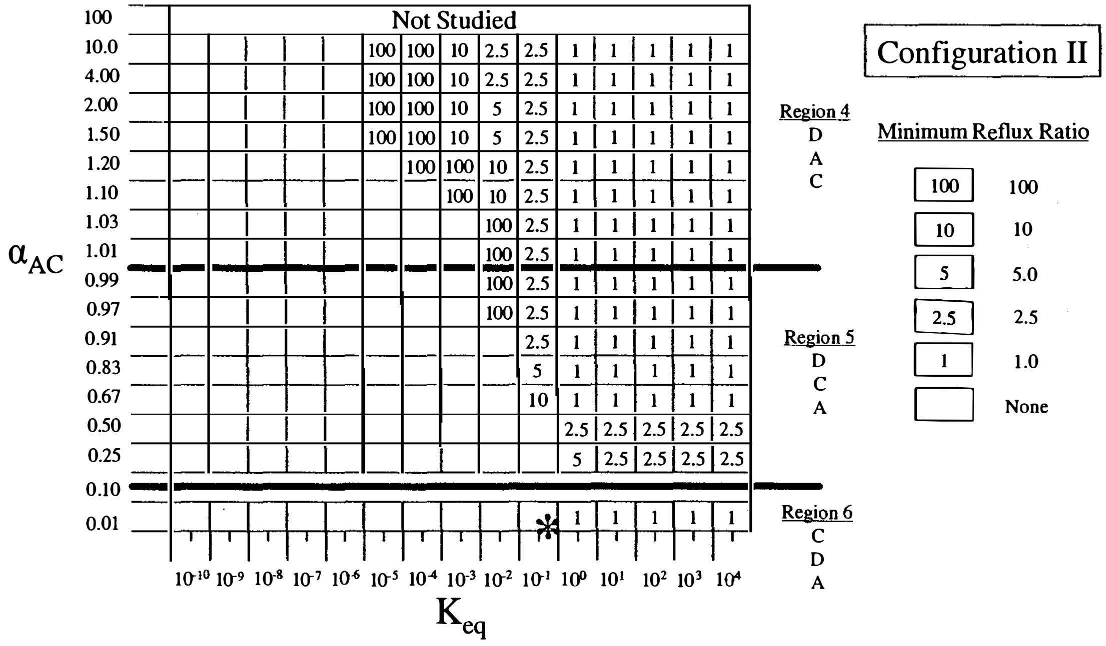
production of pure isopropylene. The chemical reaction equilibrium constant for cumene production has been estimated as $K_{eq} = 5$ (Giessler et al., 1999), which for the reverse reaction results in a $K_{eq} = 0.2$. This chemical reaction equilibrium constant was assumed to be independent of temperature for the temperature range within the reactive distillation column. Non-reactive azeotropes are not present for this mixture at a pressure of one atmosphere based on the results from the Wilson equation in Aspen Technology Aspen Plus®, which was used to model the vapor-liquid equilibrium (VLE) for this example. The production of benzene has a $\alpha_{AD} \approx 0.1$ and $\alpha_{AC} \approx 0.002$, which is plotted in Figure 35 using a '*' symbol. The production of isopropylene was also studied as an example for the $A \leftrightarrow C+D$ heuristics with the isopropylene production plotted using a '*' symbol in Figure 36.

The Rough Economic Feasibility Diagrams for the production of benzene (Figure 35) and isopropylene (Figure 36) indicate that a reactive distillation column of Configuration II may or may not be able to meet the economic feasibility criteria for a reflux ratio ≤ 100 because the cumene reactive systems fall on the border of economic feasibility. A review of the Rough Economic Feasibility Diagrams for Configurations I and III indicate that these configurations are essentially no better or worse than Configuration II (Figures 53 and 54), except for the production of isopropylene via a reactive distillation column of Configuration III, which should meet the economic feasibility criteria for a reflux ratio of 1.0 – 10.

Since the cumene reactive system relative volatility and chemical reaction equilibrium constant fall on the border of economic feasibility, the Rough Economic Feasibility Diagrams do not precisely indicate the minimum reflux ratio required to meet the economic feasibility criteria for reactive distillation. However, since the cumene reactive system does fall on the border, the Rough Economic Feasibility Diagrams do indicate that the system would be close to meeting the economic feasibility criteria if it did not actually meet the criteria.

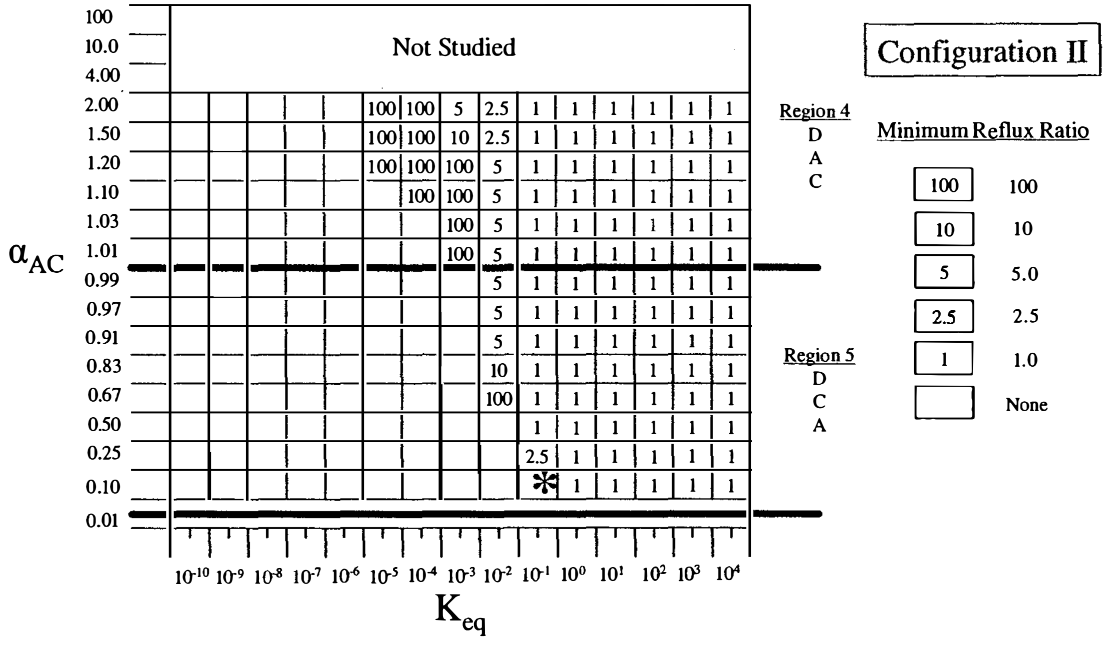
In order to check the results indicated by the Rough Economic Feasibility Diagrams for the production of benzene and isopropylene, all three reactive distillation configurations were simulated using Aspen Plus. The expected reflux ratios from the Rough Economic Feasibility Diagrams and the actual Aspen Plus simulation reflux ratios for the production of both cumene decomposition products are shown in Table 11.

The actual Aspen Plus simulation results show that the decomposition of cumene to produce benzene and isopropylene was economically feasible for all reactive distillation column configurations with a minimum reflux ratio of 1.0. Since the relative volatility of isopropylene and cumene is lower than the lowest studied relative volatility by approximately a factor of ten (i.e. $0.002 < 0.01$), the fact that the production of benzene and isopropylene met the economic feasibility criteria for a reflux ratio of 1.0 was not surprising. The economic feasibility of reactive distillation is usually extended by chemical reactive systems where the reactant and product relative volatilities are far



α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100	Not Studied														
10.0						100	100	10	2.5	2.5	1	1	1	1	1
4.00						100	100	10	2.5	2.5	1	1	1	1	1
2.00						100	100	10	5	2.5	1	1	1	1	1
1.50						100	100	10	5	2.5	1	1	1	1	1
1.20							100	100	10	2.5	1	1	1	1	1
1.10								100	10	2.5	1	1	1	1	1
1.03									100	2.5	1	1	1	1	1
1.01									100	2.5	1	1	1	1	1
0.99									100	2.5	1	1	1	1	1
0.97									100	2.5	1	1	1	1	1
0.91										2.5	1	1	1	1	1
0.83										5	1	1	1	1	1
0.67										10	1	1	1	1	1
0.50											2.5	2.5	2.5	2.5	2.5
0.25											5	2.5	2.5	2.5	2.5
0.10															
0.01										*	1	1	1	1	1

Figure 35. Benzene Production from Cumene ($\alpha_{AD} = 0.1$): Configuration II



α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100	Not Studied														
10.0															
4.00															
2.00						100	100	5	2.5	1	1	1	1	1	1
1.50						100	100	10	2.5	1	1	1	1	1	1
1.20						100	100	100	5	1	1	1	1	1	1
1.10							100	100	5	1	1	1	1	1	1
1.03								100	5	1	1	1	1	1	1
1.01								100	5	1	1	1	1	1	1
0.99									5	1	1	1	1	1	1
0.97									5	1	1	1	1	1	1
0.91									5	1	1	1	1	1	1
0.83									10	1	1	1	1	1	1
0.67									100	1	1	1	1	1	1
0.50										1	1	1	1	1	1
0.25										2.5	1	1	1	1	1
0.10										*	1	1	1	1	1
0.01															

Fig

Figure 36. Isopropylene Production from Cumene ($\alpha_{AD} = 0.01$): Configuration II

Table 11. Cumene Literature Example Economic Feasibility Reflux Ratios

Chemical Reaction $A \leftrightarrow C + D$	Reflux Ratio	
	Heuristic	Actual
Configuration I, II, and III		
Cumene ↔ Benzene + isopropylene	1.0 to NF*	1.0
Cumene ↔ isopropylene + Benzene	1.0 to NF*	1.0

*NF = Not economically feasible

apart. For $\alpha_{AC} < 1.0$ and the same K_{eq}, reactive systems with smaller relative volatilities than those reactive systems that are on the economic feasibility border will usually meet the economic feasibility criteria because of the advantages caused by better separation of the two components. Conversely, for $\alpha_{AC} > 1.0$ and the same K_{eq}, reactive systems with larger relative volatilities than those reactive systems that are on the economic feasibility border will usually meet the economic feasibility because of the same separation advantages.

This example highlights the ability of the Rough Economic Feasibility Diagram to indicate if a particular reactive system of interest is worth further investigation and which reactive distillation column configurations should be investigated.

Observation/Heuristics

Observations

1. Reactive azeotropes for the $A \leftrightarrow C+D$ system are not present for $K_{eq} > 1.0$.
2. Reactive azeotropes do not limit the economic feasibility of $A \leftrightarrow C+D$ systems.
3. Reactive azeotropes will not be present in Regions 3 and 4 for $A \leftrightarrow C+D$ systems of constant relative volatility (Barbosa and Doherty, 1988d).

Heuristics – General

1. A reactive distillation column of Configuration II is usually the best configuration for all $A \leftrightarrow C+D$ systems.
2. The separation of the desired product and by-product is the primary factor limiting reactive distillation economic feasibility for $A \leftrightarrow C+D$ systems with $K_{eq} > 1.0$.
3. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 100, the relative volatility of the by-product and product must be less than approximately 0.91 or greater than 1.10. ($\alpha_{DC} > 1.10$ or $\alpha_{DC} < 0.91$).

4. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 10, the relative volatility of the by-product and product must be less than approximately 0.80 or greater than 1.25. ($\alpha_{DC} > 1.25$ or $\alpha_{DC} < 0.80$).
5. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 5, the relative volatility of the by-product and product must be less than approximately 0.69 or greater than 1.45. ($\alpha_{DC} > 1.45$ or $\alpha_{DC} < 0.69$).
6. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 2.5, the relative volatility of the by-product and product must be less than approximately 0.48 or greater than 2.1. ($\alpha_{DC} > 2.1$ or $\alpha_{DC} < 0.48$).

Heuristics – Region 1: $T_{bp,A} < T_{bp,D} < T_{bp,C}$

7. All A↔C+D systems within this region must have a $K_{eq} > 0.1$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A↔C+D system relative volatilities.
8. Reactive azeotropes do exist in this region, but do not directly limit the economic feasibility of the desired product.

Heuristics – Region 2: $T_{bp,A} < T_{bp,C} < T_{bp,D}$

9. All A↔C+D systems within this region must have a $K_{eq} > 0.1$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A↔C+D system relative volatilities.
10. Reactive azeotropes do exist in this region, but do not appear to have a direct limitation on the economic feasibility of the desired product.

Heuristics – Region 3: $T_{bp,C} < T_{bp,A} < T_{bp,D}$

11. All A↔C+D systems within this region must have a $K_{eq} > 10^{-5}$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A↔C+D system relative volatilities.
12. Reactive azeotropes will not be present in this region for A↔C+D systems of constant relative volatility.

Heuristics – Region 4: $T_{bp,D} < T_{bp,A} < T_{bp,C}$

13. All A↔C+D systems within this region must have a $K_{eq} > 10^{-5}$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A↔C+D system relative volatilities.
14. Reactive azeotropes will not be present in this region for A↔C+D systems of constant relative volatility.

Heuristics – Region 5: $T_{bp,D} < T_{bp,C} < T_{bp,A}$

15. All A↔C+D systems within this region must have a $K_{eq} > 10^{-3}$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A↔C+D system relative volatilities.
16. Reactive azeotropes do exist in this region, but do not appear to have a direct limitation on the economic feasibility of the desired product.

Heuristics – Region 6: $T_{bp,C} < T_{bp,D} < T_{bp,A}$

17. All A↔C+D systems within this region must have a $K_{eq} > 10^{-3}$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A↔C+D system relative volatilities.
18. Reactive azeotropes do exist in this region, but do not directly limit the economic feasibility of the desired product.

Economic feasibility criteria:

1. reactant conversion $\geq$ 95.0%
2. product purity $\geq$ 99.0%
3. total column stages $\leq$ 100.
4. reflux ratio $\leq$ 100 (economic reflux ratios depend on product value).

These heuristics are based on data collected with the following assumptions:

1. The reactant is a single feed and is fed directly on the reactive stage.
2. Chemical reaction equilibrium is attained on every reactive stage.
3. Vapor-liquid equilibrium is attained on every stage.
4. Vapor and liquid phases are ideal.
5. The feed is 100% reactant.
6. Any heat effects cancel within the reactive distillation column.
7. The reactive distillation column has a total condenser.

Summary

In this chapter, a set of heuristics was proposed for the initial feasibility assessment and conceptual design of reactive distillation columns involving the reaction A↔C+D. These heuristics were developed from a data set collected from Aspen Plus simulations using a generic A↔C+D reactive system. For this generic system, a range of relative volatilities and chemical reaction equilibrium constants were chosen to cover the expected range of potential reactive systems. The potential component boiling points for the A↔C+D system were divided into six regions of similar volatility orderings. Three different reactive distillation column configurations were evaluated for each region. The first configuration had a reactive section above a non-reactive stripping section. The second configuration had a non-reactive rectifying section, a reactive section, and a non-reactive stripping section. The third configuration had a reactive zone below a non-reactive rectifying section. Diagrams were created for each studied component relative volatility and chemical reaction equilibrium constant combination indicating the economic feasibility of each reactive distillation column configuration. Reactive azeotropes were found to be present in Regions 1, 2, 5, and 6, but do not appear to limit the economic feasibility of reactive distillation for A↔C+D systems. The primary limiting factor for A↔C+D systems and reactive distillation feasibility was the separation of the by-product and desired product. For each of the six A↔C+D regions, a minimum required chemical reaction equilibrium constant was proposed for the economic feasibility of reactive distillation. The heuristics and simulation results for the generic reactive system were verified using the decomposition of cumene as an example, which is available in the reactive distillation literature.

VII. SYSTEMS WITH TWO REACTANTS AND ONE PRODUCT

Introduction

The A+B↔C system is different from the previous two chemical reactive systems because it has two reactants instead of just one. The presence of two reactants adds an additional design concern for reactive distillation because the reactants must both be present in the reactive zone and in the liquid phase in order to produce the product. The A↔C system and A↔C+D system only require that the lone reactant be present in the liquid phase of the reactive zone in order to produce product. The presence of two reactants also adds an additional design option of feeding the reactants together in a single feed or feeding the reactants in separate feeds to the reactive distillation column. Both of these feed designs, a single feed reactive distillation column and double feed reactive distillation column, were evaluated for economic feasibility for the A+B↔C system.

The reactant and product boiling points for the A+B↔C system were divided into three volatility order regions, which are defined in Table 2. Reactant A was always designated as the lowest boiling reactant for the A+B↔C system. The relative volatility combinations within each region share similar characteristics for reactive distillation feasibility and design. Therefore, each region for the A+B↔C system will be evaluated individually with the commonalities within each region condensed into a final set of observations and heuristics for this ternary reactive system.

The component boiling points within each region were broken into a fixed set of relative volatilities covering the potential range of component boiling points. In general, the relative volatilities for the reactant and product (α_{AC}) and the reactants (α_{AB}) were 0.01, 0.10, 0.25, 0.50, 0.67, 0.83, 0.91, 0.97, 0.99, 1.01, 1.03, 1.10, 1.20, 1.50, 2.0, 4.0, 10.0, and 100 with each combination of α_{AC} and α_{AB} fitting into one of the three regions. Simulations for each relative volatility combination were run with the chemical reaction equilibrium constant (K_{eq}) sequentially reduced from 10,000 by a factor of 10 until the reactive distillation column no longer met the economic feasibility criteria. The acceptance criteria for an economically feasible reactive distillation column was set so that the total column stages must be less than 100, the reactant conversion greater than 95.0%, and the product purity greater than 99.0%.

Single Feed/Double Feed Reactive Distillation Columns

In the previous chemical reactive systems, there was only one reactant and the feed to the reactive distillation column was always a single feed of pure reactant. In the A+B↔C system, there are two reactants which can be fed together in a single feed or independently in separate feeds. When the reactants are fed together in the same feed stream, it is called a single feed reactive distillation column (Figure 73). When the reactants are fed separately in two different feed streams, it is called a double feed reactive distillation column (Figure 74).

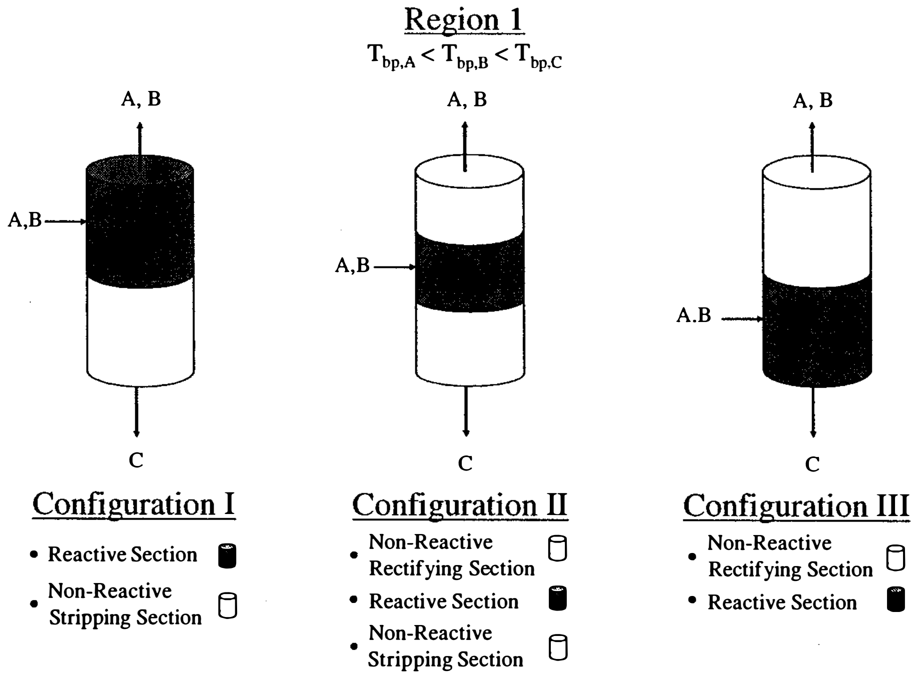


Figure 73. A+B↔C Region 1, Single Feed Reactive Distillation Column

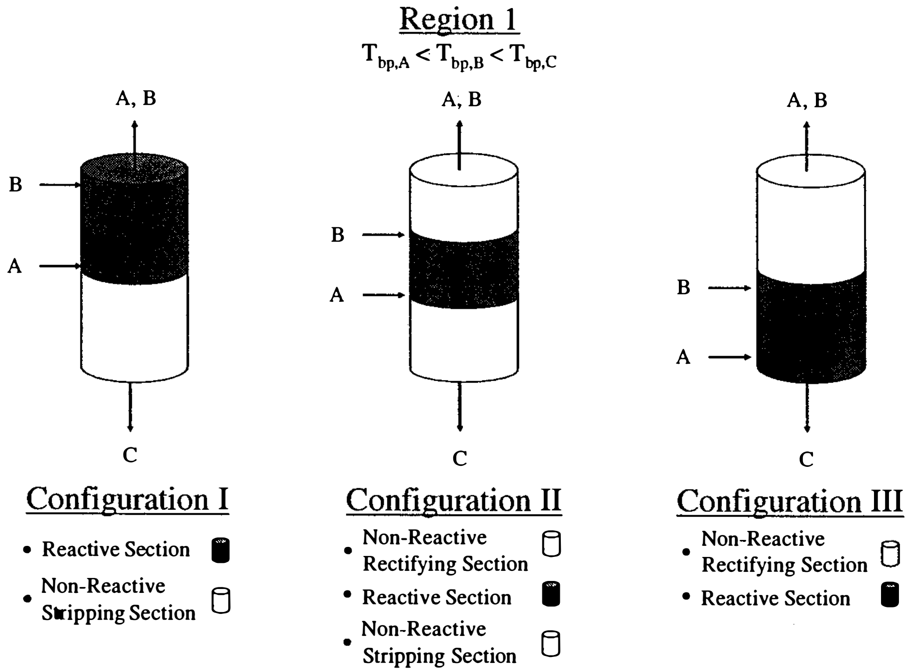


Figure 74. A+B↔C Region 1, Double Feed Reactive Distillation Column

A single feed reactive distillation column is shown in Figure 73 for an A+B↔C system with a boiling point ordering that falls within Region 1. The reactants are fed together to the reactive zone in a single feed with the unconverted reactants leaving the reactive distillation column in the distillate stream and the product leaving the reactive distillation column in the bottoms stream. For the A+B↔C systems in this study, the reactants were fed to the reactive distillation column stoichiometrically, which for a single feed reactive distillation column means the feed mol fraction was x_A=0.5 and x_B=0.5.

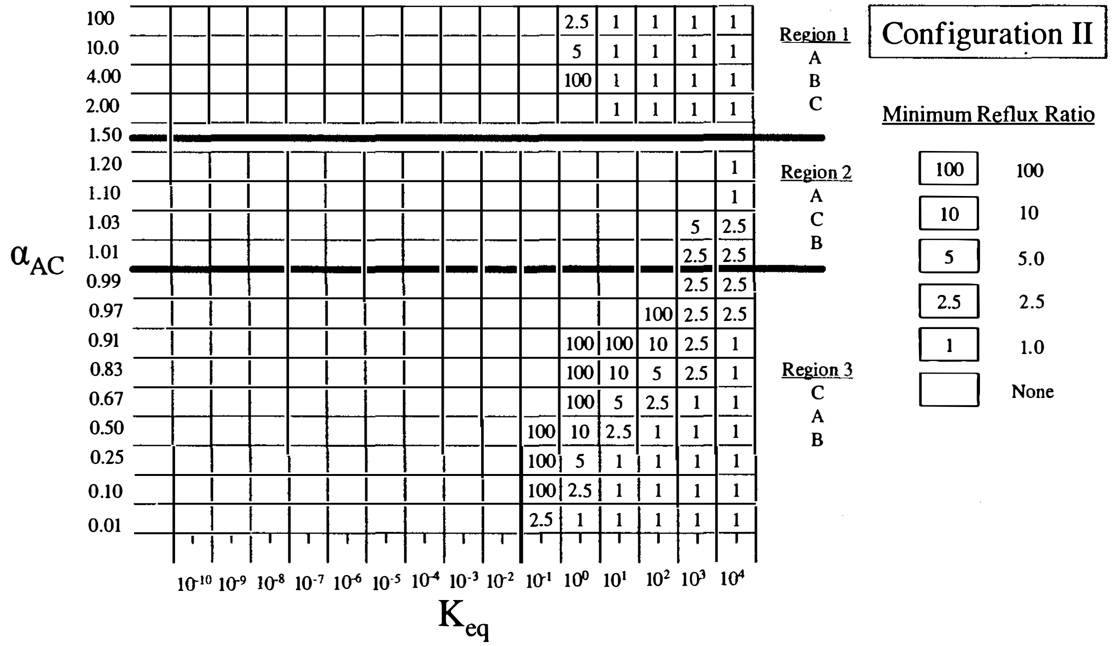
The other feed design evaluated for economic feasibility was a double feed reactive distillation column where the reactants are fed in separate feed streams (Figure 74). The overall reactant feed to the double feed column was stoichiometric just like the single feed case with the reactant A feed rate to the column equal to the reactant B feed rate. A double feed design can improve reactant conversion for certain boiling point orderings because each reactant feed stage will have a local excess of the one of the reactants, which can help to drive reactant conversion. Additionally, since the low boiling reactant A is fed lower than the higher boiling reactant B, the reactants will flow in opposite directions in the reactive distillation column. The heavier reactant B will fall down the column and the lighter reactant A will travel up the column. This cross flow of reactants may help drive reactant conversion, but the key issue for an effective double feed reactive distillation column design is that the reactants must both be relatively high in concentration in the liquid phase within the reactive zone. If both reactants are not present in the reacting liquid phase, the reactants cannot be converted to product and a double feed reactive distillation column design will probably not be the most economical process design.

For the A+B↔C system, both single and double feed reactive distillation columns were evaluated to determine the economic feasibility of each design. The feed locations were confined to the reactive zone and for the double feed design, reactant A was always the lower feed since it was always the lowest boiling reactant.

When the reactant boiling points are all lower (Region 1) or higher (Region 3) than the desired product boiling point, a reactive distillation column with the distillate stream completely returned to column (Region 1) or the bottoms stream completely returned to the column (Region 3) may be another economically acceptable design.

Rough Economic Feasibility Diagrams

A unique Rough Economic Feasibility Diagram was created from the simulation results for each studied combination of reactants (α_{AB}) and reactive distillation configuration. The Rough Economic Feasibility Diagrams for the A+B↔C system can be found in Appendix B (Figures 88-105). Figure 75 shows an example of a Rough Economic Feasibility Diagram for a single feed reactive distillation column and an A+B↔C system with α_{AB}=1.50.



α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100											2.5	1	1	1	1
10.0											5	1	1	1	1
4.00											100	1	1	1	1
2.00												1	1	1	1
1.50															
1.20															1
1.10															1
1.03														5	2.5
1.01														2.5	2.5
0.99														2.5	2.5
0.97													100	2.5	2.5
0.91											100	100	10	2.5	1
0.83											100	10	5	2.5	1
0.67											100	5	2.5	1	1
0.50										100	10	2.5	1	1	1
0.25										100	5	1	1	1	1
0.10										100	2.5	1	1	1	1
0.01										2.5	1	1	1	1	1

Figure 75. A+B↔C Rough Economic Feasibility Diagram $\alpha_{AB}=1.50$, Single Feed: Configuration II

A Rough Economic Feasibility Diagram consists of the chemical reaction equilibrium constant (K_{eq}) plotted on the x-axis, the relative volatility of the reactant and product (α_{AC}) on the y-axis, a region boundary where $\alpha_{AC} = \alpha_{AB}$, and another region boundary where $\alpha_{AC}=1.0$. The K_{eq} is plotted on the x-axis on a logarithmic scale while the α_{AC} is not plotted to scale. The regions between the boundaries are identified on the diagram and have the boiling point orderings described in Table 2. The component boiling point ordering list for the region is shown below the region title with the lowest boiling component on top of the list and the highest boiling component on the bottom.

For example, Region 1 in Figure 75 is where the reactant (A) is the lowest boiling component and is on the top, the other reactant (B) is the intermediate boiling component shown in the middle, and the product (C) is the highest boiling component and is on the bottom. Each block within the Rough Economic Feasibility Diagram consists of a specific α_{AB}, α_{AC}, and K_{eq} combination and within this block is written the minimum reflux ratio required for the reactive distillation column to meet the economic feasibility criteria. For example, an A+B↔C system with $\alpha_{AB} = 1.50$, $\alpha_{AC} = 0.67$, and a $K_{eq} = 10$ requires a minimum reflux ratio of 5 to meet the economic feasibility criteria.

Most A+B↔C systems have a combination of relative volatility and chemical reaction equilibrium constant that fall in between the blocks shown in the Rough Economic Feasibility Diagrams. The blocks within the Rough Economic Feasibility Diagrams are not intended to provide detailed boundaries, but can be used to provide initial guidance for economic feasibility with the understanding that the actual minimum reflux ratio for a particular A+B↔C system falls within the range of reflux ratios indicated by adjacent blocks. For example, an A↔C+D system with $\alpha_{AB} = 1.50$, $\alpha_{AC} = 0.5$, and a $K_{eq} = 2.0$ will require a reflux ratio between 2.5 and 10 as indicated in Figure 75. A more detailed study of this particular system shows that the actual minimum reflux ratio required to meet the economic feasibility criteria is 5 for a reactive distillation column of Configuration II, which is between the minimum reflux ratios shown in adjacent blocks.

The region boundaries within the Economic Feasibility Diagrams for the A+B↔C systems are arbitrary boundaries set to define regions where the boiling point orderings change from one ordering to another. Region boundaries for the A+B↔C system are not actual boundaries to economic feasibility. The region boundaries are just arbitrary boundaries defined to indicate changes in boiling point orderings for the components involved in the chemical reaction. The A+B↔C region boundary where $\alpha_{AC} = 1.0$ is similar to the $\alpha_{AC} = 1.0$ region boundaries for the A↔C and A↔C+D systems because the region boundary can be overcome by chemical systems with a K_{eq} that is large enough to react away the separation limiting reactant. The A+B↔C region boundary where $\alpha_{AC} = \alpha_{AB}$ can also be overcome by chemical systems with a large K_{eq}, which is in contrast to the A↔C+D system boundary where $\alpha_{AC} = \alpha_{AD}$. The A↔C+D system boundary where $\alpha_{AC} = \alpha_{AD}$ is an actual boundary to the economic feasibility of reactive distillation because the product and by-product can not be separated by distillation. Unlike the A↔C+D boundary, the $\alpha_{AC} = \alpha_{AB}$ boundary for the A+B↔C system is not an actual physical boundary to economic feasibility because there is only one product and the potential separation limiting reactants can be eliminated by the presence of chemical reaction.

The Rough Economic Feasibility Diagrams in Appendix B (Figures 88-105) for both the single and double feed reactive distillation columns along with the Refined Economic Feasibility Diagrams (Figures 76-77) will serve as the basis for the development of observations, heuristics, and trends for the A+B↔C chemical reactive system.

Refined Economic Feasibility Diagrams

The Rough Economic Feasibility Diagrams for the A+B↔C system where $\alpha_{AB} = 1.50$ were studied in much greater detail to show what the actual economic feasibility boundaries look like for given a combination of relative volatility and chemical reaction equilibrium constant. Figure 76 shows the Refined Economic Feasibility Diagrams for a single feed reactive distillation column and Figure 77 shows the Refined Economic Feasibility Diagrams for a double feed reactive distillation column. There are three Refined Economic Feasibility Diagrams each feed design, one diagram for each reactive distillation configuration.

The Refined Economic Feasibility Diagrams show that the separation of the product and reactants has a significant affect on the shape of the economic feasibility boundaries for the A+B↔C system, as is the case for the other reactive systems as well. The closer the product and reactants boiling points are the larger the K_{eq} constant has to be to meet the

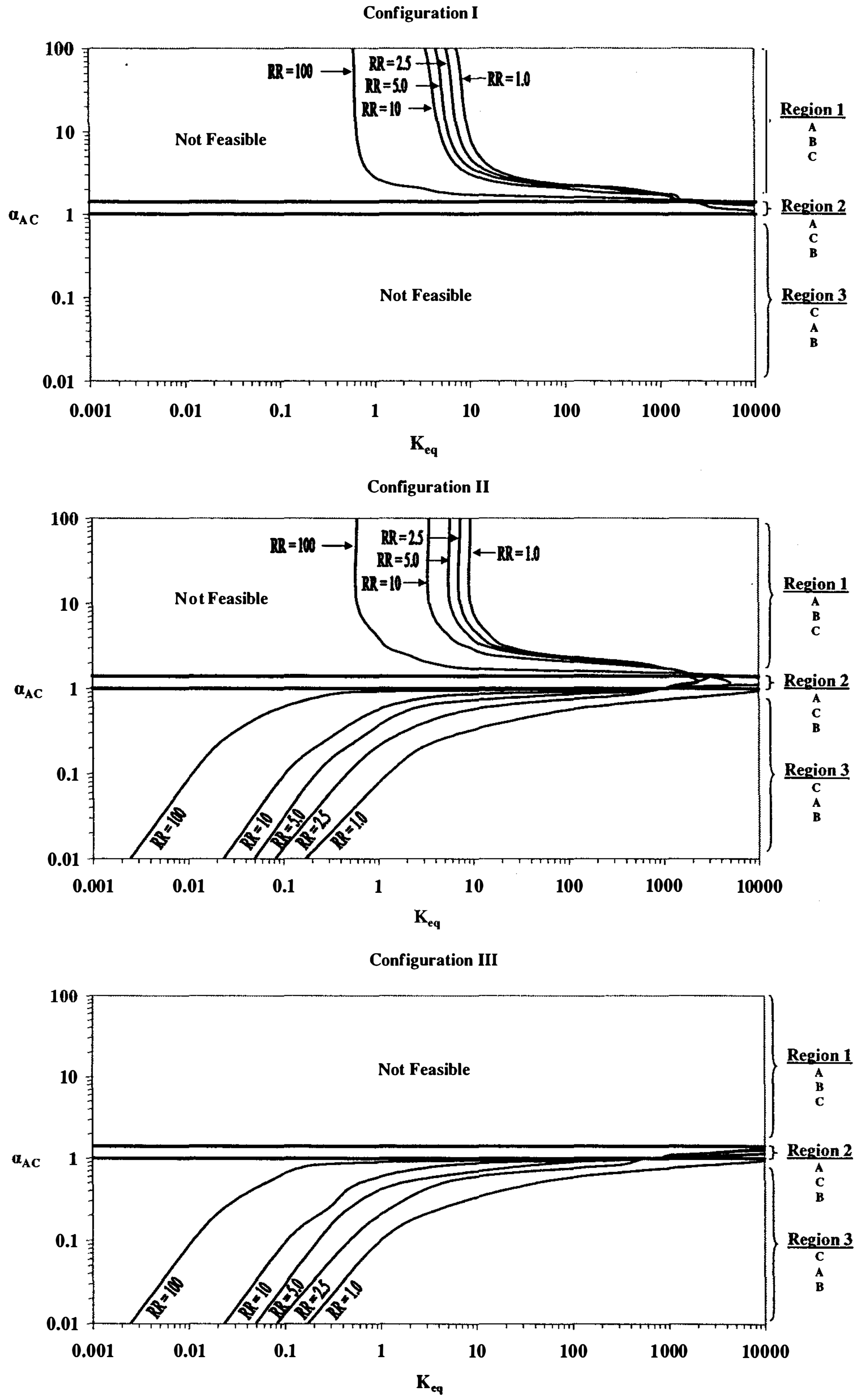


Figure 76. A+B↔C Refined Economic Feasibility Diagrams, Single Feed: $\alpha_{AB}=1.50$

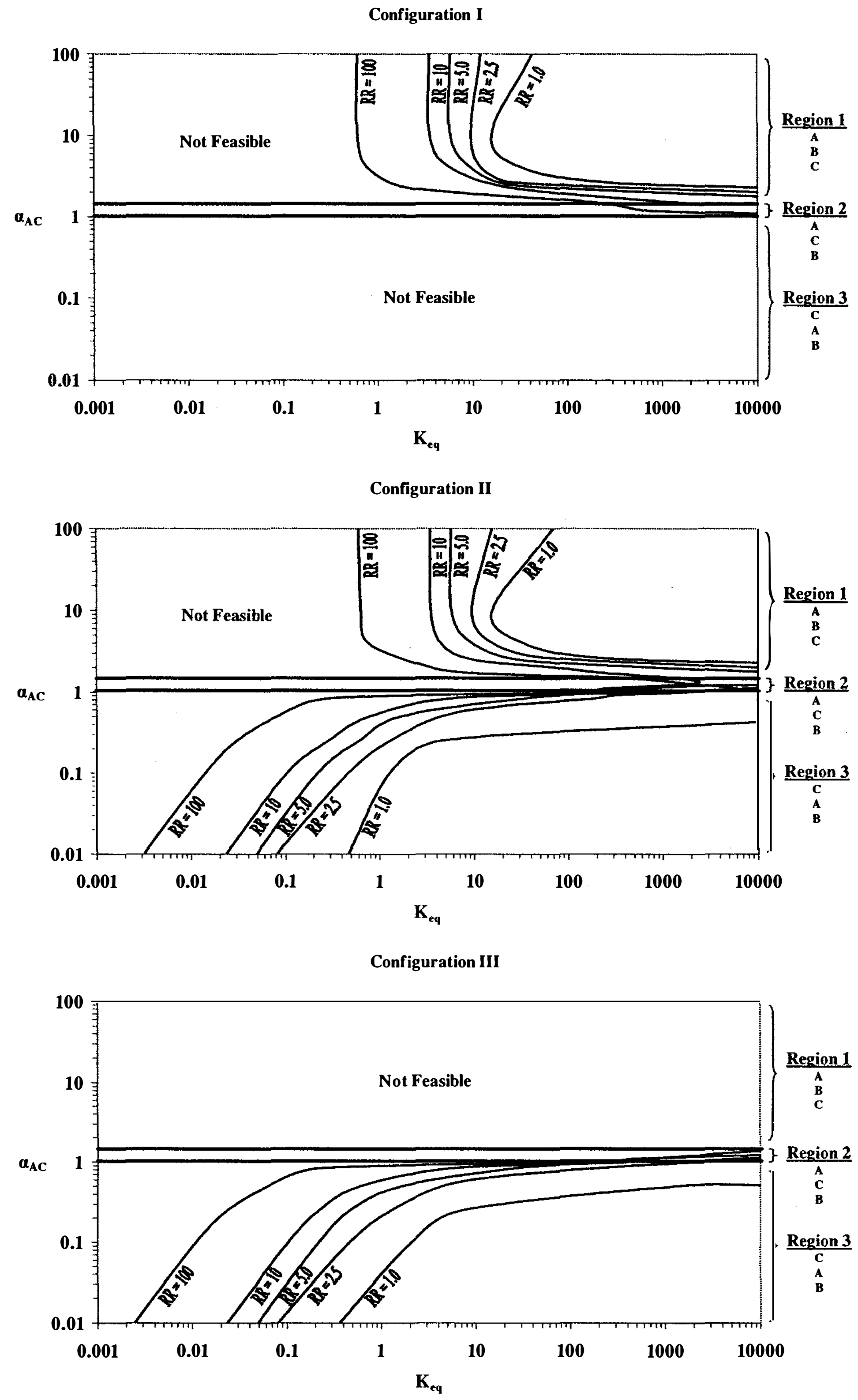


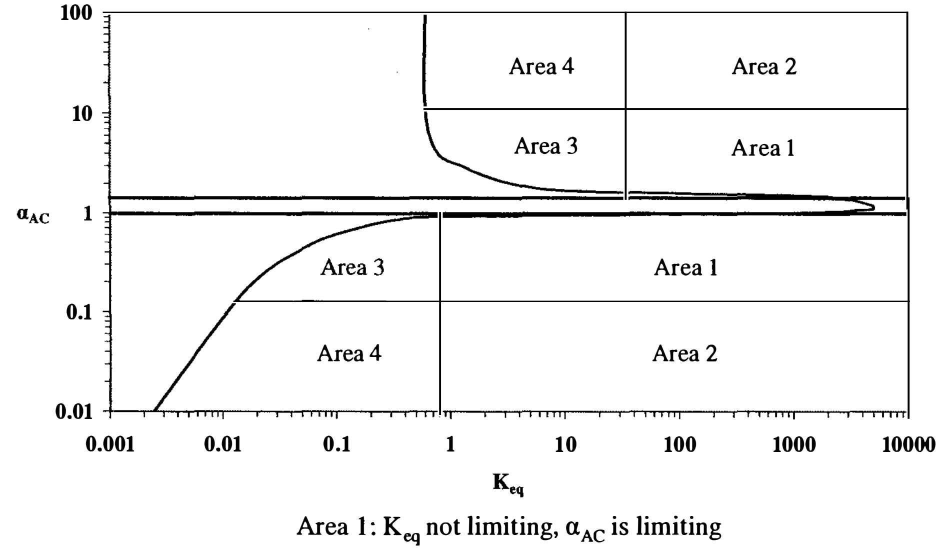
Figure 77. A+B↔C Refined Economic Feasibility Diagrams, Double Feed: α_{AB}=1.50

economic feasibility for reactive distillation. This is true for both a single feed reactive distillation column and a double feed reactive distillation column.

Qualitative Areas

The Refined Economic Feasibility Diagram boundaries shown in Figures 76 and 77 indicate that the economic feasibility boundaries for the A+B↔C system (Figure 78) have the same qualitative limiting areas found in the A↔C system (Figures 8 and 9) and the A↔C+D system (Figures 22 and 23).

For all studied chemical reactive systems, the Economic Feasibility Diagram boundaries have the same defined qualitative areas. Area 1 is where the separation of the product and reactant is limiting the economic feasibility of reactive distillation. Area 2 is where the chemical reaction equilibrium constant and the separation of the product and reactant are both enhancing the feasibility of reactive distillation. Area 3 is where both the chemical reaction equilibrium constant and the separation of the product and reactant are limiting the feasibility of reactive distillation. Area 4 is where the chemical reaction equilibrium constant is limiting the feasibility of reactive distillation. These areas are present for both a single feed reactive distillation column and a double feed reactive distillation column design.



Area 1: K_{eq} not limiting, α_{AC} is limiting
Area 2: K_{eq} not limiting, α_{AC} not limiting
Area 3: K_{eq} is limiting, α_{AC} is limiting
Area 4: K_{eq} is limiting, α_{AC} is not limiting

Figure 78. A+B↔C Economic Feasibility Diagram Single Feed, α_{AB}=1.50, RR=100: Limiting Areas

It is expected that all chemical reactive systems will have the same four qualitative areas, where the economic feasibility of reactive distillation is limited by chemical reaction, limited by separation, limited by both separation and reaction, and not limited by reaction or separation.

Reactive Azeotropes

Reactive azeotropes are not present for all A↔C+D systems, just like the previously studied reactive systems. Barbosa and Doherty (1988d) have shown that for constant relative volatility systems, reactive azeotropes can only occur if the volatility of all the reactants is either higher or lower than the volatility of all the products. Assuming that the relative volatilities are constant for the A+B↔C systems in this study, only those systems that fall within Regions 1 and 3 can have reactive azeotropes. For the A+B↔C systems within Region 2, the reactant is the middle boiling component and these systems will not have reactive azeotropes.

The presence of reactive azeotropes was determined for each studied combination of relative volatility and chemical reaction equilibrium constant using Hyprotech Distil 2.0.1. The results were organized by α_{AB} and contain a diagram showing the combinations of relative volatilities and chemical reaction equilibrium constant that have a reactive azeotrope indicated by a reference number(s). The reactive azeotrope diagrams for the A+B↔C system are located in Appendix B (Figures 106-114).

The transformed coordinates used in the A↔C+D systems to visually show the affects of reactive azeotropes do not visually add to the understanding of A+B↔C systems because the stoichiometric reactant feed and pure product have the same transformed coordinates. A stoichiometric feed of both reactants ($x_A=x_B=0.5$) has a transformed composition of $X_A=0.5$ and $X_B=0.5$ according to Equations 7.1 and 7.2 when the product is chosen as the reference component, as required by the Distil 2.0.1 software.

$$X_A = \frac{(x_A - \nu_C x_C)}{(1 - \nu_C x_C)} \tag{7.1}$$

$$X_B = \frac{(x_B - \nu_C x_C)}{(1 - \nu_C x_C)} \tag{7.2}$$

If the A+B↔C reaction goes to completion ($x_C=1.0$), the transformed composition of the pure product is $X_A=0.5$ and $X_B=0.5$, which is the same as the feed transformed coordinates. Therefore, transformed coordinates do not provide a profound, easily understandable visual explanation of the limitations of reactive azeotropes for the A+B↔C reactive system. However, the concepts of stable (highest boiling) nodes, saddles, and unstable (lowest boiling) nodes do provide an understanding of the limitations caused by reactive azeotropes.

For A+B↔C systems with a boiling point ordering that falls within Region 1 ($T_{b,A} < T_{b,B} < T_{b,C}$), existing reactive azeotropes were found to all be stable (highest boiling) nodes. Since the product is the highest boiling component in this region for a non-reactive system, it is expected that the final product purity will be limited to the reactive azeotrope composition for reactive distillation columns of Configuration III for reactive systems where a reactive azeotrope exists. If the reactive azeotrope does not have a product mole fraction greater than 0.99, reactive distillation columns of Configuration III will not be able to meet the economic feasibility criteria because Configuration III does not have a non-reactive stripping section. Reactive distillation columns of Configurations I and II are expected to be able to overcome the reactive azeotrope because these configurations have a non-reactive stripping section that will break the reactive azeotrope composition. Additionally, it is of note that the higher boiling reactant always has a higher mole fraction for any reactive azeotropes within this region.

For A+B↔C systems with a boiling point ordering that falls within Region 3 ($T_{b,C} < T_{b,A} < T_{b,B}$), existing reactive azeotropes were found to all be unstable (lowest boiling) nodes. Since the product is the lowest boiling component in this region for a non-reactive system, it is expected that the final product purity will be limited to the reactive azeotrope composition for reactive distillation columns of Configuration I for reactive systems where a reactive azeotrope exists. If the reactive azeotrope does not have a product mole fraction greater than 0.99, reactive distillation columns of Configuration I will not be able to meet the economic feasibility criteria because Configuration I does not have a non-reactive rectifying section. Reactive distillation columns of Configurations II and III are expected to be able to overcome the reactive azeotrope because these configurations have a non-reactive stripping section that will break the reactive azeotrope composition. Additionally, it is of note that the higher boiling reactant always has a lower mole fraction for any reactive azeotropes within this region.

For A+B↔C systems with a boiling point ordering that falls within Region 2 ($T_{b,A} < T_{b,C} < T_{b,B}$), there were no reactive azeotropes found for any relative volatility and chemical reaction equilibrium constant combination that was part of this study, as was expected.

A+B↔C Economic Feasibility: Region 1

Volatility order Region 1 is defined as where the boiling points for reactant A, reactant B, and the product are of the order $T_{bp,A} < T_{bp,B} < T_{bp,C}$. In all regions for the A+B↔C system, a sharp split is required between the product and the reactants so that the product purity can be greater than 99.0% and meet the economic feasibility criteria. If this sharp split is not obtained, the reactants will contaminate the product and limit the final product purity. Therefore for A+B↔C systems in Region 1, the reactants must be the primary component in the distillate stream and the product must be the primary component in the bottoms stream since the reactants are lower boiling than the product. All reactive distillation columns for this region were designed with a molar distillate to feed ratio of 0.05 to allow the unconverted reactants to leave in the distillate stream and maximize the product purity in the bottoms stream.

As was previously noted, since the distillate stream for A+B↔C systems in Region 1 consists primarily of reactants, the entire distillate stream could actually be returned back to the reactive distillation column. This deadheading of the reactive distillation column could help drive the complete conversion of the reactant to product and result in another economically acceptable design in addition to the configurations included in this research project.

The economic feasibility of both single feed and double feed reactive distillation columns were evaluated for the A+B↔C reactive system. The single feed reactive distillation design is shown in Figure 73 and the double feed design is shown in Figure 74 for the three different reactive distillation configurations studied in this research project.

It is possible to design a reactive distillation column such that the distillate or bottoms stream from the reactive distillation column is completely returned to the column as was shown previously for A↔C+D systems in Figure 25. However, for A+B↔C systems only one product is leaving the reactive distillation column and the additional non-reactive distillation column is not necessary to further purify the product as was required for the A↔C+D systems. The primary advantage for A+B↔C systems in this design is the same as it was for similar A↔C+D systems in that the reactants fed to the reactive distillation column are kept in the distillation column and are completely converted to product because they never leave the reactive distillation column. It is expected that this design would be economically advantageous for A+B↔C systems with boiling point orderings that fall in Regions 1 and 3, but this design was not fully evaluated in this research project.

The top sections of the Rough Economic Feasibility Diagrams in Appendix B (Figures 88-105), the single feed Refined Economic Feasibility Diagrams (Figure 76), and double feed Refined Economic Feasibility Diagrams (Figure 77) contain the simulation results for Region 1. A review of these diagrams shows that a reactive distillation column of Configuration III is the most economically limited reactive distillation configuration for this region. These results along with the reactive azeotrope data for this region show that a column of Configuration III is not economically feasible for any A+B↔C system because of the presence of high boiling reactive azeotropes. All A+B↔C systems in this region with a K_{eq} greater than 1-10 have reactive azeotropes with a boiling point that is higher than the individual component boiling points. This results in the reactive azeotrope being the stable (highest boiling) node and the expected component composition in the bottoms stream for all reactive distillation columns without a non-reactive stripping section. Since almost all reactive azeotropes have a product mole fraction that is less than 0.99, it is not possible for a reactive distillation column of Configuration III to meet the economic feasibility criteria of a product purity that is greater than 99.0%. These reactive azeotropes are present whether or not the feed is a single feed or double feed and the only way to overcome the feasibility limits imposed by the maximum boiling reactive azeotropes is to use a reactive distillation column with a non-reactive stripping section.

Single feed reactive distillation columns with non-reactive stripping sections are able to break the reactive azeotrope and have a chance to produce a product that is greater than 99.0% pure. Columns of Configurations I and II have non-reactive stripping sections and have A+B↔C systems that are economically feasible. A detailed review of the data in the Rough Economic Feasibility Diagrams and Refined Economic Feasibility Diagrams show that Configurations I and II for a single feed reactive distillation column have almost the same economic feasibility boundaries for a given reflux ratio. This result demonstrates that the key design criteria for an economically feasible reactive distillation column for A+B↔C systems in this region is the requirement of a non-reactive stripping section to break the maximum boiling reactive azeotropes.

As was the case for a single feed reactive distillation column, double feed reactive distillation columns of Configurations I or II are able to break the reactive azeotrope as well and have the chance to produce product that meets the economic feasibility criteria for A+B↔C systems within this region. Double feed reactive distillation columns of Configurations I or II have similar economic feasibility boundaries for a given reflux ratio demonstrating that the key design issue for this region is a non-reactive stripping section within the column, just like the single feed case.

The boiling point ordering boundary for this region is where $\alpha_{AC} = \alpha_{AB}$. When the product and reactant boiling points are the same or relatively close to the same, the economic feasibility of both the single feed and double feed reactive distillation column configurations are significantly reduced, just like similar systems in the A↔C system and the A↔C+D system. This reduction in economic feasibility is caused by the difficulty in separating any unconverted reactant from the product, which can only be overcome by reactive systems with large chemical reaction equilibrium constants. The systems with a large K_{eq} can react away the separation limiting reactant allowing the reactive distillation column to produce a product purity that meets the economic feasibility criteria.

For both the single feed and double feed reactive distillation columns, A+B↔C systems within this region must have a $K_{eq} > 0.1$ to be economically feasible regardless of reflux ratio or column staging. A K_{eq} of at least 0.1 does not guarantee an economically feasible reactive distillation column, but any A+B↔C system with a $K_{eq} < 0.1$ will not be economically feasible for any relative volatility combination. Increasing the reflux ratio of the reactive distillation column does increase the number of economically feasible A+B↔C systems for both separation limited and chemical reaction equilibrium limited systems. The additional reflux ratio improves economic feasibility by either returning the unconverted reactant(s) to the reactive zone to increase reactant conversion or improving the separation of the product from the separation limiting reactant(s).

For A+B↔C systems within this region with a $\alpha_{AC} > 10$, the economic feasibility of a double feed reactive distillation is not enhanced by a large boiling point difference between a low boiling reactant and a heavy product (Figure 77). This appears to go against what may initially be expected for A+B↔C systems with this set of product and reactant relative volatilities. Since the reactant boiling point(s) is much lower than the product boiling point, one would initially expect the economic feasibility of a double feed reactive distillation column to be enhanced because the product is easily separated from the unconverted reactant. However, this anticipated advantage is actually a disadvantage for these A+B↔C systems for a double feed reactive distillation column of Configurations I and II. Since the reactant boiling point is significantly lower than the product, any unconverted reactant will concentrate at the top of the reactive distillation column. Since the double feed reactive distillation columns of Configuration I and II have non-reactive rectifying sections at the top of the column, the low boiling unconverted reactant(s) at the top of the column will have to concentrate together in the reactive zone for further conversion. If one of the unconverted reactants is not present the liquid phase within the reactive zone, the unconverted reactant will eventually leave the reactive distillation column in the distillate stream. So the economic feasibility of these particular A+B↔C systems is limited by reactant losses for a double feed column, just like the A↔C+D systems within Region 1 and 4. This phenomenon is also found in the Rough Economic Feasibility Diagrams in Appendix B (Figures 97-105) for double feed reactive distillation columns of Configuration I and II.

It is interesting to note that single feed reactive distillation columns of Configuration I and II do not suffer from this problem (Figure 76), while the double feed columns do. This result indicates that the single feed reactive distillation column may be better than the double feed column at concentrating both reactants within the reactive zone liquid phase for these particular A+B↔C systems. This will allow the reactants in the single feed reactive distillation column to undergo further reaction and generate more product.

The A+B↔C systems within Region 1 have similar boiling point orderings as the Region 1 A↔C systems and the Region 1 and Region 4 A+B↔C systems. In these regions, the reactants are lower boiling than the product and the product is expected to be the primary component in the bottoms stream from the reactive distillation column. Table 12 shows the minimum K_{eq} that is required to meet the economic feasibility criteria for a reactive distillation column configuration for the first three chemical reactive systems studied in this research project. This minimum K_{eq} does not guarantee an economically feasible reactive distillation column, but any chemical reactive system that does not have at least this K_{eq} will not be economically feasible for any relative volatility combination. The minimum K_{eq} for the A+B↔C systems is the minimum for both the double feed and single feed reactive distillation columns. The boiling point ordering for each region is also summarized in Table 12 with the lowest boiling component on top and the heavier component shown on the bottom. For example, for the A+B↔C systems in Region 1, reactant A is the lowest boiling component and is on the top of the list, reactant B is the intermediate boiling component shown in the middle, and the product C is the highest boiling component and is on the bottom.

For an economically feasible reactive distillation column, the A+B↔C systems within Region 1 require a K_{eq} of at least 0.1 as do the Region 1 A↔C systems and Region 1 A↔C+D systems (Table 12). The common thread between these three reactive system regions is that the reactants are lower boiling than the product and the product is the

Table 12. Chemical Reactive Systems Minimum Required K_{eq}

Chemical Reactive System					
A↔C		A↔C+D		A+B↔C	
Region 1 A C	I: $K_{eq} > 0.1$	Region 1 A D C	I: $K_{eq} > 0.1$	Region 1 A B C	I: $K_{eq} > 0.1$
			II: $K_{eq} > 0.1$		
	II: $K_{eq} > 0.1$		III: $K_{eq} > 0.1$		II: $K_{eq} > 0.1$
		Region 4 D A C	I: $K_{eq} > 10^{-5}$		
	III: Reactive Azeotropes		II: $K_{eq} > 10^{-5}$		III: Reactive Azeotropes
			III: $K_{eq} > 10^{-5}$		
-		Region 2 A C D	I: $K_{eq} > 0.1$	Region 2 A C B	I: $K_{eq} > 100$
			II: $K_{eq} > 0.1$		
			III: $K_{eq} > 0.1$		II: $K_{eq} > 100$
		Region 5 D C A	I: $K_{eq} > 0.01$		
			II: $K_{eq} > 0.01$		III: $K_{eq} > 100$
			III: $K_{eq} > 0.01$		
Region 2 C A	I: Reactive Azeotropes	Region 3 C A D	I: $K_{eq} > 10^{-5}$	Region 3 C A B	I: Reactive Azeotropes
			II: $K_{eq} > 10^{-5}$		
	II: $K_{eq} > 10^{-3}$		III: $K_{eq} > 10^{-5}$		II: $K_{eq} > 10^{-3}$
		Region 6 C D A	I: $K_{eq} > 10^{-3}$		
	III: $K_{eq} > 10^{-3}$		II: $K_{eq} > 10^{-3}$		III: $K_{eq} > 10^{-3}$
			III: $K_{eq} > 10^{-3}$		

highest boiling component in the system. All reactive distillation configurations (I, II, III, single feed, and double feed), have the same economic feasibility limit except for Configuration III for the A↔C systems and A+B↔C systems, which are both economically limited by maximum boiling reactive azeotropes. The product generated from the A↔C+D systems is not limited by reactive azeotropes, although reactive azeotropes are present in Region 1.

A+B↔C Economic Feasibility: Region 2

Volatility order Region 2 is defined as where the boiling points for reactant A, reactant B, and the product are of the order $T_{bp,A} < T_{bp,C} < T_{bp,B}$. In all regions for the A+B↔C system, a sharp split was required between the product and the reactants so that the product purity can be greater than 99.0% and meet the economic feasibility criteria. If this sharp split is not obtained, the reactants will contaminate the product and limit the final product purity. Since the product is the intermediate boiling component in this region, it is not possible to have a sharp split between both reactants and the product. In fact, not many A+B↔C systems with this particular boiling point ordering were initially expected to be economically feasible and the simulation results for the single feed and double feed reactive distillation columns bear this point out.

The difficulty for this system is that the product boiling point falls between the reactant boiling points. This makes it impossible to separate the product from the reactants in either the distillate or bottoms stream by distillation alone. The only way a reactive distillation column can be economically feasible for an A+B↔C system within this region is for the separation limiting reactant to be almost completely converted to product and thus, allow the product to leave the reactive distillation column at a purity > 99.0%.

Because the product boiling point falls in between the reactant boiling points, the product can be designed to leave the reactive distillation column in either the distillate or bottoms stream depending on whether the product boiling point is closer to the low boiling reactant or the high boiling reactant. Since the product can leave in either stream, the molar distillate to feed ratio for the reactive distillation column was designed to be either 0.05 when the product was closest to the higher boiling reactant or 0.475 when the product was closest to the lower boiling reactant. This was done to maximize the chance that the product could leave the reactive distillation column with a high enough purity to meet the economic feasibility criteria set for this research project.

Reactive azeotropes were not found within this region because volatilities of all the reactants are not higher or lower than the volatilities of all the products, which is a requirement for reactive azeotropes to be present.

The economic feasibility of both single feed and double feed reactive distillation columns was evaluated for the A+B↔C reactive system. The single feed reactive distillation design is shown in Figure 79 and the double feed design is shown in Figure 80 for the three different reactive distillation configurations studied in this research project. The

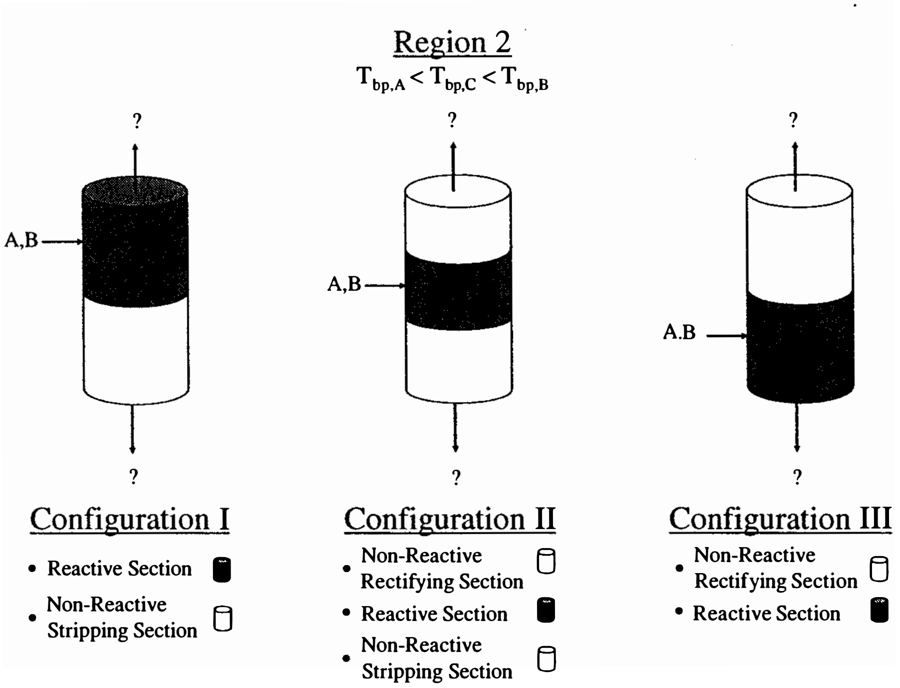


Figure 79. A+B↔C Region 2: Single Feed Configurations I, II, III

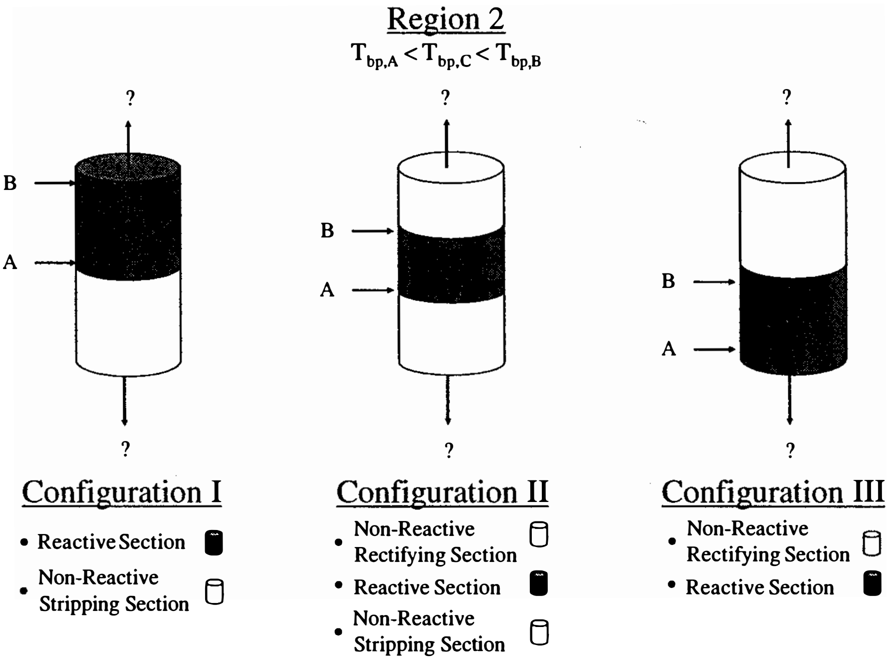


Figure 80. A+B↔C Region 2: Double Feed Configurations I, II, III

expected components in the distillate and bottoms streams are not indicated in Figure 79 and Figure 80 because the product was designed to leave the reactive distillation column in either the distillate or bottoms stream depending on whether the product boiling point was closer to the low boiling reactant or the high boiling reactant. For example, if the A+B↔C system had a $\alpha_{AC} = 1.01$ and $\alpha_{AB} = 1.5$, the product was designed to leave in the distillate stream. If the A+B↔C system had a $\alpha_{AC} = 1.4$ and $\alpha_{AB} = 1.5$, the product was designed to leave in the bottoms stream.

The middle sections of the Rough Economic Feasibility Diagrams in Appendix B (Figures 88-105) and the Refined Economic Feasibility Diagrams in Figure 76 and Figure 77 contain the reactive distillation column simulation results for Region 2. As was expected, the A+B↔C systems within this region must have very large chemical reaction equilibrium constants for reactive distillation to be economically feasible. Reactive systems with smaller chemical reaction equilibrium constants cannot overcome the separation limitations caused by an intermediate boiling product. All A+B↔C systems within this region must have a $K_{eq} > 100$ for a reactive distillation column to be economically feasible regardless of reflux ratio, column staging, or feed design. A K_{eq} of greater than 100 does not guarantee an economically feasible reactive distillation column, but any A+B↔C system with a $K_{eq} < 100$ will not be economically feasible for any relative volatility combination within this region. Increasing the reflux ratio of the reactive distillation column may improve the economic feasibility of the chemical reactive systems within this region, but reactive distillation is not expected to be the most effective process design for A+B↔C systems within Region 2.

There are two region boundaries for this system, one is where $\alpha_{AC} = \alpha_{AB}$ and the other is where $\alpha_{AC} = 1.0$. The region boundaries are not actual boundaries to economic feasibility, but the region boundaries do define the A+B↔C systems that contain the boiling point orderings that cause reactive distillation the most difficulty. The economic feasibility of any reactive distillation column configuration is significantly reduced when the product and reactant boiling points are the same or relatively close to the same, just like in the A↔C system and the A↔C+D system. When the product is an intermediate boiling component, the economic feasibility of reactive distillation is even worse than when the product has the same boiling point as one of the reactants. This reduction in economic feasibility is caused by the difficulty in separating an intermediate boiling product from any unconverted reactant. If any of the separation limiting reactant is left in the reactive distillation column, it will come out with the product because the product is the middle boiler and the sharp split from one reactant will cause the other reactant to leave with the intermediate boiling product. This is the difficulty of producing a pure product via reactive distillation for A+B↔C systems in Region 2.

The A+B↔C systems within Region 2 have similar boiling point orderings as the A↔C+D systems within Region 2 and Region 5 (Table 12). The similarity within these regions is that the product is the intermediate boiling component. The A↔C system does not have a region where the product is the intermediate boiling component because there are only two components in the system, so the product has to be either higher or lower boiling than the reactant. For an economically feasible reactive distillation column, the Region 2 A+B↔C systems require a K_{eq} of at least 100, while the Region 2 A↔C+D systems require a K_{eq} of 0.1, and Region 5 A↔C+D systems require a K_{eq} of 0.01.

Although these systems all have an intermediate boiling product, the required minimum K_{eq} for an economically feasible reactive distillation column is significantly different. The Region 2 A+B↔C systems have a product boiling point that is in between both reactant boiling points, which makes it very difficult for reactive distillation to separate the product from the reactants and still have significant concentrations of both reactants within the reactive zone of the reactive distillation column. This is why the required minimum K_{eq} very large for the A+B↔C systems in Region 2. The A↔C+D systems within Region 2 and Region 5 also have a product that is intermediate boiling, but have more chemical systems that are economically feasible. The A↔C+D systems have more economically feasible systems because the system has only one reactant that has to present in the liquid phase of the reactive zone instead of two reactants, as is the case in the A+B↔C system. Another enhancing factor in the A↔C+D system is the removal of the by-product, which helps to drive the conversion of the reactant following Le Chatelier's principle. This improvement in reactive distillation feasibility is shown by the required minimum K_{eq} of 0.1 for the Region 2 A↔C+D system and K_{eq} of 0.01 for the Region 5 A↔C+D system.

A+B↔C Economic Feasibility: Region 3

Volatility order Region 3 is defined as where the boiling points for reactant A, reactant B , and the product are of the order $T_{bp,C} < T_{bp,A} < T_{bp,B}$. In all regions for the A+B↔C system, a sharp split is required between the product and the reactants so that the product purity can be greater than 99.0% and meet the economic feasibility criteria. If this sharp split is not obtained, the reactants will contaminate the product and limit the final product purity. Therefore for A+B↔C systems in Region 3, the reactants must be the primary component in the bottoms stream and the product must be the primary component in the distillate stream since the reactants are higher boiling than the product. Since the reactants are the lowest boiling components in this region, all reactive distillation columns for this region were designed with a molar distillate to feed ratio of 0.475 to allow the product to leave in the distillate stream and the unconverted reactants to leave in the bottoms stream.

As was previously noted, since the bottoms stream for A+B↔C systems in Region 3 consists primarily of reactants, the entire bottoms stream could actually be returned back to the reactive distillation column. This deadheading of the reactive distillation column could help drive the complete conversion of the reactant to product and result in another economically acceptable design in addition to the configurations included in this research project.

The economic feasibility of both single feed and double feed reactive distillation columns were evaluated for the A+B↔C reactive system. The single feed reactive distillation design is shown in Figure 81 and the double feed design is shown in Figure 82 for the three different reactive distillation configurations studied in this research project.

An additional reactive distillation column design is to completely return the bottoms stream from the column (Figure 25) and not allow the reactants to leave the reactive distillation column. This would allow the reactants to be completely converted to product if the product could be separated from the reactants in the reactive zone. As was previously discussed for A+B↔C systems in Region 1, it is expected that this design would be economically advantageous for A+B↔C systems with boiling point orderings that fall in Regions 1 and 3, but this design was not fully evaluated in this research project.

The bottom sections of the Rough Economic Feasibility Diagrams in Appendix B (Figures 88-105), the single feed Refined Economic Feasibility Diagrams (Figure 76), and double feed Refined Economic Feasibility Diagrams (Figure 77) contain the simulation results for Region 3. A review of these diagrams shows that a reactive distillation column of Configuration I is the most economically limited reactive distillation configuration for this region. These results along with the reactive azeotrope data for this region show that a column of Configuration I is not economically feasible for any A+B↔C system because of the presence of low boiling reactive azeotropes. Most A+B↔C systems in this region with a K_{eq} greater than 0.01-0.1 have reactive azeotropes with a boiling point that is lower than the individual component boiling points, which results in the reactive azeotrope being the unstable (lowest boiling) node and the expected component composition in the distillate stream for all reactive distillation columns without a non-reactive rectifying section. Since most reactive azeotropes have a product mole fraction that are less than 0.99, it is not possible for a reactive distillation column of Configuration I to meet the economic feasibility criteria of a product purity that is greater than 99.0%. These reactive azeotropes are present whether or not the feed is a single feed or double feed and the only way to overcome the feasibility limits imposed by the minimum boiling reactive azeotropes is to use a reactive distillation column with a non-reactive rectifying section.

Single feed reactive distillation columns with non-reactive stripping sections are able to break the reactive azeotrope and have a chance to produce a product that is greater than 99.0% pure. Columns of Configurations II and III have non-reactive stripping sections and have A+B↔C systems that are economically feasible. A detailed review of the data in the Rough Economic Feasibility Diagrams and Refined Economic Feasibility Diagrams show that Configurations II and III for a single feed reactive distillation column have almost the same economic feasibility boundaries for a given reflux ratio. This result demonstrates that the key design criteria for an economically feasible reactive distillation column for A+B↔C systems in this region is the requirement of a non-reactive rectifying section to break the minimum boiling reactive azeotropes.

As was the case for a single feed reactive distillation column, double feed reactive distillation columns of Configurations II or III are able to break the reactive azeotrope as

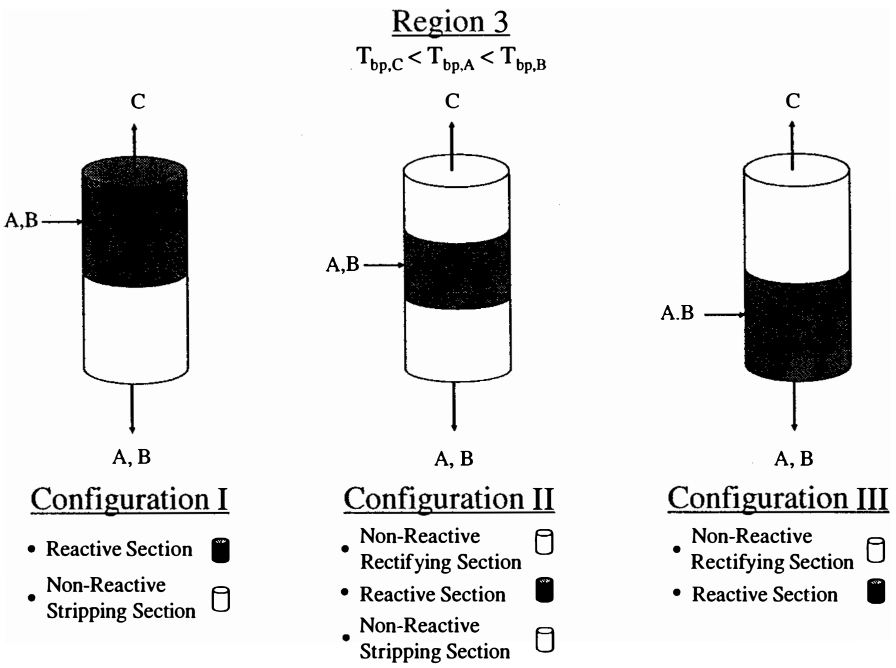


Figure 81. A+B↔C Region 3: Single Feed Configurations I, II, III

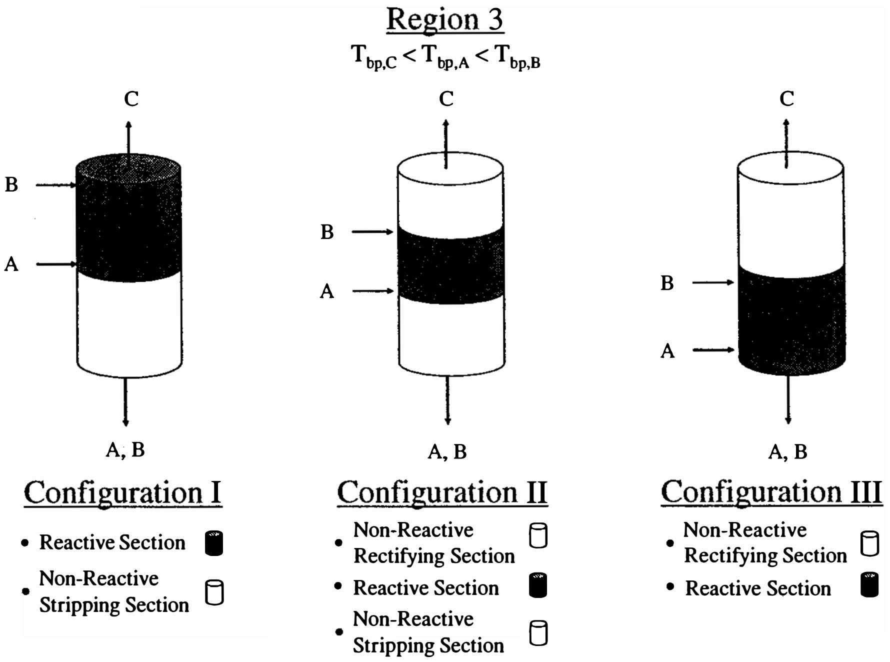


Figure 82. A+B↔C Region 3: Double Feed Configurations I, II, III

well and have the chance to produce product that meets the economic feasibility criteria for A+B↔C systems within this region. Double feed reactive distillation columns of Configurations II or III have similar economic feasibility boundaries for a given reflux ratio demonstrating that the key design issue for this region is a non-reactive rectifying section within the column, just like the single feed case.

The boiling point ordering boundary for this region is where $\alpha_{AC} = 1.0$. When the product and reactant boiling points are the same or relatively close to the same, the economic feasibility of any single feed reactive distillation column configuration is significantly reduced, just like the A↔C system and the A↔C+D system. This reduction in economic feasibility is caused by the difficulty in separating any unconverted reactant from the product, which can only be overcome by reactive systems with large chemical reaction equilibrium constants. The systems with a large K_{eq} can react away the separation limiting reactant allowing the reactive distillation column to produce a product purity that meets the economic feasibility criteria.

All A+B↔C systems within this region must have a $K_{eq} > 0.001$ for a reactive distillation column to be economically feasible regardless of reflux ratio, column staging, or feed design. A K_{eq} of at least 0.001 does not guarantee an economically feasible reactive distillation column, but any A+B↔C system with a $K_{eq} < 0.001$ will not be economically feasible for any relative volatility combination. Increasing the reflux ratio of the reactive distillation column does increase the number of economically feasible A+B↔C systems for both separation limited and chemical reaction equilibrium limited systems. The additional reflux ratio improves economic feasibility by either returning the unconverted reactants to the reactive zone to increase reactant conversion or improving the separation of the product from the separation limiting reactants.

The A+B↔C systems within Region 3 have similar boiling point orderings as the Region 2 A↔C systems and the Region 3 and Region 6 A↔C+D systems. In these regions, the reactants are higher boiling than the product and the product is expected to be the primary component in the distillate stream from the reactive distillation column. For an economically feasible reactive distillation column, the A+B↔C systems within Region 3 require a K_{eq} of at least 0.001 as do the Region 2 A↔C systems and Region 6 A↔C+D systems (Table 12). The common thread between these three reactive system regions is that the reactants are higher boiling than the product and the product is the lowest boiling component in the system. All reactive distillation configurations (I, II, III, single feed, and double feed), have the same economic feasibility limit except for Configuration I for the A↔C systems and A+B↔C systems, which are both limited by minimum boiling reactive azeotropes. The product generated from the A↔C+D systems is not limited by reactive azeotropes, although reactive azeotropes are present in Region 6.

The other chemical reactive system with a similar boiling point ordering is the Region 3 A↔C+D system. Within this region, the product is still the lowest boiling component just like the A↔C, A+B↔C, and A↔C+D systems, but the lone reactant is now an intermediate boiling component. This change in boiling point ordering leads to a significant improvement in reactive distillation economic feasibility, as shown by the required minimum K_{eq} of 10^{-5}. This improvement in economic feasibility over the other regions is caused by the high boiling by-product. The presence of the high boiling by-product enhances the economic feasibility of reactive distillation by keeping the unconverted reactant in the reactive distillation column and, following Le Chatelier's principle, by leaving the reactive liquid phase. Keeping the reactant in the reactive distillation column allows the reactant to undergo further conversion to more product and by leaving the reactive zone of the reactive distillation column; the high boiling by-product forces the lone reactant to undergo further conversion in order to maintain the required liquid phase K_{eq}. Both of these situations help to enhance the economic feasibility of reactive distillation for the $A \leftrightarrow C+D$ systems within Region 3.

Single Feed vs. Double Feed Reactive Distillation

Double feed reactive distillation columns have been shown to have advantages over single feed columns for certain reactive systems (Barbosa and Doherty,1988c; Agreda et al.,1984; Chadda et al., 2002). A double feed reactive distillation column can provide a more feasible design option than a single feed reactive distillation column when the reactants have significantly different boiling points. In a single feed reactive distillation column, reactants with significantly different boiling points can separate so quickly that they both are not present in the liquid phase of the reactive zone and therefore cannot react to form the product. A double feed column can overcome this problem by feeding the low boiling reactant at a lower stage in the column than the higher boiling reactant, thereby allowing the light reactant to travel up the column and the heavier reactant to travel down the column. This cross flow of reactants can improve the contact of the reactants within the liquid phase of the reactive zone and with this improved contact comes more reaction and more product generation.

This expected double feed advantage over a single feed reactive distillation column was found to exist for the $A+B \leftrightarrow C$ systems in this study where the reactants had significantly different boiling points. Figure 83 shows the relative volatility and chemical reaction equilibrium constant combinations for the $A+B \leftrightarrow C$ systems with $\alpha_{AB}=100$ where a double feed reactive distillation column requires a smaller reflux ratio than a single feed column to meet the economic feasibility criteria.

The blocks that are highlighted in solid light grey with a thick, black outline are the combinations where a double feed reactive distillation column has an economic advantage over a single feed reactive distillation column. The blocks that are clear and have a normal, black outline show the relative volatility and chemical reaction equilibrium constant combinations that require the same minimum reflux ratio for a single feed and double feed reactive distillation column to be economically feasible. The combinations that do not have any outlined blocks did not meet the economic feasibility criteria for reflux ratios ≤ 100.

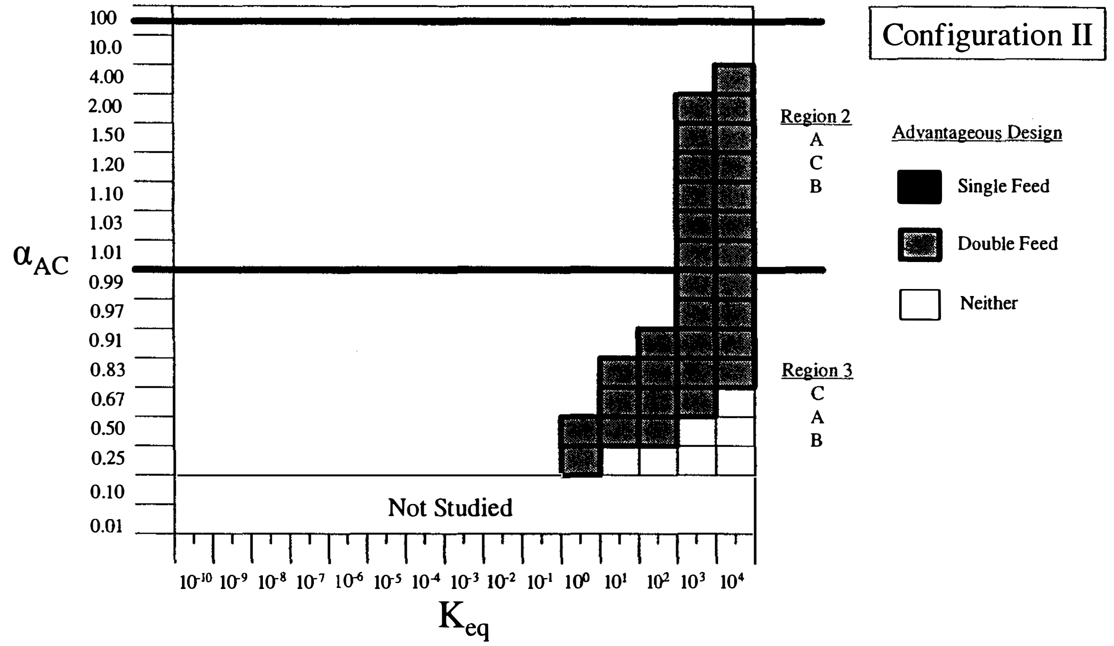


Figure 83. A+B↔C α_{AB}=100, Single vs. Double Feed: Configuration II

As Figure 83 shows, a double feed reactive distillation column does have an economic advantage over a single feed reactive distillation for the A+B↔C system when the reactants have a relative volatility of 100 and have boiling points that are very far apart. This advantage can be found when reviewing the Rough Economic Feasibility Diagrams for other boiling point orderings with significantly different reactant boiling points, $\alpha_{AB} \geq 4.0$.

However, this research also shows that a double feed reactive distillation column is not always the most economically feasible design. For certain A+B↔C systems, a single feed reactive distillation column is the economically advantageous design because the reactant boiling points are close together and do not have difficulty "seeing" each other in the reacting liquid phase. Figure 84 shows that A+B↔C systems with α_{AB}=1.03, a single feed reactive distillation column has an economic advantage over a double feed column.

The combination blocks with the solid dark grey and the thick, black outlines are the relative volatility and chemical reactive equilibrium constant combinations where a single feed reactive distillation column requires a smaller reflux ratio than a double feed column. The clear blocks with the normal, black outline shows the combinations where the minimum reflux ratio to meet the economic feasibility criteria were the same for both feed designs. The combinations that do not have any outlined blocks did not meet the economic feasibility criteria for reflux ratios less than 100.

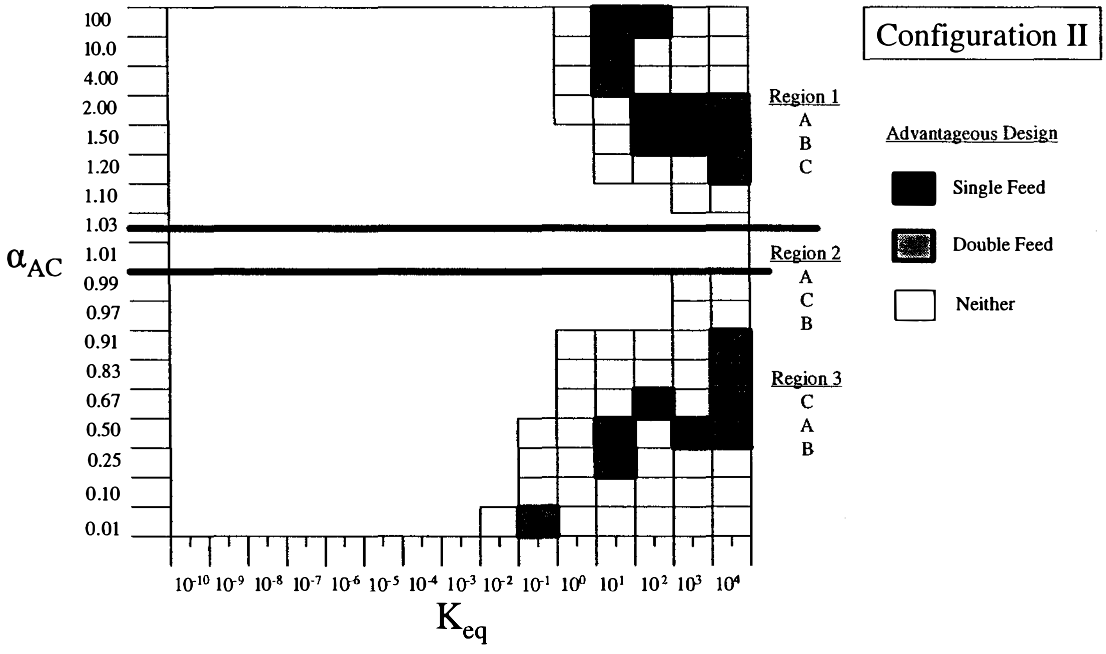


Figure 84. A+B↔C α_{AB}=1.03, Single vs. Double Feed: Configuration II

A single feed reactive distillation column, in general, has the economic advantage over a double feed column for A+B↔C systems where $\alpha_{AB} \leq 1.2$. With these systems, the reactant boiling points are close and do not have difficulty "seeing" each other in the liquid phase of the reactive zone. Feeding the reactants together on the same reactive stage of the reactive distillation column maximizes the contact of the reactants and delivers them in a high local concentration together, which helps drive the reaction to completion. Also helping to drive reactant conversion is the fact that reactants with similar boiling points will travel up and/or down the reactive distillation column together, which will allow them to continue to react and produce more product. If a double feed reactive distillation column is employed for A+B↔C systems with close boiling reactants, the separate reactant feeds will force the reactants to "find" each other in the reactive zone liquid phase. If the local reactant excess around the feed stages for the double feed column does not provide adequate reactant contact, the reactants can pass by each other in the vapor and liquid phases of the reactive distillation column and not react to produce the product. The single feed reactive distillation column guarantees that the reactants will both be present in the liquid phase of the reactive zone and maximize the contact between the close boiling reactants in the reactive zone of the reactive distillation column.

For A+B↔C systems with $1.2 < \alpha_{AB} < 4.0$, the reactant boiling points are such that for certain cases, a double feed column may be the best choice, a single feed column may be the best choice, or both designs give equal results. The data from this research project indicate that a single feed reactive distillation column is, in general, the economically feasible design for these intermediate reactant boiling point orderings for A+B↔C systems in Region 1 and 3 and a double feed reactive distillation column is the economically feasible design for A+B↔C systems in Region 2. Figure 85 shows the single feed vs. double feed economic feasibility results for an A+B↔C system with α_{AB}=1.5.

Literature Example

The reactive distillation literature was reviewed with the intent of finding real chemical reactive systems that could be used to verify the heuristics and observations proposed in this research project. The production of cumene (isopropylbenzene) is present in the reactive distillation literature (Shoemaker and Jones, 1987; Stadig, 1987) and can be used as an example of an A+B↔C system. For the purpose of this study, it was assumed that cumene will not react with the isopropylene product to form di-alkyl or tri-alkyl substituted cumene compounds and isopropylene does not oligomerize with itself. The system boiling points, relative volatilities, and chemical reaction equilibrium constant for this particular reactive system are shown in Table 13.

Cumene Reactive Azeotropes

A review of the reactive azeotrope diagrams for the production of cumene (Figure 86) indicate that reactive azeotropes may or may not be present because the cumene reactive system falls on the border between the studied A+B↔C combinations that have reactive azeotropes and combinations that do not have reactive azeotropes. The '*' symbol in Figure 86 is an approximate mark of where the cumene system falls in the diagram.

A reactive feasibility assessment of the cumene decomposition using Hyprotech Distil 2.0.1 indicates that reactive azeotropes are not present for this particular reactive system and therefore, will not be a direct limitation on the economic feasibility of any reactive distillation configuration for the production cumene.

Economic Feasibility: Cumene Production

The economic feasibility of cumene production was evaluated using both single feed and double feed reactive distillation columns of Configurations I, II, and III at an operating

Table 13. A+B↔C Literature Example

Reactive Distillation System A+B↔C	Boiling Points (°C)	Relative Volatilities (α_{Ai})	K_{eq}
isopropylene (A) +benzene (B) ↔ cumene (C)	A = -48 B = 80 C = 152	$\alpha_{AB} = 50$ $\alpha_{AC} = 500$	5

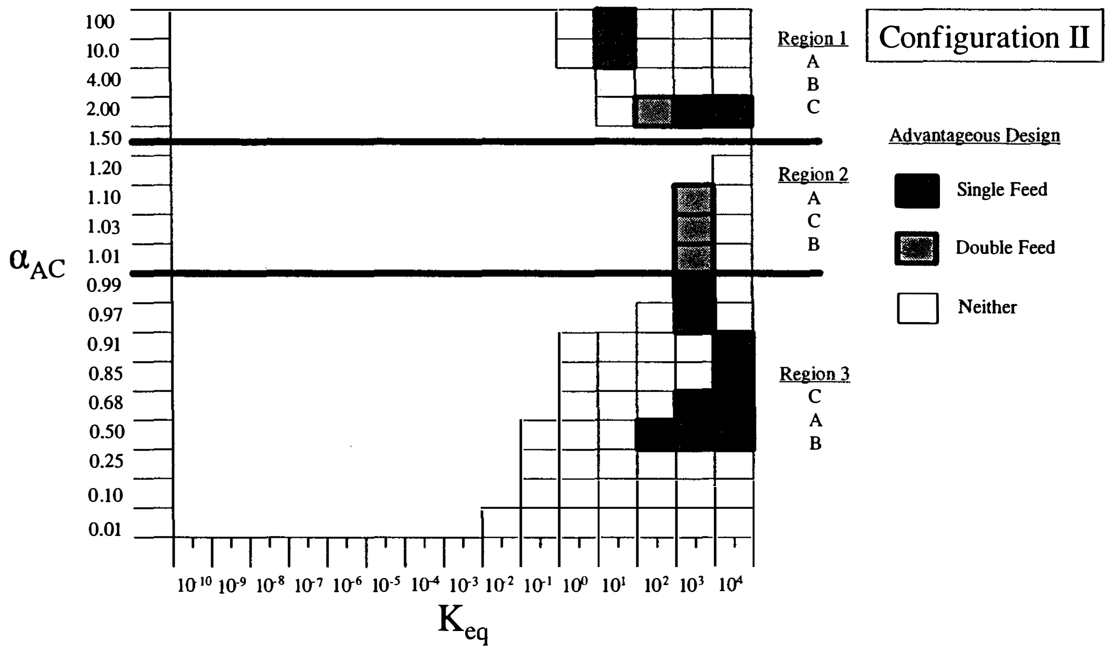


Figure 85. A+B↔C α_{AB}=1.5, Single vs. Double Feed: Configuration II

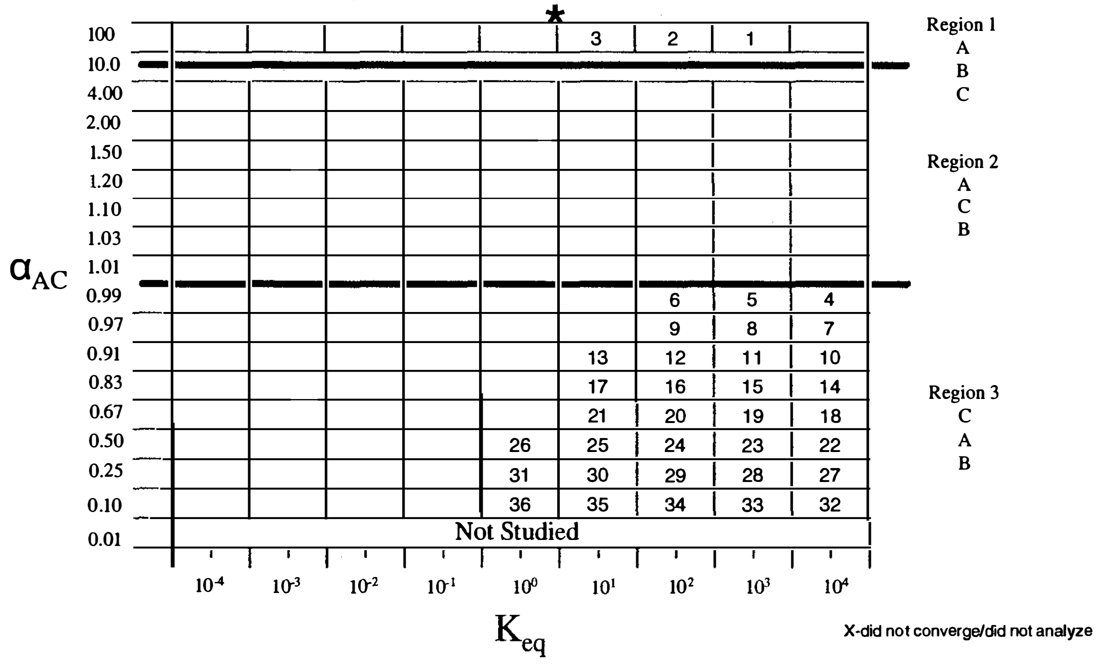


Figure 86. Cumene Production (α_{AB} = 10): Reactive Azeotropes

pressure of one atm. The cumene reactive system has a boiling point ordering that falls within Region 1 and has a estimated chemical reaction equilibrium constant of $K_{eq} = 5$ (Giessler et al., 1999). This chemical reaction equilibrium constant was assumed to be independent of temperature for the temperature range within the reactive distillation column. Non-reactive azeotropes are not present for this mixture at a pressure of one atmosphere based on the results from the Wilson equation in Aspen Technology Aspen Plus®, which was used to model the vapor-liquid equilibrium (VLE) for this example. The production of cumene has a $\alpha_{AB} \approx 50$ and $\alpha_{AC} \approx 500$, which is plotted in Figure 87 using a '*' symbol for a single feed reactive distillation column of Configuration II.

The Rough Economic Feasibility Diagrams for the production of cumene indicate that a single feed and double feed reactive distillation column of Configuration II may or may not be able to meet the economic feasibility criteria for a reflux ratio $\leq$ 100 because the cumene reactive system falls on the border of economic feasibility. A review of the Rough Economic Feasibility Diagrams for a single feed reactive distillation column of

Configuration I indicate that this configuration may have a slightly better chance of being economically feasible than any other configuration. A single feed or double feed reactive distillation column of Configuration III does not appear to have a chance of being economically feasible based on the Rough Economic Feasibility Diagrams.

Since the cumene reactive system relative volatility and chemical reaction equilibrium constant fall on the border of economic feasibility, the Rough Economic Feasibility

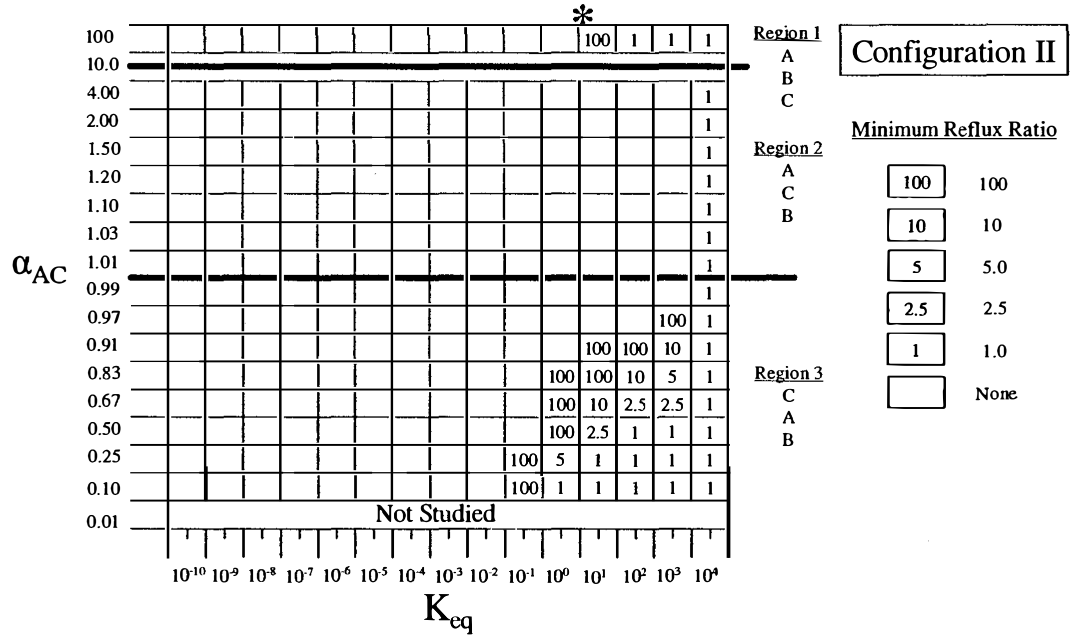


Figure 87. Cumene Production ($\alpha_{AB} = 10$), Single Feed: Configuration II

Diagrams do not precisely indicate the minimum reflux ratio required to meet the economic feasibility criteria for reactive distillation. However, since the cumene reactive system does fall on the border, the Rough Economic Feasibility Diagrams do indicate that the system would be close to meeting the economic feasibility criteria if it did not actually meet the criteria.

In order to check the results indicated by the Rough Economic Feasibility Diagrams for the production of cumene, all three reactive distillation configurations with both feed designs were simulated using Aspen Plus. The expected reflux ratios from the Rough Economic Feasibility Diagrams and the actual Aspen Plus simulation reflux ratios for the production of cumene are shown in Table 14.

The actual Aspen Plus simulation results show that the production of cumene was economically feasible for both single and double feed reactive distillation columns of Configuration I with a required minimum reflux ratio of 100. The single and double feed reactive distillation columns of Configurations II and III did not meet the economic feasibility criteria. The reactive distillation columns of Configuration I were successful in meeting the economic feasibility criteria because the reactive zone extended to the very top of the reactive distillation column where the isopropylene reactant accumulated. Since the low boiling isopropylene reactant accumulated in vapor phase within the reactive distillation column, the reactive distillation column required that the benzene reactant be fed at the top of the column. This maximizes the isopropylene and benzene concentration in the liquid phase of the top reactive stage. Once produced, the heavy cumene product drops out of the reactive zone and is preferentially separated from the reactants in the non-reactive stripping section of the column.

A single feed or double feed reactive distillation column of Configuration II did not meet the economic feasibility criteria because the required non-reactive rectifying section

Table 14. Cumene Literature Example Economic Feasibility Reflux Ratios

Reactive Distillation Configuration	Reflux Ratio	
	Heuristic	Actual
isopropylene + Benzene ↔ Cumene		
I (Single and Double Feed)	10 to NF*	100
II (Single and Double Feed)	100 to NF	NF
III (Single and Double Feed)	NF	NF

*NF = Not economically feasible

limited the isopropylene and benzene concentrations within in the reactive zone of the column. The same situation occurs for a reactive distillation column of Configuration III, which also did not meet the economic feasibility criteria. In practice, the distillate stream is probably completely returned to the reactive distillation column so that the highly volatile isopropylene can be completely converted to cumene (Shoemaker and Jones, 1987).

This example highlights the ability of the Rough Economic Feasibility Diagram to indicate if a particular reactive system of interest is worth further investigation and which reactive distillation column configurations should be investigated.

Observations and Heuristics

Note: For all $A+B\leftrightarrow C$ systems, the low boiling reactant is always designated as reactant A, which results in all reactant relative volatilities being greater than 1.0.

Observations

1. Reactive azeotropes can limit the economic feasibility of $A+B\leftrightarrow C$ systems with boiling point orderings that fall in Regions 1 and 3.

2. Reactive azeotropes will not be present in Region 2 for $A+B\leftrightarrow C$ systems of constant relative volatility.

Heuristics – Single Feed vs. Double Feed Reactive Distillation Columns

1. A double feed reactive distillation column is usually the best feed design for reactive $A+B\leftrightarrow C$ systems where the reactant boiling points are far apart, $\alpha_{AB} \geq 4.0$.
2. A single feed reactive distillation column is usually the best feed design for reactive $A+B\leftrightarrow C$ systems where the reactant boiling points are close together, $1.0 \leq \alpha_{AB} \leq 1.2$.
3. For $A+B\leftrightarrow C$ systems in Region 2 with a relative volatility of $1.2 < \alpha_{AB} < 4.0$, a double feed reactive distillation column is usually the best feed design.
4. For $A+B\leftrightarrow C$ systems in Regions 1 and 3 with a relative volatility of $1.2 < \alpha_{AB} < 4.0$, a single feed reactive distillation column is usually the best feed design.

Heuristics – Region 1: $T_{bp,A} < T_{bp,B} < T_{bp,C}$

5. All $A+B\leftrightarrow C$ systems within this region must have a $K_{eq} > 0.1$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the $A+B\leftrightarrow C$ system relative volatilities.
6. Maximum boiling reactive azeotropes are present in this region for $K_{eq} > 1\text{-}10$.

7. For all A+B↔C systems within this region, both single feed and double feed reactive distillation columns must have at least one non-reactive stripping stage to produce a product in the bottoms stream that will meet the economic feasibility criteria.

Heuristics – Region 2: $T_{bp,A} < T_{bp,C} < T_{bp,B}$

8. All A+B↔C systems within this region must have a $K_{eq} > 100$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A+B↔C system relative volatilities.
9. Reactive azeotropes do not exist in this region for systems of constant relative volatility.
10. A double feed reactive distillation column is usually the best feed design for systems within this region.

Heuristics – Region 3: $T_{bp,C} < T_{bp,A} < T_{bp,B}$

11. All A+B↔C systems within this region must have a $K_{eq} > 10^{-3}$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A+B↔C system relative volatilities.
12. Minimum boiling reactive azeotropes are present in this region.
13. For all A+B↔C systems within this region, both single feed and double feed reactive distillation columns must have at least one non-reactive rectifying stage to produce a product in the distillate stream that will meet the economic feasibility criteria.

Economic feasibility criteria:
1. reactant conversion $\geq 95.0\%$
2. product purity $\geq 99.0\%$
3. total column stages ≤ 100.
4. reflux ratio ≤ 100 (economic reflux ratios depend on product value).

These heuristics are based on data collected with the following assumptions:

1. The reactant feed stage(s) is confined to the reactive zone.
2. Chemical reaction equilibrium is attained on every reactive stage.
3. Vapor-liquid equilibrium is attained on every stage.
4. Vapor and liquid phases are ideal.
5. The feed(s) is 100% reactant.
6. The overall feed to the reactive distillation column is stoichiometric.
7. Any heat effects cancel within the reactive distillation column.
8. The reactive distillation column has a total condenser.

Summary

In this chapter, a set of heuristics was proposed for the initial feasibility assessment and conceptual design of reactive distillation columns involving the reaction A+B↔C. These heuristics were developed from a data set collected from Aspen Plus simulations using a generic A+B↔C reactive system. For this generic system, a range of relative volatilities and chemical reaction equilibrium constants were chosen to cover the expected range of potential reactive systems. The potential component boiling points for the A+B↔C system was divided into three regions of similar boiling points orderings. Three different reactive distillation column configurations were evaluated for each region. The first configuration had a reactive section above a non-reactive stripping section. The second configuration had a non-reactive rectifying section, a reactive section, and a non-reactive stripping section. The third configuration had a reactive zone below a non-reactive rectifying section. Diagrams were created for each studied component relative volatility and chemical reaction equilibrium constant combination indicating the economic feasibility of each reactive distillation column configuration. Reactive azeotropes were found to be present in Regions 1 and 3 with only the economic feasibility of Configuration III being limited for A+B↔C systems in Region 1 and Configuration I for Region 3. The primary limiting factor for A+B↔C systems and reactive distillation feasibility was maximizing the contact of the reactants in the liquid phase of the reactive zone within the reactive distillation column. The use of a single feed reactive distillation column was found to be the best design for A+B↔C systems with close boiling reactants, while a double feed column was found to be the best for reactants that had significantly different boiling points. For each of the three A+B↔C regions, a minimum required chemical reaction equilibrium constant was proposed for the economic feasibility of reactive distillation. The heuristics and simulation results for the generic reactive system were verified using the production of cumene as an example, which is available in the reactive distillation literature.

VIII. SYSTEMS WITH TWO REACTANTS AND TWO PRODUCTS

Introduction

An actively studied chemical reactive system for reactive distillation is the four component A+B↔C+D system. Real chemical systems of interest, both academically and industrially, include the production of esters such as methyl acetate, ethyl acetate, isopropyl acetate, and butyl acetate; the hydrolysis of esters such as methyl acetate and butyl acetate; and the production of dimethyl carbonate to name just a few.

Moving from a three component to a four component chemical reactive system adds significantly to the complexity and depth of potential boiling point orderings. Because of the large number of relative volatility and chemical reaction equilibrium constant combinations within the A+B↔C+D system, exhaustive reactive distillation simulations were not included in this study. However, the results from three previously studied chemical reactive systems were used to provide guidance for the development of an initial set of observations and heuristics for the A+B↔C+D system. In this chapter, the boiling point orderings for the A↔C, A+B↔C, and A↔C+D systems were grouped with similar boiling point orderings for the A+B↔C+D system. The results from three studied systems were then extended to the defined regions within the A+B↔C+D system and an initial set of observations and heuristics were proposed for the four component system.

A+B↔C+D Regions

The reactant and product boiling points for the A+B↔C+D system were divided into twelve volatility order regions, which are defined in Table 15. Reactant A is always designated as the lowest boiling reactant for the system, which limits the study of duplicate boiling point orderings for this chemical reactive system. Component C is always the desired product and component D is always the by-product. The relative volatility combinations within each region are expected to share similar characteristics for reactive distillation feasibility and design based on the results from the three previously studied chemical systems.

Reactive Azeotropes

Reactive azeotropes are not present in all A+B↔C+D systems, just like non-reactive azeotropes are not present in all A+B↔C+D systems. As shown in Table 15, the only A+B↔C+D systems in this study that are expected to contain reactive azeotropes are those systems within Regions 1, 2, 11, and 12. Reactive azeotropes are limited to these regions because the volatility of both reactants is either higher or lower than the volatility of both products and the component volatilities are essentially constant for systems in this study (Barbosa and Doherty, 1988d).

Table 15. $A+B \leftrightarrow C+D$ Relative Volatility Ordering Regions

Region	Boiling Point Ordering	Reactive Azeotropes
1	$(T_{bp,A} < T_{bp,B} < T_{bp,D} < T_{bp,C})$ $\alpha_{AB} > 1.0$, $\alpha_{AB} < \alpha_{AD}$, $\alpha_{AD} < \alpha_{AC}$	Reactive Azeotropes may exist
2	$(T_{bp,A} < T_{bp,B} < T_{bp,C} < T_{bp,D})$ $\alpha_{AB} > 1.0$, $\alpha_{AB} < \alpha_{AD}$, $\alpha_{AD} > \alpha_{AC}$	Reactive Azeotropes may exist
3	$(T_{bp,A} < T_{bp,C} < T_{bp,B} < T_{bp,D})$ $\alpha_{AC} > 1.0$, $\alpha_{AC} < \alpha_{AB}$, $\alpha_{AB} < \alpha_{AD}$	
4	$(T_{bp,A} < T_{bp,D} < T_{bp,B} < T_{bp,C})$ $\alpha_{AD} > 1.0$, $\alpha_{AD} < \alpha_{AB}$, $\alpha_{AB} < \alpha_{AC}$	
5	$(T_{bp,A} < T_{bp,C} < T_{bp,D} < T_{bp,B})$ $\alpha_{AC} > 1.0$, $\alpha_{AC} < \alpha_{AD}$, $\alpha_{AD} < \alpha_{AB}$	
6	$(T_{bp,A} < T_{bp,D} < T_{bp,C} < T_{bp,B})$ $\alpha_{AD} > 1.0$, $\alpha_{AD} < \alpha_{AC}$, $\alpha_{AC} < \alpha_{AB}$	
7	$(T_{bp,C} < T_{bp,A} < T_{bp,B} < T_{bp,D})$ $\alpha_{AC} < 1.0$, $\alpha_{AB} > 1.0$, $\alpha_{AB} < \alpha_{AD}$	
8	$(T_{bp,D} < T_{bp,A} < T_{bp,B} < T_{bp,C})$ $\alpha_{AD} < 1.0$, $\alpha_{AB} > 1.0$, $\alpha_{AB} < \alpha_{AC}$	
9	$(T_{bp,C} < T_{bp,A} < T_{bp,D} < T_{bp,B})$ $\alpha_{AC} < 1.0$, $\alpha_{AD} > 1.0$, $\alpha_{AD} < \alpha_{AB}$	
10	$(T_{bp,D} < T_{bp,A} < T_{bp,C} < T_{bp,B})$ $\alpha_{AD} < 1.0$, $\alpha_{AC} > 1.0$, $\alpha_{AC} < \alpha_{AB}$	
11	$(T_{bp,C} < T_{bp,D} < T_{bp,A} < T_{bp,B})$ $\alpha_{AC} < 1.0$, $\alpha_{AD} < 1.0$, $\alpha_{AC} < \alpha_{AD}$, $\alpha_{AB} > 1.0$	Reactive Azeotropes may exist
12	$(T_{bp,D} < T_{bp,C} < T_{bp,A} < T_{bp,B})$ $\alpha_{AC} < 1.0$, $\alpha_{AD} < 1.0$, $\alpha_{AC} > \alpha_{AD}$, $\alpha_{AB} > 1.0$	Reactive Azeotropes may exist

Just as in the previous three chemical reactive systems, reactive azeotropes may limit the economic feasibility of reactive distillation for certain A+B↔C+D relative volatility and K_{eq} combinations. A brief study of systems within Regions 1, 2, 11, and 12 indicate that the reactive azeotropes, if present, are all saddles. Since the reactive azeotropes are not an unstable (lowest boiling) or stable (highest boiling) node, the reactive azeotrope composition will not be the expected distillate or bottoms composition for reactive distillation columns of Configurations I or III. However, the presence of a reactive azeotrope saddle in the reactive system still limits the economic feasibility of these regions where the desired product is not the highest or lowest boiling component. This means that the economic feasibility of systems within Regions 2 and 12 may be limited by the presence of reactive azeotropes, while systems within Regions 1 and 11 will not.

It is expected that certain relative volatility and K_{eq} combinations within Regions 2 and 12 will be economically feasible because reactive azeotropes are not present in all A+B↔C+D systems. However, some systems within Regions 2 and 12 have reactive azeotropes that do limit the economic feasibility of reactive distillation. For example, Figure 115 shows a reactive residue curve map for an A+B↔C+D system within Region 12 with $\alpha_{AB} = 1.03$, $\alpha_{AC} = 0.67$, $\alpha_{AD} = 0.25$, and a $K_{eq} = 1.0$. For a completely reactive distillation column with a stoichiometric feed, Figure 115 shows that reactant B is the expected bottoms product and by-product D is the expected distillate product. A completely reactive distillation column will not be able to produce product C in the bottoms stream because the reactive azeotrope saddle provides a boundary that cannot be crossed by reactive distillation. This reactive residue curve map indicates that for A+B↔C+D systems within Region 12 that have saddle reactive azeotropes, pure product C cannot be produced in a reactive distillation column without a non-reactive stripping section.

Similarly for A+B↔C+D systems in Region 2 with a saddle reactive azeotrope, a reactive distillation column cannot produce pure product C because the saddle reactive azeotrope once again produces a boundary that cannot be passed by a reactive distillation. Therefore, the only way these systems can produce pure desired product C is with a reactive distillation column with a non-reactive rectifying section which will break the reactive azeotrope.

As was the case for systems within Regions 2 and 12, A+B↔C+D systems in Regions 1 and 11 may have reactive azeotropes and if so, the reactive azeotropes will be saddles. However, the systems within Regions 1 and 11 are not limited by these reactive azeotropes because the desired product is now either the highest boiling or lowest boiling component in the reactive system. As Figure 116 shows, when the desired product is the lowest boiling component in the system, a completely reactive distillation column with a stoichiometric reactant feed will be able to produce the desired product as the expected distillate product because the desired product is now on the same side of the boundary produced by the reactive azeotrope saddle as the stoichiometric feed. Figure 116 shows a

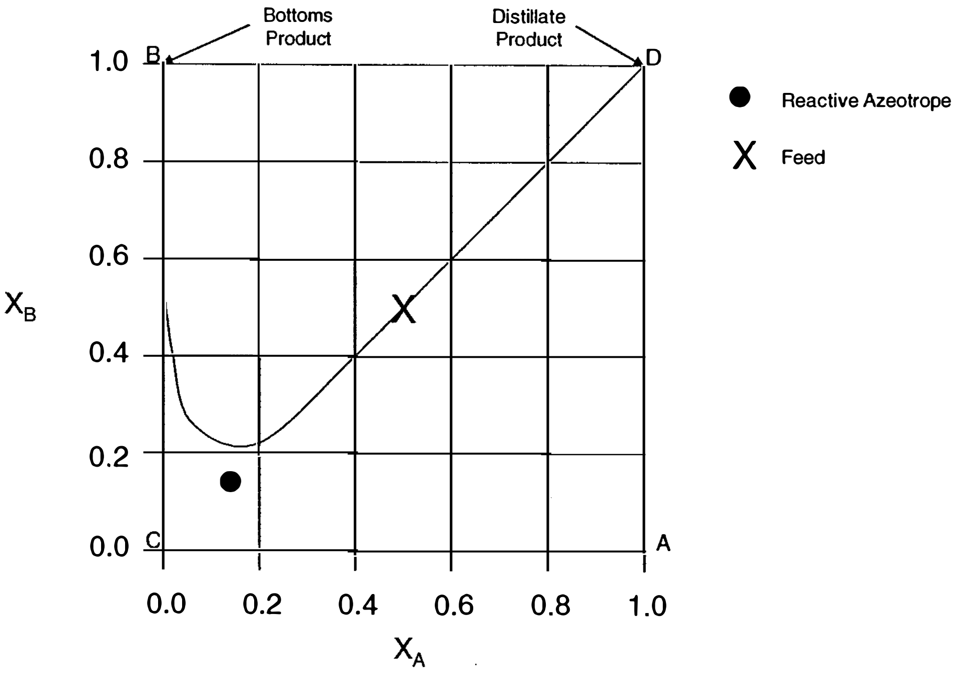


Figure 115. A+B↔C+D Region 12: Reactive Residue Curve Map

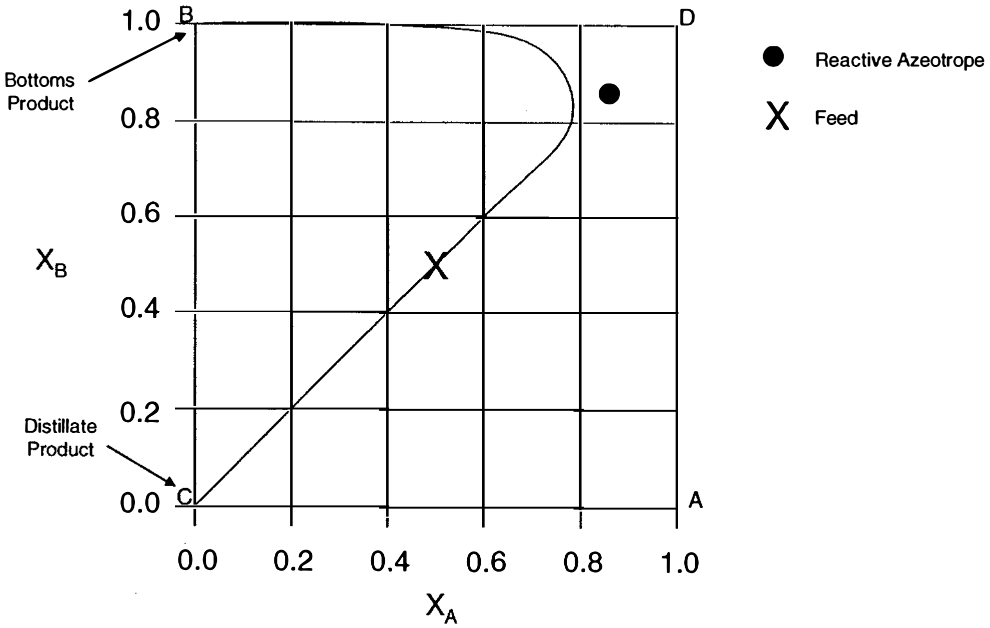


Figure 116. A+B↔C+D Region 11: Reactive Residue Curve Map

reactive residue curve map for a A+B↔C+D system within Region 12 with $\alpha_{AB} = 1.03$, $\alpha_{AC} = 0.25$, $\alpha_{AD} = 0.67$, and a $K_{eq} = 1.0$. This reactive residue curve map indicates that for A+B↔C+D systems within Region 12 that have saddle reactive azeotropes, pure product C can be produced in a reactive distillation column with a stoichiometric feed without a non-reactive stripping section.

Similarly for A+B↔C+D systems in Region 1 with a saddle reactive azeotrope, a completely reactive distillation column can produce pure product C because the stoichiometric feed is on the same side of the boundary as product C. Therefore, these systems can produce pure desired product C with a completely reactive distillation column and a stoichiometric reactant feed.

It should be understood that reactive azeotropes are not limited to just the regions identified in this study for non-ideal chemical reactive systems. For example, the isopropyl acetate reactive system has a boiling point ordering that falls within Region 5 and would not have a reactive azeotrope if the components within the system were all ideal with constant volatility. However, the system is non-ideal and has non-reactive azeotropes along with a reactive azeotrope (Song et al., 1997; Chadda et al., 2002). This reactive azeotrope is an unstable (lowest boiling) node within the reactive isopropyl acetate system, which makes the reactive azeotrope composition the expected distillate composition for a reactive distillation column of Configuration I. Reactive azeotropes are not limited to just the regions identified in Tables 4 and 15 if the A+B↔C+D system is non-ideal or has component volatilities that are not constant.

Single Feed vs. Double Feed Reactive Distillation

The A+B↔C+D systems are like the A+B↔C systems in that the chemical reactive systems both have two reactants. This adds an additional design concern for reactive distillation because the reactants must both be present in the reactive zone liquid phase in relatively high concentration in order to produce the desired product. The presence of two reactants also adds an additional design option of feeding the reactants together in a single feed or feeding the reactants in separate feeds to the reactive distillation column. Both of these feed designs, a single feed reactive distillation column and double feed reactive distillation column, are expected to have similar heuristics for A+B↔C+D systems as for A+B↔C systems.

For the A+B↔C system, a single feed reactive distillation column was found to be the economic reactive distillation design of choice for systems where the reactants have boiling points that were relatively close to each other. A double feed reactive distillation column was found to be the design of choice for systems where the reactants have boiling points that are far apart. For A+B↔C systems where the reactant boiling points fall somewhere in between being close together or far apart, a single feed or double feed reactive distillation column may be the design of choice depending on the exact system of interest.

The same general findings are expected to hold true for the A+B↔C+D systems. A single feed reactive distillation column is expected to be the design of choice for systems where the reactant boiling points are close together. Using the A+B↔C system results as a guideline, A+B↔C+D systems with a $\alpha_{AB} \leq 1.2$ are expected to benefit from a single feed reactive distillation column. A double feed reactive distillation column is expected to be the design of choice for A+B↔C+D systems where the reactant boiling points are far apart, $\alpha_{AB} \geq 4.0$. The A+B↔C+D systems that have reactant boiling points in between these guidelines, $1.2 < \alpha_{AB} < 4.0$, are expected to have mixed results when comparing single feed vs. double feed reactive distillation columns.

A+B↔C+D Economic Feasibility: Group 1

The desired product C in the A+B↔C+D systems in Regions 1, 4, and 8 has a boiling point that is higher than the other components in the reactive system. Therefore, the desired product is designed to be the primary component in the bottoms stream for a single feed (Figure 117) or double feed (Figure 118) reactive distillation column. A sharp split between the desired product and by-product must occur in the reactive distillation column in order for the desired product to meet the economic feasibility criteria set in this research project. Therefore, the by-product and unconverted reactants are designed to leave the reactive distillation column in the distillate steam allowing the reactive distillation column to produce essentially pure product C in the bottoms stream.

For A+B↔C+D systems in Region 1, it may be economically beneficial to design the reactive distillation column so that both the by-product and desired product leave the reactive distillation column in the bottoms steam and be sent for further refinement in a non-reactive distillation column, just like similar boiling point orderings in the A↔C+D systems (Figure 25). Although this process configuration may be a better design, the focus of this research project was on the economic feasibility of a single reactive distillation column and so this design was not investigated in more detail.

Reactive azeotropes are present in the Region 1 A+B↔C+D systems, but as was discussed in the reactive azeotrope section of this chapter, the reactive azeotropes in this region are not expected to limit the economic feasibility of any reactive distillation configurations with a stoichiometric feed. This is true for both a single feed or double feed reactive distillation column designs.

In order to develop a set of heuristics for the A+B↔C+D system, the boiling points orderings in Table 15 are grouped with similar boiling point orderings from the previously studied chemical reactive systems. The A↔C, A+B↔C, A↔C+D, and A+B↔C+D system regions where the desired product is the highest boiling component are grouped together in Table 16. This grouping is defined as Group 1 and shows the minimum K_{eq} required to meet the economic feasibility criteria for the A↔C, A+B↔C, and A↔C+D systems. This minimum K_{eq} does not guarantee an economically feasible reactive distillation column, but a reactive system that does not have a K_{eq} > minimum

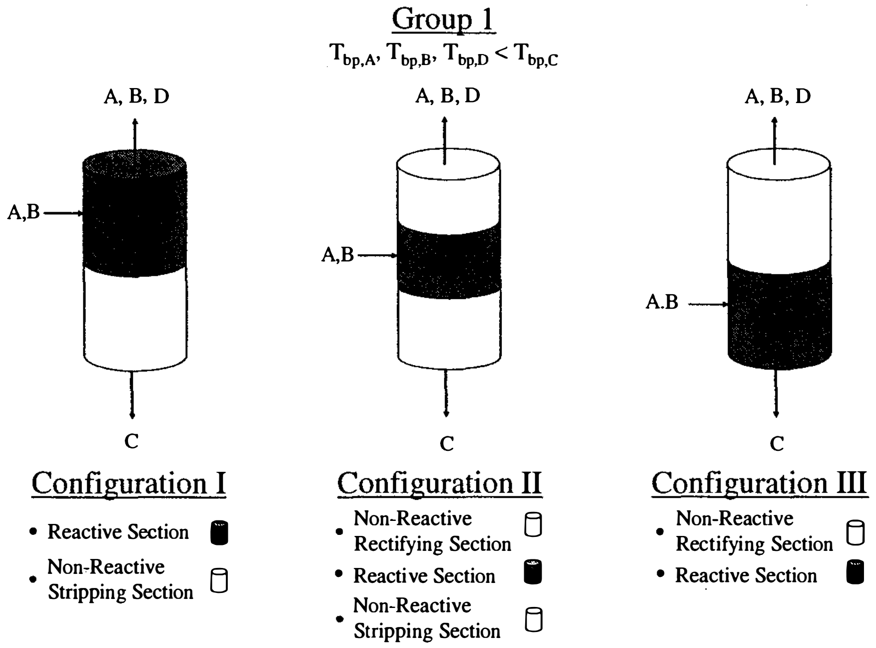


Figure 117. A+B↔C+D Group 1, Single Feed: Configurations I, II, III

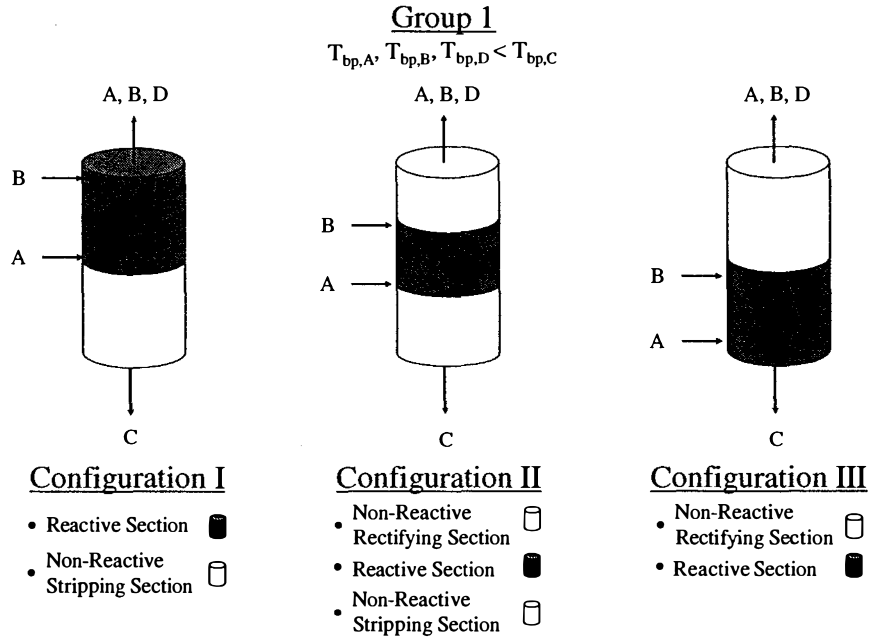


Figure 118. A+B↔C+D Group 1, Double Feed: Configurations I, II, III

Table 16. Group 1 Chemical Reactive Systems Minimum Required K_{eq}

Chemical Reactive System							
A↔C		A+B↔C		A↔C+D		A+B↔C+D	
Region 1 A C	I, II $K_{eq} > 0.1$	Region 1 A B C	I, II $K_{eq} > 0.1$	Region 1 A D C	I, II, III $K_{eq} > 0.1$	Region 1 A B D C	I, II, III $K_{eq} > 0.1$ (expected)
	III Reactive Azeos		III Reactive Azeos			Region 4 A D B C	I, II, III $K_{eq} > 0.1$ (expected)
-		-		Region 4 D A C	I, II, III $K_{eq} > 10^{-5}$	Region 8 D A B C	I, II, III $K_{eq} > 10^{-5}$ (expected)

K_{eq} will not be economically feasible regardless of the specific system component relative volatilities.

The Region 1 A↔C, Region 1 A+B↔C, and Region 1 A↔C+D systems all have a required minimum $K_{eq} > 0.1$, whereas the Region 4 A↔C+D systems have a smaller minimum K_{eq} of 10^{-5}. This difference comes from the fact that the reactant is the intermediate boiling component in the Region 4 A↔C+D systems and the reactants in the other regions are the lowest boiling components. When the reactant is the intermediate boiling component, the reactant is continually returned to the reactive zone, while the products are continually removed from the reactive zone which helps to drive reactant conversion following Le Chatelier's principle. When the reactant is the lowest boiling component, the reactant tends to concentrate at the top of the reactive distillation column and stay in the vapor phase. This limits the reactant concentration in the liquid phase of reactive zone and hinders product production in the reactive distillation column.

For A+B↔C+D systems, Regions 1, 4, and 8 are the regions where the desired product is the highest boiling component. These regions are grouped together in Table 16 along with the other Group 1 systems. The A+B↔C+D systems in Region 1 have reactants that are both lower boiling than the desired product and by-product, which is like the Region 1 A↔C, Region 1 A+B↔C, and Region 1 A↔C+D systems. Therefore, it is expected that the minimum K_{eq} for A+B↔C+D systems in Region 1 will be 0.1 based on comparison with the results from the other three reactive systems. The A+B↔C+D systems in Region 8 have reactants that are both intermediate boiling components, just like the Region 4 A↔C+D systems. Since both reactants are intermediate boiling for the

Region 8 A+B↔C+D systems, they both are continually returned to the reactive zone of the reactive distillation column like the reactant in the Region 4 A↔C+D systems. Therefore, it is expected that the minimum K_{eq} for A+B↔C+D systems in Region 8 will be 10^{-5} based on the results from the Region 4 A↔C+D systems.

The A+B↔C+D systems in Region 4 have a boiling point ordering that is similar to the Region 1 A↔C+D systems because one of the reactants is the lowest boiling component in the system, but the by-product boiling point falls in between the reactant boiling points. This particular boiling point ordering may hinder the reactant conversion for these A+B↔C+D systems because the reactants may have difficulty "seeing" each other in the liquid phase of the reactive zone. However, based on the understanding that the limiting factor in the other Group 1 chemical reactive systems was keeping the lowest boiling component in the reactive zone liquid phase, the minimum K_{eq} of the A+B↔C+D systems in Region 4 is expected to be 0.1, just like the other reactive systems in Group 1.

A+B↔C+D Economic Feasibility: Group 2

The A+B↔C+D systems within Regions 2, 3, 5, 6, 10, and 12 have an intermediate boiling product C. The desired product C can be either the distillate product or the bottoms product depending on the by-product boiling point. A sharp split between the desired product and by-product is required for the reactive distillation column to meet the economic feasibility criteria set in this research project. For A+B↔C+D systems in Regions 2, 3, and 5, the by-product has a boiling point that is higher than the desired product and the reactive distillation column is required to take the desired product out in the distillate stream. For A+B↔C+D systems in Regions 6, 10, and 12, the by-product has a boiling point that is lower than the desired product and the reactive distillation column is required to take the desired product out in the bottoms stream. Since the desired product is an intermediate boiling component, at least one of the unconverted reactants is going to have to leave the reactive distillation column with the desired product. The actual reactive distillation designs for a single feed (Figure 119) or double feed (Figure 120) reactive distillation column are shown without indicating the desired product location because each A+B↔C+D region in Group 2 has a unique design.

For A+B↔C+D systems in Regions 2 and 12, it may be economically beneficial to design the reactive distillation column so that both the by-product and desired product leave the reactive distillation column in the same stream and be sent for further refinement in a non-reactive distillation column, just like similar boiling point orderings in the A↔C+D system (Figure 25). Although this process configuration may be a better design, the focus of this research project was on the economic feasibility of a single reactive distillation column and so this design was not investigated in more detail.

Reactive azeotropes are present in the Region 2 and 12 A+B↔C+D systems and as was discussed in the reactive azeotrope section in this chapter, the reactive azeotropes limit the economic feasibility of a reactive distillation column with a stoichiometric feed. The reactive azeotropes present in the Region 2 A+B↔C+D systems will limit the economic

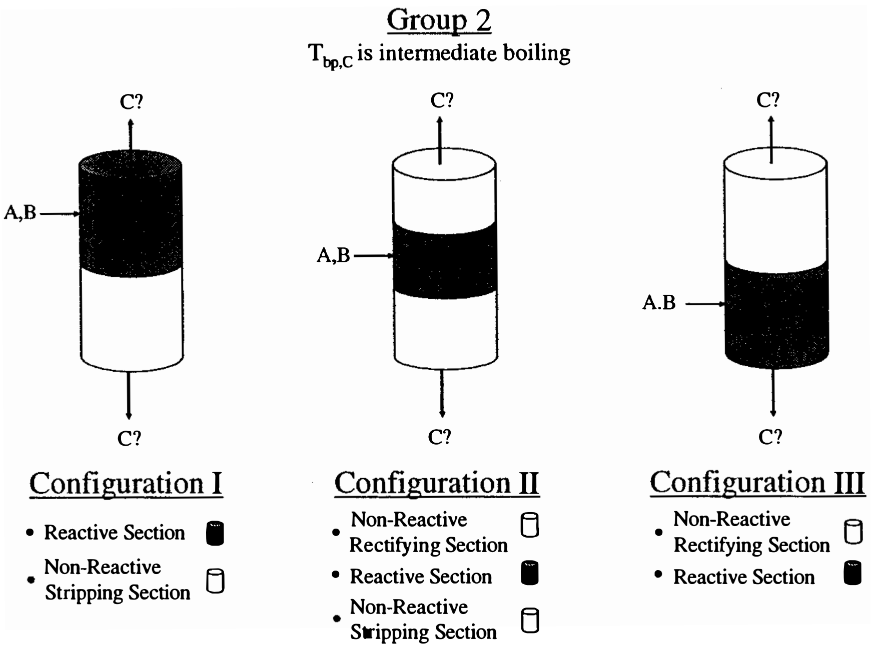


Figure 119. A+B↔C+D Group 2, Single Feed: Configurations I, II, III

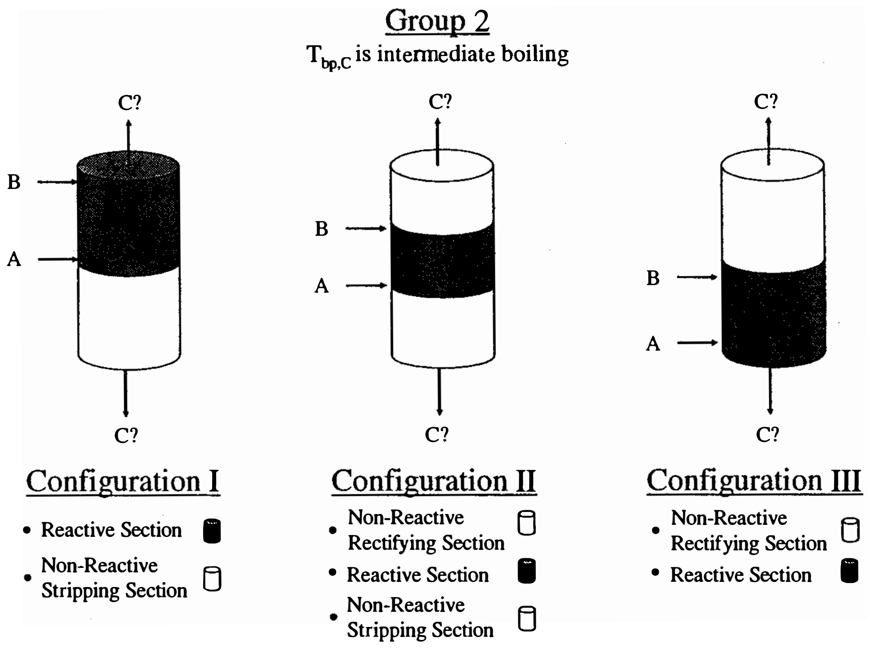


Figure 120. A+B↔C+D Group 2, Double Feed: Configurations I, II, III

feasibility of reactive distillation columns of Configuration I. The reactive azeotropes present in the Region 12 A+B↔C+D systems will limit the economic feasibility of reactive distillation columns of Configuration III. Reactive azeotropes are not present for all A+B↔C+D volatility and K_{eq} combinations in Regions 2 and 12. But for those combinations that do have reactive azeotropes, a reactive distillation column should have an appropriately placed non-reactive section to ensure that reactive azeotropes do not limit the economic feasibility of the reactive distillation column. For Region 2 A+B↔C+D systems with reactive azeotropes, a non-reactive rectifying section is necessary to break the reactive azeotrope. For Region 12 A+B↔C+D systems with reactive azeotropes, a non-reactive stripping section is necessary to break the reactive azeotrope. This is true for both a single feed or double feed reactive distillation column design.

The A↔C, A+B↔C, A↔C+D, and A+B↔C+D system regions where the desired product is an intermediate boiling component are shown in Table 17. This grouping is defined as Group 2 and shows the minimum K_{eq} required to meet the economic feasibility criteria for the A↔C, A+B↔C, and A↔C+D systems. This minimum K_{eq} does not guarantee an economically feasible reactive distillation column, but a reactive system that does not have a K_{eq} > minimum K_{eq} will not be economically feasible regardless of the specific system component relative volatilities.

There are three similar boiling point orderings within Group 2. The first set of regions is Region 2 A↔C+D, Region 2 A+B↔C+D, and Region 3 A+B↔C+D. The chemical reactive systems in these regions all have a high boiling by-product and an intermediate boiling desired product. The chemical reactive systems within these regions will require that the desired product be the primary distillate product and the by-product be the primary bottoms product. The economically limiting factor for the chemical systems in these regions is that the low boiling reactant(s) will have to be almost completely converted to product so that the desired product can leave the reactive distillation column in an essentially pure state. The economic feasibility of all systems in these regions is enhanced by the fact that the by-product will leave the reactive zone and allow the reactants to undergo further conversion to more product following Le Chatelier's principle. The minimum K_{eq} required to meet the economic feasibility criteria is expected to be 10^{-2}, except for A+B↔C+D in Region 2 which may be limited by reactive azeotropes for a reactive distillation column of Configuration I.

The next similar boiling point orderings within Group 2 are the Region 5 A↔C+D, Region 10 A+B↔C+D, and Region 12 A+B↔C+D boiling point orderings. The chemical reactive systems in these regions all have a low boiling by-product and an intermediate boiling desired product. The chemical reactive systems within these regions will require that the desired product be the primary bottoms product and the by-product be the primary distillate product. The economically limiting factor for the chemical systems in these regions is that the high boiling reactant(s) will have to be almost completely converted to product so that the desired product can leave the reactive

Table 17. Group 2 Chemical Reactive Systems Minimum Required K_{eq}

Chemical Reactive System						
A↔C	A+B↔C		A↔C+D		A+B↔C+D	
-	-		Region 2 A C D	I, II, III $K_{eq} > 10^{-2}$	Region 2 A B C D	I Reactive Azeos? II, III $K_{eq} > 10^{-2}$ (expected)
					Region 3 A C B D	I, II, III $K_{eq} > 10^{-2}$ (expected)
	-		Region 5 D C A	I, II, III $K_{eq} > 10^{-3}$	Region 12 D C A B	I, II $K_{eq} > 10^{-3}$ (expected) III Reactive Azeos?
					Region 10 D A C B	I, II, III $K_{eq} > 10^{-3}$ (expected)
	Region 2 A C B	I, II, III $K_{eq} > 100$	-		Region 5 A C D B	I, II, III $K_{eq} > 100$ (expected)
					Region 6 A D C B	I, II, III $K_{eq} > 100$ (expected)

distillation column in an essentially pure state. The economic feasibility of all systems in these regions is enhanced by the fact that the by-product will leave the reactive zone and allow the reactants to undergo further conversion to more product following Le Chatelier's principle. The minimum K_{eq} required to meet the economic feasibility criteria is expected to be 10^{-3}, except for A+B↔C+D in Region 12 which may be limited by reactive azeotropes for a reactive distillation column of Configuration III.

The other similar boiling point orderings within Group 2 are the Region 2 A+B↔C, Region 5 A+B↔C+D, and Region 6 A+B↔C+D boiling point orderings. Since the products in these regions are all intermediate boiling, the reactants must be completely converted for the desired product to leave the reactive distillation column in an essentially pure state. Additionally, since both products are intermediate boiling, neither the by-product nor desired product is leaving the reactive zone to enhance reactant conversion. In fact, the reactants are trying to leave the reactive zone liquid phase which tends to drive the overall reaction backwards to produce more reactants and maintain the chemical reaction equilibrium constant. Both of these situations limit the economic feasibility of reactive distillation for chemical systems within these regions where the all products are intermediate boiling components. The sharp split for the Region 5 A+B↔C+D systems require that the desired product leave in the distillate stream, the Region 6 A+B↔C+D systems require that the desired product leave in the bottoms stream, and the product in the Region 2 A+B↔C systems can leave in either the distillate or bottoms stream. The minimum K_{eq} required to meet the economic feasibility criteria is expected to be 100 for all of the A+B↔C+D systems in Regions 5 and 6 based on the significant difficulties associated with the intermediate boiling products found in these regions.

A+B↔C+D Economic Feasibility: Group 3

The A+B↔C+D systems in Regions 7, 9, and 11 have a desired product C boiling point that is lower than the other components in the reactive system. Therefore, the desired product is designed to be the primary component in the distillate stream for a single feed (Figure 121) or double feed (Figure 122) reactive distillation column. A sharp split between the desired product and by-product must occur in the reactive distillation column in order for the desired product to meet the economic feasibility criteria set in this research project. Therefore, the by-product and unconverted reactants are designed to leave the reactive distillation column in the bottoms steam allowing the reactive distillation column to produce essentially pure product in the distillate stream.

For A+B↔C+D systems in Region 11, it may be economically beneficial to design the reactive distillation column so that both the by-product and desired product leave the reactive distillation column in the distillate steam and be sent for further refinement in a non-reactive distillation column, just like similar boiling point orderings in the A↔C+D system (Figure 25). Although this process configuration may be a better design, the focus of this research project was on the economic feasibility of a single reactive distillation column and so this design was not investigated in more detail.

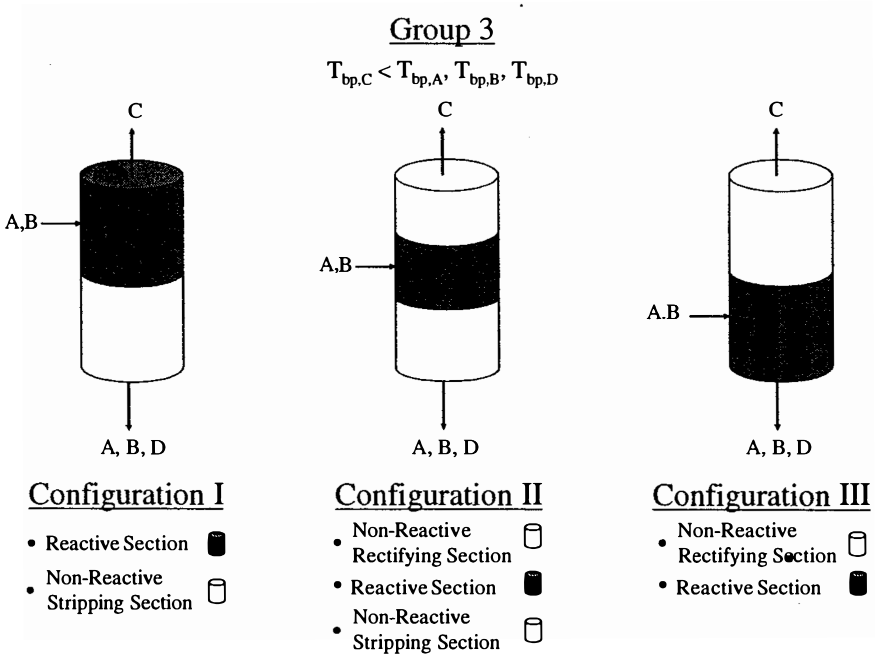


Figure 121. A+B↔C+D Group 3, Single Feed: Configurations I, II, III

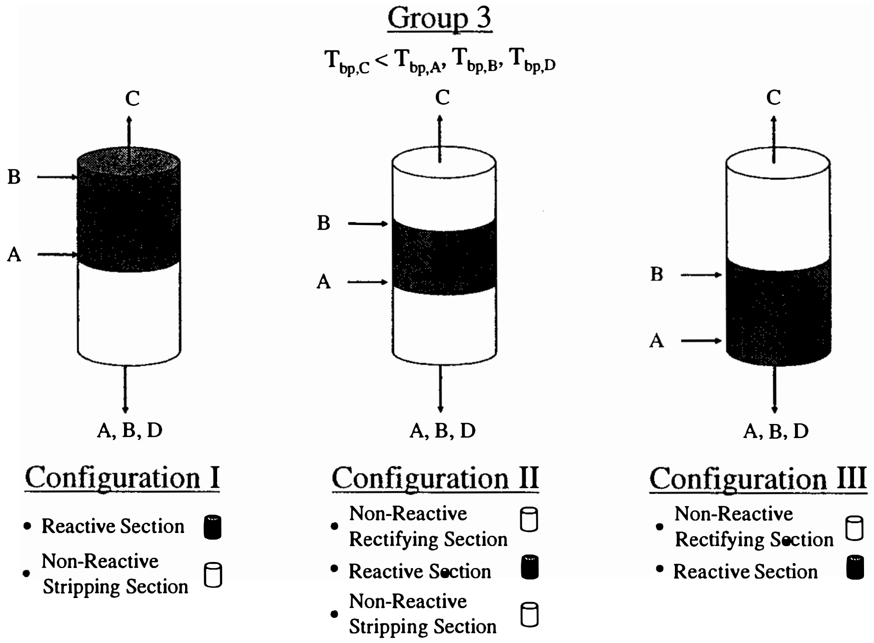


Figure 122. A+B↔C+D Group 3, Double Feed: Configurations I, II, III

Reactive azeotropes are present in the Region 11 A+B↔C+D systems, but as was discussed in the reactive azeotrope section of this chapter, the reactive azeotropes are not expected to limit the economic feasibility of any reactive distillation configurations with a stoichiometric feed. This is true for both a single feed or double feed reactive distillation column designs.

The A↔C, A+B↔C, A↔C+D, and A+B↔C+D system regions where the desired product is the lowest boiling component are shown in Table 18. This grouping is defined as Group 3 and shows the minimum K_{eq} required to meet the economic feasibility criteria for the A↔C, A+B↔C, and A↔C+D systems. This minimum K_{eq} does not guarantee an economically feasible reactive distillation column, but a reactive system that does not have a $K_{eq} >$ minimum K_{eq} will not be economically feasible regardless of the specific system component relative volatilities.

The Region 2 A↔C, Region 3 A+B↔C, and Region 6 A↔C+D systems all have a required minimum $K_{eq} > 10^{-3}$, whereas the Region 3 A↔C+D systems have a smaller minimum K_{eq} of 10^{-5}. This difference comes from the fact that the reactant is the intermediate boiling component in the Region 3 A↔C+D systems and the reactants in the other regions are the highest boiling components. When the reactant is the intermediate boiling component, the reactant is continually returned to the reactive zone, while both products are continually removed from the reactive zone which helps to drive reactant conversion following Le Chatelier's principle. When the reactant is the highest boiling component, the reactant tends to concentrate in the bottom of the reactive distillation column which can limit the reactant concentration in the liquid phase of reactive zone, especially for reactive distillation columns of Configurations I and II.

Table 18. Group 3 Chemical Reactive Systems Minimum Required K_{eq}

A↔C		A+B↔C		A↔C+D		A+B↔C+D	
Region 2 C A	I Reactive Azeos	Region 3 C A B	I Reactive Azeos	Region 6 C D A	I, II, III $K_{eq} > 10^{-3}$	Region 11 C D A B	I, II, III $K_{eq} > 10^{-3}$ (expected)
	II, III $K_{eq} > 10^{-3}$		II, III $K_{eq} > 10^{-3}$			Region 9 C A D B	I, II, III $K_{eq} > 10^{-3}$ (expected)
-		-		Region 3 C A D	I, II, III $K_{eq} > 10^{-5}$	Region 7 C A B D	I, II, III $K_{eq} > 10^{-5}$ (expected)

For the A+B↔C+D system, Regions 7, 9, and 11 are the regions where the desired product is the lowest boiling component with the actual boiling point orderings for these regions shown in Table 18 along with the other Group 3 systems. The A+B↔C+D systems in Region 11 have reactants that are both higher boiling than the desired product and by-product, which is like the Region 2 A↔C, Region 3 A+B↔C, and Region 6 A↔C+D systems. Therefore, it is expected that the minimum K_{eq} for A+B↔C+D systems in Region 11 will be 10^{-3} based on comparison with the results from the other three reactive systems. The A+B↔C+D systems in Region 7 have reactants that are both intermediate boiling components, just like the Region 3 A↔C+D systems. Since both reactants are intermediate boiling for the Region 7 A+B↔C+D systems, they both are continually returned to the reactive zone of the reactive distillation column like the reactant in the Region 3 A↔C+D systems. Therefore, it is expected that the minimum K_{eq} for A+B↔C+D systems in Region 7 will be 10^{-5} based on the results from the Region 3 A↔C+D systems.

The A+B↔C+D systems in Region 9 have a boiling point ordering that is similar to the Region 3 A↔C+D systems because one of the reactants is the highest boiling component in the system, but the by-product boiling point falls in between the reactant boiling points. This particular boiling point ordering may hinder the reactant conversion for these A+B↔C+D systems because the reactants may have difficulty "seeing" each other in the liquid phase of the reactive zone. However, based on the understanding that the limiting factor in the other Group 3 chemical reactive systems was keeping the reactants in the reactive zone liquid phase, the minimum K_{eq} of the A+B↔C+D systems in Region 9 is expected to be 10^{-3}, just like the other reactive systems in Group 3.

Product and By-Product Separation Limitations

The A+B↔C+D reactive systems have two products just like the A↔C+D systems and are expected to have the same separation difficulties associated with a close boiling by-product and desired product. For A+B↔C+D systems with $\alpha_{AC} = \alpha_{AD}$, the boiling points of the by-product and product are exactly the same and cannot be separated by distillation. Reactive distillation will not be able to separate the by-product from the product regardless of the chemical reaction equilibrium constant for A+B↔C+D systems with the product and by-product relative volatility. For A+B↔C+D systems with α_{AC} close to α_{AD}, the separation of the product and by-product can be improved by higher column reflux ratios, but the same limitations found for the A↔C+D systems are expected for the A+B↔C+D systems because the purification of the desired product from the by-product is not improved by the presence of an additional reactant in the reactive system. Therefore, the minimum reflux ratio heuristics proposed for the A↔C+D systems are expected to be exactly the same for the A+B↔C+D systems.

Literature Examples

The reactive distillation literature was reviewed with the intent of finding real chemical reactive systems that could be used to verify the heuristics and observations proposed in this chapter. The metathesis of 2-pentene is present in the reactive distillation literature (Okasinski and Doherty, 1998; Chen et al., 2000; Lee et al., 2003) and can be used as an example for the A+B↔C+D system. The 2-pentene reaction is actually an A+A↔C+D system, but can be used to verify the heuristics for a 4-component system with $\alpha_{AB} = 1.0$. The system boiling points, relative volatilities, and chemical reaction equilibrium constant for this particular reactive system are shown in Table 19. The other reactions shown in Table 19 are not ideal reactive systems, but will be used to discuss the heuristics for a single feed vs. double feed reactive distillation column. For the purpose of this study, it was assumed that the chemical reaction equilibrium constants shown in Table 19 are temperature independent.

Economic Feasibility: 2-Pentene Metathesis

The economic feasibility of the 2-pentene metathesis reaction was evaluated using a single feed reactive distillation column of Configurations I, II, and III at an operating pressure of one atm. A double feed reactive distillation column was not evaluated because it is not possible to actually separate the reactants in separate feeds for this particular reactive system. The boiling point ordering for the 2-pentene metathesis reactive system falls within Region 7 for the production of 2-butene and Region 8 for the production of 3-hexene. The chemical reaction equilibrium constant is reported to be 0.25 (Okasinski and Doherty, 1998) and there are no non-reactive azeotropes present in this reactive system.

The production of 2-butene and 3-hexene via reactive distillation both met the economic feasibility criteria for all column configurations with a minimum reflux ratio of 1.0. The chemical reaction equilibrium constant of 0.25 is within the expected minimum economic feasibility K_{eq} of 10^{-5} for A+B↔C+D systems in Regions 7 and 8 (Tables 16 and 18).

Single Feed vs. Double Feed: Reactive Distillation Production of Esters

Single feed and double feed reactive distillation columns have been evaluated for several ester systems by Chadda el al. (2002). It should be noted that all of these esterification systems are non-ideal and do contain non-reactive azeotropes, which are outside of the scope of this research project. However, the heuristics proposed in this research project for single feed and double feed reactive distillation columns should be applicable to non-ideal reactive systems because the primary design criteria for choosing a feed design is to maximize the contact of reactants in the reactive zone liquid phase, which is not expected to be highly dependant on the presence of non-reactive azeotropes.

The first system studied was the production of n-butyl acetate using a single feed reactive distillation column. The component boiling point ordering for n-butyl acetate falls within Region 8 for A+B↔C+D systems. The reported K_{eq} for this reaction is 12.5, which is well above the expected minimum economically feasible K_{eq} of 10^{-5} in the proposed heuristics for this region. This would indicate that an economically feasible reactive distillation column design should be found unless the non-reactive azeotropes present in

Table 19. A+B↔C+D Literature Examples

Reactive Distillation System A+B↔C+D	Boiling Points (°C)	Relative Volatilities (α_{Ai})	K_{eq}	Region
2-Pentene (A) + 2-Pentene (B) ↔ 2-Butene (C) + 3-Hexene (D)	A = 37 B = 37 C = 3.7 D = 66	$\alpha_{AB} = 1.00$ $\alpha_{AC} = 0.33$ $\alpha_{AD} = 2.84$	0.25	7
2-Pentene (A) + 2-Pentene (B) ↔ 2-Butene (D) + 3-Hexene (C)	A = 37 B = 37 C = 66 D = 3.7	$\alpha_{AB} = 1.00$ $\alpha_{AC} = 2.84$ $\alpha_{AD} = 0.33$	0.25	8
Methanol (A) + Acetic Acid (B) ↔ Methyl Acetate (C) + Water (D)	A = 64 B = 118 C = 56 D = 100	$\alpha_{AB} = 6.5$ $\alpha_{AC} = 0.87$ $\alpha_{AD} = 3.7$	20	9
Acetic Acid (A) + Butanol (B) ↔ Butyl Acetate (C) + Water (D)	A = 118 B = 118 C = 126 D = 100	$\alpha_{AB} = 1.01$ $\alpha_{AC} = 1.28$ $\alpha_{AD} = 0.54$	12.5	8
iso-Propanol (A) + Acetic Acid (B) ↔ iso-Propyl Acetate (C) + Water (D)	A = 82.6 B = 118 C = 88.9 D = 100	$\alpha_{AB} = 3.6$ $\alpha_{AC} = 1.28$ $\alpha_{AD} = 1.97$	8.7	5

the reactive system inhibit product purification. Additionally, the relative volatility of the reactants is approximately $\alpha_{AB} = 1.01$, which would indicate that a single feed reactive distillation column would be the design of choice based on the proposed heuristics for A+B↔C+D systems. The results from Chadda et al. show that a single feed reactive distillation of Configuration II was found to be an economically feasible design for production of n-butyl acetate, which supports the proposed heuristics. Unfortunately, a double feed reactive distillation column was not evaluated for the production of n-butyl acetate in that paper.

The next system studied was the production of methyl acetate using a double feed reactive distillation column. The component boiling point ordering for methyl acetate falls within Region 9 for A+B↔C+D systems. The calculated K_{eq} for this reaction over the expected temperature range within the reactive distillation column is approximately 20, which is well above the minimum economically feasible K_{eq} of 10^{-5} reported in the proposed heuristics for this region. This would indicate that an economically feasible reactive distillation column design should be found unless the non-reactive azeotropes present in the reactive system inhibit product purification. The relative volatility of the reactants for this system is approximately $\alpha_{AB} = 6.5$, which indicates that a double feed reactive distillation column would be the design of choice based on the proposed heuristics in this research project. Chadda et al. found that a double feed column was required to produce high purity methyl acetate because a single feed reactive distillation column did not provide adequate reactant contact within the reactive distillation column reactive zone, which supports the proposed heuristics in this research project.

The final esterification system studied by Chadda et al. was the production of isopropyl acetate, which has a component boiling point ordering that falls within Region 5 for the A+B↔C+D systems. The reported K_{eq} for this reaction is 8.7, which is below the minimum economically feasible K_{eq} of 100 reported in the proposed heuristics for systems in Region 5. This would indicate that an economically feasible reactive distillation column design should not be found for this particular reactive system. The isopropyl acetate system has a reactant relative volatility of approximately $\alpha_{AB} = 3.6$, which falls in the "in between" range for the proposed single of double feed heuristics. Extending the heuristic results for the Region 2 A+B↔C system, a double feed column would most likely produce the best results for an A+B↔C+D system with an intermediate boiling product. Chadda et al. found both the single feed and double reactive distillation column designs to be economically limited, primarily because of the presence of non-reactive and reactive azeotropes inherent to the isopropyl acetate system. However, a double feed column did produce the best isopropyl acetate purity at 58%, while a single feed column was able to produce the product at only 54% purity. Even if the non-reactive and reactive azeotropes were not present, the isopropyl acetate system would not be economically feasible based on the heuristics proposed in this research project.

Observations and Heuristics

Note: For all $A+B \leftrightarrow C+D$ systems, the low boiling reactant is always designated as reactant A, which results in all reactant relative volatilities being greater than 1.0.

Observations

1. Reactive azeotropes, if present, limit the economic feasibility of $A+B \leftrightarrow C+D$ systems with boiling point orderings that fall in Regions 2 and 12. The reactive azeotropes present in Regions 2 and 12 are all saddles.

2. Reactive azeotropes are present in Regions 1 and 11, but are not economically limiting for $A+B \leftrightarrow C+D$ systems of constant relative volatility. The reactive azeotropes present in Regions 1 and 11 are all saddles.

3. Reactive azeotropes are not present in Regions 3-10 for the ideal, constant volatility $A+B \leftrightarrow C+D$ systems in this study.

Heuristics – Single Feed vs. Double Feed Reactive Distillation Columns

1. A double feed reactive distillation column is usually the best feed design for reactive $A+B \leftrightarrow C+D$ systems where the reactant boiling points are far apart, $\alpha_{AB} \geq 4.0$.
2. A single feed reactive distillation column is usually the best feed design for reactive $A+B \leftrightarrow C+D$ systems where the reactant boiling points are close together, $1.0 \leq \alpha_{AB} \leq 1.2$.
3. For $A+B \leftrightarrow C$ systems with a reactant relative volatility of $1.2 < \alpha_{AB} < 4.0$, a double feed or single feed reactive distillation column may be the best feed design depending on which design produces the best reactant contact in the reactive zone liquid phase.

Heuristics – Minimum Reflux Ratios For Product and By-Product Separation

4. A reactive distillation column of Configuration II is usually the best configuration for all $A+B \leftrightarrow C+D$ systems.
5. The separation of the desired product and by-product is the primary factor limiting reactive distillation economic feasibility for $A+B \leftrightarrow C+D$ systems with $K_{eq} > 1.0$.
6. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 100, the relative volatility of the by-product and product must be less than approximately 0.91 or greater than 1.10. ($\alpha_{DC} > 1.10$ or $\alpha_{DC} < 0.91$).
7. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 10, the relative volatility of the by-product and product must be less than approximately 0.80 or greater than 1.25. ($\alpha_{DC} > 1.25$ or $\alpha_{DC} < 0.80$).
8. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 5, the relative volatility of the by-product and product must be less than approximately 0.69 or greater than 1.45. ($\alpha_{DC} > 1.45$ or $\alpha_{DC} < 0.69$).

9. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 2.5, the relative volatility of the by-product and product must be less than approximately 0.48 or greater than 2.1. ($\alpha_{DC} > 2.1$ or $\alpha_{DC} < 0.48$).

Heuristics – Group 1: Desired Product is Highest Boiling Component

10. The A+B↔C+D systems within this group are expected to require a $K_{eq} > 0.1$ to be economically feasible, except for systems in Region 8 which are expected to require a $K_{eq} > 10^{-5}$. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A+B↔C+D system relative volatilities.

Heuristics – Group 2: Desired Product is Intermediate Boiling Component

11. The A+B↔C+D systems within Regions 5 and 6 are expected to require a $K_{eq} > 100$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A+B↔C+D system relative volatilities.
12. The A+B↔C+D systems within Regions 10 and 12 are expected to require a $K_{eq} > 10^{-3}$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A+B↔C+D system relative volatilities.
13. The A+B↔C+D systems within Regions 2 and 3 are expected to require a $K_{eq} > 10^{-2}$ to be economically feasible. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A+B↔C+D system relative volatilities.
14. For Region 2 A+B↔C+D systems with reactive azeotropes, a non-reactive rectifying section is necessary for the reactive distillation column to break the reactive azeotrope and produce a pure desired product.
15. For Region 12 A+B↔C+D systems with reactive azeotropes, a non-reactive stripping section is necessary to break the reactive azeotrope and produce a pure desired product.

Heuristics – Group 3: Desired Product is Lowest Boiling Component

16. All A+B↔C+D systems within this region must have a $K_{eq} > 10^{-3}$ to be economically feasible, except for systems in Region 7 which must have a $K_{eq} > 10^{-5}$. This K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the A+B↔C+D system relative volatilities.

Economic feasibility criteria:

1. reactant conversion $\geq 95.0\%$
2. product purity $\geq 99.0\%$
3. total column stages ≤ 100.
4. reflux ratio ≤ 100 (economic reflux ratios depend on product value).

These heuristics are based on data collected with the following assumptions:

1. The reactant feed stage(s) is confined to the reactive zone.
2. Chemical reaction equilibrium is attained on every reactive stage.
3. Vapor-liquid equilibrium is attained on every stage.
4. Vapor and liquid phases are ideal.
5. The feed(s) is 100% reactant.
6. The overall feed to the reactive distillation column is stoichiometric.
7. Any heat effects cancel within the reactive distillation column.
8. The reactive distillation column has a total condenser.

Summary

In this chapter, a set of heuristics was proposed for the initial feasibility assessment and conceptual design of reactive distillation columns involving the reaction A+B↔C+D. The potential component boiling points for the A+B↔C+D systems were divided into twelve regions of similar boiling points orderings. These regions were grouped with similar regions for the A↔C, A↔C+D, and A+B↔C systems with the similarities within these groups used to generate a set of heuristics for the A+B↔C+D system. A small study indicated that reactive azeotropes were present in Regions 1, 2, 11 and 12 with only the economic feasibility of Configuration I being limited for A+B↔C+D systems in Region 2 and Configuration III for Region 12. For each of the twelve A+B↔C+D regions, a minimum required chemical reaction equilibrium constant was proposed for the economic feasibility of reactive distillation based on analogy with the previously studied reactive systems. Similarly, the use of a single feed reactive distillation column was proposed to be the best design for A+B↔C+D systems with close boiling reactants, while a double feed column was proposed to be the best for reactants that had significantly different boiling points. The heuristics for the A+B↔C+D system were checked using the 2-pentene metathesis reaction and the ester production results from Chadda et al. (2002) as examples.

IX. CONCLUSIONS AND FUTURE RESEARCH

Conclusions

A parametric study was conducted using four ideal generic chemical reactive systems: A↔C, A↔C+D, A+B↔C, and A+B↔C+D. The study evaluated the affects that changing relative volatility and chemical equilibrium have on reactive distillation economic feasibility and design. Each reactive chemical system was divided into regions of potential component boiling point orderings which were expected to have similar single column reactive distillation feasibility and design characteristics.

Economic Feasibility Diagrams were developed to display the reflux required for a high conversion, high product purity, 100-tray reactive distillation column as a function of reactive system type, component relative volatilities, and reaction equilibrium constant. In each specific situation, other considerations including energy consumption and product value will place practical limits on the maximum reflux ratio that is economically acceptable.

Rough Economic Feasibility Diagrams were created to document the economic feasibility results for the three potential reactive distillation column configurations. A smaller number of these rough diagrams were selected for further study with Refined Economic Feasibility Diagrams being created to show the actual economic feasibility boundaries in greater detail. These Economic Feasibility Diagrams show that each individual chemical reactive system was located within one of four qualitative areas: systems limited by reaction, systems limited by separation, systems limited by reaction and separation, or systems where reaction and separation are both enhancing the economic feasibility of reactive distillation.

Additionally, the Economic Feasibility Diagrams show that the economic feasibility boundaries for low and high boiling reactants are not symmetric. Reactive systems with low boiling reactants require a larger chemical reaction equilibrium constant than systems with higher boiling reactants. This is primary caused by the difficulties in keeping the low boiling reactants in the reactive zone liquid phase. Lower boiling reactants concentrate in the vapor phase of the reactive distillation column, which makes it difficult to keep them in the reactive zone liquid phase. Higher boiling reactants will concentrate in the liquid phase of the reactive distillation column, which enhances their conversion to the desired product. This non-symmetry was found in all Economic Feasibility Diagrams for these particular reactive systems.

Economic Feasibility Diagrams are a useful screening tool which can be used to identify systems likely to benefit from single column reactive distillation.

A set of heuristics was proposed for the initial feasibility assessment and conceptual design of reactive distillation columns for A↔C, A↔C+D, A+B↔C, and A+B↔C+D chemical reactive systems. These heuristics can be condensed into a final set of key observations and heuristics.

Observations

1. Every A↔C reactive system has one and only one reactive azeotrope, which is independent of relative volatility and only depends on the value of the chemical reaction equilibrium constant.
2. Reactive azeotropes for the A↔C+D system are not present for $K_{eq} > 1.0$ and, if present, do not limit the economic feasibility of A↔C+D systems.
3. For A+B↔C systems, reactive azeotropes can limit systems with low or high boiling products (i.e. Regions 1 or 3).
4. All reactive azeotropes for A+B↔C+D systems are intermediate boiling and, if present, can limit systems that have boiling point orderings that fall within Regions 2 and 12.

Heuristics – Reactive Distillation Column Configuration

1. Chemical reactive systems with low boiling reactive azeotropes and a low boiling product must have a non-reactive rectifying section in the reactive distillation column so that the column can produce pure product and break the reactive azeotrope.
2. Chemical reactive systems with high boiling reactive azeotropes and a high boiling product must have a non-reactive stripping section in the reactive distillation column so that the column can produce pure product and break the reactive azeotrope.
3. Reactive distillation columns with a non-reactive rectifying section and non-reactive stripping section will not be economically limited by reactive azeotropes.

Heuristics – Single Feed vs. Double Feed Two-Reactant Reactive Distillation Columns

4. A double feed reactive distillation column is usually the best feed design for reactive systems where the reactant boiling points are far apart, $\alpha_{AB} \geq 4.0$.
5. A single feed reactive distillation column is usually the best feed design for reactive systems where the reactant boiling points are close together, $1.0 \leq \alpha_{AB} \leq 1.2$.
6. For reactive systems with a reactant relative volatility of $1.2 < \alpha_{AB} < 4.0$, a double feed or single feed reactive distillation column may be the best feed design depending on which design produces the best reactant contact in the reactive zone liquid phase.

Heuristics – Minimum Reflux Ratios For Product and By-Product Separation

7. A reactive distillation column of Configuration II is usually the best configuration for all A↔C+D and A+B↔C+D systems.
8. The separation of the desired product and by-product is the primary factor limiting reactive distillation economic feasibility for A↔C+D and A+B↔C+D systems and a $K_{eq} > 1.0$.

9. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 100, the relative volatility of the by-product and product must be less than approximately 0.91 or greater than 1.10. ($\alpha_{DC} > 1.10$ or $\alpha_{DC} < 0.91$).
10. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 10, the relative volatility of the by-product and product must be less than approximately 0.80 or greater than 1.25. ($\alpha_{DC} > 1.25$ or $\alpha_{DC} < 0.80$).
11. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 5, the relative volatility of the by-product and product must be less than approximately 0.69 or greater than 1.45. ($\alpha_{DC} > 1.45$ or $\alpha_{DC} < 0.69$).
12. For a reactive distillation column to be economically feasible and have a reflux ratio ≤ 2.5, the relative volatility of the by-product and product must be less than approximately 0.48 or greater than 2.1. ($\alpha_{DC} > 2.1$ or $\alpha_{DC} < 0.48$).

Heuristics – Economic Feasibility

Note: These economic feasibility limits are for single column reactive distillation with a reflux ratio ≤ 100 and the reported minimum K_{eq} does not guarantee economic feasibility, but any K_{eq} less than this value will not be economically feasible regardless of the component relative volatilities.

13. For chemical reactive systems where the reactants are all intermediate boiling and the products are the highest and lowest boiling components, a minimum K_{eq} of 10^{-5} is required for an economically feasible reactive distillation column.
14. For chemical reactive systems where the products are all intermediate boiling and the reactants are the highest and lowest boiling components, a minimum K_{eq} of 100 is required for an economically feasible reactive distillation column.
15. For chemical reactive systems where the desired product is the highest boiling component, a minimum K_{eq} of 10^{-1} is required for an economically feasible reactive distillation column.
16. For chemical reactive systems where the desired product is the lowest boiling component, a minimum K_{eq} of 10^{-3} is required for an economically feasible reactive distillation column
17. For chemical reactive systems where the by-product is the lowest boiling component and the desired product is intermediate boiling, a minimum K_{eq} of 10^{-3} is required for an economically feasible reactive distillation column.
18. For chemical reactive systems where the by-product is the highest boiling component and the desired product is intermediate boiling, a minimum K_{eq} of 10^{-2} is required for an economically feasible reactive distillation column.

Future Research

Non-Ideal Reactive System Heuristics for Single Column Reactive Distillation

The heuristics proposed in this research project were developed using ideal reactive systems. Although these heuristics can be extended to certain non-ideal reactive systems, it is clear that the presence of non-reactive azeotropes can limit the economic feasibility of reactive distillation (Venimadhavan et al., 1999a; Lee and Westerberg, 2001; Chadda et al., 2002). For example, the production of pure methyl acetate is limited by the presence of a minimum boiling methyl acetate-methanol azeotrope. Methyl acetate is the lowest boiling pure component in this reactive system. However, methyl acetate forms a minimum boiling azeotrope with methanol, which is not destroyed by reaction because the azeotrope consists of a reactant and product. Since the azeotrope exists in both the reactive and non-reactive sections of a reactive distillation column, the low boiling methyl acetate-methanol non-reactive azeotrope is the expected distillate product for all reactive distillation column configurations. Therefore, a pure methyl acetate product is not economically possible and has a significant impact on the feasibility and design of reactive distillation.

As this example demonstrates, it is important to consider the limitations of non-reactive azeotropes when evaluating the initial feasibility and design of reactive distillation columns. A set of heuristics for non-ideal reactive systems would be very beneficial and the next logical progression in heuristic development for reactive distillation.

Reactive Distillation Enhancing Non-Reactive Component

It is possible that the reactive distillation economic feasibility of certain reactive systems may be enhanced by the addition of a low boiling or high boiling non-reactive component. This non-reactive component is not extractive in nature, but will provide a higher reactant concentration in the reactive zone by forcing the reactant(s) back into in the liquid phase of the reactive distillation column. For example, $A \leftrightarrow C$ reactive systems in Region 2 have a high boiling product and a low boiling reactant, which is proposed to require a minimum K_{eq} of 0.1 to meet the economic feasibility criteria set in this research project. Similarly, $A \leftrightarrow C+D$ systems in Region 4 have a high boiling product, but have an intermediate boiling reactant along with a low boiling by-product. These Region 4 $A \leftrightarrow C+D$ systems require a minimum K_{eq} of 10^{-5} in order to meet the economic feasibility criteria. As was discussed in the previous chapters, one of the primary reasons that the required K_{eq}'s for Region 4 $A \leftrightarrow C+D$ systems are smaller than comparable Region 2 $A \leftrightarrow C$ systems is because the low boiling by-product keeps the intermediate boiling reactant in the liquid phase of the reactive distillation column. Adding a low boiling non-reactive component to the $A \leftrightarrow C$ reactive systems in Region 2 should force the low boiling reactant back into the liquid phase of the reactive zone to produce more desired product and potentially enhance the economics of reactive distillation. It is expected that any reactive system with low boiling or high boiling reactants can potentially have greater reactive distillation economic feasibility if a non-reactive component is selected such that the reactants are the intermediate boiling components after the addition of the non-reactive component.

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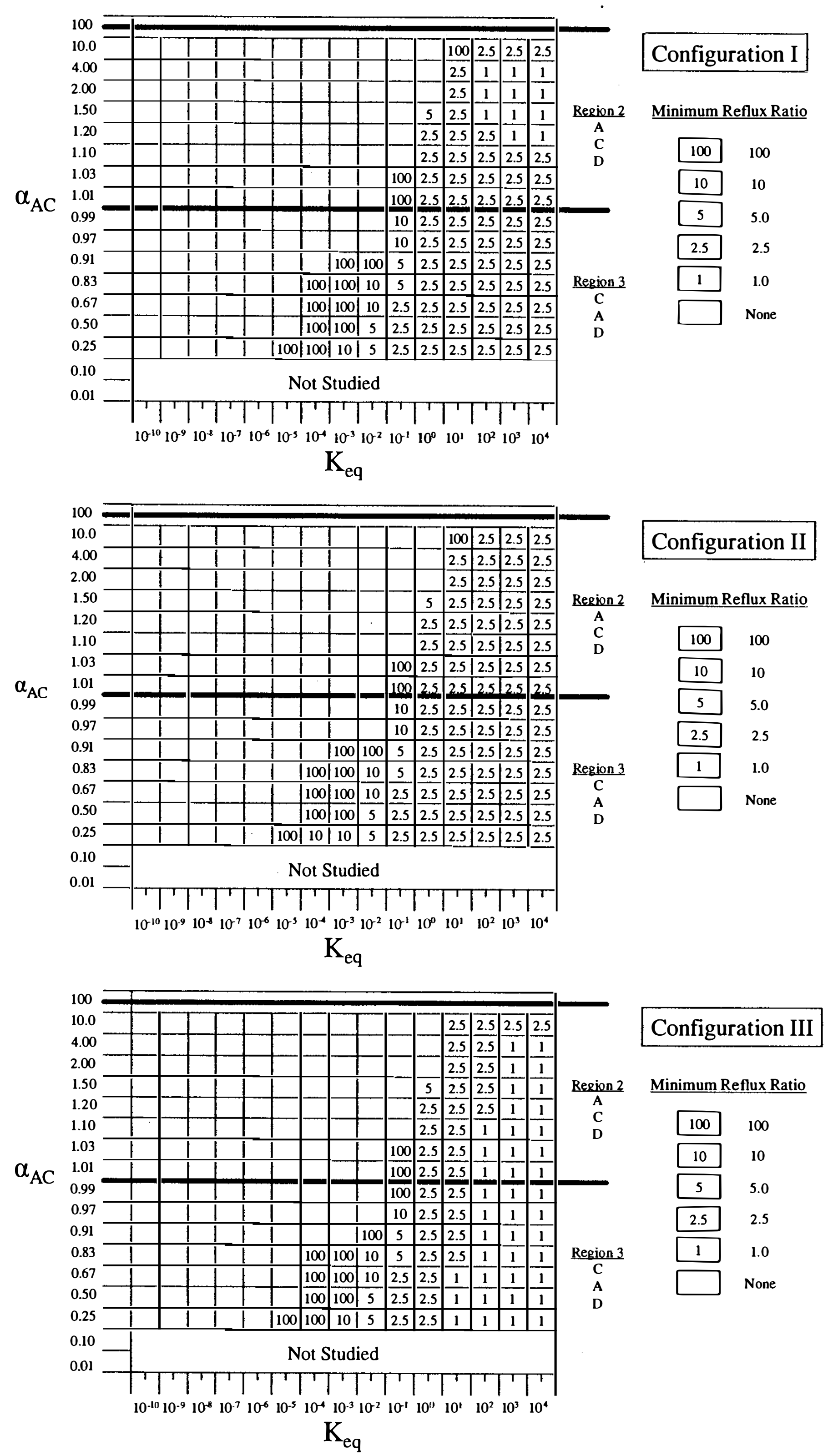
APPENDICES

Appendix A

A↔C+D System Figures



Configuration I

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
10.0												100	2.5	2.5	2.5
4.00												2.5	1	1	1
2.00												2.5	1	1	1
1.50											5	2.5	1	1	1
1.20											2.5	2.5	2.5	1	1
1.10											2.5	2.5	2.5	2.5	2.5
1.03										100	2.5	2.5	2.5	2.5	2.5
1.01										100	2.5	2.5	2.5	2.5	2.5
0.99										10	2.5	2.5	2.5	2.5	2.5
0.97										10	2.5	2.5	2.5	2.5	2.5
0.91								100	100	5	2.5	2.5	2.5	2.5	2.5
0.83							100	100	10	5	2.5	2.5	2.5	2.5	2.5
0.67							100	100	10	2.5	2.5	2.5	2.5	2.5	2.5
0.50							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
0.25						100	100	10	5	2.5	2.5	2.5	2.5	2.5	2.5

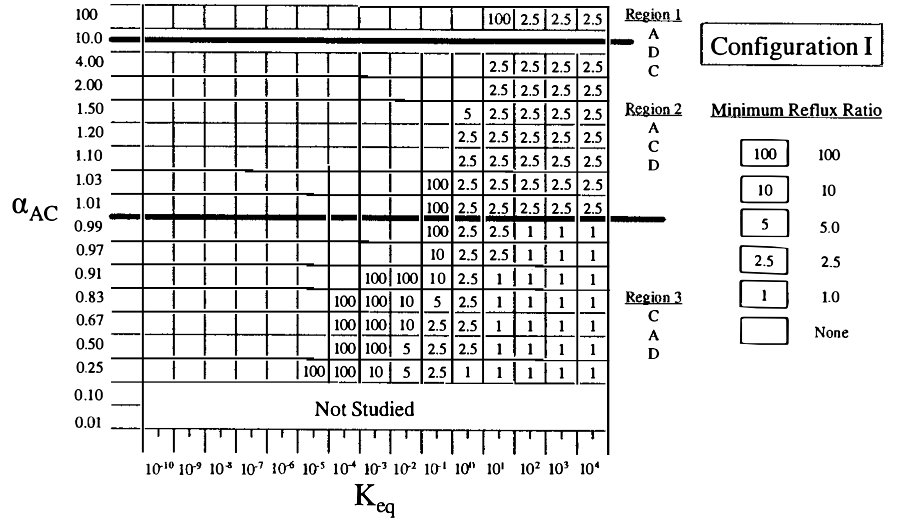
Configuration II

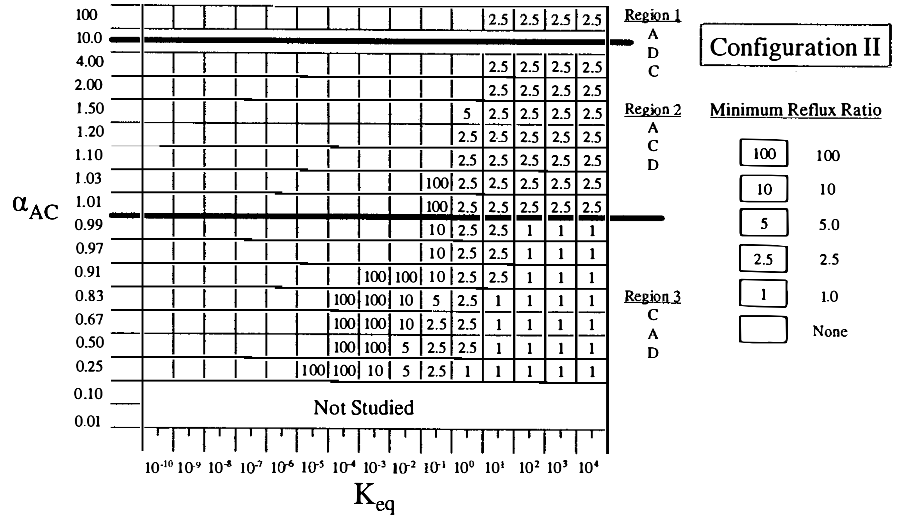
α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
10.0												100	2.5	2.5	2.5
4.00												2.5	2.5	2.5	2.5
2.00												2.5	2.5	2.5	2.5
1.50											5	2.5	2.5	2.5	2.5
1.20											2.5	2.5	2.5	2.5	2.5
1.10											2.5	2.5	2.5	2.5	2.5
1.03										100	2.5	2.5	2.5	2.5	2.5
1.01										100	2.5	2.5	2.5	2.5	2.5
0.99										10	2.5	2.5	2.5	2.5	2.5
0.97										10	2.5	2.5	2.5	2.5	2.5
0.91								100	100	5	2.5	2.5	2.5	2.5	2.5
0.83							100	100	10	5	2.5	2.5	2.5	2.5	2.5
0.67							100	100	10	2.5	2.5	2.5	2.5	2.5	2.5
0.50							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
0.25						100	10	10	5	2.5	2.5	2.5	2.5	2.5	2.5

Configuration III

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
10.0												2.5	2.5	2.5	2.5
4.00												2.5	2.5	1	1
2.00												2.5	2.5	1	1
1.50											5	2.5	2.5	1	1
1.20											2.5	2.5	2.5	1	1
1.10											2.5	2.5	1	1	1
1.03										100	2.5	2.5	1	1	1
1.01										100	2.5	2.5	1	1	1
0.99										100	2.5	2.5	1	1	1
0.97										10	2.5	2.5	1	1	1
0.91									100	5	2.5	2.5	1	1	1
0.83							100	100	10	5	2.5	2.5	1	1	1
0.67							100	100	10	2.5	2.5	1	1	1	1
0.50							100	100	5	2.5	2.5	1	1	1	1
0.25						100	100	10	5	2.5	2.5	1	1	1	1

Figure 37. A↔C+D α_{AD} =100: Configuration I, II, III





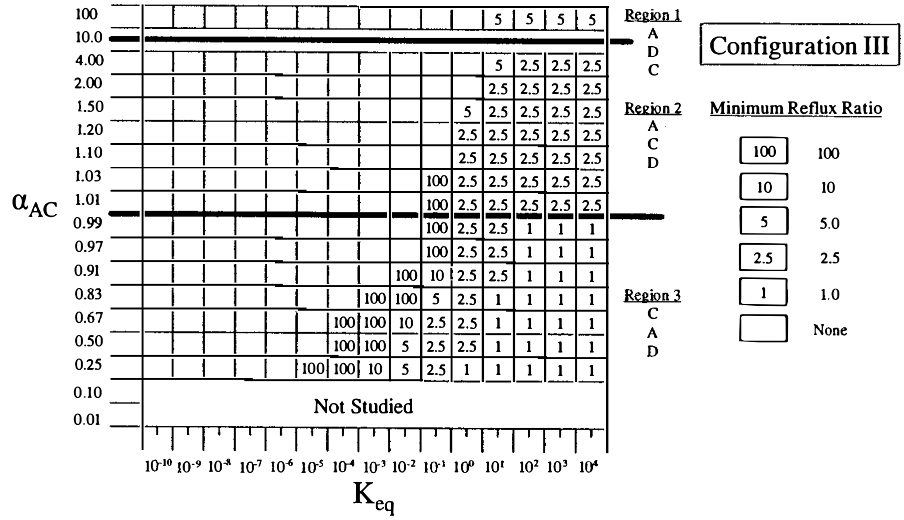
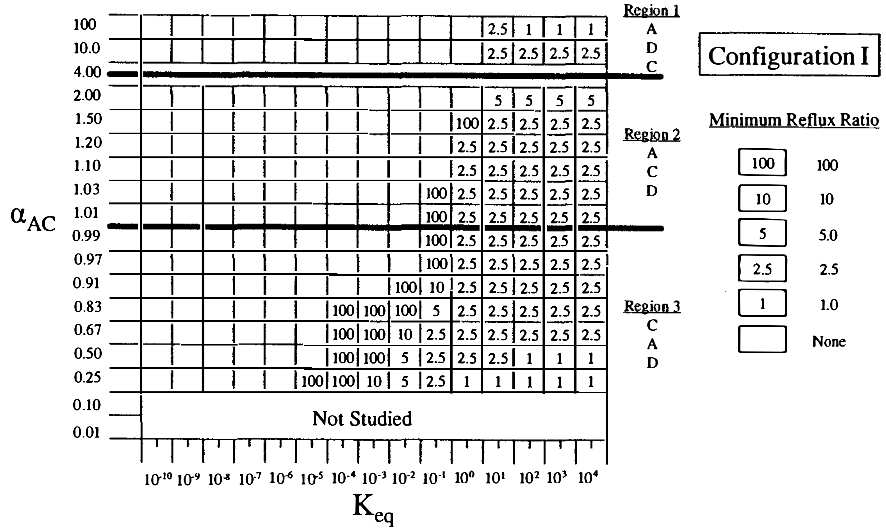
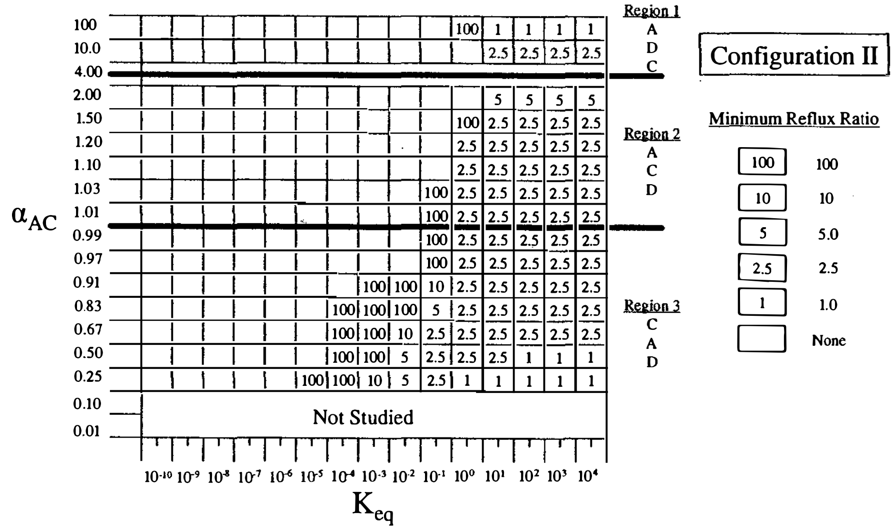


Figure 38. A↔C+D α_{AD} =10: Configuration I, II, III





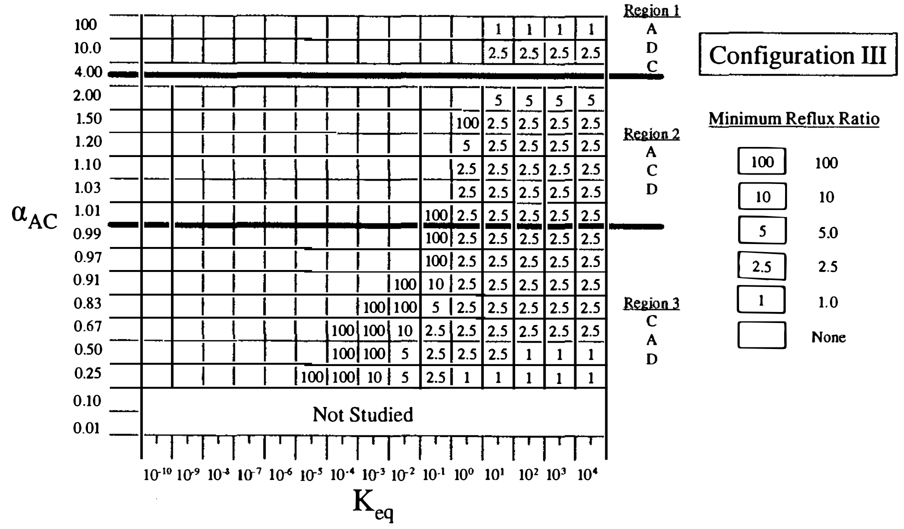


Figure 39. A↔C+D α_{AD} =4.0: Configuration I, II, III

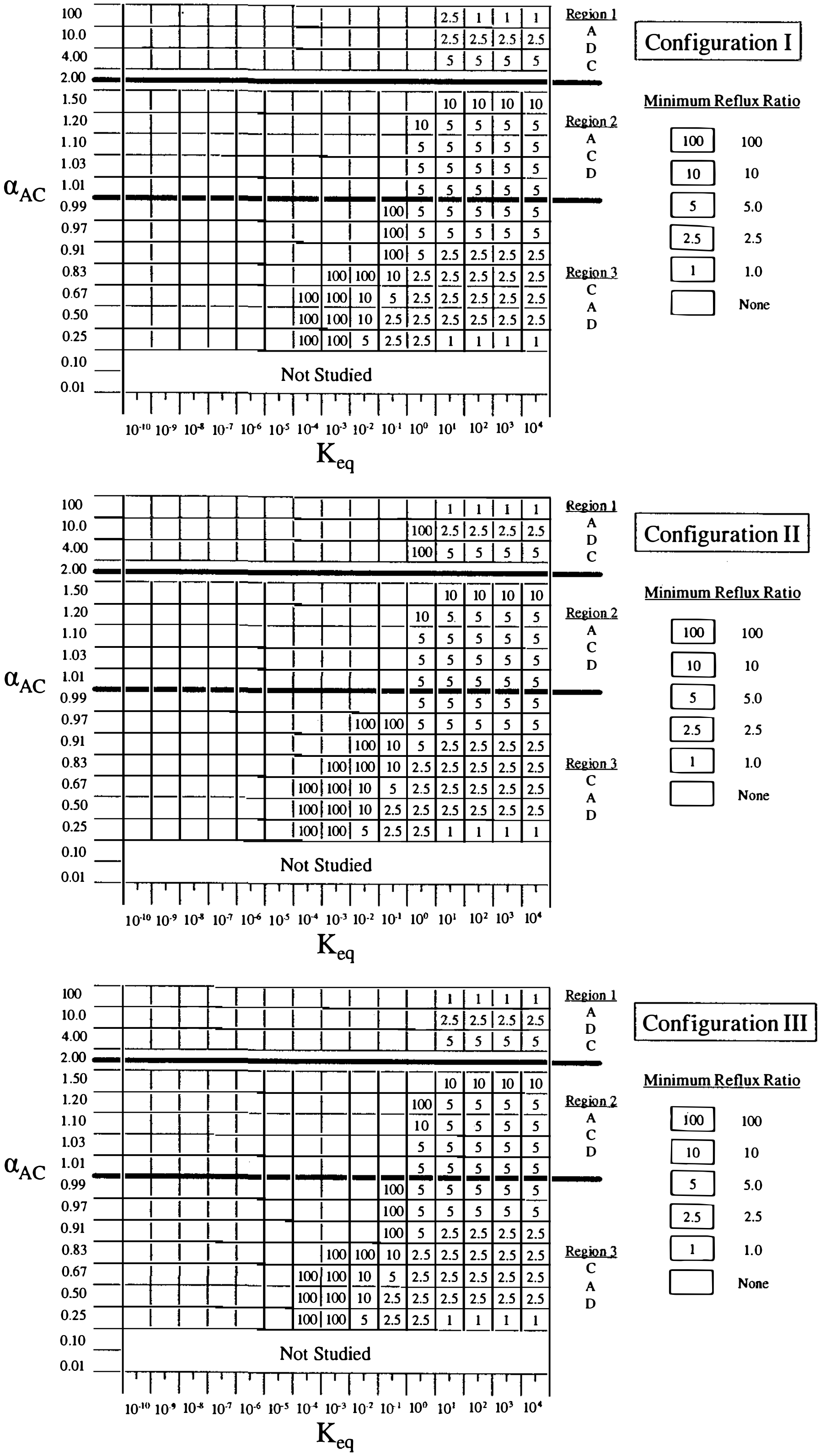
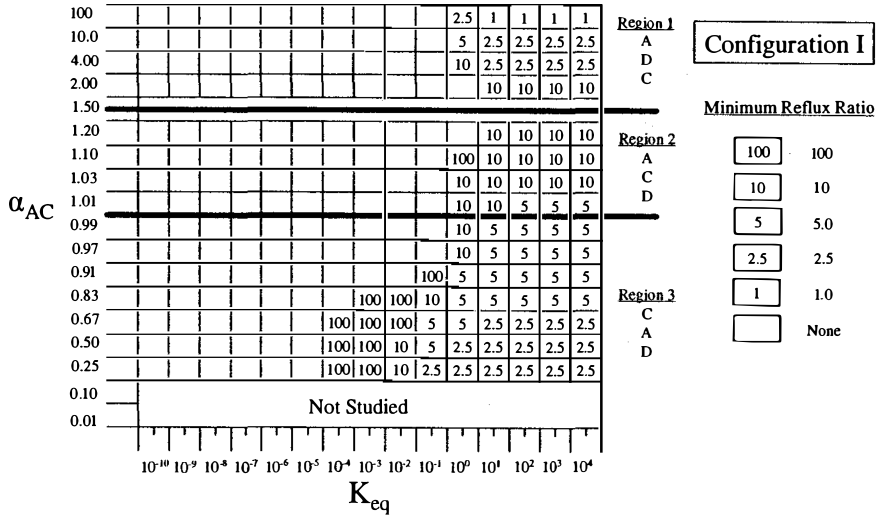
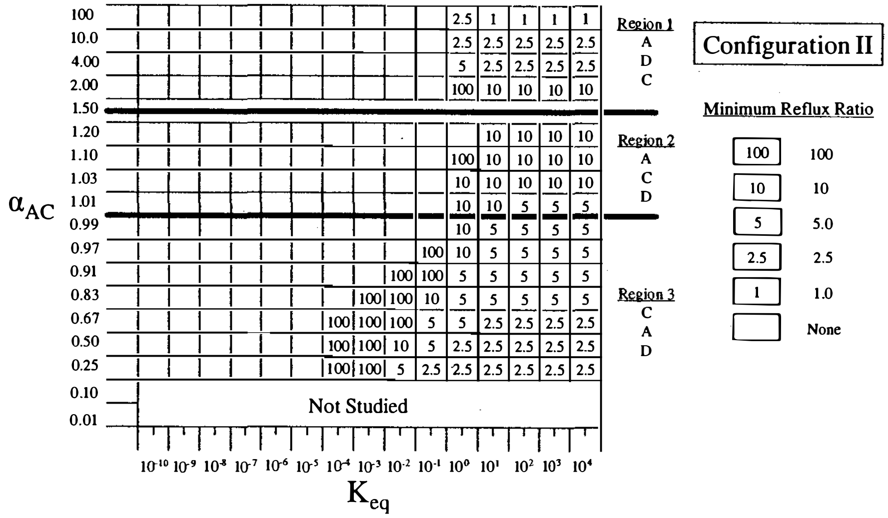


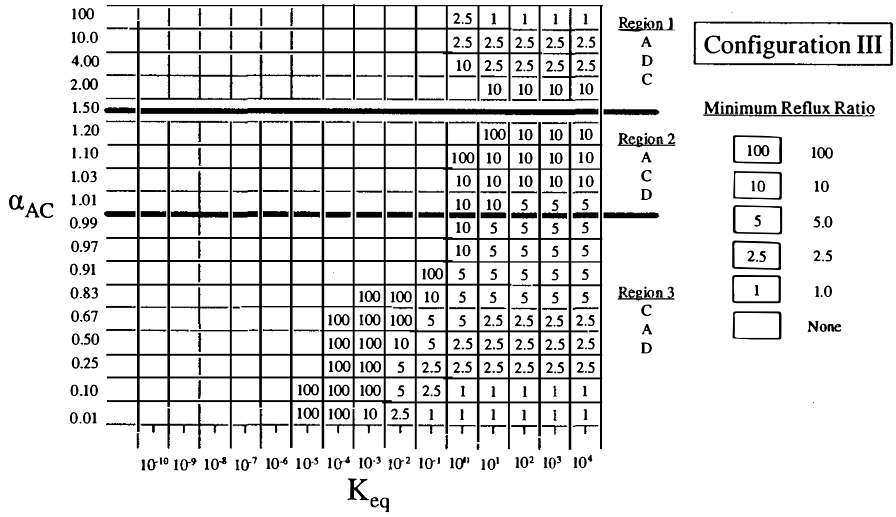
Figure 40. A↔C+D α_{AD} =2.0: Configuration I, II, III



α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100											2.5	1	1	1	1
10.0											5	2.5	2.5	2.5	2.5
4.00											10	2.5	2.5	2.5	2.5
2.00												10	10	10	10
1.50															
1.20												10	10	10	10
1.10											100	10	10	10	10
1.03											10	10	10	10	10
1.01											10	10	5	5	5
0.99											10	5	5	5	5
0.97											10	5	5	5	5
0.91										100	5	5	5	5	5
0.83								100	100	10	5	5	5	5	5
0.67							100	100	100	5	5	2.5	2.5	2.5	2.5
0.50							100	100	10	5	2.5	2.5	2.5	2.5	2.5
0.25							100	100	10	2.5	2.5	2.5	2.5	2.5	2.5
0.10	Not Studied														
0.01															

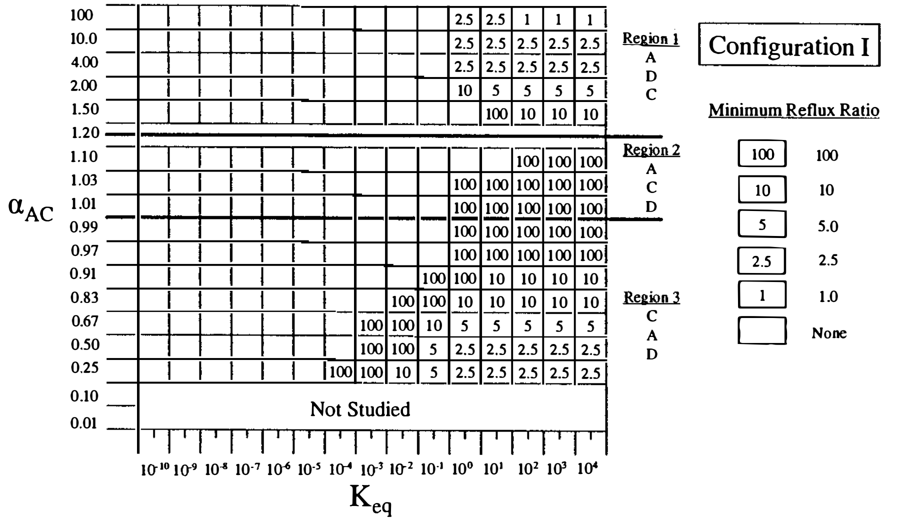


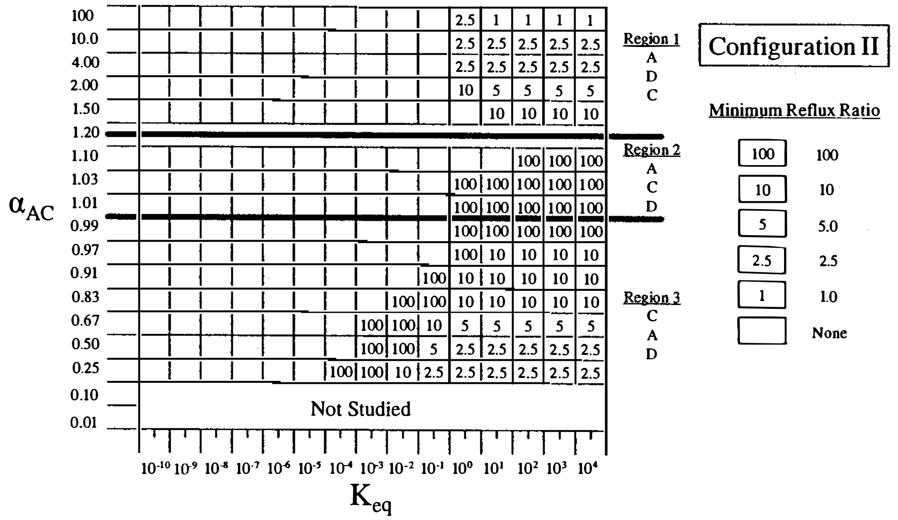
α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100											2.5	1	1	1	1
10.0											2.5	2.5	2.5	2.5	2.5
4.00											5	2.5	2.5	2.5	2.5
2.00											100	10	10	10	10
1.50															
1.20												10	10	10	10
1.10											100	10	10	10	10
1.03											10	10	10	10	10
1.01											10	10	5	5	5
0.99											10	5	5	5	5
0.97										100	10	5	5	5	5
0.91									100	100	5	5	5	5	5
0.83								100	100	10	5	5	5	5	5
0.67							100	100	100	5	5	2.5	2.5	2.5	2.5
0.50							100	100	10	5	2.5	2.5	2.5	2.5	2.5
0.25							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
0.10	Not Studied														
0.01															



α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100											2.5	1	1	1	1
10.0											2.5	2.5	2.5	2.5	2.5
4.00											10	2.5	2.5	2.5	2.5
2.00												10	10	10	10
1.50															
1.20												100	10	10	10
1.10											100	10	10	10	10
1.03											10	10	10	10	10
1.01											10	10	5	5	5
0.99											10	5	5	5	5
0.97											10	5	5	5	5
0.91										100	5	5	5	5	5
0.83								100	100	10	5	5	5	5	5
0.67							100	100	100	5	5	2.5	2.5	2.5	2.5
0.50							100	100	10	5	2.5	2.5	2.5	2.5	2.5
0.25							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
0.10						100	100	100	5	2.5	1	1	1	1	1
0.01						100	100	10	2.5	1	1	1	1	1	1

Figure 41. A↔C+D α_{AD} =1.5: Configuration I, II, III





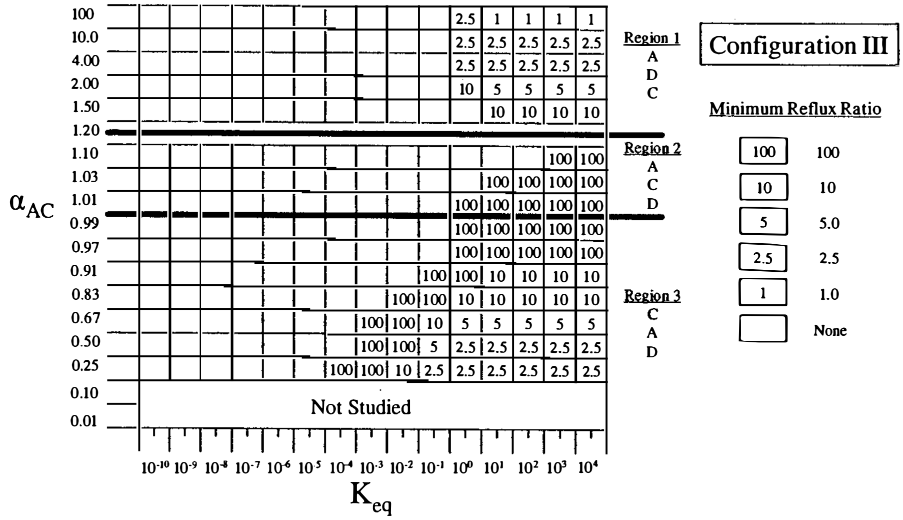


Figure 42. A↔C+D α_{AD} =1.2: Configuration I, II, III

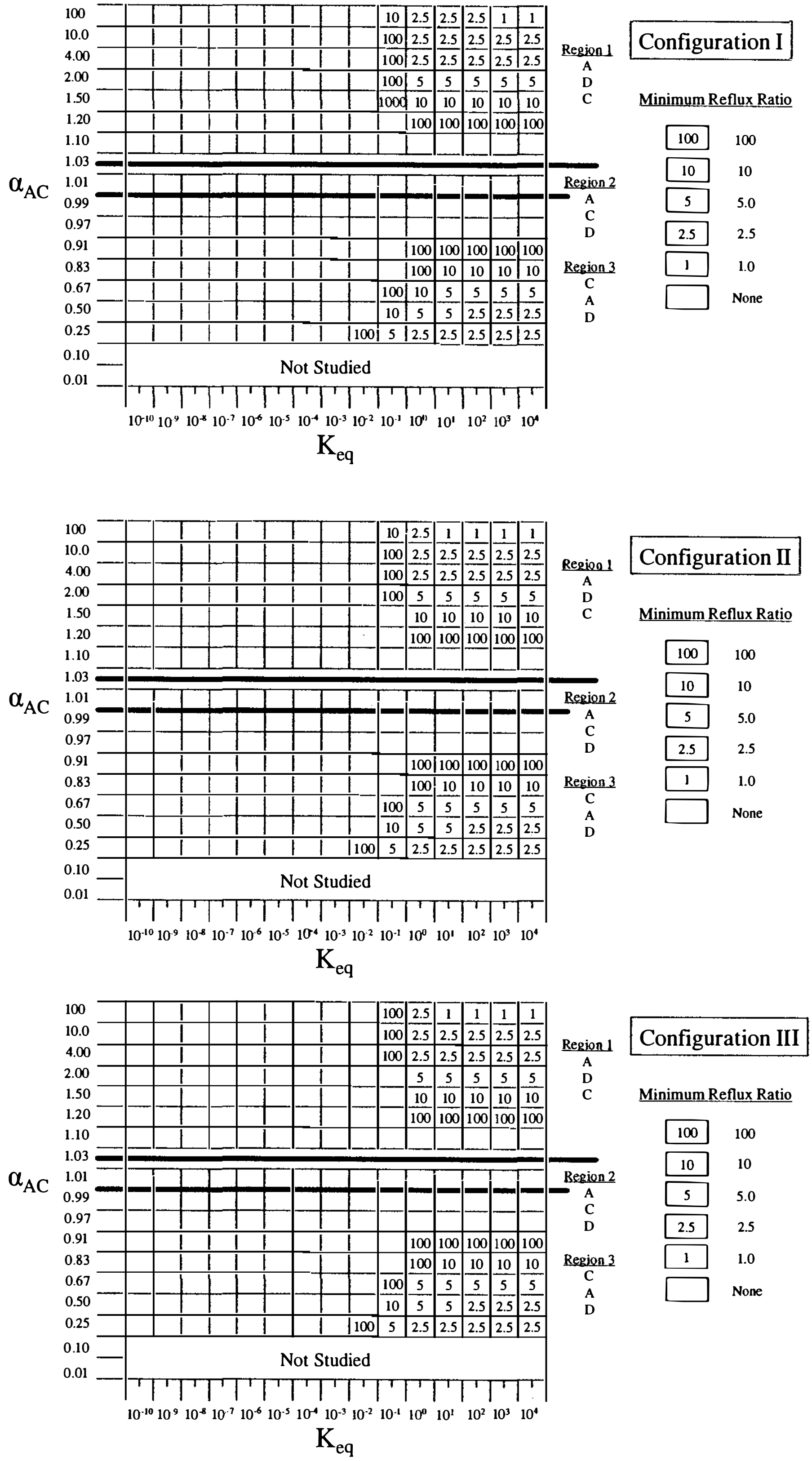


Figure 43. A↔C+D α_{AD} =1.1: Configuration I, II, III

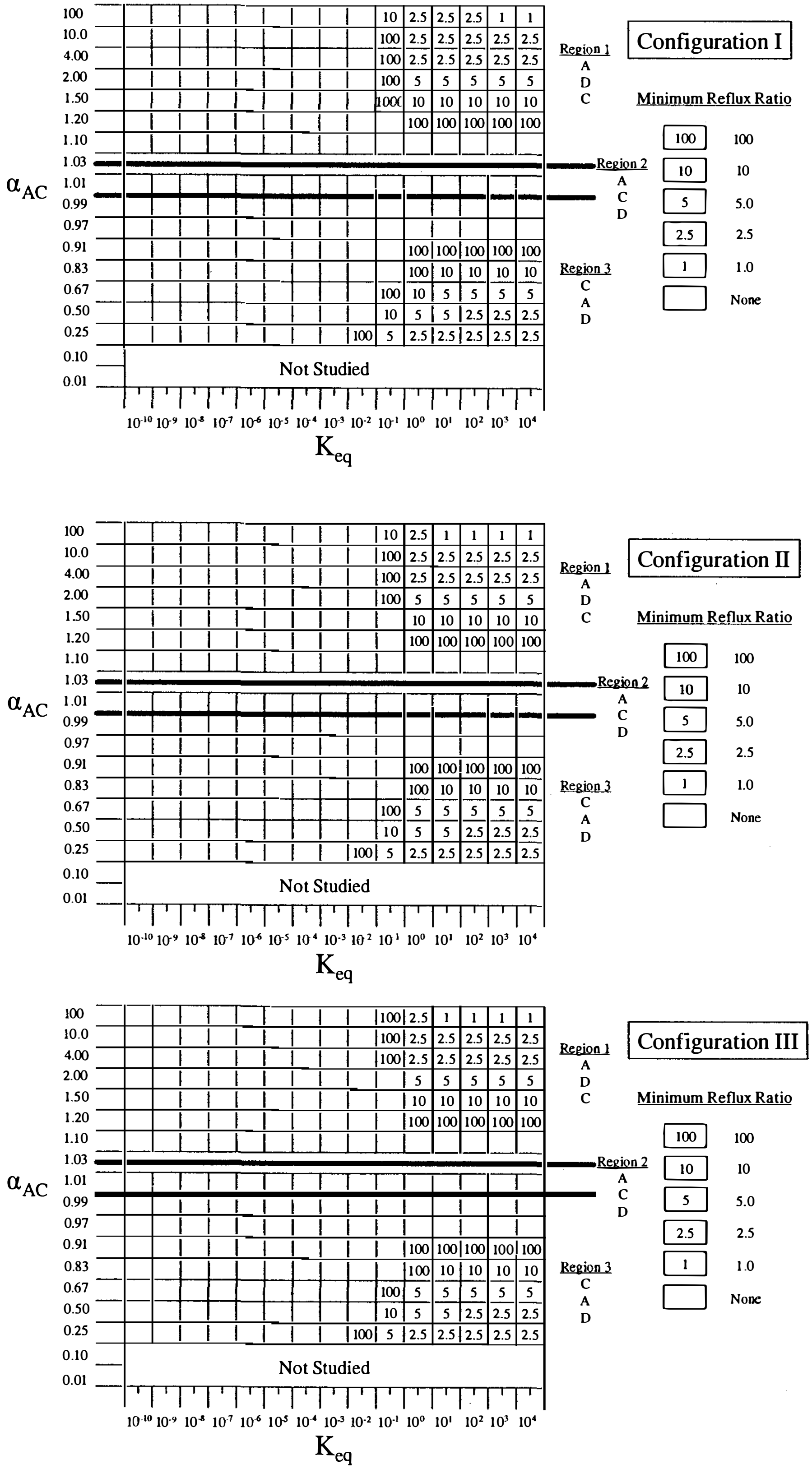


Figure 44. A↔C+D α_{AD} =1.03: Configuration I, II, III

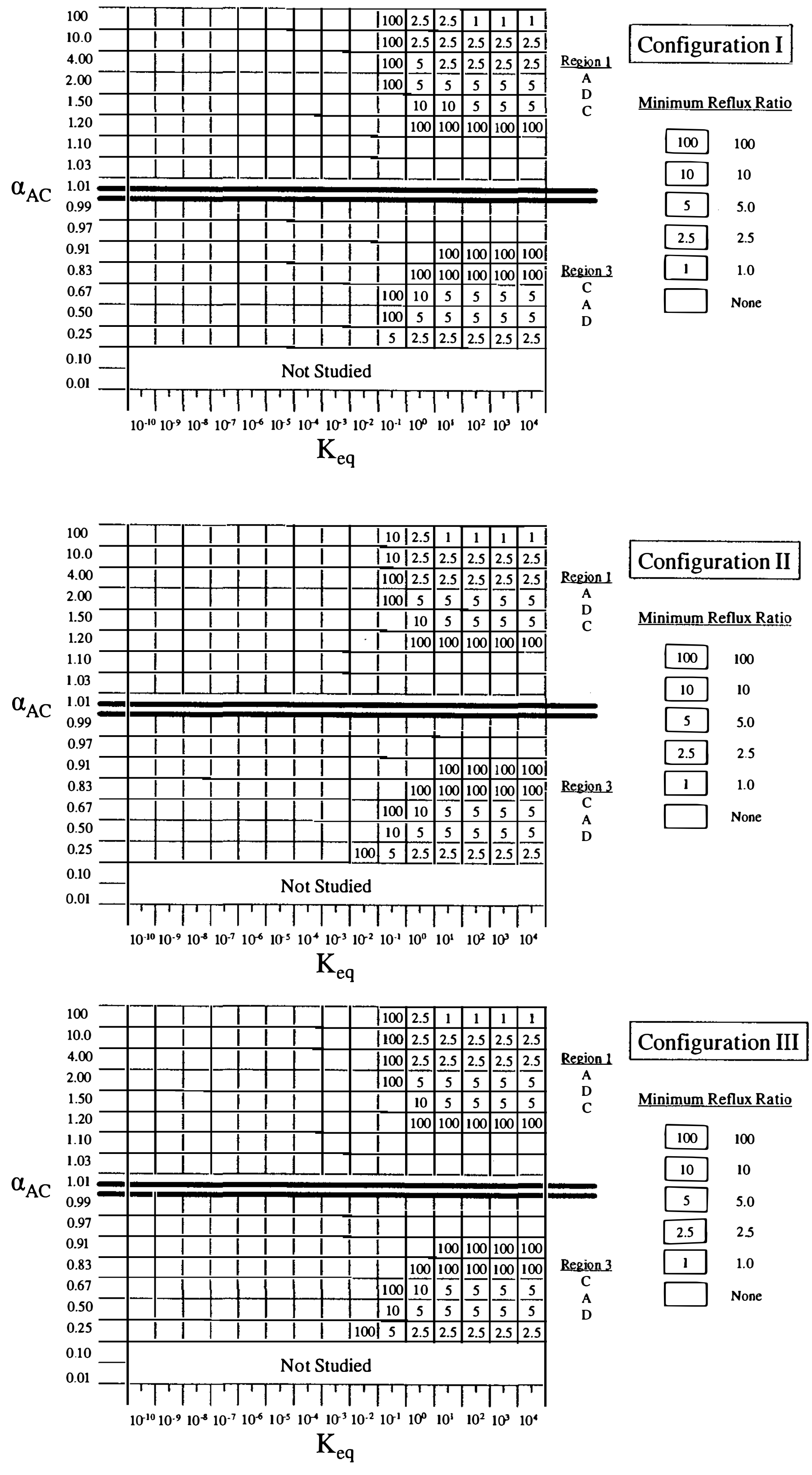
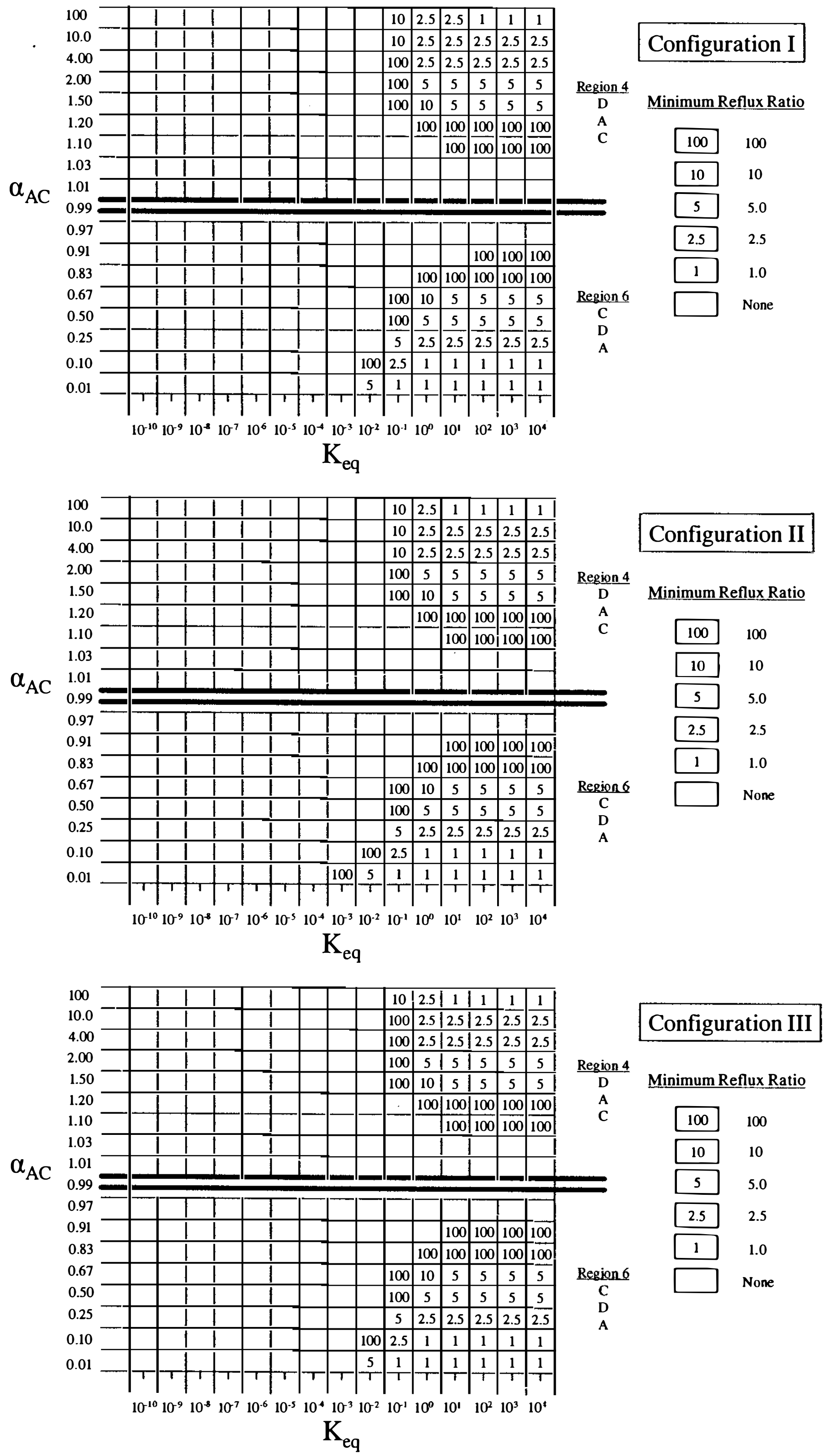


Figure 45. A↔C+D α_{AD} =1.01: Configuration I, II, III



Configuration I

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100										10	2.5	2.5	1	1	1
10.0										10	2.5	2.5	2.5	2.5	2.5
4.00										100	2.5	2.5	2.5	2.5	2.5
2.00										100	5	5	5	5	5
1.50										100	10	5	5	5	5
1.20											100	100	100	100	100
1.10												100	100	100	100
1.03															
1.01															
0.99															
0.97															
0.91													100	100	100
0.83											100	100	100	100	100
0.67										100	10	5	5	5	5
0.50										100	5	5	5	5	5
0.25										5	2.5	2.5	2.5	2.5	2.5
0.10									100	2.5	1	1	1	1	1
0.01									5	1	1	1	1	1	1

K_{eq}

Region 4
D
A
C

Region 6
C
D
A

Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
☐	None

Configuration II

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100										10	2.5	1	1	1	1
10.0										10	2.5	2.5	2.5	2.5	2.5
4.00										10	2.5	2.5	2.5	2.5	2.5
2.00										100	5	5	5	5	5
1.50										100	10	5	5	5	5
1.20											100	100	100	100	100
1.10												100	100	100	100
1.03															
1.01															
0.99															
0.97															
0.91												100	100	100	100
0.83											100	100	100	100	100
0.67										100	10	5	5	5	5
0.50										100	5	5	5	5	5
0.25										5	2.5	2.5	2.5	2.5	2.5
0.10									100	2.5	1	1	1	1	1
0.01								100	5	1	1	1	1	1	1

K_{eq}

Region 4
D
A
C

Region 6
C
D
A

Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
☐	None

Configuration III

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100										10	2.5	1	1	1	1
10.0										100	2.5	2.5	2.5	2.5	2.5
4.00										100	2.5	2.5	2.5	2.5	2.5
2.00										100	5	5	5	5	5
1.50										100	10	5	5	5	5
1.20											100	100	100	100	100
1.10												100	100	100	100
1.03															
1.01															
0.99															
0.97															
0.91												100	100	100	100
0.83											100	100	100	100	100
0.67										100	10	5	5	5	5
0.50										100	5	5	5	5	5
0.25										5	2.5	2.5	2.5	2.5	2.5
0.10									100	2.5	1	1	1	1	1
0.01									5	1	1	1	1	1	1

K_{eq}

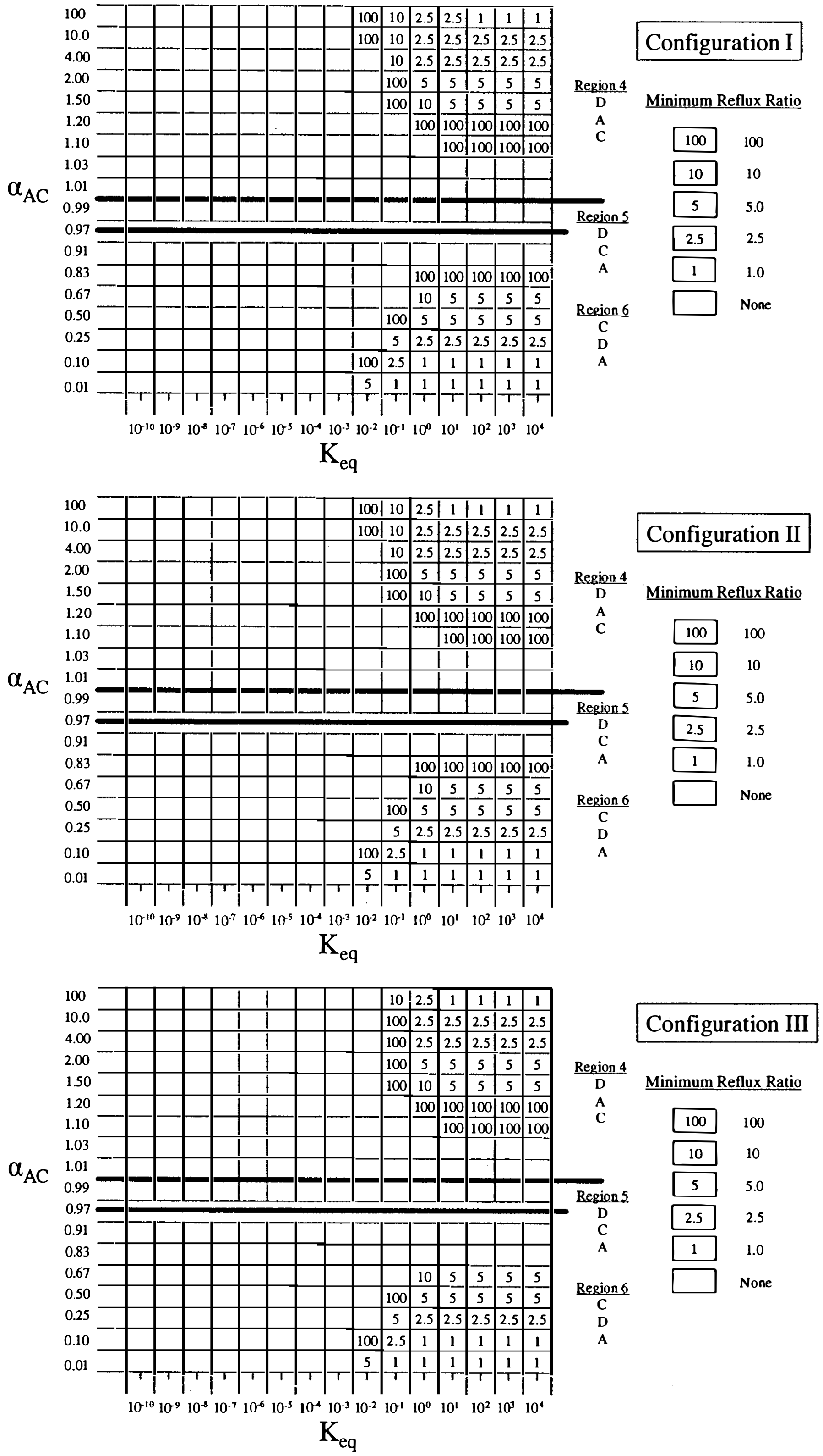
Region 4
D
A
C

Region 6
C
D
A

Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
☐	None

Figure 46. A↔C+D α_{AD} =0.99: Configuration I, II, III



Configuration I

	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100									100	10	2.5	2.5	1	1	1
10.0									100	10	2.5	2.5	2.5	2.5	2.5
4.00										10	2.5	2.5	2.5	2.5	2.5
2.00										100	5	5	5	5	5
1.50										100	10	5	5	5	5
1.20											100	100	100	100	100
1.10												100	100	100	100
1.03															
1.01															
0.99															
0.97															
0.91															
0.83											100	100	100	100	100
0.67											10	5	5	5	5
0.50										100	5	5	5	5	5
0.25										5	2.5	2.5	2.5	2.5	2.5
0.10									100	2.5	1	1	1	1	1
0.01									5	1	1	1	1	1	1

Configuration II

	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100									100	10	2.5	1	1	1	1
10.0									100	10	2.5	2.5	2.5	2.5	2.5
4.00										10	2.5	2.5	2.5	2.5	2.5
2.00										100	5	5	5	5	5
1.50										100	10	5	5	5	5
1.20											100	100	100	100	100
1.10												100	100	100	100
1.03															
1.01															
0.99															
0.97															
0.91															
0.83											100	100	100	100	100
0.67											10	5	5	5	5
0.50										100	5	5	5	5	5
0.25										5	2.5	2.5	2.5	2.5	2.5
0.10									100	2.5	1	1	1	1	1
0.01									5	1	1	1	1	1	1

Configuration III

	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100										10	2.5	1	1	1	1
10.0										100	2.5	2.5	2.5	2.5	2.5
4.00										100	2.5	2.5	2.5	2.5	2.5
2.00										100	5	5	5	5	5
1.50										100	10	5	5	5	5
1.20											100	100	100	100	100
1.10												100	100	100	100
1.03															
1.01															
0.99															
0.97															
0.91															
0.83															
0.67											10	5	5	5	5
0.50										100	5	5	5	5	5
0.25										5	2.5	2.5	2.5	2.5	2.5
0.10									100	2.5	1	1	1	1	1
0.01									5	1	1	1	1	1	1

Figure 47. A↔C+D α_{AD} =0.97: Configuration I, II, III

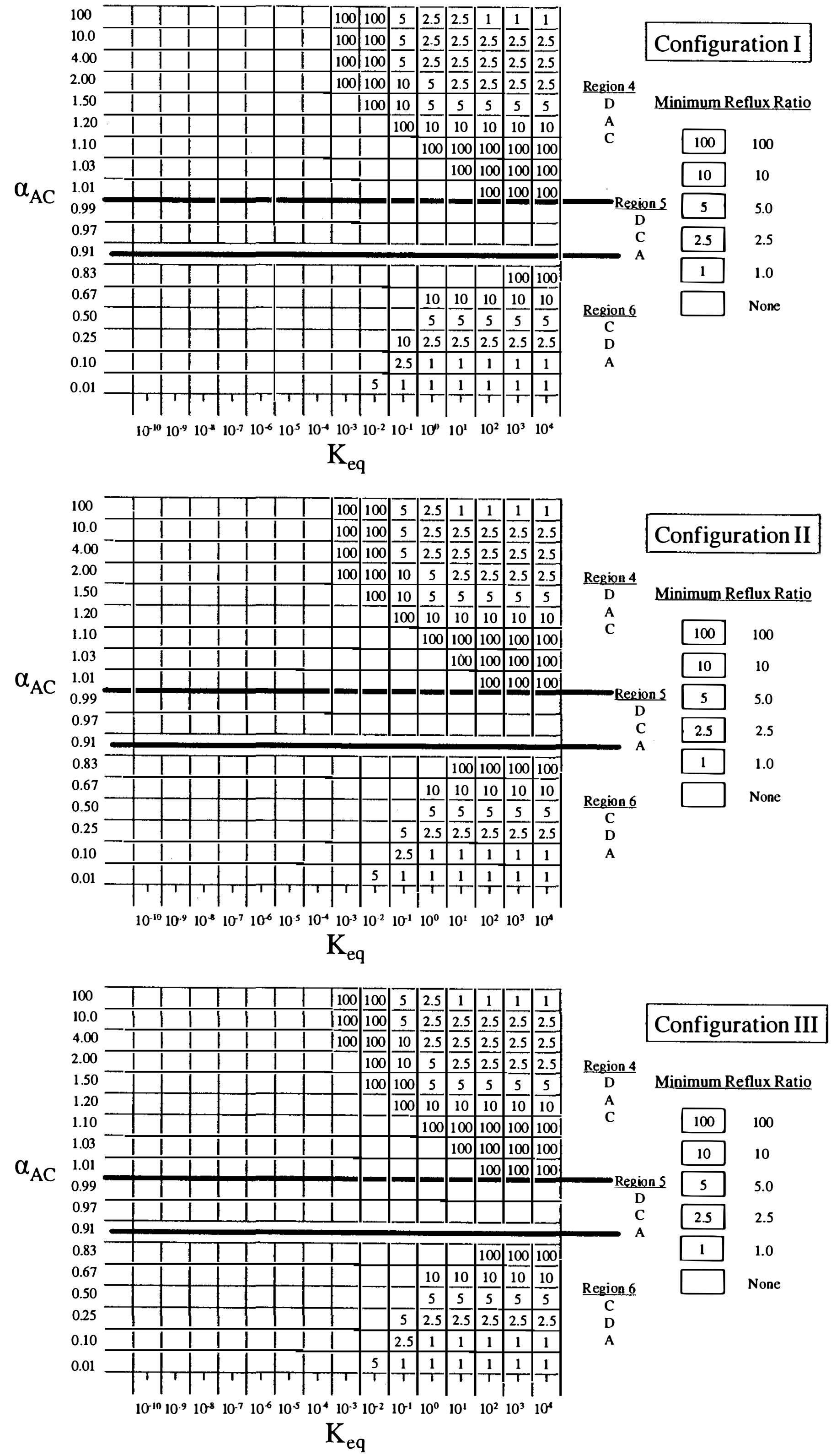


Figure 48. A↔C+D α_{AD} =0.91: Configuration I, II, III

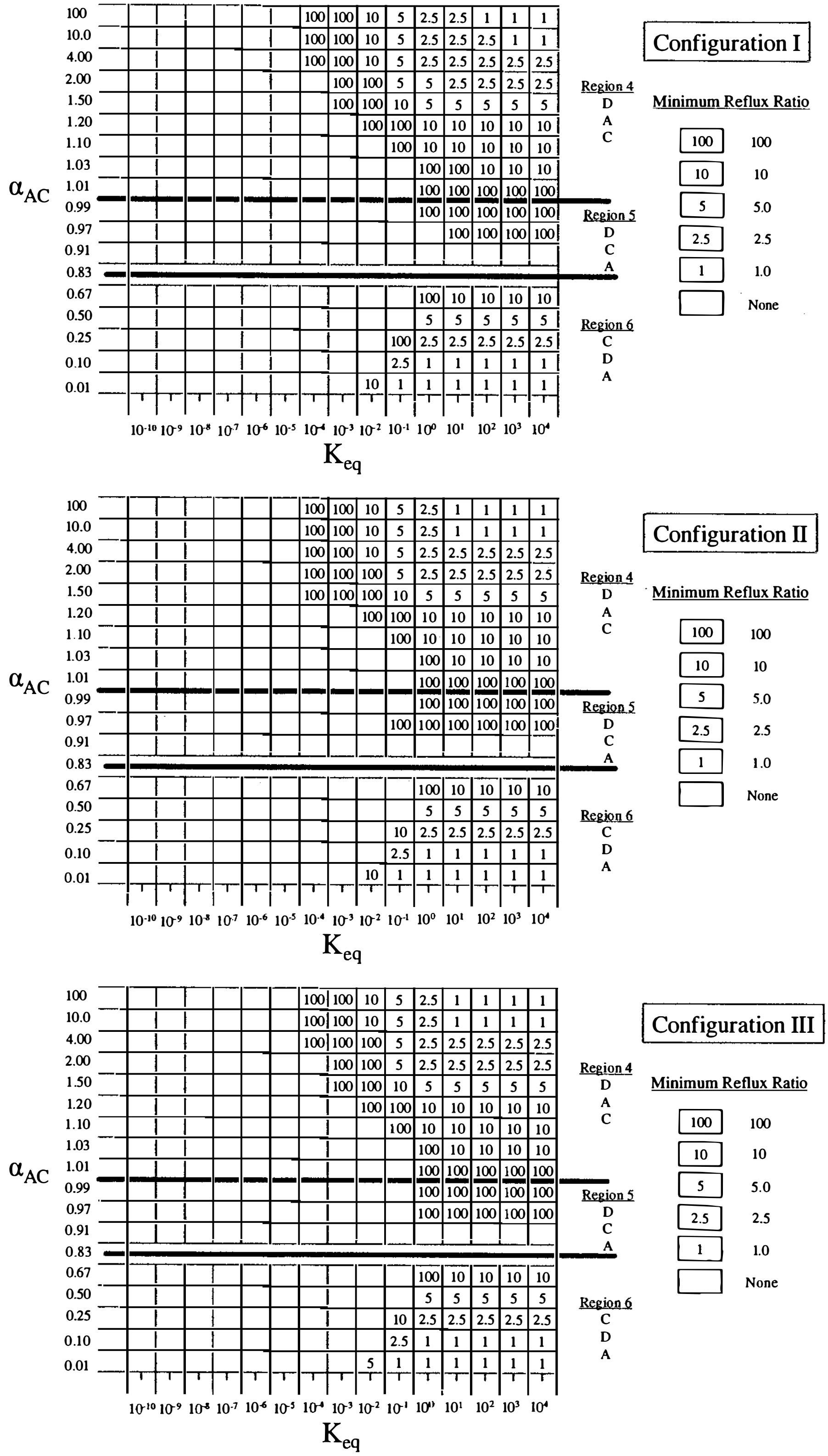


Figure 49. A↔C+D α_{AD} =0.83: Configuration I, II, III

Configuration I

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100							100	100	10	2.5	2.5	2.5	2.5	1	1
10.0							100	100	10	2.5	2.5	1	1	1	1
4.00							100	100	10	2.5	2.5	2.5	2.5	2.5	2.5
2.00							100	100	10	5	2.5	2.5	2.5	2.5	2.5
1.50							100	100	100	5	5	2.5	2.5	2.5	2.5
1.20									100	10	5	5	5	5	5
1.10										100	5	5	5	5	5
1.03										100	10	5	5	5	5
1.01											10	5	5	5	5
0.99											10	5	5	5	5
0.97											10	5	5	5	5
0.91											100	10	10	10	10
0.83												10	10	10	10
0.67															
0.50												10	10	10	10
0.25											2.5	2.5	2.5	2.5	2.5
0.10										5	1	1	1	1	1
0.01									100	1	1	1	1	1	1

K_{eq}

Region 4
D
A
C

Region 5
D
C
A

Region 6
C
D
A

Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
	None

Configuration II

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100							100	100	10	2.5	2.5	1	1	1	1
10.0							100	100	10	2.5	2.5	1	1	1	1
4.00							100	100	10	2.5	2.5	2.5	2.5	2.5	2.5
2.00							100	10	10	5	2.5	2.5	2.5	2.5	2.5
1.50							100	100	100	5	5	2.5	2.5	2.5	2.5
1.20									100	10	5	5	5	5	5
1.10									100	100	5	5	5	5	5
1.03										100	10	5	5	5	5
1.01										100	10	5	5	5	5
0.99											10	5	5	5	5
0.97											10	5	5	5	5
0.91											100	10	10	10	10
0.83											100	10	10	10	10
0.67															
0.50											100	10	10	10	10
0.25											2.5	2.5	2.5	2.5	2.5
0.10										5	1	1	1	1	1
0.01									100	1	1	1	1	1	1

K_{eq}

Region 4
D
A
C

Region 5
D
C
A

Region 6
C
D
A

Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
	None

Configuration III

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100							100	100	10	2.5	2.5	1	1	1	1
10.0							100	100	10	2.5	2.5	1	1	1	1
4.00							100	100	10	2.5	2.5	2.5	2.5	2.5	2.5
2.00							100	100	10	5	2.5	2.5	2.5	2.5	2.5
1.50							100	100	100	5	5	2.5	2.5	2.5	2.5
1.20									100	10	5	5	5	5	5
1.10									100	100	5	5	5	5	5
1.03										100	10	5	5	5	5
1.01										100	100	5	5	5	5
0.99											10	5	5	5	5
0.97											10	5	5	5	5
0.91											100	10	10	10	10
0.83											100	10	10	10	10
0.67															
0.50											100	10	10	10	10
0.25											2.5	2.5	2.5	2.5	2.5
0.10										5	1	1	1	1	1
0.01									100	1	1	1	1	1	1

K_{eq}

Region 4
D
A
C

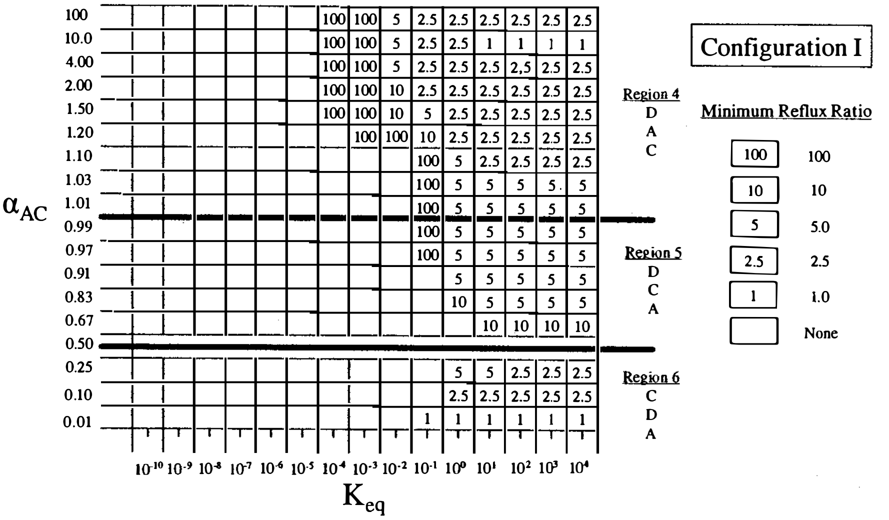
Region 5
D
C
A

Region 6
C
D
A

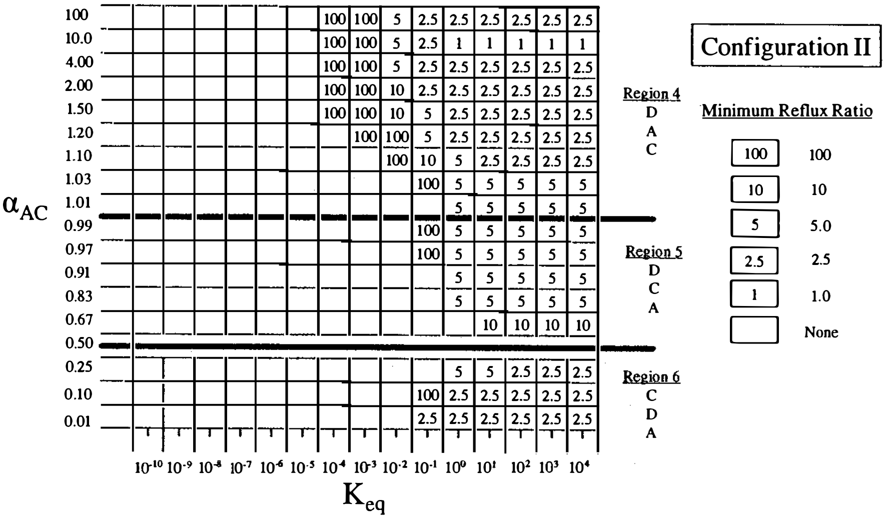
Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
	None

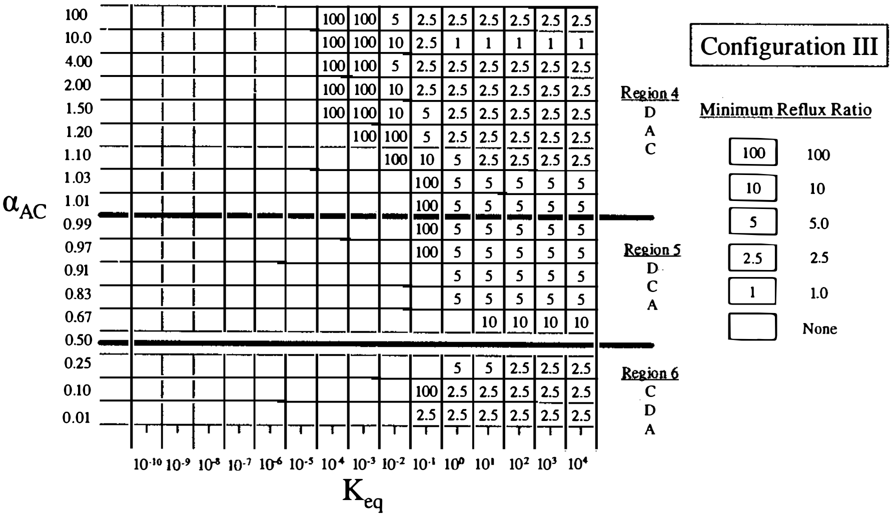
Figure 50. A↔C+D α_{AD} =0.67: Configuration I, II, III



α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
10.0							100	100	5	2.5	2.5	1	1	1	1
4.00							100	100	5	2.5	2.5	2.5	2,5	2.5	2.5
2.00							100	100	10	2.5	2.5	2.5	2.5	2.5	2.5
1.50							100	100	10	5	2.5	2.5	2.5	2.5	2.5
1.20								100	100	10	2.5	2.5	2.5	2.5	2.5
1.10										100	5	2.5	2.5	2.5	2.5
1.03										100	5	5	5	5	5
1.01										100	5	5	5	5	5
0.99										100	5	5	5	5	5
0.97										100	5	5	5	5	5
0.91											5	5	5	5	5
0.83											10	5	5	5	5
0.67												10	10	10	10
0.50															
0.25											5	5	2.5	2.5	2.5
0.10											2.5	2.5	2.5	2.5	2.5
0.01										1	1	1	1	1	1



α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
10.0							100	100	5	2.5	1	1	1	1	1
4.00							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
2.00							100	100	10	2.5	2.5	2.5	2.5	2.5	2.5
1.50							100	100	10	5	2.5	2.5	2.5	2.5	2.5
1.20								100	100	5	2.5	2.5	2.5	2.5	2.5
1.10									100	10	5	2.5	2.5	2.5	2.5
1.03										100	5	5	5	5	5
1.01											5	5	5	5	5
0.99										100	5	5	5	5	5
0.97										100	5	5	5	5	5
0.91											5	5	5	5	5
0.83											5	5	5	5	5
0.67												10	10	10	10
0.50															
0.25											5	5	2.5	2.5	2.5
0.10										100	2.5	2.5	2.5	2.5	2.5
0.01										2.5	2.5	2.5	2.5	2.5	2.5



α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
10.0							100	100	10	2.5	1	1	1	1	1
4.00							100	100	5	2.5	2.5	2.5	2.5	2.5	2.5
2.00							100	100	10	2.5	2.5	2.5	2.5	2.5	2.5
1.50							100	100	10	5	2.5	2.5	2.5	2.5	2.5
1.20								100	100	5	2.5	2.5	2.5	2.5	2.5
1.10									100	10	5	2.5	2.5	2.5	2.5
1.03										100	5	5	5	5	5
1.01										100	5	5	5	5	5
0.99										100	5	5	5	5	5
0.97										100	5	5	5	5	5
0.91											5	5	5	5	5
0.83											5	5	5	5	5
0.67												10	10	10	10
0.50															
0.25											5	5	2.5	2.5	2.5
0.10										100	2.5	2.5	2.5	2.5	2.5
0.01										2.5	2.5	2.5	2.5	2.5	2.5

Figure 51. A↔C+D α_{AD} =0.50: Configuration I, II, III

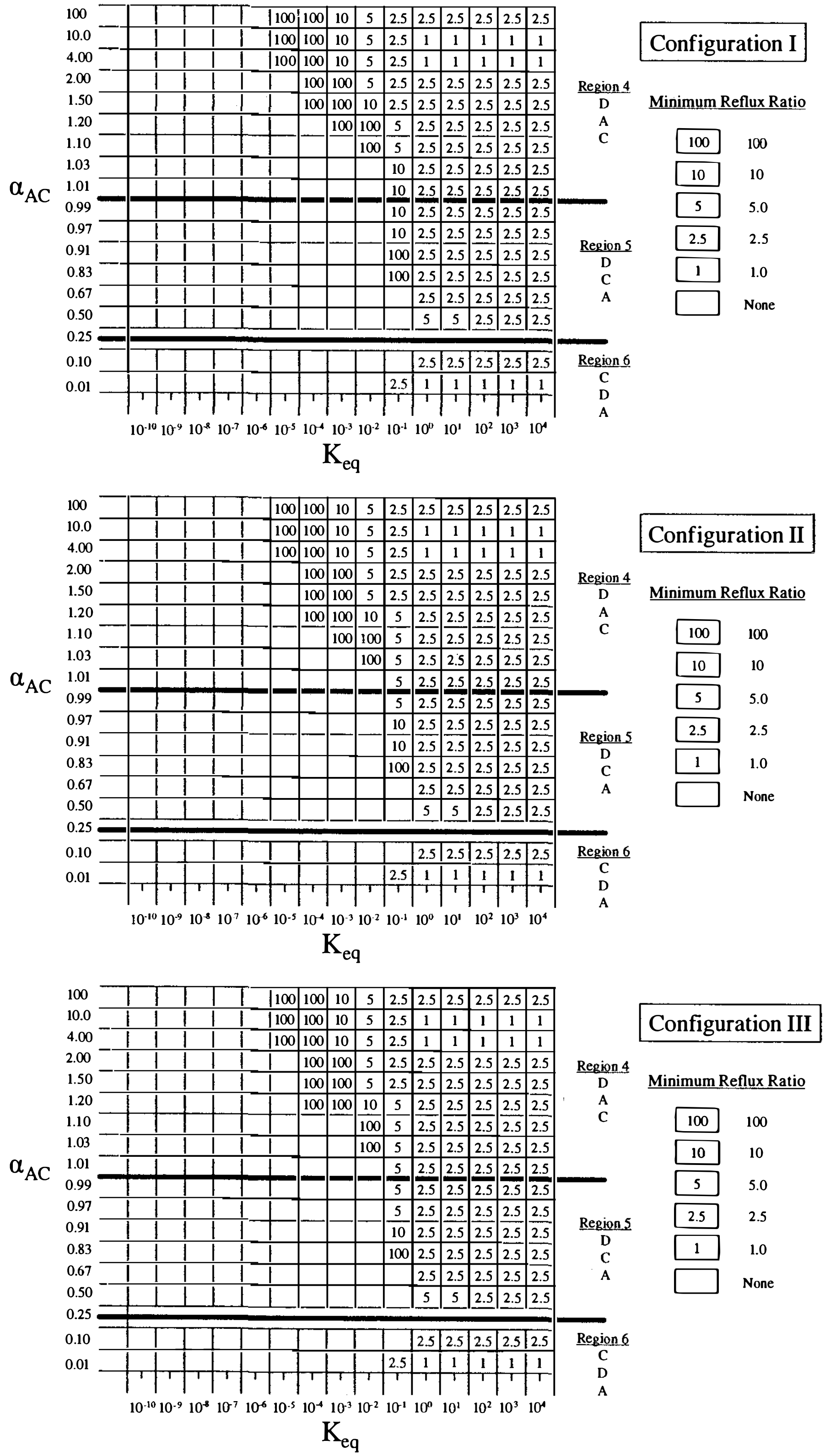
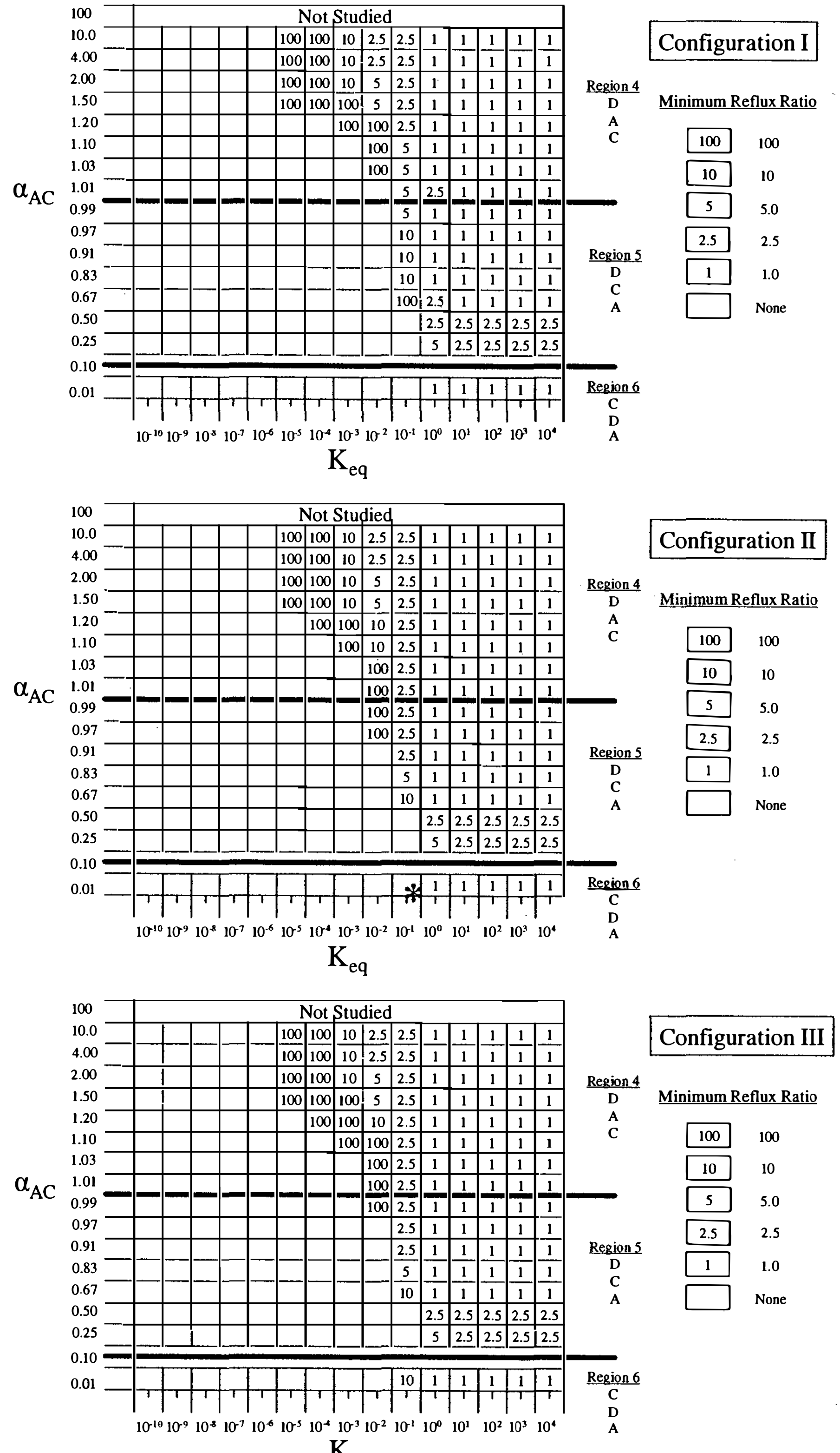


Figure 52. A↔C+D α_{AD} =0.25: Configuration I, II, III



Configuration I

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100	Not Studied														
10.0						100	100	10	2.5	2.5	1	1	1	1	1
4.00						100	100	10	2.5	2.5	1	1	1	1	1
2.00						100	100	10	5	2.5	1	1	1	1	1
1.50						100	100	100	5	2.5	1	1	1	1	1
1.20								100	100	2.5	1	1	1	1	1
1.10									100	5	1	1	1	1	1
1.03									100	5	1	1	1	1	1
1.01										5	2.5	1	1	1	1
0.99										5	1	1	1	1	1
0.97										10	1	1	1	1	1
0.91										10	1	1	1	1	1
0.83										10	1	1	1	1	1
0.67										100	2.5	1	1	1	1
0.50											2.5	2.5	2.5	2.5	2.5
0.25											5	2.5	2.5	2.5	2.5
0.10															
0.01											1	1	1	1	1

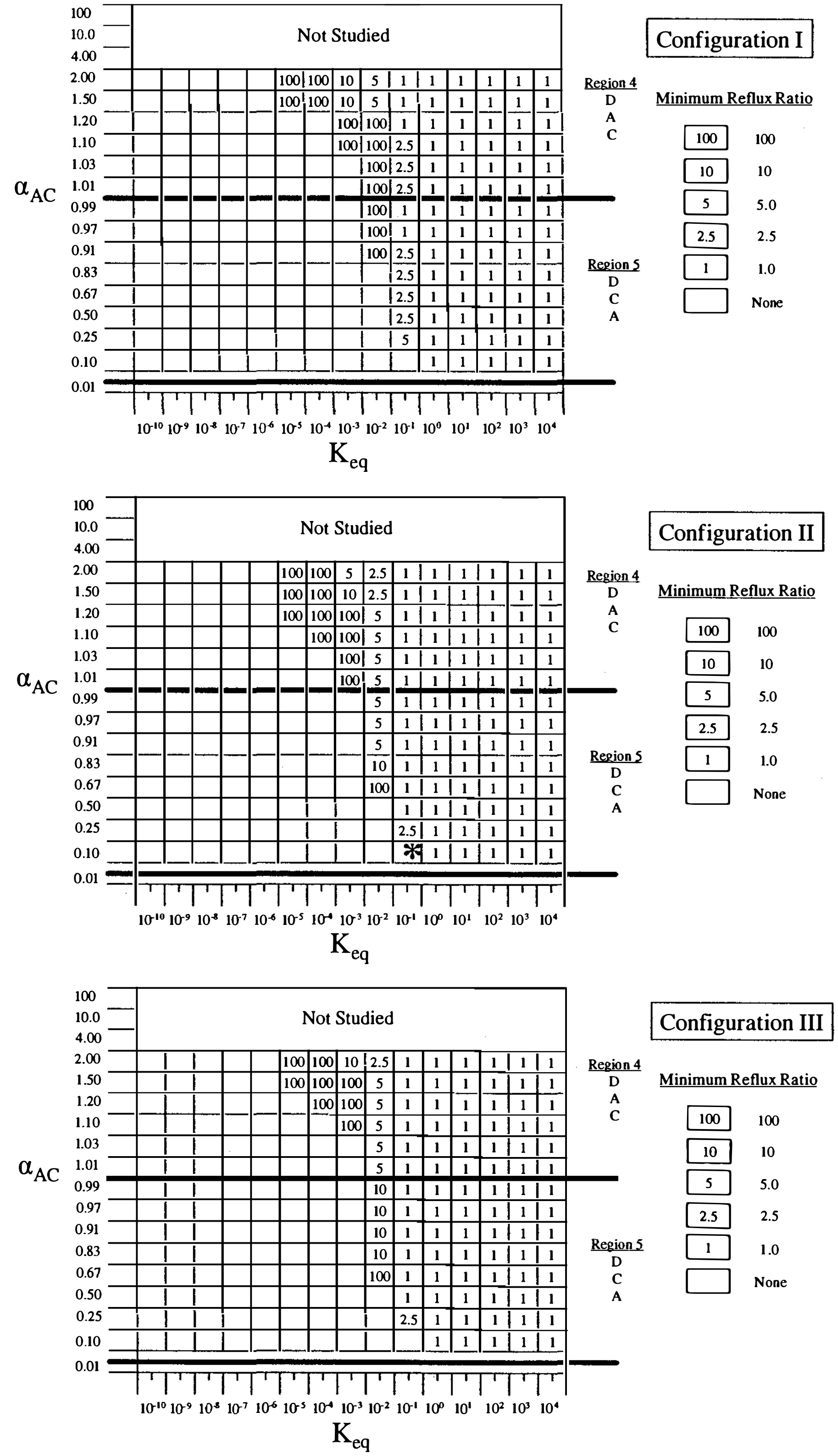
Configuration II

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100	Not Studied														
10.0						100	100	10	2.5	2.5	1	1	1	1	1
4.00						100	100	10	2.5	2.5	1	1	1	1	1
2.00						100	100	10	5	2.5	1	1	1	1	1
1.50						100	100	10	5	2.5	1	1	1	1	1
1.20							100	100	10	2.5	1	1	1	1	1
1.10								100	10	2.5	1	1	1	1	1
1.03									100	2.5	1	1	1	1	1
1.01									100	2.5	1	1	1	1	1
0.99									100	2.5	1	1	1	1	1
0.97									100	2.5	1	1	1	1	1
0.91										2.5	1	1	1	1	1
0.83										5	1	1	1	1	1
0.67										10	1	1	1	1	1
0.50											2.5	2.5	2.5	2.5	2.5
0.25											5	2.5	2.5	2.5	2.5
0.10															
0.01										*	1	1	1	1	1

Configuration III

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100	Not Studied														
10.0						100	100	10	2.5	2.5	1	1	1	1	1
4.00						100	100	10	2.5	2.5	1	1	1	1	1
2.00						100	100	10	5	2.5	1	1	1	1	1
1.50						100	100	100	5	2.5	1	1	1	1	1
1.20							100	100	10	2.5	1	1	1	1	1
1.10								100	100	2.5	1	1	1	1	1
1.03									100	2.5	1	1	1	1	1
1.01									100	2.5	1	1	1	1	1
0.99									100	2.5	1	1	1	1	1
0.97										2.5	1	1	1	1	1
0.91										2.5	1	1	1	1	1
0.83										5	1	1	1	1	1
0.67										10	1	1	1	1	1
0.50											2.5	2.5	2.5	2.5	2.5
0.25											5	2.5	2.5	2.5	2.5
0.10															
0.01										10	1	1	1	1	1

Figure 53. A↔C+D α_{AD} =0.10: Configuration I, II, III



Configuration I

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
2.00						100	100	10	5	1	1	1	1	1	1
1.50						100	100	10	5	1	1	1	1	1	1
1.20								100	100	1	1	1	1	1	1
1.10								100	100	2.5	1	1	1	1	1
1.03									100	2.5	1	1	1	1	1
1.01									100	2.5	1	1	1	1	1
0.99									100	1	1	1	1	1	1
0.97									100	1	1	1	1	1	1
0.91									100	2.5	1	1	1	1	1
0.83										2.5	1	1	1	1	1
0.67										2.5	1	1	1	1	1
0.50										2.5	1	1	1	1	1
0.25										5	1	1	1	1	1
0.10											1	1	1	1	1
0.01															

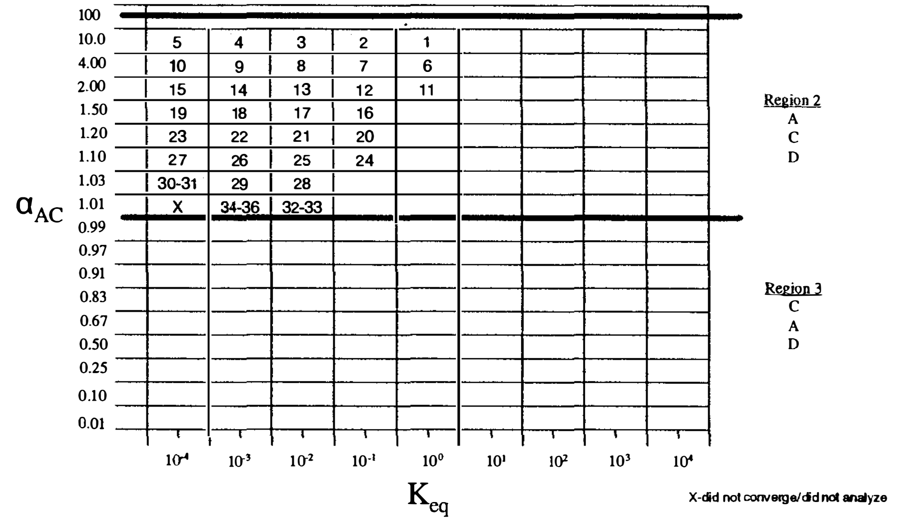
Configuration II

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
2.00						100	100	5	2.5	1	1	1	1	1	1
1.50						100	100	10	2.5	1	1	1	1	1	1
1.20						100	100	100	5	1	1	1	1	1	1
1.10							100	100	5	1	1	1	1	1	1
1.03								100	5	1	1	1	1	1	1
1.01								100	5	1	1	1	1	1	1
0.99									5	1	1	1	1	1	1
0.97									5	1	1	1	1	1	1
0.91									5	1	1	1	1	1	1
0.83									10	1	1	1	1	1	1
0.67									100	1	1	1	1	1	1
0.50										1	1	1	1	1	1
0.25										2.5	1	1	1	1	1
0.10										*	1	1	1	1	1
0.01															

Configuration III

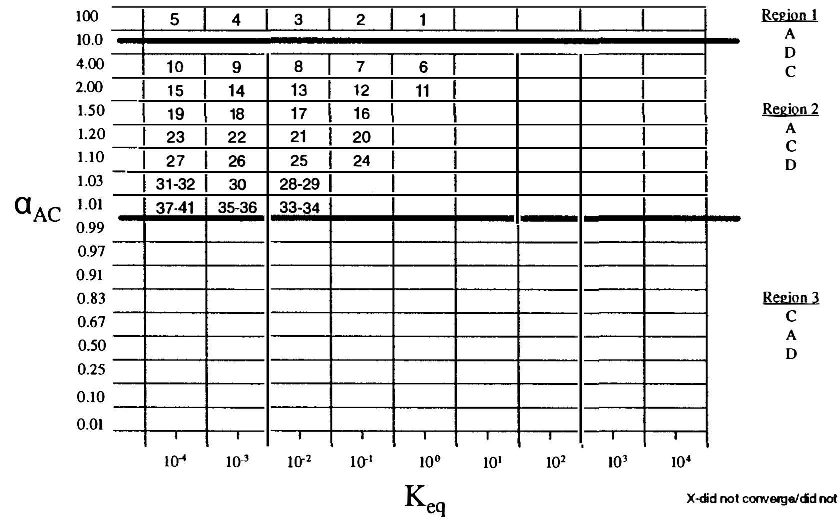
α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
2.00						100	100	10	2.5	1	1	1	1	1	1
1.50						100	100	100	5	1	1	1	1	1	1
1.20							100	100	5	1	1	1	1	1	1
1.10								100	5	1	1	1	1	1	1
1.03									5	1	1	1	1	1	1
1.01									5	1	1	1	1	1	1
0.99									10	1	1	1	1	1	1
0.97									10	1	1	1	1	1	1
0.91									10	1	1	1	1	1	1
0.83									10	1	1	1	1	1	1
0.67									100	1	1	1	1	1	1
0.50										1	1	1	1	1	1
0.25										2.5	1	1	1	1	1
0.10											1	1	1	1	1
0.01															

Figure 54. A↔C+D α_{AD} =0.01: Configuration I, II, III



	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB,azeo	XC,azeo	XB,F	XC,F
1	-14.4	119.7	57.6	0.1696	0.3630	0.4674	31.1	Unstable Strip/Rect	0.455	0.545	0.50	0.50
2	-14.4	119.7	57.6	0.5365	0.2237	0.2398	1.1	Unstable Strip/Rect	0.495	0.505	0.50	0.50
3	-14.4	119.7	57.6	0.8190	0.0885	0.0925	-9.6	Unstable Strip/Rect	0.499	0.501	0.50	0.50
4	-14.4	119.7	57.6	0.9387	0.0300	0.0312	-12.9	Unstable Rectifying	0.500	0.500	0.50	0.50
5	-14.4	119.7	57.6	0.9802	0.0097	0.0101	-13.9	Unstable Rectifying	0.500	0.500	0.50	0.50
6	-11.3	117.2	31.5	0.1519	0.2570	0.5911	24.4	Unstable Strip/Rect	0.355	0.645	0.50	0.50
7	-11.3	117.2	31.5	0.5336	0.2011	0.2654	2.7	Unstable Strip/Rect	0.479	0.521	0.50	0.50
8	-11.3	117.2	31.5	0.8182	0.8207	0.0997	-6.8	Unstable Rectifying	0.901	0.505	0.50	0.50
9	-11.3	117.2	31.5	0.9385	0.0281	0.0033	-9.9	Unstable Rectifying	0.499	0.486	0.50	0.50
10	-11.3	117.2	31.5	0.9801	0.0091	0.0178	-10.9	Unstable Rectifying	0.500	0.504	0.50	0.50
11	-11.3	111.2	10.0	0.0486	0.0451	0.8973	9.9	Unstable Strip/Rect	0.089	0.902	0.50	0.50
12	-11.3	111.2	10.0	0.5111	0.1515	0.3374	-0.6	Unstable Rectifying	0.438	0.562	0.50	0.50
13	-11.3	111.2	10.0	0.8119	0.0671	0.1210	-7.6	Unstable Rectifying	0.485	0.515	0.50	0.50
14	-11.3	111.2	10.0	0.9366	0.0233	0.0401	-10.1	Unstable Rectifying	0.496	0.504	0.50	0.50
15	-11.3	111.2	10.0	0.9795	0.0076	0.0129	-10.9	Unstable Rectifying	0.499	0.501	0.50	0.50
16	-11.3	110.3	0.9	0.4610	0.1066	0.4324	-3.3	Unstable Strip/Rect	0.389	0.611	0.50	0.50
17	-11.3	110.3	0.9	0.7971	0.0533	0.1496	-8.4	Unstable Rectifying	0.473	0.527	0.50	0.50
18	-11.3	110.3	0.9	0.9320	0.0190	0.0490	-10.3	Unstable Rectifying	0.492	0.508	0.50	0.50
19	-11.3	110.3	0.9	0.9781	0.0062	0.0157	-11.0	Unstable Rectifying	0.498	0.502	0.50	0.50
20	-11.3	109.0	-5.6	0.3168	0.0500	0.6332	-6.4	Unstable Strip/Rect	0.279	0.721	0.50	0.50
21	-11.3	109.0	-5.6	0.7536	0.0358	0.2106	-9.3	Unstable Strip/Rect	0.450	0.550	0.50	0.50
22	-11.3	109.0	-5.6	0.9183	0.0135	0.0683	-10.6	Unstable Rectifying	0.486	0.514	0.50	0.50
23	-11.3	109.0	-5.6	0.9738	0.0045	0.0218	-11.1	Unstable Rectifying	0.496	0.504	0.50	0.50
24	-11.3	108.4	-8.4	0.1022	0.0115	0.8863	-8.4	Unstable Strip/Rect	0.103	0.897	0.50	0.50
25	-11.3	108.4	-8.4	0.6884	0.0239	0.2877	-9.9	Unstable Strip/Rect	0.422	0.578	0.50	0.50
26	-11.3	108.4	-8.4	0.8974	0.0097	0.0930	-10.8	Unstable Rectifying	0.478	0.522	0.50	0.50
27	-11.3	108.4	-8.4	0.9673	0.0033	0.0294	-11.1	Unstable Rectifying	0.493	0.507	0.50	0.50
28	-11.3	108.0	-10.4	0.4861	0.0096	0.5042	-10.6	Unstable Strip/Rect	0.334	0.666	0.50	0.50
29	-11.3	108.0	-10.4	0.8354	0.0052	0.1593	-11.0	Unstable Rectifying	0.458	0.542	0.50	0.50
30	-11.3	108.0	-10.4	0.9472	0.0019	0.0510	-11.2	Unstable Rectifying	0.487	0.513	0.50	0.50
31	-11.3	108.0	-10.4	0.9473	0.0019	0.0508	-11.2	Unstable Rectifying	0.487	0.513	0.50	0.50
32	-11.3	108.0	-10.9	0.1710	0.0021	0.8269	-11.0	Unstable Stripping	0.148	0.852	0.50	0.50
33	-11.3	108.0	-10.9	0.1747	0.0021	0.8232	-11.0	Unstable Rectifying	0.151	0.849	0.50	0.50
34	-11.3	108.0	-10.9	0.7499	0.0030	0.2470	-11.1	Unstable Rectifying	0.430	0.570	0.50	0.50
35	-11.3	108.0	-10.9	0.7312	0.0027	0.2661	-11.1	Unstable Rectifying	0.424	0.576	0.50	0.50
36	-11.3	108.0	-10.9	0.7349	0.0028	0.2623	-11.1	Unstable Rectifying	0.425	0.575	0.50	0.50

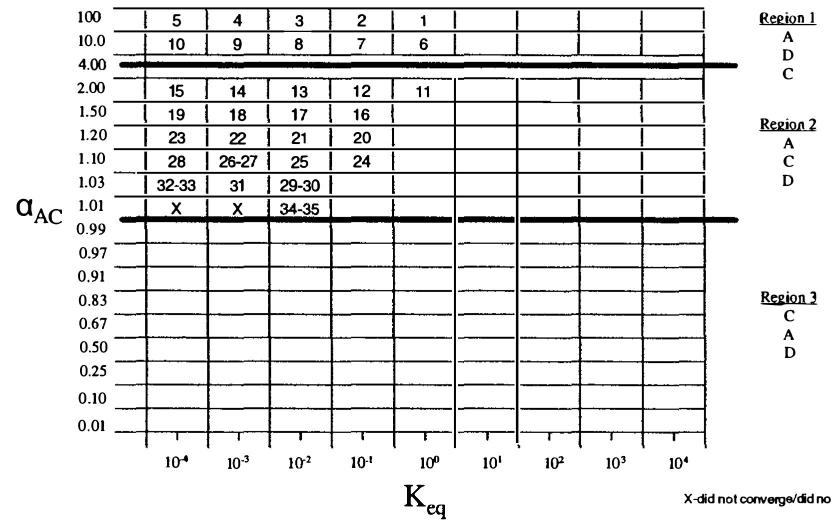
Figure 55. A↔C+D α_{AD} =100: Reactive Azeotropes



X-did not converge/did not analyze

	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB.azeo	XC.azeo	XB.F	XC.F
1	-14.4	57.6	119.7	0.1696	0.4674	0.3630	31.1	Unstable Strip/Rect	0.545	0.455	0.50	0.50
2	-14.4	57.6	119.7	0.5365	0.2398	0.2237	1.1	Unstable Strip/Rect	0.505	0.495	0.50	0.50
3	-14.4	57.6	119.7	0.8190	0.0925	0.0885	-9.6	Unstable Strip/Rect	0.501	0.499	0.50	0.50
4	-14.4	57.6	119.7	0.9387	0.0312	0.0300	-12.9	Unstable Rectifying	0.500	0.500	0.50	0.50
5	-14.4	57.6	119.7	0.9802	0.0101	0.0097	-13.9	Unstable Rectifying	0.500	0.500	0.50	0.50
6	-11.3	50.5	27.1	0.1602	0.2929	0.5469	19.8	Unstable Rectifying	0.391	0.609	0.50	0.50
7	-11.3	50.5	27.1	0.5346	0.2062	0.2593	1.6	Unstable Rectifying	0.483	0.517	0.50	0.50
8	-11.3	50.5	27.1	0.8184	0.0832	0.0983	-7.1	Unstable Rectifying	0.496	0.504	0.50	0.50
9	-11.3	50.5	27.1	0.9386	0.0284	0.0331	-10.0	Unstable Rectifying	0.499	0.501	0.50	0.50
10	-11.3	50.5	27.1	0.9801	0.0092	0.0107	-10.9	Unstable Rectifying	0.500	0.500	0.50	0.50
11	-11.3	48.3	7.5	0.0537	0.0606	0.8857	7.3	Unstable Strip/Rect	0.108	0.892	0.50	0.50
12	-11.3	48.3	7.5	0.5110	0.1514	0.3376	-1.6	Unstable Strip/Rect	0.438	0.562	0.50	0.50
13	-11.3	48.3	7.5	0.8117	0.0667	0.1216	-7.9	Unstable Rectifying	0.485	0.515	0.50	0.50
14	-11.3	48.3	7.5	0.9365	0.0232	0.0403	-10.2	Unstable Rectifying	0.496	0.504	0.50	0.50
15	-11.3	48.3	7.5	0.9795	0.0076	0.0129	-11.0	Unstable Rectifying	0.499	0.501	0.50	0.50
16	-11.3	47.3	-0.1	0.4634	0.1081	0.4285	-4.0	Unstable Strip/Rect	0.391	0.609	0.50	0.50
17	-11.3	47.3	-0.1	0.7975	0.0535	0.1490	-8.6	Unstable Rectifying	0.473	0.527	0.50	0.50
18	-11.3	47.3	-0.1	0.9320	0.0191	0.0489	-10.4	Unstable Rectifying	0.492	0.508	0.50	0.50
19	-11.3	47.3	-0.1	0.9781	0.0062	0.0157	-11.0	Unstable Rectifying	0.498	0.502	0.50	0.50
20	-11.3	46.8	-6.1	0.3179	0.0503	0.6318	-6.8	Unstable Strip/Rect	0.279	0.721	0.50	0.50
21	-11.3	46.8	-6.1	0.7355	0.0358	0.2107	-9.4	Unstable Rectifying	0.444	0.545	0.50	0.50
22	-11.3	46.8	-6.1	0.9182	0.0134	0.0684	-10.7	Unstable Rectifying	0.486	0.514	0.50	0.50
23	-11.3	46.8	-6.1	0.9737	0.0045	0.0218	-11.1	Unstable Rectifying	0.496	0.504	0.50	0.50
24	-11.3	46.6	-8.7	0.0847	0.0093	0.9060	-8.7	Unstable Rectifying	0.087	0.913	0.50	0.50
25	-11.3	46.6	-8.7	0.6827	0.0232	0.2940	-10.0	Unstable Rectifying	0.420	0.580	0.50	0.50
26	-11.3	46.6	-8.7	0.8954	0.0094	0.0952	-10.9	Unstable Rectifying	0.477	0.523	0.50	0.50
27	-11.3	46.6	-8.7	0.9667	0.0032	0.0301	-11.2	Unstable Rectifying	0.493	0.507	0.50	0.50
28	-11.3	46.3	-10.6	0.4326	0.0077	0.5596	-10.7	Unstable Rectifying	0.307	0.693	0.50	0.50
29	-11.3	46.3	-10.6	0.4340	0.0078	0.5582	-10.7	Unstable Stripping	0.308	0.692	0.50	0.50
30	-11.3	46.3	-10.6	0.8180	0.0046	0.1773	-11.1	Unstable Rectifying	0.452	0.548	0.50	0.50
31	-11.3	46.3	-10.6	0.9424	0.0017	0.0559	-11.2	Unstable Rectifying	0.486	0.514	0.50	0.50
32	-11.3	46.3	-10.6	0.9420	0.0017	0.0564	-11.2	Unstable Rectifying	0.486	0.514	0.50	0.50
33	-11.3	46.3	-10.9	0.2024	0.0025	0.7950	-11.0	Unstable Rectifying	0.170	0.830	0.50	0.50
34	-11.3	46.3	-10.9	0.2027	0.0026	0.7948	-11.0	Unstable Stripping	0.171	0.829	0.50	0.50
35	-11.3	46.3	-10.9	0.7512	0.0031	0.2458	-11.1	Unstable Rectifying	0.431	0.569	0.50	0.50
36	-11.3	46.3	-10.9	0.7585	0.0032	0.2383	-11.1	Unstable Rectifying	0.433	0.567	0.50	0.50
37	-11.3	46.3	-10.9	0.9189	0.0012	0.0799	-11.2	Unstable Rectifying	0.479	0.521	0.50	0.50
38	-11.3	46.3	-10.9	0.9342	0.0015	0.0643	-11.2	Unstable Rectifying	0.484	0.516	0.50	0.50
39	-11.3	46.3	-10.9	0.9328	0.0014	0.0658	-11.2	Unstable Rectifying	0.483	0.517	0.50	0.50
40	-11.3	46.3	-10.9	0.9077	0.0001	0.0913	-11.2	Unstable Rectifying	0.476	0.524	0.50	0.50
41	-11.3	46.3	-10.9	0.9193	0.0012	0.0795	-11.2	Unstable Rectifying	0.480	0.520	0.50	0.50

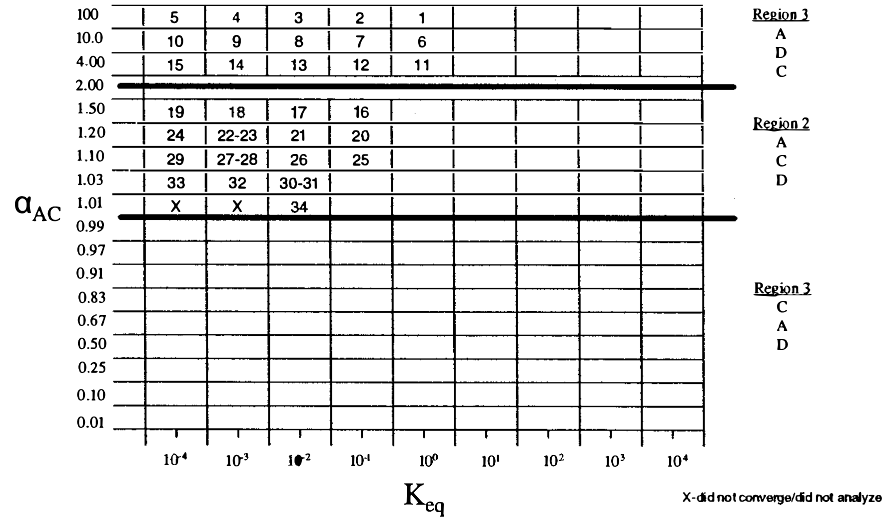
Figure 56. A↔C+D α_{AD} =10: Reactive Azeotropes



X-did not converge/did not analyze

	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB.azeo	XC.azeo	XB.F	XC.F
1	-11.3	31.5	117.2	0.1519	0.5911	0.2570	24.4	Unstable Strip/Rect	0.645	0.355	0.50	0.50
2	-11.3	31.5	117.2	0.5336	0.2654	0.2011	2.7	Unstable Strip/Rect	0.521	0.479	0.50	0.50
3	-11.3	31.5	117.2	0.8182	0.0997	0.8207	-6.8	Unstable Rectifying	0.505	0.901	0.50	0.50
4	-11.3	31.5	117.2	0.9385	0.0033	0.0281	-9.9	Unstable Rectifying	0.486	0.499	0.50	0.50
5	-11.3	31.5	117.2	0.9801	0.0178	0.0091	-10.9	Unstable Rectifying	0.504	0.500	0.50	0.50
6	-11.3	27.1	50.5	0.1602	0.5469	0.2929	19.8	Unstable Rectifying	0.609	0.391	0.50	0.50
7	-11.3	27.1	50.5	0.5346	0.2593	0.2062	1.6	Unstable Rectifying	0.517	0.483	0.50	0.50
8	-11.3	27.1	50.5	0.8184	0.0983	0.0832	-7.1	Unstable Rectifying	0.504	0.496	0.50	0.50
9	-11.3	27.1	50.5	0.9386	0.0331	0.0284	-10.0	Unstable Rectifying	0.501	0.499	0.50	0.50
10	-11.3	27.1	50.5	0.9801	0.0107	0.0092	-10.9	Unstable Rectifying	0.500	0.500	0.50	0.50
11	-11.3	24.1	7.0	0.1158	0.1600	0.7242	6.0	Unstable Strip/Rect	0.247	0.753	0.50	0.50
12	-11.3	24.1	7.0	0.5243	0.1735	0.3022	-2.7	Unstable Strip/Rect	0.458	0.542	0.50	0.50
13	-11.3	24.1	7.0	0.8154	0.0732	0.1114	-8.3	Unstable Rectifying	0.489	0.511	0.50	0.50
14	-11.3	24.1	7.0	0.9376	0.0252	0.0372	-10.3	Unstable Rectifying	0.497	0.503	0.50	0.50
15	-11.3	24.1	7.0	0.9798	0.0082	0.0120	-11.0	Unstable Rectifying	0.499	0.501	0.50	0.50
16	-11.3	23.0	-1.1	0.4815	0.1212	0.3974	-4.9	Unstable Strip/Rect	0.407	0.593	0.50	0.50
17	-11.3	23.0	-1.1	0.8026	0.0573	0.1401	-8.9	Unstable Rectifying	0.477	0.523	0.50	0.50
18	-11.3	23.0	-1.1	0.9336	0.0202	0.0462	-10.5	Unstable Rectifying	0.493	0.507	0.50	0.50
19	-11.3	23.0	-1.1	0.9786	0.0066	0.0148	-11.1	Unstable Rectifying	0.498	0.502	0.50	0.50
20	-11.3	23.1	-6.7	0.3402	0.0564	0.6034	-7.4	Unstable Rectifying	0.296	0.704	0.50	0.50
21	-11.3	23.1	-6.7	0.7600	0.0375	0.2025	-9.7	Unstable Rectifying	0.453	0.547	0.50	0.50
22	-11.3	23.1	-6.7	0.9202	0.0140	0.0658	-10.8	Unstable Rectifying	0.487	0.513	0.50	0.50
23	-11.3	23.1	-6.7	0.9744	0.0046	0.0210	-11.1	Unstable Rectifying	0.496	0.504	0.50	0.50
24	-11.3	23.0	-8.9	0.1254	0.0146	0.8600	-9.0	Unstable Stripping	0.124	0.876	0.50	0.50
25	-11.3	23.0	-8.9	0.6948	0.0248	0.2804	-10.2	Unstable Rectifying	0.425	0.575	0.50	0.50
26	-11.3	23.0	-8.9	0.9018	0.0103	0.0879	-10.9	Unstable Rectifying	0.480	0.520	0.50	0.50
27	-11.3	23.0	-8.9	0.9000	0.0100	0.0900	-10.9	Unstable Rectifying	0.479	0.521	0.50	0.50
28	-11.3	23.0	-8.9	0.9679	0.0034	0.0288	-11.2	Unstable Rectifying	0.494	0.506	0.50	0.50
29	-11.3	23.0	-10.6	0.4790	0.0094	0.5117	-10.8	Unstable Stripping	0.330	0.670	0.50	0.50
30	-11.3	23.0	-10.6	0.4863	0.0096	0.5041	-10.8	Unstable Rectifying	0.334	0.666	0.50	0.50
31	-11.3	23.0	-10.6	0.8417	0.0055	0.1528	-11.1	Unstable Rectifying	0.460	0.540	0.50	0.50
32	-11.3	23.0	-10.6	0.9466	0.0018	0.0516	-11.2	Unstable Rectifying	0.487	0.513	0.50	0.50
33	-11.3	23.0	-10.6	0.9469	0.0018	0.0513	-11.2	Unstable Rectifying	0.487	0.513	0.50	0.50
34	-11.3	23.0	-10.9	0.2704	0.0037	0.7259	-11.0	Unstable Stripping	0.216	0.784	0.50	0.50
35	-11.3	23.0	-10.9	0.2489	0.0033	0.7478	-11.0	Unstable Rectifying	0.202	0.798	0.50	0.50

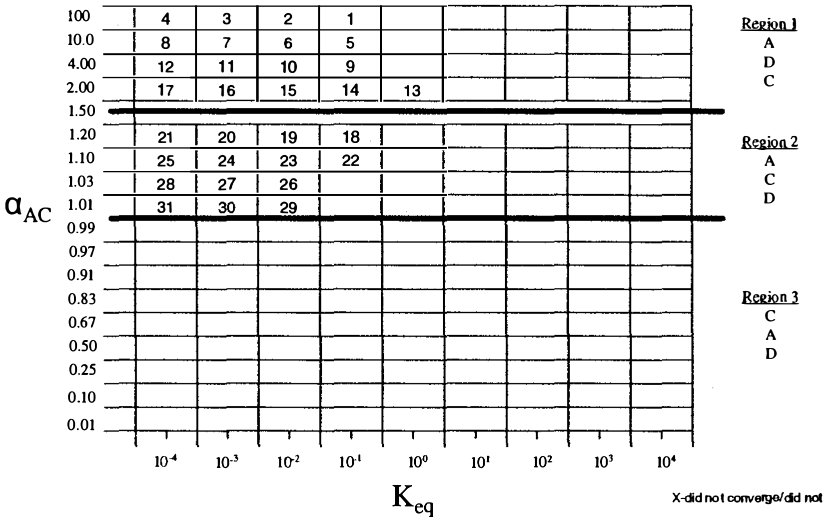
Figure 57. A↔C+D α_{AD} =4.0: Reactive Azeotropes



X-did not converge/did not analyze

	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB.azeo	XC.azeo	XB.F	XC.F
1	-11.3	10.0	111.2	0.0486	0.8973	0.0451	9.9	Unstable Strip/Rect	0.902	0.089	0.50	0.50
2	-11.3	10.0	111.2	0.5111	0.3374	0.1515	-0.6	Unstable Rectifying	0.562	0.438	0.50	0.50
3	-11.3	10.0	111.2	0.8119	0.1210	0.0671	-7.6	Unstable Rectifying	0.515	0.485	0.50	0.50
4	-11.3	10.0	111.2	0.9366	0.0401	0.0233	-10.1	Unstable Rectifying	0.504	0.496	0.50	0.50
5	-11.3	10.0	111.2	0.9795	0.0129	0.0076	-10.9	Unstable Rectifying	0.501	0.499	0.50	0.50
6	-11.3	7.5	48.3	0.0537	0.8857	0.0606	7.3	Unstable Strip/Rect	0.892	0.108	0.50	0.50
7	-11.3	7.5	48.3	0.5110	0.3376	0.1514	-1.6	Unstable Strip/Rect	0.562	0.438	0.50	0.50
8	-11.3	7.5	48.3	0.8117	0.1216	0.0667	-7.9	Unstable Rectifying	0.515	0.485	0.50	0.50
9	-11.3	7.5	48.3	0.9365	0.0403	0.0232	-10.2	Unstable Rectifying	0.504	0.496	0.50	0.50
10	-11.3	7.5	48.3	0.9795	0.0129	0.0076	-11.0	Unstable Rectifying	0.501	0.499	0.50	0.50
11	-11.3	7.0	24.1	0.1158	0.7242	0.1600	6.0	Unstable Strip/Rect	0.753	0.247	0.50	0.50
12	-11.3	7.0	24.1	0.5243	0.3022	0.1735	-2.7	Unstable Strip/Rect	0.542	0.458	0.50	0.50
13	-11.3	7.0	24.1	0.8154	0.1114	0.0732	-8.3	Unstable Rectifying	0.511	0.489	0.50	0.50
14	-11.3	7.0	24.1	0.9376	0.0372	0.0252	-10.3	Unstable Rectifying	0.503	0.497	0.50	0.50
15	-11.3	7.0	24.1	0.9798	0.0120	0.0082	-11.0	Unstable Rectifying	0.501	0.499	0.50	0.50
16	-11.3	6.0	-1.1	0.5234	0.1716	0.3050	-6.1	Unstable Strip/Rect	0.456	0.544	0.50	0.50
17	-11.3	6.0	-1.1	0.8150	0.0724	0.1126	-9.4	Unstable Rectifying	0.489	0.511	0.50	0.50
18	-11.3	6.0	-1.1	0.9375	0.0249	0.0376	-10.7	Unstable Rectifying	0.497	0.503	0.50	0.50
19	-11.3	6.0	-1.1	0.9798	0.0081	0.0121	-11.1	Unstable Rectifying	0.499	0.501	0.50	0.50
20	-11.3	5.8	-6.9	0.4266	0.0878	0.4856	-8.1	Unstable Strip/Rect	0.361	0.639	0.50	0.50
21	-11.3	5.8	-6.9	0.7868	0.0470	0.1672	-10.0	Unstable Rectifying	0.467	0.534	0.50	0.50
22	-11.3	5.8	-6.9	0.9283	0.0170	0.0548	-10.9	Unstable Rectifying	0.490	0.510	0.50	0.50
23	-11.3	5.8	-6.9	0.9284	0.0170	0.0546	-10.9	Unstable Rectifying	0.490	0.510	0.50	0.50
24	-11.3	5.8	-6.9	0.9769	0.0056	0.0175	-11.2	Unstable Rectifying	0.497	0.503	0.50	0.50
25	-11.3	5.8	-8.9	0.2773	0.0407	0.6820	-9.2	Unstable Strip/Rect	0.249	0.751	0.50	0.50
26	-11.3	5.8	-8.9	0.7406	0.0327	0.2267	-10.4	Unstable Rectifying	0.444	0.556	0.50	0.50
27	-11.3	5.8	-8.9	0.9141	0.0124	0.0735	-11.0	Unstable Rectifying	0.484	0.516	0.50	0.50
28	-11.3	5.8	-8.9	0.9124	0.0121	0.0755	-11.0	Unstable Rectifying	0.483	0.517	0.50	0.50
29	-11.3	5.8	-8.9	0.9724	0.0042	0.0234	-11.2	Unstable Rectifying	0.495	0.505	0.50	0.50
30	-11.3	5.8	-10.6	0.5683	0.0136	0.4181	-10.8	Unstable Rectifying	0.371	0.629	0.50	0.50
31	-11.3	5.8	-10.6	0.5725	0.0138	0.4137	-10.8	Unstable Rectifying	0.373	0.627	0.50	0.50
32	-11.3	5.8	-10.6	0.8622	0.0066	0.1312	-11.1	Unstable Rectifying	0.467	0.533	0.50	0.50
33	-11.3	5.8	-10.6	0.9557	0.0023	0.0420	-11.2	Unstable Rectifying	0.490	0.510	0.50	0.50
34	-11.3	5.8	-10.9	0.4023	0.0068	0.5909	-11.0	Unstable Rectifying	0.292	0.708	0.50	0.50

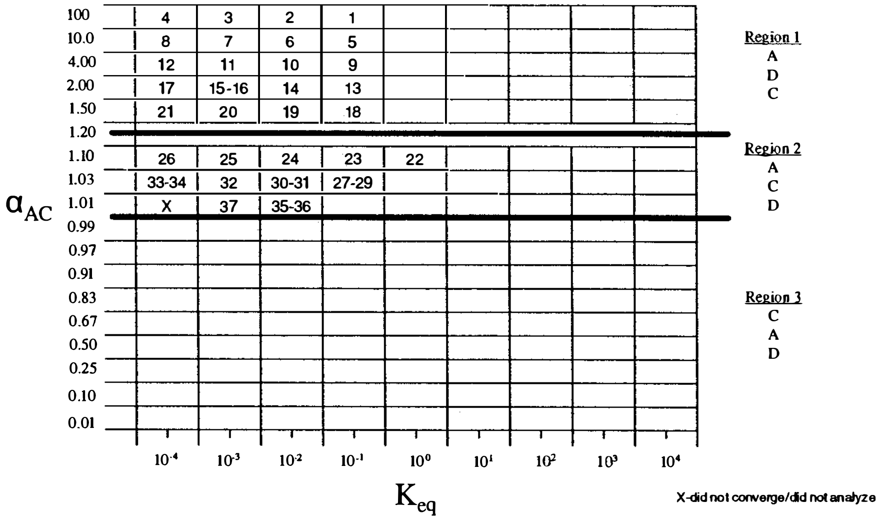
Figure 58. A↔C+D α_{AD} =2.0: Reactive Azeotropes



X-did not converge/did not analyze

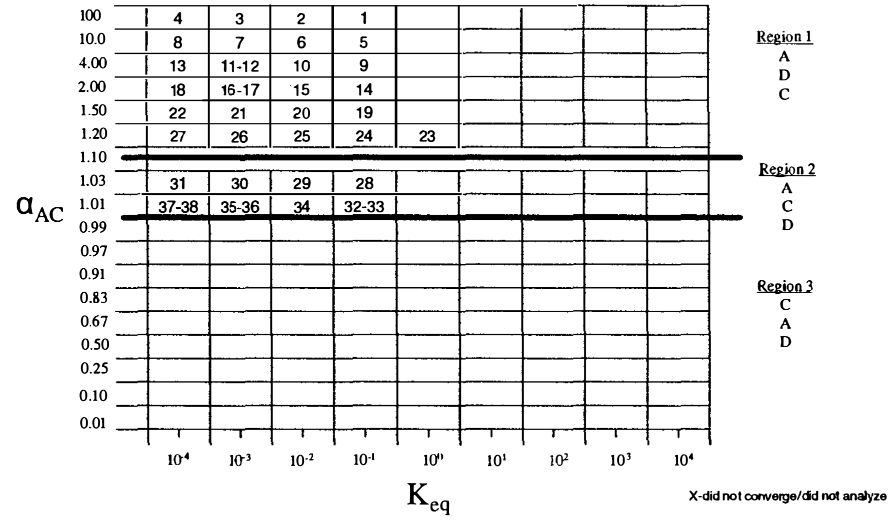
	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB,azeo	XC,azeo	XB,F	XC,F
1	-11.3	0.9	110.3	0.4610	0.4324	0.1066	-3.3	Unstable Strip/Rect	0.611	0.389	0.50	0.50
2	-11.3	0.9	110.3	0.7971	0.1496	0.0533	-8.4	Unstable Rectifying	0.527	0.473	0.50	0.50
3	-11.3	0.9	110.3	0.9320	0.0490	0.0190	-10.3	Unstable Rectifying	0.508	0.492	0.50	0.50
4	-11.3	0.9	110.3	0.9781	0.0157	0.0062	-11.0	Unstable Rectifying	0.502	0.498	0.50	0.50
5	-11.3	-0.1	47.3	0.4634	0.4285	0.1081	-4.0	Unstable Strip/Rect	0.609	0.391	0.50	0.50
6	-11.3	-0.1	47.3	0.7975	0.1490	0.0535	-8.6	Unstable Rectifying	0.527	0.473	0.50	0.50
7	-11.3	-0.1	47.3	0.9320	0.0489	0.0191	-10.4	Unstable Rectifying	0.508	0.492	0.50	0.50
8	-11.3	-0.1	47.3	0.9781	0.0157	0.0062	-11.0	Unstable Rectifying	0.502	0.498	0.50	0.50
9	-11.3	-1.1	23.0	0.4815	0.3974	0.1212	-4.9	Unstable Strip/Rect	0.593	0.407	0.50	0.50
10	-11.3	-1.1	23.0	0.8026	0.1401	0.0573	-8.9	Unstable Rectifying	0.523	0.477	0.50	0.50
11	-11.3	-1.1	23.0	0.9336	0.0462	0.0202	-10.5	Unstable Rectifying	0.507	0.493	0.50	0.50
12	-11.3	-1.1	23.0	0.9786	0.0148	0.0066	-11.1	Unstable Rectifying	0.502	0.498	0.50	0.50
13	-11.3	-1.1	6.0	0.1141	0.7295	0.1564	-1.5	Unstable Strip/Rect	0.757	0.243	0.50	0.50
14	-11.3	-1.1	6.0	0.5234	0.3050	0.1716	-6.1	Unstable Strip/Rect	0.544	0.456	0.50	0.50
15	-11.3	-1.1	6.0	0.8150	0.1126	0.0724	-9.4	Unstable Rectifying	0.511	0.489	0.50	0.50
16	-11.3	-1.1	6.0	0.9375	0.0376	0.0249	-10.7	Unstable Rectifying	0.503	0.497	0.50	0.50
17	-11.3	-1.1	6.0	0.9798	0.0121	0.0081	-11.1	Unstable Rectifying	0.501	0.499	0.50	0.50
18	-11.3	-1.4	-6.9	0.4938	0.1320	0.3742	-8.6	Unstable Rectifying	0.419	0.581	0.50	0.50
19	-11.3	-1.4	-6.9	0.8060	0.0603	0.1336	-10.2	Unstable Rectifying	0.480	0.520	0.50	0.50
20	-11.3	-1.4	-6.9	0.9347	0.0211	0.0442	-10.9	Unstable Rectifying	0.494	0.506	0.50	0.50
21	-11.3	-1.4	-6.9	0.9789	0.0069	0.0142	-11.2	Unstable Rectifying	0.498	0.502	0.50	0.50
22	-11.3	-1.4	-8.9	0.3928	0.0736	0.5336	-9.4	Unstable Rectifying	0.335	0.665	0.50	0.50
23	-11.3	-1.4	-8.9	0.7755	0.0426	0.1819	-10.5	Unstable Rectifying	0.461	0.539	0.50	0.50
24	-11.3	-1.4	-8.9	0.9248	0.0155	0.0597	-11.0	Unstable Rectifying	0.489	0.511	0.50	0.50
25	-11.3	-1.4	-8.9	0.9759	0.0051	0.0190	-11.2	Unstable Rectifying	0.497	0.503	0.50	0.50
26	-11.3	-1.4	-10.6	0.6553	0.0202	0.3246	-10.9	Unstable Rectifying	0.408	0.592	0.50	0.50
27	-11.3	-1.4	-10.6	0.8853	0.0083	0.1064	-11.2	Unstable Rectifying	0.474	0.526	0.50	0.50
28	-11.3	-1.4	-10.6	0.9631	0.0028	0.0341	-11.3	Unstable Rectifying	0.492	0.508	0.50	0.50
29	-11.3	-1.4	-10.9	0.6435	0.0191	0.3374	-11.0	Unstable Rectifying	0.403	0.597	0.50	0.50
30	-11.3	-1.4	-10.9	0.8436	0.0056	0.1508	-11.2	Unstable Rectifying	0.461	0.539	0.50	0.50
31	-11.3	-1.4	-10.9	0.9497	0.0020	0.0483	-11.3	Unstable Rectifying	0.488	0.512	0.50	0.50

Figure 59. A↔C+D α_{AD} =1.5: Reactive Azeotropes



	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB,azeo	XC,azeo	XB,F	XC,F
1	-11.3	-5.6	109.0	0.3168	0.6332	0.0500	-6.4	Unstable Strip/Rect	0.721	0.279	0.50	0.50
2	-11.3	-5.6	109.0	0.7536	0.2106	0.0358	-9.3	Unstable Strip/Rect	0.550	0.450	0.50	0.50
3	-11.3	-5.6	109.0	0.9183	0.0683	0.0135	-10.6	Unstable Rectifying	0.514	0.486	0.50	0.50
4	-11.3	-5.6	109.0	0.9738	0.0218	0.0045	-11.1	Unstable Rectifying	0.504	0.496	0.50	0.50
5	-11.3	-6.1	46.8	0.3179	0.6318	0.0503	-6.8	Unstable Strip/Rect	0.721	0.279	0.50	0.50
6	-11.3	-6.1	46.8	0.7355	0.2107	0.0358	-9.4	Unstable Rectifying	0.545	0.444	0.50	0.50
7	-11.3	-6.1	46.8	0.9182	0.0684	0.0134	-10.7	Unstable Rectifying	0.514	0.486	0.50	0.50
8	-11.3	-6.1	46.8	0.9737	0.0218	0.0045	-11.1	Unstable Rectifying	0.504	0.496	0.50	0.50
9	-11.3	-6.7	23.1	0.3402	0.6034	0.0564	-7.4	Unstable Rectifying	0.704	0.296	0.50	0.50
10	-11.3	-6.7	23.1	0.7600	0.2025	0.0375	-9.7	Unstable Rectifying	0.547	0.453	0.50	0.50
11	-11.3	-6.7	23.1	0.9202	0.0658	0.0140	-10.8	Unstable Rectifying	0.513	0.487	0.50	0.50
12	-11.3	-6.7	23.1	0.9744	0.0210	0.0046	-11.1	Unstable Rectifying	0.504	0.496	0.50	0.50
13	-11.3	-6.9	5.8	0.4266	0.4856	0.0878	-8.1	Unstable Strip/Rect	0.639	0.361	0.50	0.50
14	-11.3	-6.9	5.8	0.7868	0.1672	0.0470	-10.0	Unstable Rectifying	0.534	0.467	0.50	0.50
15	-11.3	-6.9	5.8	0.9283	0.0548	0.0170	-10.9	Unstable Rectifying	0.510	0.490	0.50	0.50
16	-11.3	-6.9	5.8	0.9284	0.0546	0.0170	-10.9	Unstable Rectifying	0.510	0.490	0.50	0.50
17	-11.3	-6.9	5.8	0.9769	0.0175	0.0056	-11.2	Unstable Rectifying	0.503	0.497	0.50	0.50
18	-11.3	-6.9	-1.4	0.4938	0.3742	0.1320	-8.6	Unstable Rectifying	0.581	0.419	0.50	0.50
19	-11.3	-6.9	-1.4	0.8060	0.1336	0.0603	-10.2	Unstable Rectifying	0.520	0.480	0.50	0.50
20	-11.3	-6.9	-1.4	0.9347	0.0442	0.0211	-10.9	Unstable Rectifying	0.506	0.494	0.50	0.50
21	-11.3	-6.9	-1.4	0.9789	0.0142	0.0069	-11.2	Unstable Rectifying	0.502	0.498	0.50	0.50
22	-11.3	-6.8	-8.9	0.0416	0.0456	0.9128	-9.0	Unstable Strip/Rect	0.084	0.916	0.50	0.50
23	-11.3	-6.8	-8.9	0.5062	0.1452	0.3485	-9.9	Unstable Rectifying	0.433	0.567	0.50	0.50
24	-11.3	-6.8	-8.9	0.8098	0.0643	0.1259	-10.7	Unstable Rectifying	0.483	0.517	0.50	0.50
25	-11.3	-6.8	-8.9	0.9358	0.0224	0.0418	-11.1	Unstable Rectifying	0.495	0.505	0.50	0.50
26	-11.3	-6.8	-8.9	0.9793	0.0073	0.0134	-11.2	Unstable Rectifying	0.498	0.502	0.50	0.50
27	-11.3	-6.8	-10.6	0.2600	0.0370	0.7030	-10.6	Unstable Stripping	0.236	0.764	0.50	0.50
28	-11.3	-6.8	-10.6	0.2299	0.0311	0.7390	-10.6	Unstable Rectifying	0.212	0.788	0.50	0.50
29	-11.3	-6.8	-10.6	0.2651	0.0380	0.6969	-10.6	Unstable Rectifying	0.240	0.760	0.50	0.50
30	-11.3	-6.8	-10.6	0.7436	0.0333	0.2230	-11.0	Unstable Rectifying	0.446	0.554	0.50	0.50
31	-11.3	-6.8	-10.6	0.7433	0.0333	0.2234	-11.0	Unstable Rectifying	0.445	0.555	0.50	0.50
32	-11.3	-6.8	-10.6	0.9120	0.0120	0.0760	-11.2	Unstable Rectifying	0.483	0.517	0.50	0.50
33	-11.3	-6.8	-10.6	0.9735	0.0044	0.0221	-11.3	Unstable Rectifying	0.496	0.504	0.50	0.50
34	-11.3	-6.8	-10.6	0.9717	0.0040	0.0243	-11.3	Unstable Rectifying	0.495	0.505	0.50	0.50
35	-11.3	-6.8	-10.9	0.6407	0.0188	0.3405	-11.1	Unstable Rectifying	0.402	0.598	0.50	0.50
36	-11.3	-6.8	-10.9	0.6495	0.0196	0.3309	-11.1	Unstable Rectifying	0.406	0.594	0.50	0.50
37	-11.3	-6.8	-10.9	0.8853	0.0083	0.1064	-11.2	Unstable Rectifying	0.474	0.526	0.50	0.50

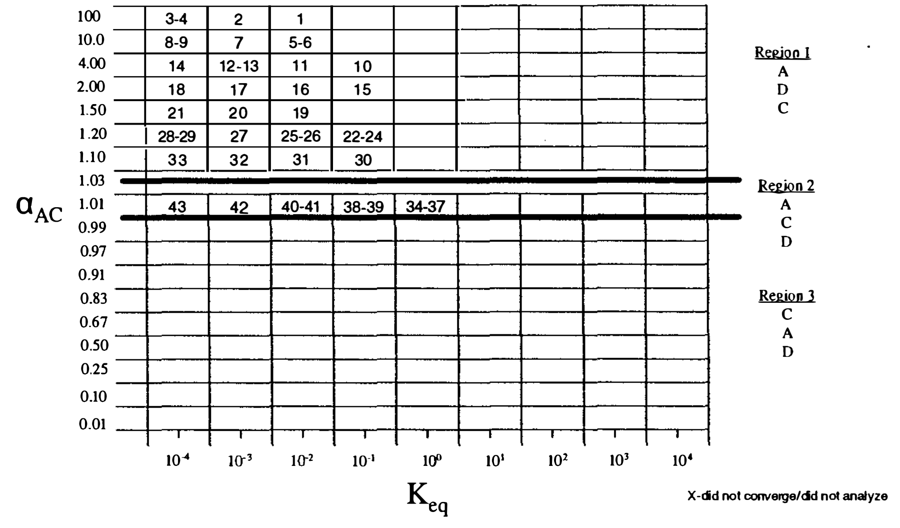
Figure 60. A↔C+D α_{AD} =1.2: Reactive Azeotropes



X-did not converge/did not analyze

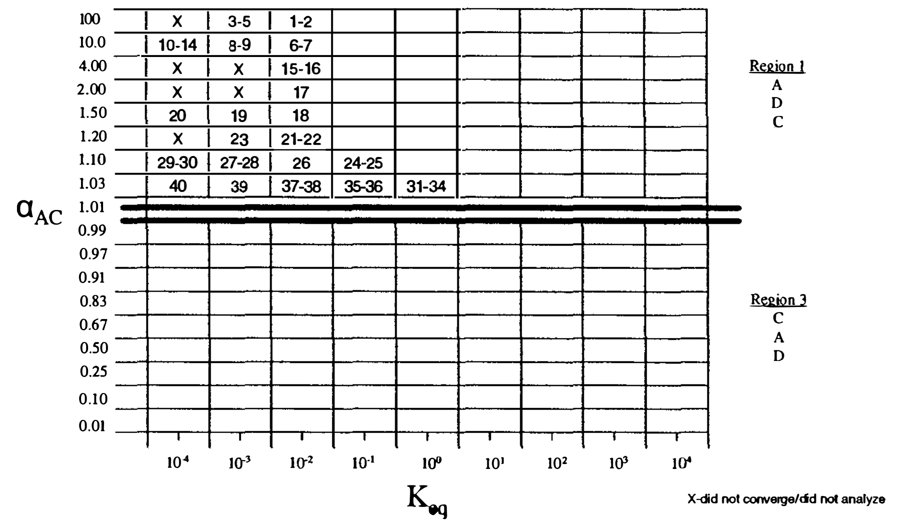
	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB.azeo	XC.azeo	XB.F	XC.F
1	-11.3	-8.4	108.4	0.1022	0.8863	0.0115	-8.4	Unstable Strip/Rect	0.897	0.103	0.50	0.50
2	-11.3	-8.4	108.4	0.6884	0.2877	0.0239	-9.9	Unstable Strip/Rect	0.578	0.422	0.50	0.50
3	-11.3	-8.4	108.4	0.8974	0.0930	0.0097	-10.8	Unstable Rectifying	0.522	0.478	0.50	0.50
4	-11.3	-8.4	108.4	0.9673	0.0294	0.0033	-11.1	Unstable Rectifying	0.507	0.493	0.50	0.50
5	-11.3	-8.7	46.6	0.0847	0.9060	0.0093	-8.7	Unstable Rectifying	0.913	0.087	0.50	0.50
6	-11.3	-8.7	46.6	0.6827	0.2940	0.0232	-10.0	Unstable Rectifying	0.580	0.420	0.50	0.50
7	-11.3	-8.7	46.6	0.8954	0.0952	0.0094	-10.9	Unstable Rectifying	0.523	0.477	0.50	0.50
8	-11.3	-8.7	46.6	0.9667	0.0301	0.0032	-11.2	Unstable Rectifying	0.507	0.493	0.50	0.50
9	-11.3	-8.9	23.0	0.1254	0.8600	0.0146	-9.0	Unstable Stripping	0.876	0.124	0.50	0.50
10	-11.3	-8.9	23.0	0.6948	0.2804	0.0248	-10.2	Unstable Rectifying	0.575	0.425	0.50	0.50
11	-11.3	-8.9	23.0	0.9018	0.0879	0.0103	-10.9	Unstable Rectifying	0.520	0.480	0.50	0.50
12	-11.3	-8.9	23.0	0.9000	0.0900	0.0100	-10.9	Unstable Rectifying	0.521	0.479	0.50	0.50
13	-11.3	-8.9	23.0	0.9679	0.0288	0.0034	-11.2	Unstable Rectifying	0.506	0.494	0.50	0.50
14	-11.3	-8.9	5.8	0.2773	0.6820	0.0407	-9.2	Unstable Strip/Rect	0.751	0.249	0.50	0.50
15	-11.3	-8.9	5.8	0.7406	0.2267	0.0327	-10.4	Unstable Rectifying	0.556	0.444	0.50	0.50
16	-11.3	-8.9	5.8	0.9141	0.0735	0.0124	-11.0	Unstable Rectifying	0.516	0.484	0.50	0.50
17	-11.3	-8.9	5.8	0.9124	0.0755	0.0121	-11.0	Unstable Rectifying	0.517	0.483	0.50	0.50
18	-11.3	-8.9	5.8	0.9724	0.0234	0.0042	-11.2	Unstable Rectifying	0.505	0.495	0.50	0.50
19	-11.3	-8.9	-1.4	0.3928	0.5336	0.0736	-9.4	Unstable Rectifying	0.665	0.335	0.50	0.50
20	-11.3	-8.9	-1.4	0.7755	0.1819	0.0426	-10.5	Unstable Rectifying	0.539	0.461	0.50	0.50
21	-11.3	-8.9	-1.4	0.9248	0.0597	0.0155	-11.0	Unstable Rectifying	0.511	0.489	0.50	0.50
22	-11.3	-8.9	-1.4	0.9759	0.0190	0.0051	-11.2	Unstable Rectifying	0.503	0.497	0.50	0.50
23	-11.3	-8.9	-6.8	0.0416	0.9128	0.0456	-9.0	Unstable Strip/Rect	0.916	0.084	0.50	0.50
24	-11.3	-8.9	-6.8	0.5062	0.3485	0.1452	-9.9	Unstable Rectifying	0.567	0.433	0.50	0.50
25	-11.3	-8.9	-6.8	0.8098	0.1259	0.0643	-10.7	Unstable Rectifying	0.517	0.483	0.50	0.50
26	-11.3	-8.9	-6.8	0.9358	0.0418	0.0224	-11.1	Unstable Rectifying	0.505	0.495	0.50	0.50
27	-11.3	-8.9	-6.8	0.9793	0.0134	0.0073	-11.2	Unstable Rectifying	0.502	0.498	0.50	0.50
28	-11.3	-9.1	-10.6	0.4306	0.0898	0.4796	-10.8	Unstable Rectifying	0.364	0.636	0.50	0.50
29	-11.3	-9.1	-10.6	0.7832	0.0458	0.1710	-11.1	Unstable Rectifying	0.465	0.535	0.50	0.50
30	-11.3	-9.1	-10.6	0.9286	0.0171	0.0543	-11.2	Unstable Rectifying	0.490	0.510	0.50	0.50
31	-11.3	-9.1	-10.6	0.9770	0.0056	0.0174	-11.3	Unstable Rectifying	0.497	0.503	0.50	0.50
32	-11.3	-9.1	-10.9	0.2466	0.0343	0.7191	-11.0	Unstable Stripping	0.225	0.775	0.50	0.50
33	-11.3	-9.1	-10.9	0.2413	0.0333	0.7255	-11.0	Unstable Rectifying	0.221	0.779	0.50	0.50
34	-11.3	-9.1	-10.9	0.7305	0.0306	0.2389	-11.1	Unstable Rectifying	0.440	0.560	0.50	0.50
35	-11.3	-9.1	-10.9	0.9115	0.0119	0.0766	-11.2	Unstable Rectifying	0.483	0.517	0.50	0.50
36	-11.3	-9.1	-10.9	0.9137	0.0124	0.0739	-11.2	Unstable Rectifying	0.484	0.516	0.50	0.50
37	-11.3	-9.1	-10.9	0.9714	0.0039	0.0025	-11.3	Unstable Rectifying	0.495	0.494	0.50	0.50
38	-11.3	-9.1	-10.9	0.9723	0.0041	0.0236	-11.3	Unstable Rectifying	0.495	0.505	0.50	0.50

Figure 61. A↔C+D α_{AD} =1.1: Reactive Azeotropes



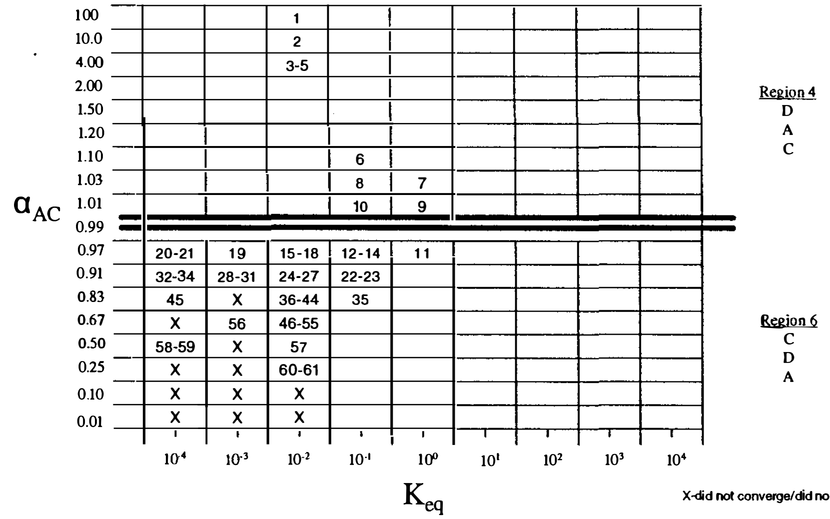
	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB.azeo	XC.azeo	XB.F	XC.F
1	-11.3	-10.4	108.0	0.4861	0.5042	0.0096	-10.6	Unstable Strip/Rect	0.666	0.334	0.50	0.50
2	-11.3	-10.4	108.0	0.8354	0.1593	0.0052	-11.0	Unstable Rectifying	0.542	0.458	0.50	0.50
3	-11.3	-10.4	108.0	0.9472	0.0510	0.0019	-11.2	Unstable Rectifying	0.513	0.487	0.50	0.50
4	-11.3	-10.4	108.0	0.9473	0.0508	0.0019	-11.2	Unstable Rectifying	0.513	0.487	0.50	0.50
5	-11.3	-10.6	46.3	0.4326	0.5596	0.0077	-10.7	Unstable Rectifying	0.693	0.307	0.50	0.50
6	-11.3	-10.6	46.3	0.4340	0.5582	0.0078	-10.7	Unstable Stripping	0.692	0.308	0.50	0.50
7	-11.3	-10.6	46.3	0.8180	0.1773	0.0046	-11.1	Unstable Rectifying	0.548	0.452	0.50	0.50
8	-11.3	-10.6	46.3	0.9424	0.0559	0.0017	-11.2	Unstable Rectifying	0.514	0.486	0.50	0.50
9	-11.3	-10.6	46.3	0.9420	0.0564	0.0017	-11.2	Unstable Rectifying	0.514	0.486	0.50	0.50
10	-11.3	-8.9	23.0	0.1254	0.8600	0.0146	-9.0	Unstable Stripping	0.876	0.124	0.50	0.50
11	-11.3	-8.9	23.0	0.6948	0.2804	0.0248	-10.2	Unstable Rectifying	0.575	0.425	0.50	0.50
12	-11.3	-8.9	23.0	0.9018	0.0879	0.0103	-10.9	Unstable Rectifying	0.520	0.480	0.50	0.50
13	-11.3	-8.9	23.0	0.9000	0.0900	0.0100	-10.9	Unstable Rectifying	0.521	0.479	0.50	0.50
14	-11.3	-8.9	23.0	0.9679	0.0288	0.0034	-11.2	Unstable Rectifying	0.506	0.494	0.50	0.50
15	-11.3	-10.6	5.8	0.5683	0.4181	0.0136	-10.8	Unstable Rectifying	0.629	0.371	0.50	0.50
16	-11.3	-10.6	5.8	0.5725	0.4137	0.0138	-10.8	Unstable Rectifying	0.627	0.373	0.50	0.50
17	-11.3	-10.6	5.8	0.8622	0.1312	0.0066	-11.1	Unstable Rectifying	0.533	0.467	0.50	0.50
18	-11.3	-10.6	5.8	0.9557	0.0420	0.0023	-11.2	Unstable Rectifying	0.510	0.490	0.50	0.50
19	-11.3	-10.6	-1.4	0.6553	0.3246	0.0202	-10.9	Unstable Rectifying	0.592	0.408	0.50	0.50
20	-11.3	-10.6	-1.4	0.8853	0.1064	0.0083	-11.2	Unstable Rectifying	0.526	0.474	0.50	0.50
21	-11.3	-10.6	-1.4	0.9631	0.0341	0.0028	-11.3	Unstable Rectifying	0.508	0.492	0.50	0.50
22	-11.3	-10.6	-6.8	0.2600	0.7030	0.0370	-10.6	Unstable Stripping	0.764	0.236	0.50	0.50
23	-11.3	-10.6	-6.8	0.2299	0.7390	0.0311	-10.6	Unstable Rectifying	0.788	0.212	0.50	0.50
24	-11.3	-10.6	-6.8	0.2651	0.6969	0.0380	-10.6	Unstable Rectifying	0.760	0.240	0.50	0.50
25	-11.3	-10.6	-6.8	0.7436	0.2230	0.0333	-11.0	Unstable Rectifying	0.554	0.446	0.50	0.50
26	-11.3	-10.6	-6.8	0.7433	0.2234	0.0333	-11.0	Unstable Rectifying	0.555	0.445	0.50	0.50
27	-11.3	-10.6	-6.8	0.9120	0.0760	0.0120	-11.2	Unstable Rectifying	0.517	0.483	0.50	0.50
28	-11.3	-10.6	-6.8	0.9735	0.0221	0.0044	-11.3	Unstable Rectifying	0.504	0.496	0.50	0.50
29	-11.3	-10.6	-6.8	0.9717	0.0243	0.0040	-11.3	Unstable Rectifying	0.505	0.495	0.50	0.50
30	-11.3	-10.6	-9.1	0.4306	0.4796	0.0898	-10.8	Unstable Rectifying	0.636	0.364	0.50	0.50
31	-11.3	-10.6	-9.1	0.7832	0.1710	0.0458	-11.1	Unstable Rectifying	0.535	0.465	0.50	0.50
32	-11.3	-10.6	-9.1	0.9286	0.0543	0.0171	-11.2	Unstable Rectifying	0.510	0.490	0.50	0.50
33	-11.3	-10.6	-9.1	0.9770	0.0174	0.0056	-11.3	Unstable Rectifying	0.503	0.497	0.50	0.50
34	-11.3	-10.6	-10.9	0.0014	0.9972	0.0014	-10.6	Stable Stripping	0.997	0.003	0.50	0.50
35	-11.3	-10.6	-10.9	0.0094	0.0096	0.9810	-10.6	Unstable Rectifying	0.019	0.981	0.50	0.50
36	-11.3	-10.6	-10.9	0.0087	0.0088	0.9825	-10.6	Unstable Rectifying	0.017	0.983	0.50	0.50
37	-11.3	-10.6	-10.9	0.0027	0.0027	0.9946	-10.6	Unstable Rectifying	0.005	0.995	0.50	0.50
38	-11.3	-10.6	-10.9	0.4967	0.1348	0.3686	-11.1	Unstable Rectifying	0.422	0.578	0.50	0.50
39	-11.3	-10.6	-10.9	0.4960	0.1340	0.3700	-11.1	Unstable Rectifying	0.421	0.579	0.50	0.50
40	-11.3	-10.6	-10.9	0.8049	0.0593	0.1348	-11.2	Unstable Rectifying	0.479	0.521	0.50	0.50
41	-11.3	-10.6	-10.9	0.8067	0.0609	0.1324	-11.2	Unstable Rectifying	0.480	0.520	0.50	0.50
42	-11.3	-10.6	-10.9	0.9348	0.0212	0.0440	-11.3	Unstable Rectifying	0.494	0.506	0.50	0.50
43	-11.3	-10.6	-10.9	0.9780	0.0069	0.0142	-11.3	Unstable Rectifying	0.498	0.502	0.50	0.50

Figure 62. A↔C+D α_{AD} =1.03: Reactive Azeotropes



	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	-11.3	-10.9	108.0	0.1710	0.8269	0.0021	-11.0	Unstable	Stripping	0.852	0.148	0.50	0.50
2	-11.3	-10.9	108.0	0.1747	0.8232	0.0021	-11.0	Unstable	Rectifying	0.849	0.151	0.50	0.50
3	-11.3	-10.9	108.0	0.7499	0.2470	0.0030	-11.1	Unstable	Rectifying	0.570	0.430	0.50	0.50
4	-11.3	-10.9	108.0	0.7312	0.2661	0.0027	-11.1	Unstable	Rectifying	0.576	0.424	0.50	0.50
5	-11.3	-10.9	108.0	0.7349	0.2623	0.0028	-11.1	Unstable	Rectifying	0.575	0.425	0.50	0.50
6	-11.3	-10.9	46.3	0.2024	0.7950	0.0025	-11.0	Unstable	Rectifying	0.830	0.170	0.50	0.50
7	-11.3	-10.9	46.3	0.2027	0.7948	0.0026	-11.0	Unstable	Stripping	0.829	0.171	0.50	0.50
8	-11.3	-10.9	46.3	0.7512	0.2458	0.0031	-11.1	Unstable	Rectifying	0.569	0.431	0.50	0.50
9	-11.3	-10.9	46.3	0.7585	0.2383	0.0032	-11.1	Unstable	Rectifying	0.567	0.433	0.50	0.50
10	-11.3	-10.9	46.3	0.9189	0.0799	0.0012	-11.2	Unstable	Rectifying	0.521	0.479	0.50	0.50
11	-11.3	-10.9	46.3	0.9342	0.0643	0.0015	-11.2	Unstable	Rectifying	0.516	0.484	0.50	0.50
12	-11.3	-10.9	46.3	0.9328	0.0658	0.0014	-11.2	Unstable	Rectifying	0.517	0.483	0.50	0.50
13	-11.3	-10.9	46.3	0.9077	0.0913	0.0001	-11.2	Unstable	Rectifying	0.524	0.476	0.50	0.50
14	-11.3	-10.9	46.3	0.9193	0.0795	0.0012	-11.2	Unstable	Rectifying	0.520	0.480	0.50	0.50
15	-11.3	-10.9	23.0	0.2704	0.7259	0.0037	-11.0	Unstable	Stripping	0.784	0.216	0.50	0.50
16	-11.3	-10.9	23.0	0.2489	0.7478	0.0033	-11.0	Unstable	Rectifying	0.798	0.202	0.50	0.50
17	-11.3	-10.9	5.8	0.4023	0.5909	0.0068	-11.0	Unstable	Rectifying	0.708	0.292	0.50	0.50
18	-11.3	-10.9	-1.4	0.6435	0.3374	0.0191	-11.0	Unstable	Rectifying	0.597	0.403	0.50	0.50
19	-11.3	-10.9	-1.4	0.8436	0.1508	0.0056	-11.2	Unstable	Rectifying	0.539	0.461	0.50	0.50
20	-11.3	-10.9	-1.4	0.9497	0.0483	0.0020	-11.3	Unstable	Rectifying	0.512	0.488	0.50	0.50
21	-11.3	-10.9	-6.8	0.6407	0.3405	0.0188	-11.1	Unstable	Rectifying	0.598	0.402	0.50	0.50
22	-11.3	-10.9	-6.8	0.6495	0.3309	0.0196	-11.1	Unstable	Rectifying	0.594	0.406	0.50	0.50
23	-11.3	-10.9	-6.8	0.8853	0.1064	0.0083	-11.2	Unstable	Rectifying	0.526	0.474	0.50	0.50
24	-11.3	-10.9	-9.1	0.2466	0.7191	0.0343	-11.0	Unstable	Stripping	0.775	0.225	0.50	0.50
25	-11.3	-10.9	-9.1	0.2413	0.7255	0.0333	-11.0	Unstable	Rectifying	0.779	0.221	0.50	0.50
26	-11.3	-10.9	-9.1	0.7305	0.2389	0.0306	-11.1	Unstable	Rectifying	0.560	0.440	0.50	0.50
27	-11.3	-10.9	-9.1	0.9115	0.0766	0.0119	-11.2	Unstable	Rectifying	0.517	0.483	0.50	0.50
28	-11.3	-10.9	-9.1	0.9137	0.0739	0.0124	-11.2	Unstable	Rectifying	0.516	0.484	0.50	0.50
29	-11.3	-10.9	-9.1	0.9714	0.0025	0.0039	-11.3	Unstable	Rectifying	0.494	0.495	0.50	0.50
30	-11.3	-10.9	-9.1	0.9723	0.0236	0.0041	-11.3	Unstable	Rectifying	0.505	0.495	0.50	0.50
31	-11.3	-10.9	-10.6	0.0014	0.0014	0.9972	-10.6	Stable	Stripping	0.003	0.997	0.50	0.50
32	-11.3	-10.9	-10.6	0.0094	0.9810	0.0096	-10.6	Unstable	Rectifying	0.981	0.019	0.50	0.50
33	-11.3	-10.9	-10.6	0.0087	0.9825	0.0088	-10.6	Unstable	Rectifying	0.983	0.017	0.50	0.50
34	-11.3	-10.9	-10.6	0.0027	0.9946	0.0027	-10.6	Unstable	Rectifying	0.995	0.005	0.50	0.50
35	-11.3	-10.9	-10.6	0.4967	0.3686	0.1348	-11.1	Unstable	Rectifying	0.578	0.422	0.50	0.50
36	-11.3	-10.9	-10.6	0.4960	0.3700	0.1340	-11.1	Unstable	Rectifying	0.579	0.421	0.50	0.50
37	-11.3	-10.9	-10.6	0.8049	0.1348	0.0593	-11.2	Unstable	Rectifying	0.521	0.479	0.50	0.50
38	-11.3	-10.9	-10.6	0.8067	0.1324	0.0609	-11.2	Unstable	Rectifying	0.520	0.480	0.50	0.50
39	-11.3	-10.9	-10.6	0.9348	0.0440	0.0212	-11.3	Unstable	Rectifying	0.506	0.494	0.50	0.50
40	-11.3	-10.9	-10.6	0.9780	0.0142	0.0069	-11.3	Unstable	Rectifying	0.502	0.498	0.50	0.50

Figure 63. A↔C+D α_{AD} =1.01: Reactive Azeotropes

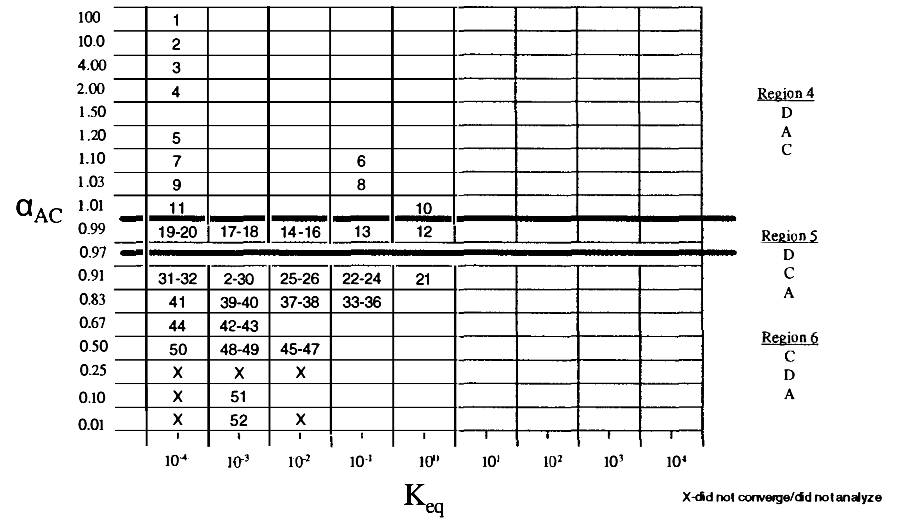


α_{AC}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100			1						
10.0			2						
4.00			3-5						
2.00									
1.50									
1.20									
1.10				6					
1.03				8	7				
1.01				10	9				
0.99									
0.97	20-21	19	15-18	12-14	11				
0.91	32-34	28-31	24-27	22-23					
0.83	45	X	36-44	35					
0.67	X	56	46-55						
0.50	58-59	X	57						
0.25	X	X	60-61						
0.10	X	X	X						
0.01	X	X	X						

X-did not converge/did not analyze

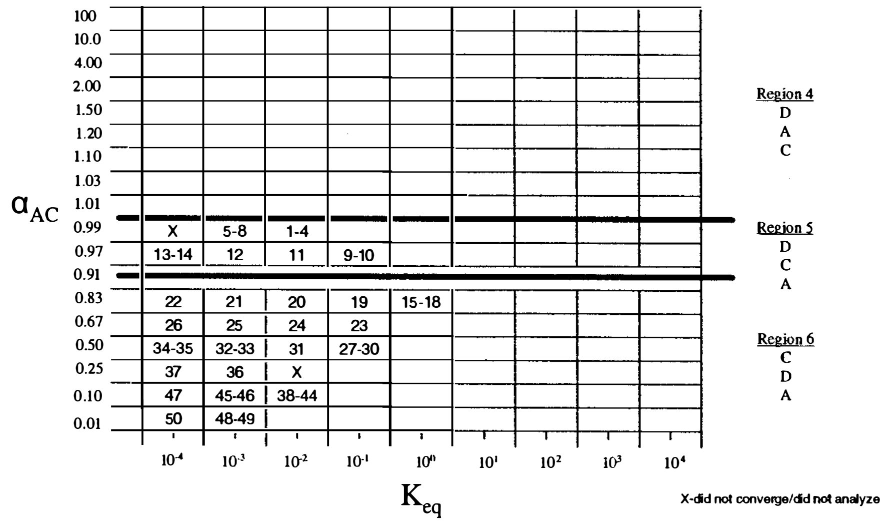
	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	-0.1	-0.4	122.4	0.0063	0.9936	0.0001	-0.4	Unstable	Rectifying	0.994	0.006	0.50	0.50
2	-0.1	-0.4	59.4	0.0063	0.9936	0.0001	-0.4	Unstable	Rectifying	0.994	0.006	0.50	0.50
3	-0.1	-0.4	35.3	0.0073	0.9926	0.0001	-0.4	Unstable	Rectifying	0.993	0.007	0.50	0.50
4	-0.1	-0.4	35.3	0.0072	0.9927	0.0001	-0.4	Unstable	Rectifying	0.993	0.007	0.50	0.50
5	-0.1	-0.4	35.3	0.0056	0.9943	0.0001	-0.4	Unstable	Rectifying	0.994	0.006	0.50	0.50
6	-0.1	-0.4	2.3	0.0091	0.9900	0.0009	-0.4	Unstable	Rectifying	0.990	0.010	0.50	0.50
7	-0.1	-0.4	0.6	0.0014	0.9972	0.0014	-0.4	Unstable	Rectifying	0.997	0.003	0.50	0.50
8	-0.1	-0.4	0.6	0.0092	0.9898	0.0009	-0.4	Unstable	Rectifying	0.990	0.010	0.50	0.50
9	-0.1	-0.4	0.2	0.0014	0.9972	0.0014	-0.4	Unstable	Rectifying	0.997	0.003	0.50	0.50
10	-0.1	-0.4	0.2	0.0927	0.9898	0.0009	-0.4	Unstable	Rectifying	0.991	0.086	0.50	0.50
11	121.6	121.3	120.7	0.0014	0.9972	0.0014	121.3	Stable	Stripping	0.997	0.003	0.50	0.50
12	121.6	121.3	120.7	0.3545	0.5849	0.0606	121.4	Stable	Stripping	0.694	0.306	0.50	0.50
13	121.6	121.3	120.7	0.3463	0.5955	0.0582	121.4	Stable	Stripping	0.700	0.300	0.50	0.50
14	121.6	121.3	120.7	0.0098	0.9892	0.0010	121.3	Unstable	Rectifying	0.989	0.011	0.50	0.50
15	121.6	121.3	120.7	0.7811	0.1741	0.0449	121.5	Stable	Stripping	0.536	0.464	0.50	0.50
16	121.6	121.3	120.7	0.0098	0.9901	0.0001	121.3	Unstable	Rectifying	0.990	0.010	0.50	0.50
17	121.6	121.3	120.7	0.0079	0.9920	0.0001	121.3	Unstable	Rectifying	0.992	0.008	0.50	0.50
18	121.6	121.3	120.7	0.0045	0.9955	0.0000	121.3	Unstable	Rectifying	0.996	0.004	0.50	0.50
19	121.6	121.3	120.7	0.9235	0.0615	0.0150	121.5	Stable	Stripping	0.512	0.488	0.50	0.50
20	121.6	121.3	120.7	0.9752	0.0198	0.0049	121.5	Stable	Stripping	0.504	0.496	0.50	0.50
21	121.6	121.3	120.7	0.9735	0.0221	0.0044	121.5	Stable	Stripping	0.504	0.496	0.50	0.50
22	121.6	121.3	118.3	0.0057	0.9937	0.0006	121.3	Stable	Stripping	0.994	0.006	0.50	0.50
23	121.6	121.3	118.3	0.0122	0.9865	0.0012	121.3	Stable	Stripping	0.987	0.013	0.50	0.50
24	121.6	121.3	118.3	0.5872	0.3981	0.0148	121.4	Stable	Stripping	0.621	0.379	0.50	0.50
25	121.6	121.3	118.3	0.5724	0.4138	0.0138	121.4	Stable	Stripping	0.627	0.373	0.50	0.50
26	121.6	121.3	118.3	0.0122	0.9877	0.0001	121.3	Unstable	Rectifying	0.988	0.012	0.50	0.50
27	121.6	121.3	118.3	0.0047	0.9953	0.0000	121.3	Unstable	Rectifying	0.995	0.005	0.50	0.50
28	121.6	121.3	118.3	0.8536	0.1403	0.0061	121.5	Stable	Stripping	0.536	0.464	0.50	0.50
29	121.6	121.3	118.3	0.8869	0.1046	0.0085	121.5	Stable	Stripping	0.525	0.475	0.50	0.50
30	121.6	121.3	118.3	0.8515	0.1425	0.0060	121.5	Stable	Stripping	0.537	0.463	0.50	0.50
31	121.6	121.3	118.3	0.8376	0.1571	0.0053	121.5	Stable	Stripping	0.541	0.459	0.50	0.50
32	121.6	121.3	118.3	0.9587	0.0388	0.0025	121.5	Stable	Stripping	0.509	0.491	0.50	0.50
33	121.6	121.3	118.3	0.9124	0.0866	0.0011	121.5	Stable	Stripping	0.522	0.478	0.50	0.50
34	121.6	121.3	118.3	0.8969	0.1022	0.0009	121.5	Stable	Stripping	0.527	0.473	0.50	0.50
35	121.6	121.3	115.2	0.0092	0.9899	0.0009	121.3	Stable	Stripping	0.990	0.010	0.50	0.50
36	121.6	121.3	115.2	0.4862	0.5042	0.0096	121.4	Stable	Stripping	0.666	0.334	0.50	0.50
37	121.6	121.3	115.2	0.4863	0.5041	0.0096	121.4	Stable	Stripping	0.666	0.334	0.50	0.50
38	121.6	121.3	115.2	0.4417	0.5503	0.0080	121.4	Stable	Stripping	0.688	0.312	0.50	0.50
39	121.6	121.3	115.2	0.5099	0.4795	0.0106	121.4	Stable	Stripping	0.655	0.345	0.50	0.50
40	121.6	121.3	115.2	0.5255	0.4632	0.0113	121.4	Stable	Stripping	0.648	0.352	0.50	0.50
41	121.6	121.3	115.2	0.5262	0.4624	0.0114	121.4	Stable	Stripping	0.648	0.352	0.50	0.50
42	121.6	121.3	115.2	0.5265	0.4621	0.0114	121.4	Stable	Stripping	0.648	0.352	0.50	0.50
43	121.6	121.3	115.2	0.0240	0.9949	0.0001	121.3	Unstable	Rectifying	0.995	0.023	0.50	0.50
44	121.6	121.3	115.2	0.0050	0.9949	0.0001	121.3	Unstable	Rectifying	0.995	0.005	0.50	0.50
45	121.6	121.3	115.2	0.9427	0.0557	0.0017	121.5	Stable	Stripping	0.514	0.486	0.50	0.50
46	121.6	121.3	108.0	0.0560	0.9434	0.0006	121.3	Unstable	Stripping	0.946	0.054	0.50	0.50
47	121.6	121.3	108.0	0.2441	0.7527	0.0032	121.3	Stable	Stripping	0.801	0.199	0.50	0.50
48	121.6	121.3	108.0	0.0318	0.9678	0.0003	121.3	Unstable	Stripping	0.969	0.031	0.50	0.50
49	121.6	121.3	108.0	0.0189	0.9809	0.0002	121.3	Unstable	Stripping	0.981	0.019	0.50	0.50
50	121.6	121.3	108.0	0.2641	0.7323	0.0036	121.3	Stable	Stripping	0.788	0.212	0.50	0.50
51	121.6	121.3	108.0	0.2656	0.7308	0.0036	121.3	Stable	Stripping	0.787	0.213	0.50	0.50
52	121.6	121.3	108.0	0.0103	0.9896	0.0001	121.3	Unstable	Stripping	0.990	0.010	0.50	0.50
53	121.6	121.3	108.0	0.2817	0.7143	0.0039	121.3	Stable	Stripping	0.777	0.223	0.50	0.50
54	121.6	121.3	108.0	0.1635	0.8346	0.0020	121.3	Stable	Rectifying	0.858	0.142	0.50	0.50
55	121.6	121.3	108.0	0.1128	0.8859	0.0013	121.3	Stable	Rectifying	0.898	0.102	0.50	0.50
56	121.6	121.3	108.0	0.6735	0.3244	0.0021	121.4	Stable	Stripping	0.596	0.404	0.50	0.50
57	121.6	121.3	98.0	0.0093	0.9906	0.0001	121.3	Stable	Stripping	0.991	0.009	0.50	0.50
58	121.6	121.3	98.0	0.8462	0.1532	0.0006	121.5	Stable	Stripping	0.541	0.459	0.50	0.50
59	121.6	121.3	98.0	0.8281	0.1714	0.0005	121.5	Stable	Stripping	0.547	0.453	0.50	0.50
60	121.6	121.3	75.1	0.0053	0.9947	0.0001	121.3	Stable	Stripping	0.995	0.005	0.50	0.50
61	121.6	121.3	75.1	0.0060	0.9939	0.0001	121.3	Stable	Stripping	0.994	0.006	0.50	0.50

Figure 64. A↔C+D α_{AD} =0.99: Reactive Azeotropes



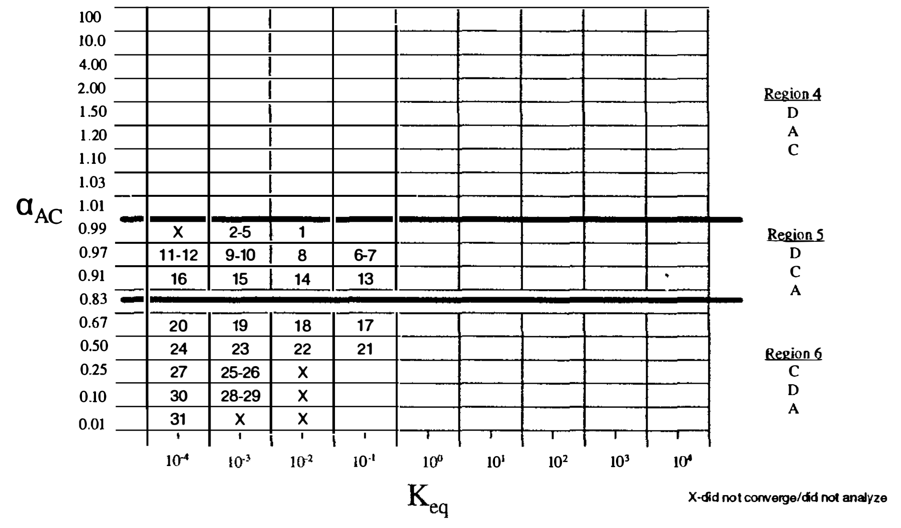
	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
1	-0.1	-0.9	122.4	0.0023	0.9977	0.0000	-0.9	Unstable	Rectifying	0.998	0.002	0.50	0.50
2	-0.1	-0.9	59.3	0.0021	0.9979	0.0000	-1.0	Unstable	Rectifying	0.998	0.002	0.50	0.50
3	-0.1	-0.9	35.3	0.0021	0.9979	0.0000	-1.0	Unstable	Rectifying	0.998	0.002	0.50	0.50
4	-0.1	-0.9	17.5	0.0021	0.9979	0.0000	-1.0	Unstable	Rectifying	0.998	0.002	0.50	0.50
5	-0.1	-0.8	4.4	0.0044	0.9956	0.0000	-0.8	Unstable	Rectifying	0.996	0.004	0.50	0.50
6	-0.1	-0.8	2.2	0.0027	0.9971	0.0003	-0.8	Unstable	Rectifying	0.997	0.003	0.50	0.50
7	-0.1	-0.8	2.2	0.0044	0.9956	0.0000	-0.8	Unstable	Rectifying	0.996	0.004	0.50	0.50
8	-0.1	-0.8	0.6	0.0027	0.9971	0.0003	-0.8	Unstable	Rectifying	0.997	0.003	0.50	0.50
9	-0.1	-0.8	0.6	0.0044	0.9956	0.0000	-0.8	Unstable	Rectifying	0.996	0.004	0.50	0.50
10	-0.1	-0.8	0.2	0.0014	0.9972	0.0014	-0.8	Unstable	Rectifying	0.997	0.003	0.50	0.50
11	-0.1	-0.8	0.2	0.0044	0.9956	0.0000	-0.8	Unstable	Rectifying	0.996	0.004	0.50	0.50
12	121.6	121.3	120.7	0.0014	0.9972	0.0014	120.7	Unstable	Rectifying	0.997	0.003	0.50	0.50
13	121.6	121.3	120.7	0.3550	0.0607	0.5843	1212.4	Stable	Stripping	0.307	0.693	0.50	0.50
14	121.6	121.3	120.7	0.7701	0.0407	0.1892	121.5	Stable	Stripping	0.458	0.542	0.50	0.50
15	121.6	121.3	120.7	0.7710	0.0410	0.1880	121.5	Stable	Stripping	0.458	0.542	0.50	0.50
16	121.6	121.3	120.7	0.7682	0.0401	0.1917	121.5	Stable	Stripping	0.457	0.543	0.50	0.50
17	121.6	121.3	120.7	0.9243	0.0153	0.0604	121.5	Stable	Stripping	0.488	0.512	0.50	0.50
18	121.6	121.3	120.7	0.9259	0.0159	0.0582	121.5	Stable	Stripping	0.489	0.511	0.50	0.50
19	121.6	121.3	120.7	0.9750	0.0048	0.0201	121.5	Stable	Stripping	0.496	0.504	0.50	0.50
20	121.6	120.7	121.3	0.9753	0.0049	0.0197	121.5	Stable	Stripping	0.496	0.504	0.50	0.50
21	121.6	120.7	118.3	0.0014	0.9972	0.0014	120.7	Stable	Stripping	0.997	0.003	0.50	0.50
22	121.6	120.7	118.3	0.3805	0.5504	0.0691	120.8	Stable	Stripping	0.674	0.326	0.50	0.50
23	121.6	120.7	118.3	0.4008	0.5225	0.0767	120.8	Stable	Rectifying	0.659	0.341	0.50	0.50
24	121.6	120.7	118.3	0.0091	0.9900	0.0009	120.7	Unstable	Rectifying	0.990	0.010	0.50	0.50
25	121.6	120.7	118.3	0.7751	0.1824	0.0425	121.3	Stable	Stripping	0.539	0.461	0.50	0.50
26	121.6	120.7	118.3	0.7627	0.1990	0.0383	121.3	Stable	Stripping	0.546	0.454	0.50	0.50
27	121.6	120.7	118.3	0.9237	0.0612	0.0151	121.5	Stable	Stripping	0.512	0.488	0.50	0.50
28	121.6	120.7	118.3	0.9236	0.0614	0.0150	121.5	Stable	Stripping	0.512	0.488	0.50	0.50
29	121.6	120.7	118.3	0.9154	0.0718	0.0127	121.4	Stable	Stripping	0.515	0.485	0.50	0.50
30	121.6	120.7	118.3	0.9238	0.0610	0.0151	121.4	Stable	Stripping	0.512	0.488	0.50	0.50
31	121.6	120.7	118.3	0.9755	0.0195	0.0050	121.5	Stable	Stripping	0.504	0.496	0.50	0.50
32	121.6	120.7	118.3	0.9716	0.0245	0.0040	121.5	Stable	Stripping	0.505	0.495	0.50	0.50
33	121.6	120.7	115.2	0.0531	0.9413	0.0056	120.7	Unstable	Stripping	0.944	0.056	0.50	0.50
34	121.6	120.7	115.2	0.0469	0.9482	0.0049	120.7	Unstable	Stripping	0.951	0.049	0.50	0.50
35	121.6	120.7	115.2	0.1546	0.8267	0.0187	120.7	Stable	Rectifying	0.850	0.150	0.50	0.50
36	121.6	120.7	115.2	0.0093	0.9897	0.0009	120.7	Unstable	Rectifying	0.990	0.010	0.50	0.50
37	121.6	120.7	115.2	0.6993	0.2753	0.0254	121.1	Stable	Stripping	0.574	0.426	0.50	0.50
38	121.6	120.7	115.2	0.6895	0.2864	0.0241	121.1	Stable	Stripping	0.578	0.422	0.50	0.50
39	121.6	120.7	115.2	0.9032	0.0864	0.0105	121.4	Stable	Stripping	0.520	0.480	0.50	0.50
40	121.6	120.7	115.2	0.8917	0.0993	0.0090	121.4	Stable	Stripping	0.524	0.476	0.50	0.50
41	121.6	120.7	115.2	0.9685	0.0280	0.0035	121.5	Stable	Stripping	0.506	0.494	0.50	0.50
42	121.6	120.7	108.0	0.8515	0.1425	0.0060	121.3	Stable	Stripping	0.537	0.463	0.50	0.50
43	121.6	120.7	108.0	0.8582	0.1355	0.0063	121.3	Stable	Stripping	0.535	0.465	0.50	0.50
44	121.6	120.7	108.0	0.9547	0.0430	0.0022	121.5	Stable	Stripping	0.510	0.490	0.50	0.50
45	121.6	120.7	98.0	0.3965	0.5968	0.0066	120.8	Stable	Stripping	0.711	0.289	0.50	0.50
46	121.6	120.7	98.0	0.4174	0.5754	0.0073	120.8	Stable	Stripping	0.700	0.300	0.50	0.50
47	121.6	120.7	98.0	0.3916	0.6019	0.0065	120.8	Stable	Rectifying	0.714	0.286	0.50	0.50
48	121.6	120.7	98.0	0.7950	0.2010	0.0040	121.2	Stable	Stripping	0.555	0.445	0.50	0.50
49	121.6	120.7	98.0	0.8037	0.1921	0.0042	121.2	Stable	Stripping	0.552	0.448	0.50	0.50
50	121.6	120.7	98.0	0.9375	0.0609	0.0015	121.4	Stable	Stripping	0.515	0.485	0.50	0.50
51	121.6	120.7	45.8	0.4816	0.5175	0.0009	120.9	Stable	Stripping	0.674	0.326	0.50	0.50
52	121.6	120.7	-24.6	0.0099	0.9901	0.0000	120.7	Stable	Rectifying	0.990	0.010	0.50	0.50

Figure 65. A↔C+D α_{AD} =0.97: Reactive Azeotropes



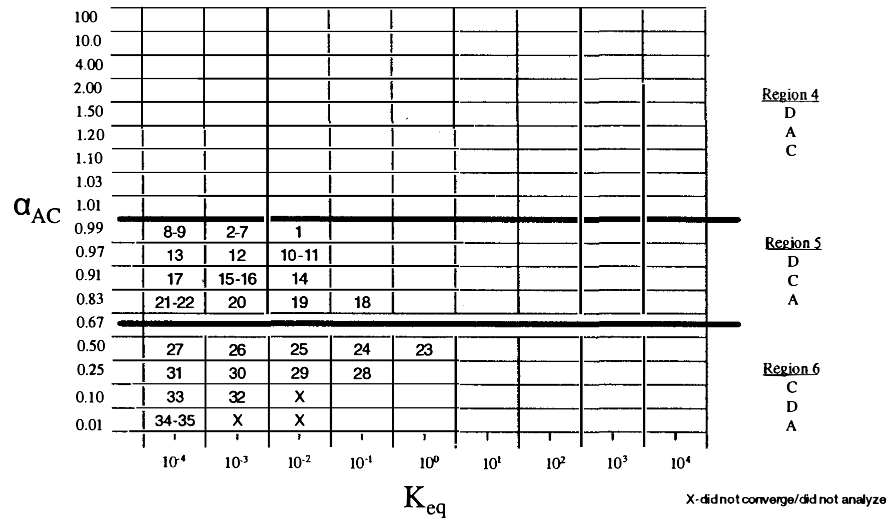
	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
1	121.6	118.3	121.3	0.6034	0.0158	0.3808	121.4	Stable	Stripping	0.386	0.614	0.50	0.50
2	121.6	118.3	121.3	0.6010	0.0157	0.3831	121.4	Stable	Stripping	0.385	0.615	0.50	0.50
3	121.6	118.3	121.3	0.6146	0.0167	0.3688	121.4	Stable	Stripping	0.391	0.609	0.50	0.50
4	121.6	118.3	121.3	0.6195	0.0170	0.3635	121.4	Stable	Stripping	0.393	0.607	0.50	0.50
5	121.6	118.3	121.3	0.8702	0.0071	0.1227	121.5	Stable	Stripping	0.469	0.531	0.50	0.50
6	121.6	118.3	121.3	0.8755	0.0075	0.1170	121.5	Stable	Stripping	0.471	0.529	0.50	0.50
7	121.6	118.3	121.3	0.8819	0.0080	0.1106	121.5	Stable	Stripping	0.473	0.527	0.50	0.50
8	121.6	118.3	121.3	0.8864	0.0084	0.1052	121.5	Stable	Stripping	0.474	0.526	0.50	0.50
9	121.6	118.3	120.7	0.3805	0.0691	0.5504	120.8	Stable	Stripping	0.326	0.674	0.50	0.50
10	121.6	118.3	120.7	0.3805	0.0691	0.5504	120.8	Stable	Rectifying	0.326	0.674	0.50	0.50
11	121.6	118.3	120.7	0.7652	0.0391	0.1957	121.3	Stable	Stripping	0.456	0.544	0.50	0.50
12	121.6	118.3	120.7	0.9237	0.0151	0.0612	121.5	Stable	Stripping	0.488	0.512	0.50	0.50
13	121.6	118.3	120.7	0.9757	0.0051	0.0193	121.5	Stable	Stripping	0.496	0.504	0.50	0.50
14	121.6	118.3	120.7	0.9755	0.0050	0.0195	121.5	Stable	Stripping	0.496	0.504	0.50	0.50
15	121.6	118.3	115.4	0.0047	0.9905	0.0048	118.3	Stable	Stripping	0.991	0.009	0.50	0.50
16	121.6	118.3	115.4	0.0050	0.9900	0.0050	118.3	Stable	Stripping	0.990	0.010	0.50	0.50
17	121.6	118.3	115.4	0.0033	0.9934	0.0033	118.3	Stable	Stripping	0.993	0.007	0.50	0.50
18	121.6	118.3	115.4	0.0065	0.9870	0.0065	118.3	Stable	Stripping	0.987	0.013	0.50	0.50
19	121.6	118.3	115.4	0.4975	0.3668	0.1356	119.5	Stable	Stripping	0.577	0.423	0.50	0.50
20	121.6	118.3	115.4	0.8072	0.1314	0.0614	120.7	Stable	Stripping	0.519	0.481	0.50	0.50
21	121.6	118.3	115.4	0.9350	0.0435	0.0215	121.3	Stable	Stripping	0.506	0.494	0.50	0.50
22	121.6	118.3	115.4	0.9790	0.0140	0.0070	121.5	Stable	Stripping	0.502	0.498	0.50	0.50
23	121.6	118.5	108.0	0.2979	0.6568	0.0454	118.8	Stable	Strip/Rect	0.736	0.264	0.50	0.50
24	121.6	118.5	108.0	0.7467	0.2192	0.0341	120.3	Stable	Stripping	0.553	0.447	0.50	0.50
25	121.6	118.5	108.0	0.9160	0.0711	0.0129	121.1	Stable	Stripping	0.515	0.485	0.50	0.50
26	121.6	118.5	108.0	0.9730	0.0227	0.0043	121.4	Stable	Stripping	0.505	0.495	0.50	0.50
27	121.6	118.5	98.0	0.0328	0.9638	0.0034	118.5	Stable	Stripping	0.965	0.035	0.50	0.50
28	121.6	118.5	98.0	0.0127	0.9860	0.0013	118.5	Stable	Stripping	0.986	0.014	0.50	0.50
29	121.6	118.5	98.0	0.0387	0.9572	0.0040	118.5	Stable	Stripping	0.959	0.041	0.50	0.50
30	121.6	118.5	98.0	0.0400	0.9558	0.0042	118.5	Stable	Stripping	0.958	0.042	0.50	0.50
31	121.6	118.5	98.0	0.6644	0.3145	0.0211	119.9	Stable	Stripping	0.588	0.412	0.50	0.50
32	121.6	118.5	98.0	0.8903	0.1009	0.0088	121.0	Stable	Stripping	0.524	0.476	0.50	0.50
33	121.6	118.5	98.0	0.8901	0.1011	0.0088	120.9	Stable	Stripping	0.524	0.476	0.50	0.50
34	121.6	118.5	98.0	0.9652	0.0318	0.0030	121.4	Stable	Stripping	0.507	0.493	0.50	0.50
35	121.6	118.5	98.0	0.9648	0.0322	0.0030	121.3	Stable	Stripping	0.507	0.493	0.50	0.50
36	121.6	118.5	76.0	0.8282	0.1668	0.0050	120.6	Stable	Stripping	0.544	0.456	0.50	0.50
37	121.6	118.5	76.0	0.9453	0.0529	0.0018	121.2	Stable	Stripping	0.513	0.487	0.50	0.50
38	121.6	118.7	45.8	0.0857	0.9134	0.0009	118.8	Stable	Stripping	0.920	0.080	0.50	0.50
39	121.6	118.7	45.8	0.0853	0.9138	0.0009	118.8	Stable	Stripping	0.921	0.079	0.50	0.50
40	121.6	118.7	45.8	0.0985	0.9004	0.0011	118.8	Stable	Stripping	0.909	0.091	0.50	0.50
41	121.6	118.7	45.8	0.1103	0.8884	0.0012	118.8	Stable	Rectifying	0.900	0.100	0.50	0.50
42	121.6	118.7	45.8	0.0108	0.9891	0.0001	118.7	Unstable	Rectifying	0.989	0.011	0.50	0.50
43	121.6	118.7	45.8	0.0077	0.9923	0.0001	118.7	Unstable	Rectifying	0.992	0.008	0.50	0.50
44	121.6	118.7	45.8	0.0053	0.9946	0.0001	118.7	Unstable	Rectifying	0.995	0.005	0.50	0.50
45	121.6	118.7	45.8	0.7170	0.2804	0.0026	120.2	Stable	Stripping	0.581	0.419	0.50	0.50
46	121.6	118.7	45.8	0.7195	0.2779	0.0026	120.2	Stable	Stripping	0.580	0.420	0.50	0.50
47	121.6	118.7	45.8	0.9090	0.0900	0.0010	121.1	Stable	Stripping	0.523	0.477	0.50	0.50
48	121.6	119.0	-24.6	0.2678	0.7318	0.0004	119.1	Stable	Stripping	0.788	0.212	0.50	0.50
49	121.6	119.0	-24.6	0.2783	0.7213	0.0004	119.1	Stable	Rectifying	0.782	0.218	0.50	0.50
50	121.6	119.0	-24.6	0.7698	0.2299	0.0003	120.3	Stable	Stripping	0.565	0.435	0.50	0.50

Figure 66. A↔C+D α_{AD} =0.91: Reactive Azeotropes



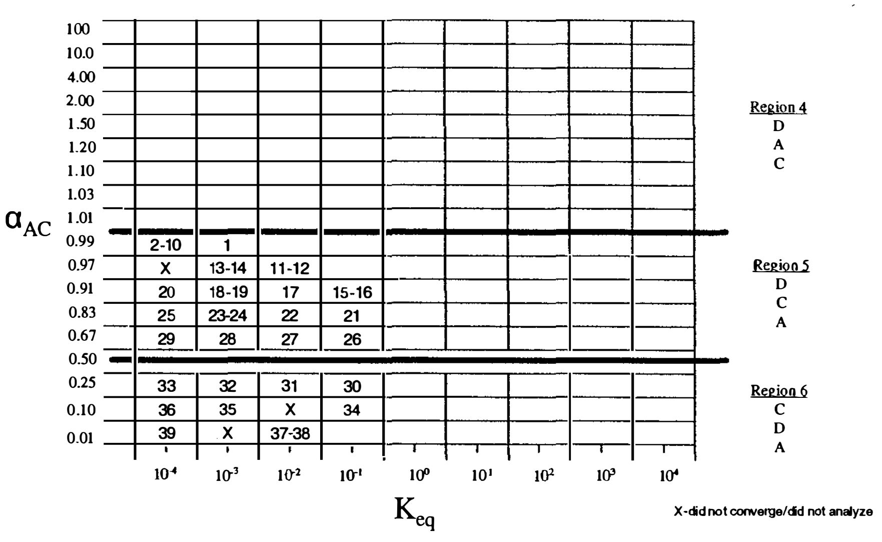
	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
1	121.6	115.3	121.3	0.4503	0.0083	0.5413	121.4	Stable	Stripping	0.316	0.684	0.50	0.50
2	121.6	115.3	121.3	0.8197	0.0047	0.1757	121.5	Stable	Stripping	0.453	0.547	0.50	0.50
3	121.6	115.3	121.3	0.8405	0.0055	0.1541	121.5	Stable	Stripping	0.460	0.540	0.50	0.50
4	121.6	115.3	121.3	0.8490	0.0059	0.1451	121.5	Stable	Stripping	0.462	0.538	0.50	0.50
5	121.6	115.3	121.3	0.8215	0.0047	0.1738	121.5	Stable	Stripping	0.454	0.546	0.50	0.50
6	121.6	115.3	120.7	0.1570	0.0191	0.8239	120.7	Stable	Stripping	0.152	0.848	0.50	0.50
7	121.6	115.3	120.7	0.1570	0.0191	0.8240	120.7	Stable	Rectifying	0.152	0.848	0.50	0.50
8	121.6	115.3	120.7	0.7050	0.0262	0.2687	121.1	Stable	Stripping	0.429	0.571	0.50	0.50
9	121.6	115.3	120.7	0.9027	0.0104	0.0869	121.4	Stable	Stripping	0.480	0.520	0.50	0.50
10	121.6	115.3	120.7	0.9055	0.0108	0.0836	121.4	Stable	Stripping	0.481	0.519	0.50	0.50
11	121.6	115.3	120.7	0.9687	0.0035	0.0278	121.5	Stable	Stripping	0.494	0.506	0.50	0.50
12	121.6	115.3	120.7	0.9703	0.0037	0.0259	121.5	Stable	Stripping	0.494	0.506	0.50	0.50
13	121.6	115.3	118.4	0.4911	0.1294	0.3796	119.5	Stable	Strip/Rect	0.416	0.584	0.50	0.50
14	121.6	115.3	118.4	0.8052	0.0595	0.1353	120.7	Stable	Stripping	0.479	0.521	0.50	0.50
15	121.6	115.3	118.4	0.9344	0.0209	0.0448	121.3	Stable	Stripping	0.494	0.506	0.50	0.50
16	121.6	115.3	118.4	0.9788	0.0068	0.0144	121.5	Stable	Stripping	0.498	0.502	0.50	0.50
17	121.6	115.3	108.0	0.4719	0.4141	0.1140	117.1	Stable	Strip/Rect	0.602	0.398	0.50	0.50
18	121.6	115.3	108.0	0.7994	0.1457	0.0549	119.7	Stable	Stripping	0.525	0.475	0.50	0.50
19	121.6	115.3	108.0	0.9326	0.0480	0.0194	120.9	Stable	Stripping	0.507	0.493	0.50	0.50
20	121.6	115.3	108.0	0.9783	0.0154	0.0064	121.3	Stable	Stripping	0.502	0.498	0.50	0.50
21	121.6	115.3	98.4	0.3273	0.6199	0.0528	116.0	Stable	Strip/Rect	0.714	0.286	0.50	0.50
22	121.6	115.3	98.4	0.7558	0.2078	0.0364	119.0	Stable	Stripping	0.549	0.451	0.50	0.50
23	121.6	115.3	98.4	0.9196	0.0666	0.0138	120.7	Stable	Stripping	0.514	0.486	0.50	0.50
24	121.6	115.3	98.4	0.9739	0.0215	0.0045	121.3	Stable	Stripping	0.504	0.496	0.50	0.50
25	121.6	115.7	76.0	0.8754	0.1171	0.0075	120.2	Stable	Stripping	0.529	0.471	0.50	0.50
26	121.6	115.7	76.0	0.8750	0.1175	0.0074	120.2	Stable	Stripping	0.529	0.471	0.50	0.50
27	121.6	115.7	76.0	0.9602	0.0373	0.0026	121.1	Stable	Stripping	0.509	0.491	0.50	0.50
28	121.6	115.9	45.8	0.7968	0.1992	0.0040	119.4	Stable	Stripping	0.554	0.446	0.50	0.50
29	121.6	115.9	45.8	0.7987	0.1973	0.0040	119.4	Stable	Stripping	0.554	0.446	0.50	0.50
30	121.6	115.9	45.8	0.9361	0.0624	0.0015	120.8	Stable	Stripping	0.516	0.484	0.50	0.50
31	121.6	116.5	-22.6	0.8414	0.1581	0.0005	120.0	Stable	Stripping	0.543	0.457	0.50	0.50

Figure 67. A↔C+D α_{AD} =0.83: Reactive Azeotropes



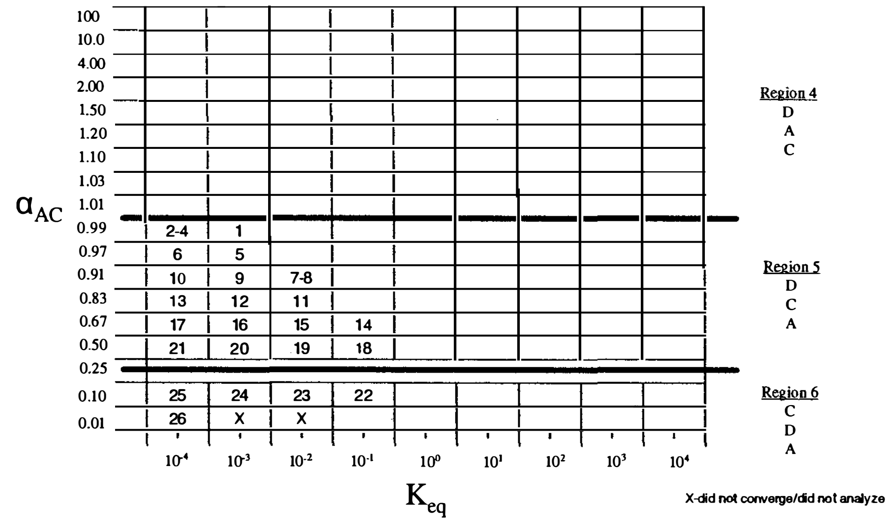
	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
1	121.6	108.0	121.2	0.2272	0.0030	0.7698	121.3	Stable	Stripping	0.168	0.812	0.50	0.50
2	121.6	108.0	121.2	0.7750	0.0035	0.2215	121.4	Stable	Stripping	0.439	0.561	0.50	0.50
3	121.6	108.0	121.2	0.7706	0.0034	0.2260	121.4	Stable	Stripping	0.437	0.563	0.50	0.50
4	121.6	108.0	121.2	0.7850	0.0037	0.2112	121.4	Stable	Stripping	0.442	0.558	0.50	0.50
5	121.6	108.0	121.2	0.8003	0.0041	0.1957	121.4	Stable	Stripping	0.447	0.553	0.50	0.50
6	121.6	108.0	121.2	0.8096	0.0044	0.1861	121.4	Stable	Stripping	0.450	0.550	0.50	0.50
7	121.6	106.0	121.2	0.8098	0.0044	0.1859	121.4	Stable	Stripping	0.450	0.550	0.50	0.50
8	121.6	108.0	121.2	0.9268	0.0013	0.0719	121.5	Stable	Stripping	0.482	0.518	0.50	0.50
9	121.6	108.0	121.2	0.9285	0.0013	0.0702	121.5	Stable	Stripping	0.482	0.518	0.50	0.50
10	121.6	108.0	120.7	0.5635	0.0133	0.4232	121.0	Stable	Stripping	0.369	0.631	0.50	0.50
11	121.6	108.0	120.7	0.5573	0.0130	0.4297	121.0	Stable	Stripping	0.366	0.634	0.50	0.50
12	121.6	108.0	120.7	0.8586	0.0064	0.1351	121.3	Stable	Stripping	0.465	0.535	0.50	0.50
13	121.6	108.0	120.7	0.9547	0.0022	0.0430	121.5	Stable	Stripping	0.490	0.510	0.50	0.50
14	121.6	108.0	115.3	0.7532	0.0357	0.2112	120.3	Stable	Stripping	0.450	0.550	0.50	0.50
15	121.6	108.0	115.3	0.9180	0.0134	0.0686	121.1	Stable	Stripping	0.486	0.514	0.50	0.50
16	121.6	108.0	115.3	0.9165	0.0130	0.0705	121.1	Stable	Stripping	0.485	0.515	0.50	0.50
17	121.6	108.0	115.3	0.9737	0.0044	0.0219	121.4	Stable	Stripping	0.496	0.504	0.50	0.50
18	121.6	108.0	115.3	0.4661	0.1099	0.4239	117.2	Stable	Strip/Rect	0.393	0.607	0.50	0.50
19	121.6	106.0	115.3	0.7977	0.0537	0.1487	119.7	Stable	Stripping	0.474	0.526	0.50	0.50
20	121.6	108.0	115.3	0.9320	0.0191	0.0489	120.9	Stable	Stripping	0.492	0.506	0.50	0.50
21	121.6	108.0	115.3	0.9780	0.0062	0.0158	121.4	Stable	Stripping	0.498	0.502	0.50	0.50
22	121.6	108.0	115.3	0.9781	0.0062	0.0157	121.3	Stable	Stripping	0.498	0.502	0.50	0.50
23	121.6	108.4	98.7	0.0001	0.9998	0.0001	108.4	Stable	Stripping	1.000	0.000	0.50	0.50
24	121.6	108.4	98.7	0.4954	0.3711	0.1335	112.6	Stable	Strip/Rect	0.579	0.421	0.50	0.50
25	121.6	108.4	98.7	0.8066	0.1325	0.0609	117.7	Stable	Stripping	0.520	0.480	0.50	0.50
26	121.6	108.4	98.7	0.9348	0.0438	0.0213	120.2	Stable	Stripping	0.506	0.494	0.50	0.50
27	121.6	108.4	98.7	0.9790	0.0141	0.0070	121.1	Stable	Stripping	0.502	0.498	0.50	0.50
28	121.6	108.8	76.0	0.2516	0.7132	0.0353	109.7	Stable	Strip/Rect	0.771	0.229	0.50	0.50
29	121.6	108.8	76.0	0.7341	0.2346	0.0313	115.7	Stable	Strip/Rect	0.559	0.441	0.50	0.50
30	121.6	108.8	76.0	0.9123	0.0756	0.0121	119.4	Stable	Stripping	0.517	0.483	0.50	0.50
31	121.6	108.8	76.0	0.9719	0.0241	0.0040	120.8	Stable	Stripping	0.505	0.495	0.50	0.50
32	121.6	109.4	46.8	0.8670	0.1262	0.0069	118.3	Stable	Stripping	0.532	0.468	0.50	0.50
33	121.6	109.4	46.8	0.9577	0.0399	0.0024	120.4	Stable	Stripping	0.510	0.490	0.50	0.50
34	121.6	110.6	-22.6	0.8956	0.1035	0.0009	119.1	Stable	Stripping	0.527	0.473	0.50	0.50
35	121.6	110.6	-22.6	0.8954	0.1038	0.0009	119.1	Stable	Stripping	0.527	0.473	0.50	0.50

Figure 68. A↔C+D α_{AD} =0.67: Reactive Azeotropes



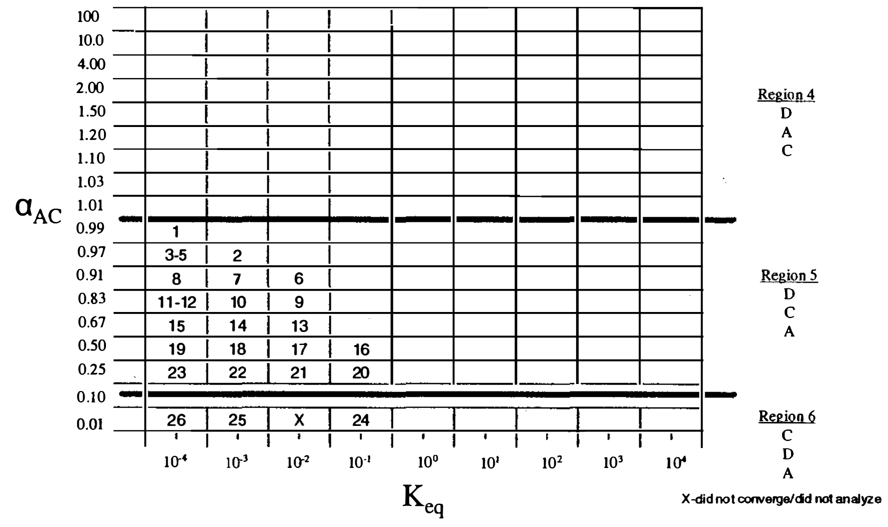
	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	121.6	98.0	1212.3	0.6194	0.0016	0.3789	121.4	Stable	Stripping	0.384	0.616	0.50	0.50
2	121.6	98.0	1212.3	0.8848	0.0008	0.1145	121.5	Stable	Stripping	0.470	0.530	0.50	0.50
3	121.6	98.0	1212.3	0.8859	0.0008	0.1133	121.5	Stable	Stripping	0.470	0.530	0.50	0.50
4	121.6	98.0	1212.3	0.8860	0.0078	0.1132	121.5	Stable	Stripping	0.474	0.530	0.50	0.50
5	121.6	98.0	1212.3	0.8681	0.0007	0.1312	121.5	Stable	Stripping	0.465	0.535	0.50	0.50
6	121.6	98.0	1212.3	0.8574	0.0006	0.1420	121.5	Stable	Stripping	0.462	0.538	0.50	0.50
7	121.6	98.0	1212.3	0.8975	0.0009	0.1016	121.5	Stable	Stripping	0.473	0.527	0.50	0.50
8	121.6	98.0	1212.3	0.9080	0.0010	0.0910	121.5	Stable	Stripping	0.476	0.524	0.50	0.50
9	121.6	98.0	1212.3	0.9104	0.0010	0.0885	121.5	Stable	Stripping	0.477	0.523	0.50	0.50
10	121.6	98.0	1212.3	0.8783	0.0007	0.1210	121.5	Stable	Stripping	0.468	0.532	0.50	0.50
11	121.6	98.4	120.7	0.4030	0.0068	0.5901	120.8	Stable	Stripping	0.292	0.708	0.50	0.50
12	121.6	98.4	120.7	0.3943	0.0066	0.5991	120.8	Stable	Rectifying	0.288	0.712	0.50	0.50
13	121.6	98.4	120.7	0.8123	0.0044	0.1833	121.3	Stable	Stripping	0.451	0.549	0.50	0.50
14	121.6	98.4	120.7	0.8202	0.0047	0.1751	121.3	Stable	Stripping	0.453	0.547	0.50	0.50
15	121.6	98.4	118.5	0.0337	0.0035	0.9628	118.5	Stable	Stripping	0.036	0.964	0.50	0.50
16	121.6	98.4	118.5	0.0390	0.0041	0.9569	118.5	Stable	Rectifying	0.041	0.959	0.50	0.50
17	121.6	98.4	118.5	0.8680	0.0215	0.3105	119.9	Stable	Stripping	0.413	0.587	0.50	0.50
18	121.6	98.4	118.5	0.8935	0.0092	0.0973	121.0	Stable	Stripping	0.477	0.523	0.50	0.50
19	121.6	98.4	118.5	0.8912	0.0089	0.0998	121.0	Stable	Stripping	0.476	0.524	0.50	0.50
20	121.6	98.4	118.5	0.9652	0.0030	0.0318	121.4	Stable	Stripping	0.493	0.507	0.50	0.50
21	121.6	98.4	115.5	0.3164	0.0499	0.6336	116.2	Stable	Strip/Rect	0.278	0.722	0.50	0.50
22	121.6	98.4	115.5	0.7526	0.0355	0.2119	119.1	Stable	Stripping	0.450	0.550	0.50	0.50
23	121.6	98.4	115.5	0.9180	0.0134	0.0687	120.7	Stable	Stripping	0.486	0.514	0.50	0.50
24	121.6	98.4	115.5	0.9179	0.0133	0.0688	120.7	Stable	Stripping	0.486	0.514	0.50	0.50
25	121.6	98.4	115.5	0.9736	0.0044	0.0220	121.3	Stable	Stripping	0.496	0.504	0.50	0.50
26	121.6	98.4	108.4	0.4939	0.1320	0.3741	112.6	Stable	Strip/Rect	0.419	0.581	0.50	0.50
27	121.6	98.4	108.4	0.8062	0.0604	0.1334	117.7	Stable	Stripping	0.480	0.520	0.50	0.50
28	121.6	98.4	108.4	0.9347	0.0212	0.0441	120.2	Stable	Stripping	0.494	0.506	0.50	0.50
29	121.6	98.4	108.4	0.9789	0.0069	0.0142	121.1	Stable	Stripping	0.498	0.502	0.50	0.50
30	121.6	99.9	77.0	0.4350	0.4731	0.0919	104.2	Stable	Strip/Rect	0.633	0.367	0.50	0.50
31	121.6	99.9	77.0	0.7891	0.1622	0.0486	113.5	Stable	Strip/Rect	0.532	0.468	0.50	0.50
32	121.6	99.9	77.0	0.9295	0.0530	0.0175	118.6	Stable	Stripping	0.509	0.491	0.50	0.50
33	121.6	99.9	77.0	0.9773	0.0169	0.0577	120.6	Stable	Stripping	0.503	0.523	0.50	0.50
34	121.6	100.9	47.8	0.1057	0.8824	0.0120	101.1	Stable	Strip/Rect	0.894	0.106	0.50	0.50
35	121.6	100.9	47.8	0.9004	0.0896	0.0101	117.0	Stable	Stripping	0.521	0.479	0.50	0.50
36	121.6	100.9	47.8	0.9685	0.0281	0.0034	120.0	Stable	Stripping	0.506	0.494	0.50	0.50
37	121.6	102.7	-19.5	0.2235	0.7736	0.0029	103.5	Stable	Strip/Rect	0.815	0.185	0.50	0.50
38	121.6	102.7	-19.5	0.2200	0.7772	0.0028	103.5	Stable	Stripping	0.817	0.183	0.50	0.50
39	121.6	102.7	-19.5	0.9263	0.0724	0.0013	118.3	Stable	Stripping	0.518	0.482	0.50	0.50

Figure 69. A↔C+D α_{AD} =0.50: Reactive Azeotropes



	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
1	121.6	75.1	121.3	0.3274	0.0005	0.6721	121.4	Stable	Stripping	0.247	0.753	0.50	0.50
2	121.6	75.1	121.3	0.8045	0.0004	0.1951	121.5	Stable	Stripping	0.446	0.554	0.50	0.50
3	121.6	75.1	121.3	0.8230	0.0005	0.1766	121.5	Stable	Stripping	0.452	0.548	0.50	0.50
4	121.6	75.1	121.3	0.8305	0.0005	0.1690	122.5	Stable	Stripping	0.454	0.546	0.50	0.50
5	121.6	75.1	120.7	0.6759	0.0021	0.3220	121.1	Stable	Stripping	0.405	0.595	0.50	0.50
6	121.6	75.1	120.7	0.8977	0.0009	0.1014	121.4	Stable	Stripping	0.474	0.526	0.50	0.50
7	121.6	75.1	118.6	0.4534	0.0084	0.5382	119.2	Stable	Stripping	0.318	0.682	0.50	0.50
8	121.6	75.1	118.6	0.4554	0.0085	0.5361	119.2	Stable	Rectifying	0.319	0.681	0.50	0.50
9	121.6	75.1	118.6	0.8204	0.0047	0.1750	120.6	Stable	Stripping	0.453	0.547	0.50	0.50
10	121.6	75.1	118.6	0.9440	0.0017	0.0543	121.2	Stable	Stripping	0.486	0.514	0.50	0.50
11	121.6	76.0	115.9	0.6082	0.0162	0.3756	118.0	Stable	Strip/Rect	0.388	0.612	0.50	0.50
12	121.6	76.0	115.9	0.8726	0.0073	0.1201	120.2	Stable	Stripping	0.470	0.530	0.50	0.50
13	121.6	76.0	115.9	0.9598	0.0026	0.0376	121.1	Stable	Stripping	0.491	0.509	0.50	0.50
14	121.6	76.0	108.8	0.2516	0.0353	0.7132	109.7	Stable	Strip/Rect	0.229	0.771	0.50	0.50
15	121.6	76.0	108.8	0.7341	0.0313	0.2346	115.7	Stable	Strip/Rect	0.441	0.559	0.50	0.50
16	121.6	76.0	108.8	0.9123	0.0121	0.0757	119.4	Stable	Stripping	0.483	0.517	0.50	0.50
17	121.6	76.0	108.8	0.9715	0.0040	0.0245	120.8	Stable	Stripping	0.495	0.505	0.50	0.50
18	121.6	77.0	99.9	0.4350	0.0919	0.4731	104.2	Stable	Stripping	0.367	0.633	0.50	0.50
19	121.6	77.0	99.9	0.7891	0.0486	0.1622	113.5	Stable	Strip/Rect	0.468	0.532	0.50	0.50
20	121.6	77.0	99.9	0.9295	0.0175	0.0530	118.6	Stable	Stripping	0.491	0.509	0.50	0.50
21	121.6	77.0	99.9	0.9773	0.0058	0.0169	120.6	Stable	Stripping	0.497	0.503	0.50	0.50
22	121.6	79.9	50.7	0.4390	0.4669	0.0940	86.7	Stable	Strip/Rect	0.630	0.370	0.50	0.50
23	121.6	79.9	50.7	0.7919	0.1580	0.0501	103.4	Stable	Strip/Rect	0.530	0.470	0.50	0.50
24	121.6	79.9	50.7	0.9306	0.0512	0.0182	114.5	Stable	Stripping	0.509	0.491	0.50	0.50
25	121.6	79.9	50.7	0.9777	0.0163	0.0060	119.1	Stable	Stripping	0.503	0.497	0.50	0.50
26	121.6	83.7	-14.4	0.9558	0.0419	0.0023	116.5	Stable	Stripping	0.510	0.490	0.50	0.50

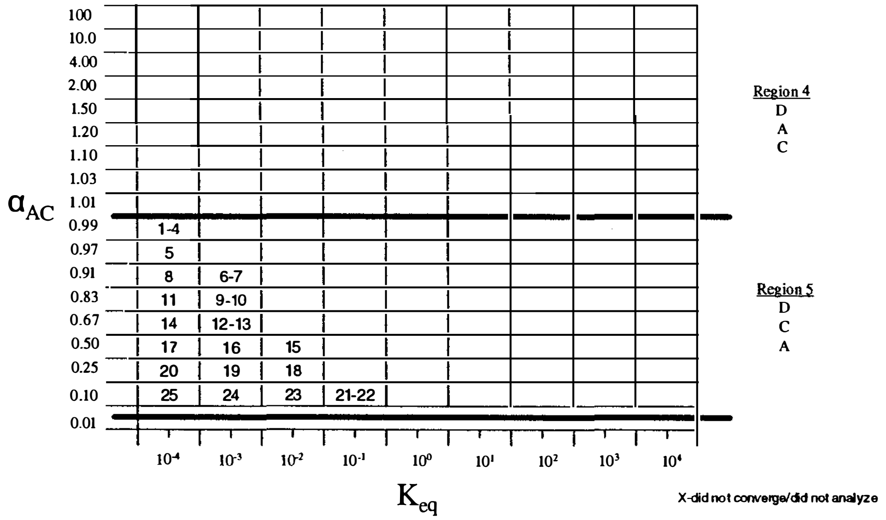
Figure 70. A↔C+D α_{AD} =0.25: Reactive Azeotropes



X-did not converge/did not analyze

	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	121.6	45.8	121.3	0.6996	0.0002	0.3001	121.4	Stable	Stripping	0.412	0.588	0.50	0.50
2	121.6	45.8	120.7	0.4872	0.0010	0.5118	120.9	Stable	Stripping	0.328	0.672	0.50	0.50
3	121.6	45.8	120.7	0.8369	0.0005	0.1625	121.3	Stable	Stripping	0.456	0.544	0.50	0.50
4	121.6	45.8	120.7	0.8328	0.0005	0.1667	121.3	Stable	Stripping	0.455	0.545	0.50	0.50
5	121.6	45.8	120.7	0.8359	0.0005	0.1636	121.3	Stable	Stripping	0.456	0.544	0.50	0.50
6	121.6	45.8	118.7	0.0985	0.0011	0.9004	118.8	Stable	Rectifying	0.091	0.909	0.50	0.50
7	121.6	45.8	118.7	0.7129	0.0025	0.2846	120.2	Stable	Stripping	0.418	0.582	0.50	0.50
8	121.6	45.8	118.7	0.9092	0.0010	0.0897	121.1	Stable	Stripping	0.477	0.523	0.50	0.50
9	121.6	45.8	115.9	0.3679	0.0059	0.6262	116.7	Stable	Stripping	0.273	0.727	0.50	0.50
10	121.6	45.8	115.9	0.7968	0.0040	0.1992	119.4	Stable	Stripping	0.446	0.554	0.50	0.50
11	121.6	45.8	115.9	0.9363	0.0015	0.0622	120.8	Stable	Stripping	0.484	0.516	0.50	0.50
12	121.6	45.8	115.9	0.9352	0.0015	0.0633	120.8	Stable	Stripping	0.484	0.516	0.50	0.50
13	121.6	46.8	109.4	0.5866	0.0147	0.3987	113.3	Stable	Strip/Rect	0.379	0.621	0.50	0.50
14	121.6	46.8	109.4	0.8669	0.0069	0.1262	118.3	Stable	Stripping	0.468	0.532	0.50	0.50
15	121.6	46.8	109.4	0.9577	0.0024	0.0399	120.4	Stable	Stripping	0.490	0.510	0.50	0.50
16	121.6	47.8	100.9	0.1057	0.0120	0.8824	101.1	Stable	Strip/Rect	0.106	0.894	0.50	0.50
17	121.6	47.8	100.9	0.6934	0.0246	0.2820	109.9	Stable	Strip/Rect	0.424	0.576	0.50	0.50
18	121.6	47.8	100.9	0.9004	0.0101	0.0896	117.0	Stable	Stripping	0.479	0.521	0.50	0.50
19	121.6	47.8	100.9	0.9682	0.0034	0.0284	120.0	Stable	Stripping	0.494	0.506	0.50	0.50
20	121.6	50.7	79.9	0.4390	0.0940	0.4669	86.7	Stable	Stripping	0.370	0.630	0.50	0.50
21	121.6	50.7	79.9	0.7919	0.0501	0.1580	103.4	Stable	Strip/Rect	0.470	0.530	0.50	0.50
22	121.6	50.7	79.9	0.9306	0.0182	0.0512	114.5	Stable	Stripping	0.491	0.509	0.50	0.50
23	121.6	50.7	79.9	0.9777	0.0060	0.0163	119.1	Stable	Stripping	0.497	0.503	0.50	0.50
24	121.6	59.5	-11.3	0.0358	0.9605	0.0037	59.6	Stable	Strip/Rect	0.962	0.038	0.50	0.50
25	121.6	59.5	-11.3	0.9039	0.0855	0.0106	101.0	Stable	Stripping	0.520	0.480	0.50	0.50
26	121.6	59.5	-11.3	0.9701	0.0262	0.0037	114.1	Stable	Stripping	0.506	0.494	0.50	0.50

Figure 71. A↔C+D α_{AD} =0.10: Reactive Azeotropes



	Tb,i (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
1	121.6	-24.6	121.3	0.2071	0.0000	0.7928	121.3	Stable	Stripping	0.172	0.828	0.50	0.50
2	121.6	-24.6	121.3	0.2012	0.0000	0.7987	121.3	Stable	Stripping	0.168	0.832	0.50	0.50
3	121.6	-24.6	121.3	0.2150	0.0000	0.7850	121.3	Stable	Stripping	0.177	0.823	0.50	0.50
4	121.6	-24.6	121.3	0.0949	0.0001	0.9051	121.3	Unstable	Stripping	0.087	0.913	0.50	0.50
5	121.6	-24.6	120.7	0.6205	0.0002	0.3793	121.0	Stable	Stripping	0.383	0.617	0.50	0.50
6	121.6	-24.6	119.0	0.2678	0.0004	0.7318	119.1	Stable	Stripping	0.212	0.788	0.50	0.50
7	121.6	-24.6	119.0	0.2677	0.0004	0.7319	119.1	Stable	Rectifying	0.211	0.789	0.50	0.50
8	121.6	-24.6	119.0	0.7649	0.0003	0.2348	120.5	Stable	Stripping	0.434	0.566	0.50	0.50
9	121.6	-24.6	116.5	0.4809	0.0009	0.5181	117.6	Stable	Stripping	0.325	0.675	0.50	0.50
10	121.6	-24.6	116.5	0.4815	0.0009	0.5176	117.6	Stable	Rectifying	0.326	0.674	0.50	0.50
11	121.6	-24.6	116.5	0.8379	0.0005	0.1616	120.0	Stable	Stripping	0.456	0.544	0.50	0.50
12	121.6	-24.6	110.7	0.6534	0.0019	0.3447	115.0	Stable	Stripping	0.396	0.604	0.50	0.50
13	121.6	-24.6	110.7	0.6537	0.0019	0.3444	115.0	Stable	Rectifying	0.396	0.604	0.50	0.50
14	121.6	-24.6	110.7	0.8923	0.0008	0.1068	119.1	Stable	Stripping	0.472	0.528	0.50	0.50
15	121.6	-19.5	102.7	0.2235	0.0029	0.7736	103.5	Stable	Strip/Rect	0.185	0.815	0.50	0.50
16	121.6	-19.5	102.7	0.7620	0.0032	0.2347	112.5	Stable	Strip/Rect	0.434	0.566	0.50	0.50
17	121.6	-19.5	102.7	0.9263	0.0013	0.0724	118.3	Stable	Stripping	0.482	0.518	0.50	0.50
18	121.6	-14.4	83.7	0.5283	0.0115	0.4602	90.9	Stable	Strip/Rect	0.353	0.647	0.50	0.50
19	121.6	-14.4	83.7	0.8571	0.0063	0.1366	107.5	Stable	Strip/Rect	0.465	0.535	0.50	0.50
20	121.6	-14.4	83.7	0.9558	0.0023	0.0419	116.5	Stable	Stripping	0.490	0.510	0.50	0.50
21	121.6	-11.3	59.5	0.0379	0.0040	0.9582	59.6	Stable	Stripping	0.040	0.960	0.50	0.50
22	121.6	-11.3	59.5	0.0358	0.0037	0.9605	59.6	Stable	Rectifying	0.038	0.962	0.50	0.50
23	121.6	-11.3	59.5	0.6879	0.0239	0.2882	77.6	Stable	Strip/Rect	0.422	0.578	0.50	0.50
24	121.6	-11.3	59.5	0.9039	0.0106	0.0855	101.0	Stable	Stripping	0.480	0.520	0.50	0.50
25	121.6	-11.3	59.5	0.9700	0.0037	0.0263	114.1	Stable	Stripping	0.494	0.506	0.50	0.50

Figure 72. A↔C+D α_{AD} =0.01: Reactive Azeotropes

Appendix B

A+B↔C System Figures

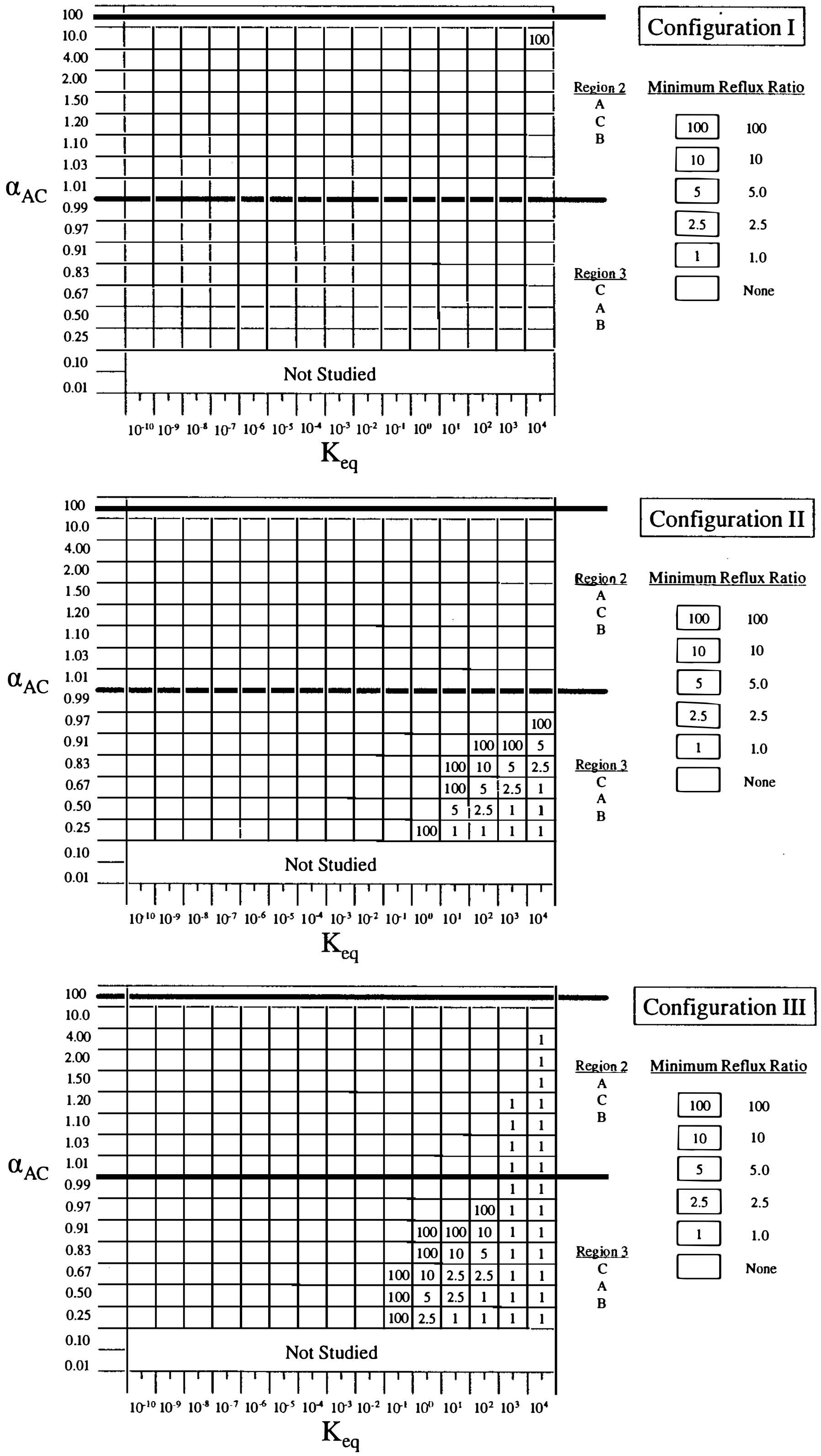


Figure 88. A+B↔C α_{AB} =100, Single Feed: Configuration I, II, III

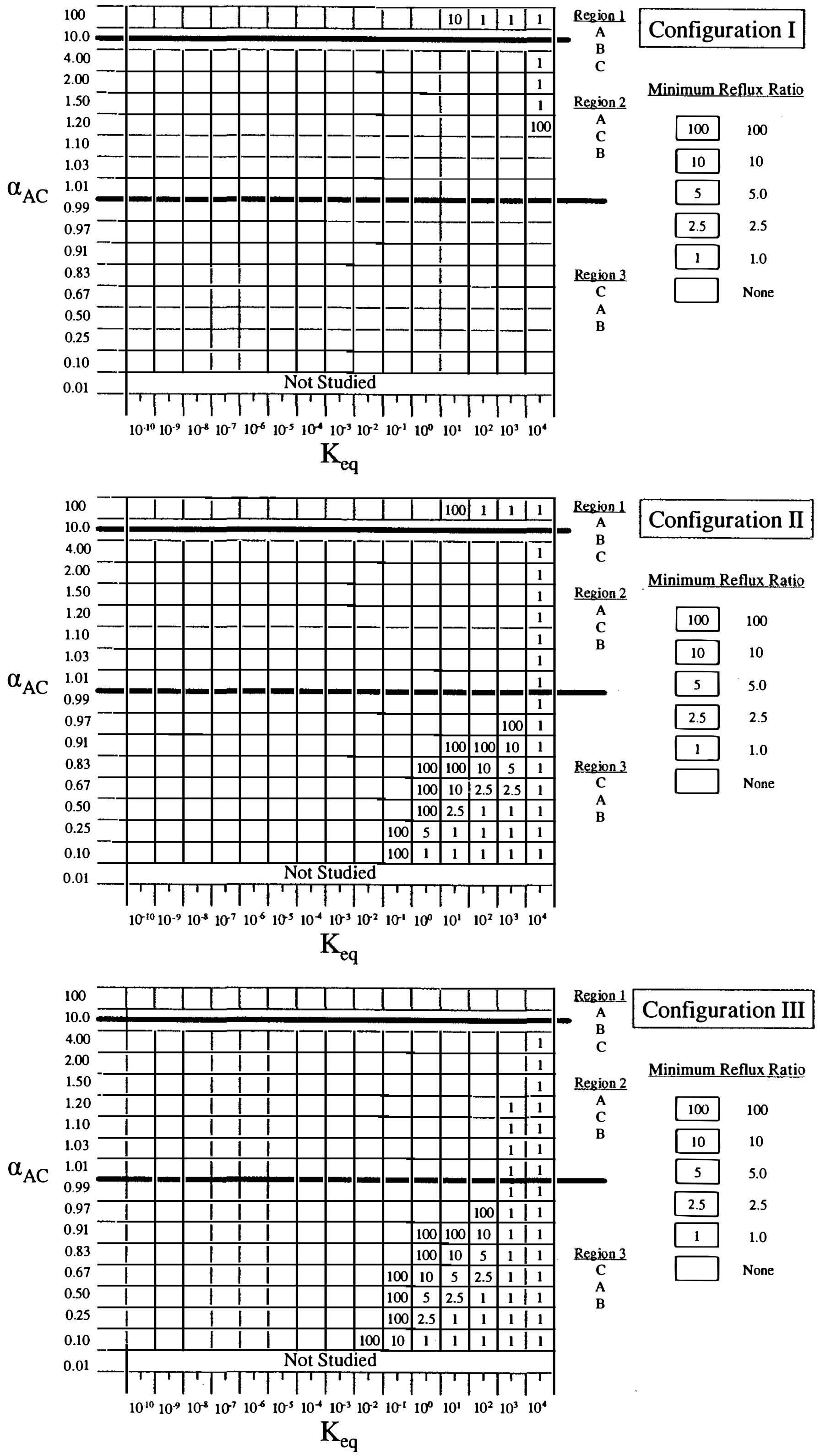


Figure 89. A+B↔C α_{AB} =10, Single Feed: Configuration I, II, III

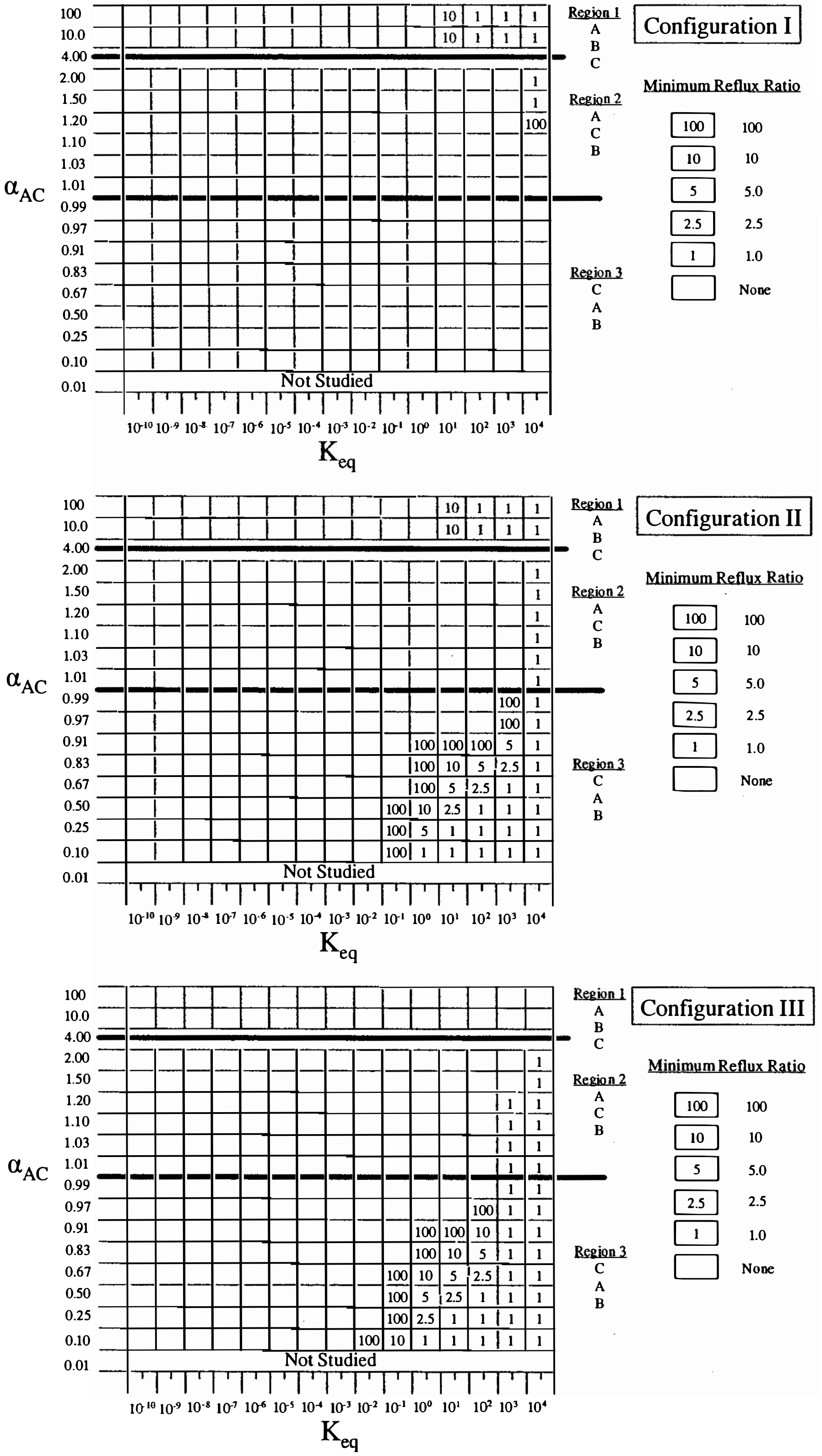


Figure 90. A+B↔C α_{AB} =4.0, Single Feed: Configuration I, II, III

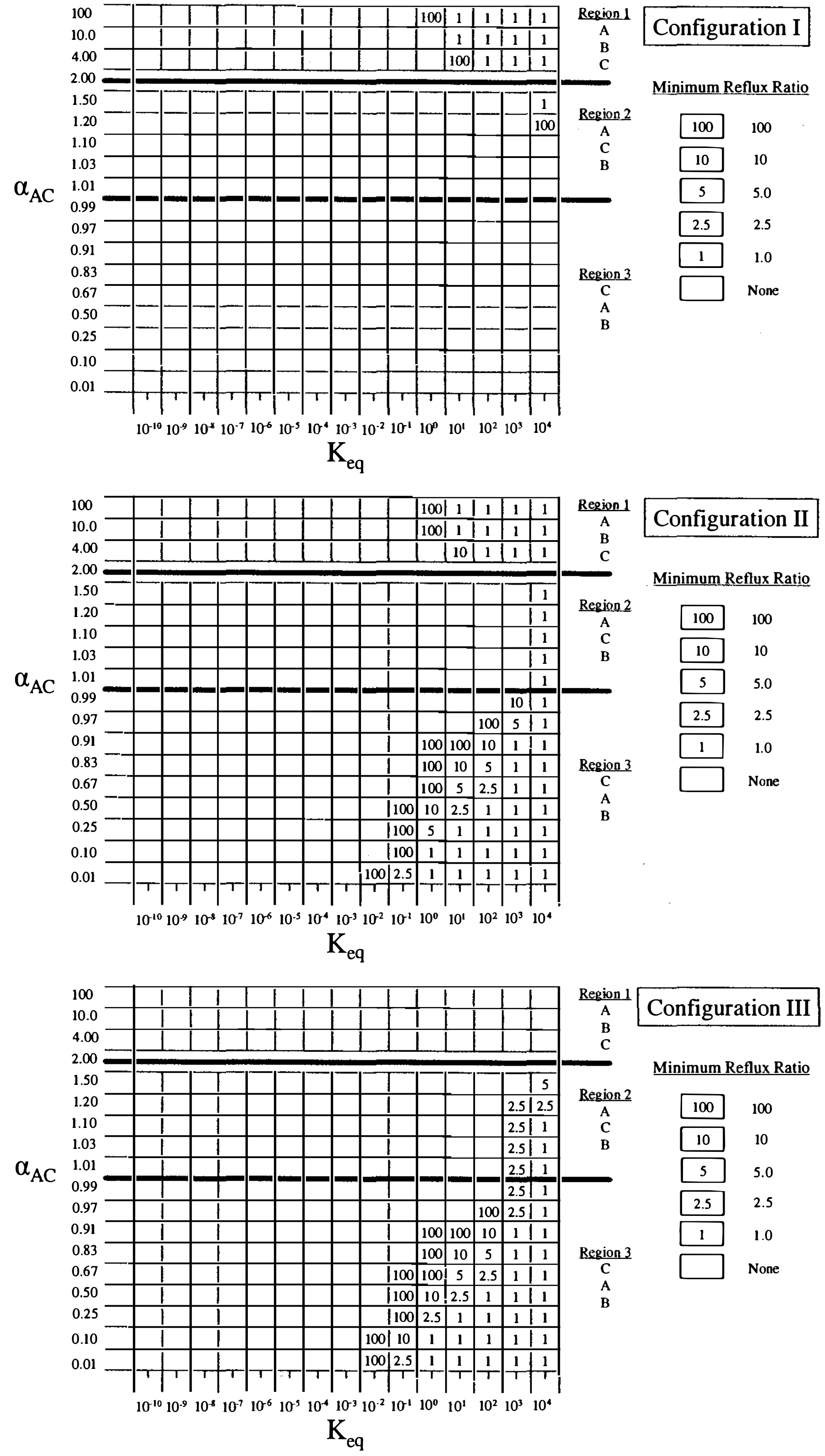


Figure 91. A+B↔C α_{AB} =2.0, Single Feed: Configuration I, II, III

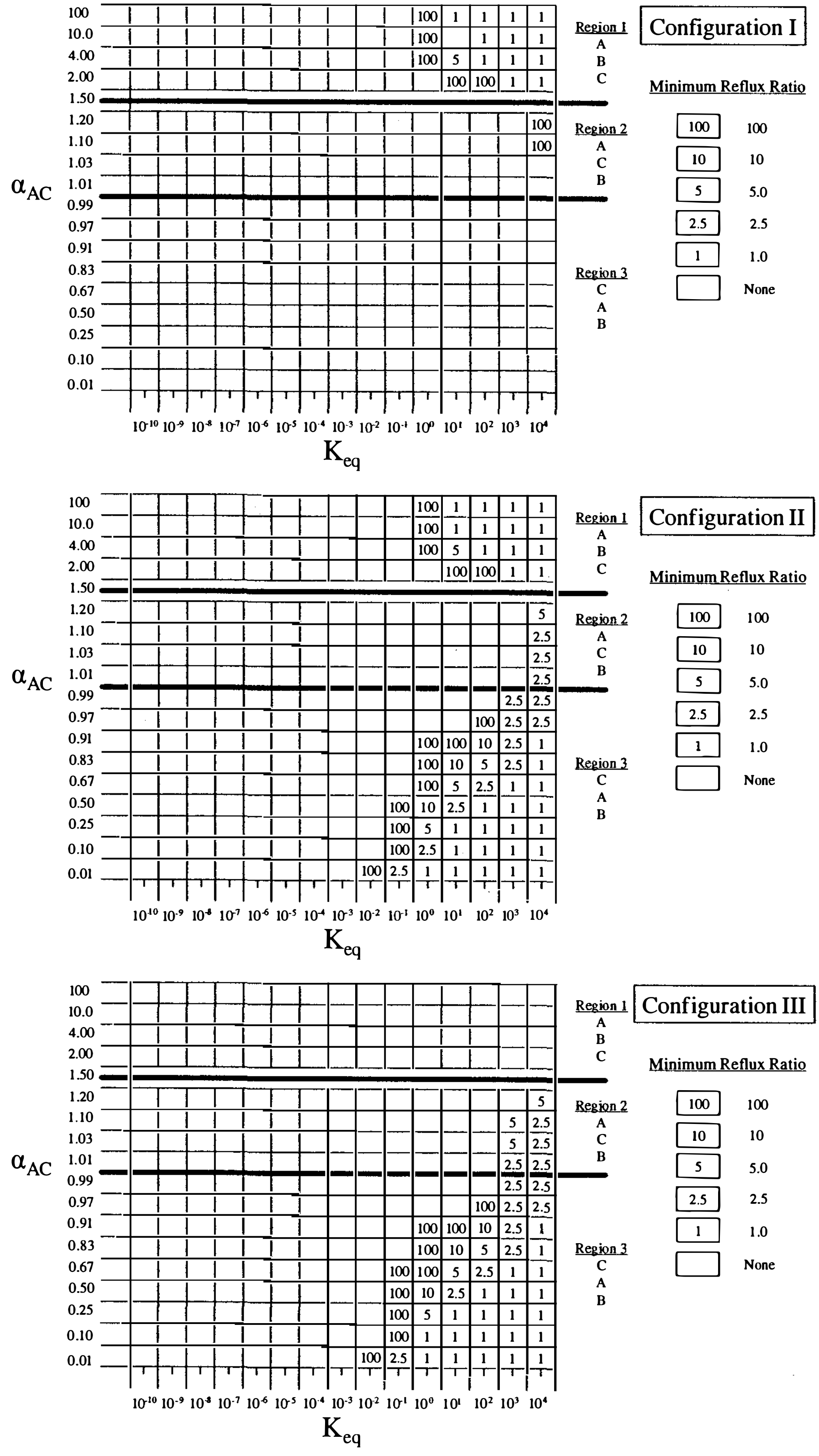


Figure 92. A+B↔C α_{AB} =1.5, Single Feed: Configuration I, II, III

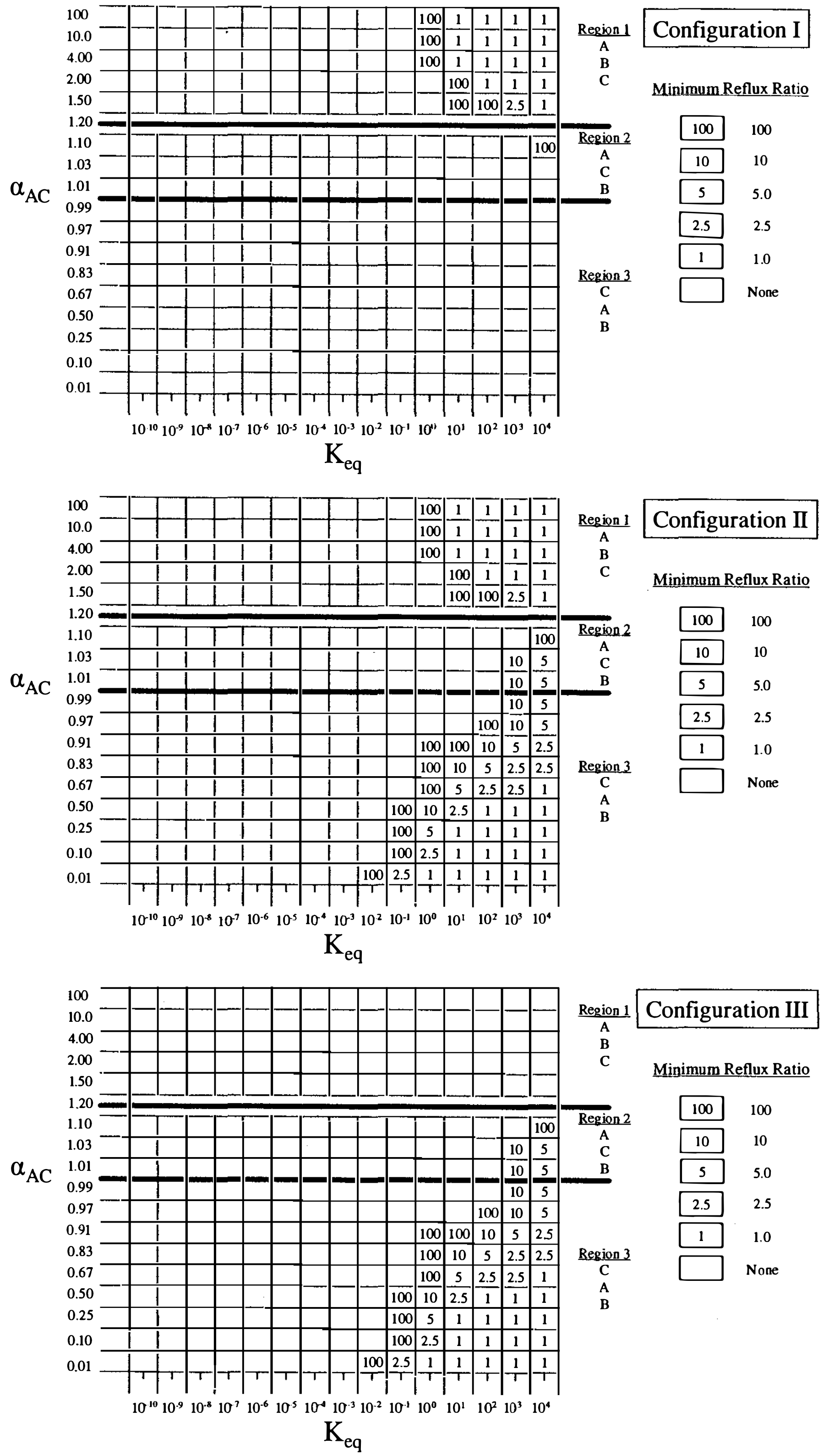


Figure 93. A+B↔C α_{AB} =1.2, Single Feed: Configuration I, II, III

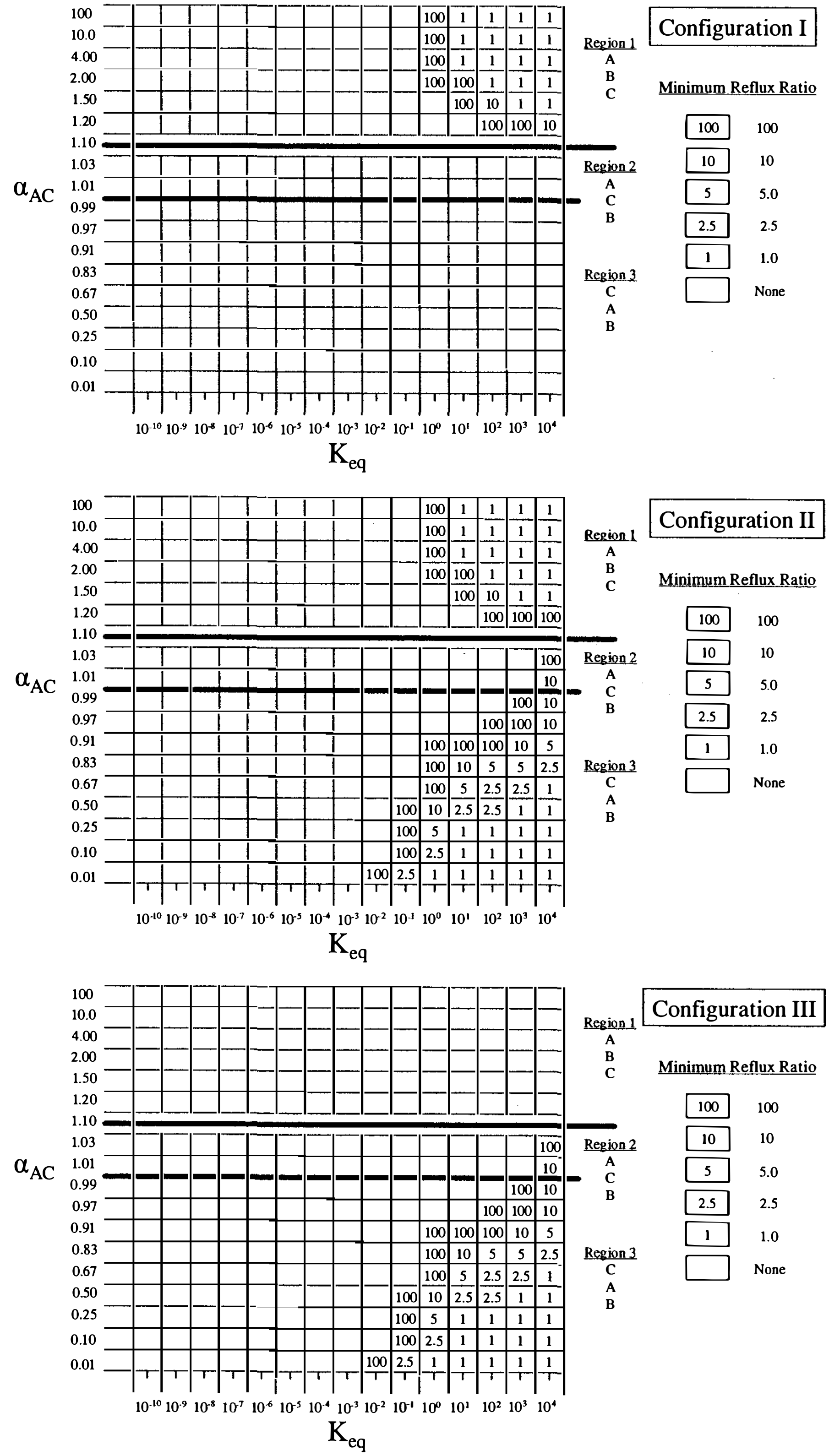


Figure 94. A+B↔C $\alpha_{AB} = 1.1$, Single Feed: Configuration I, II, III

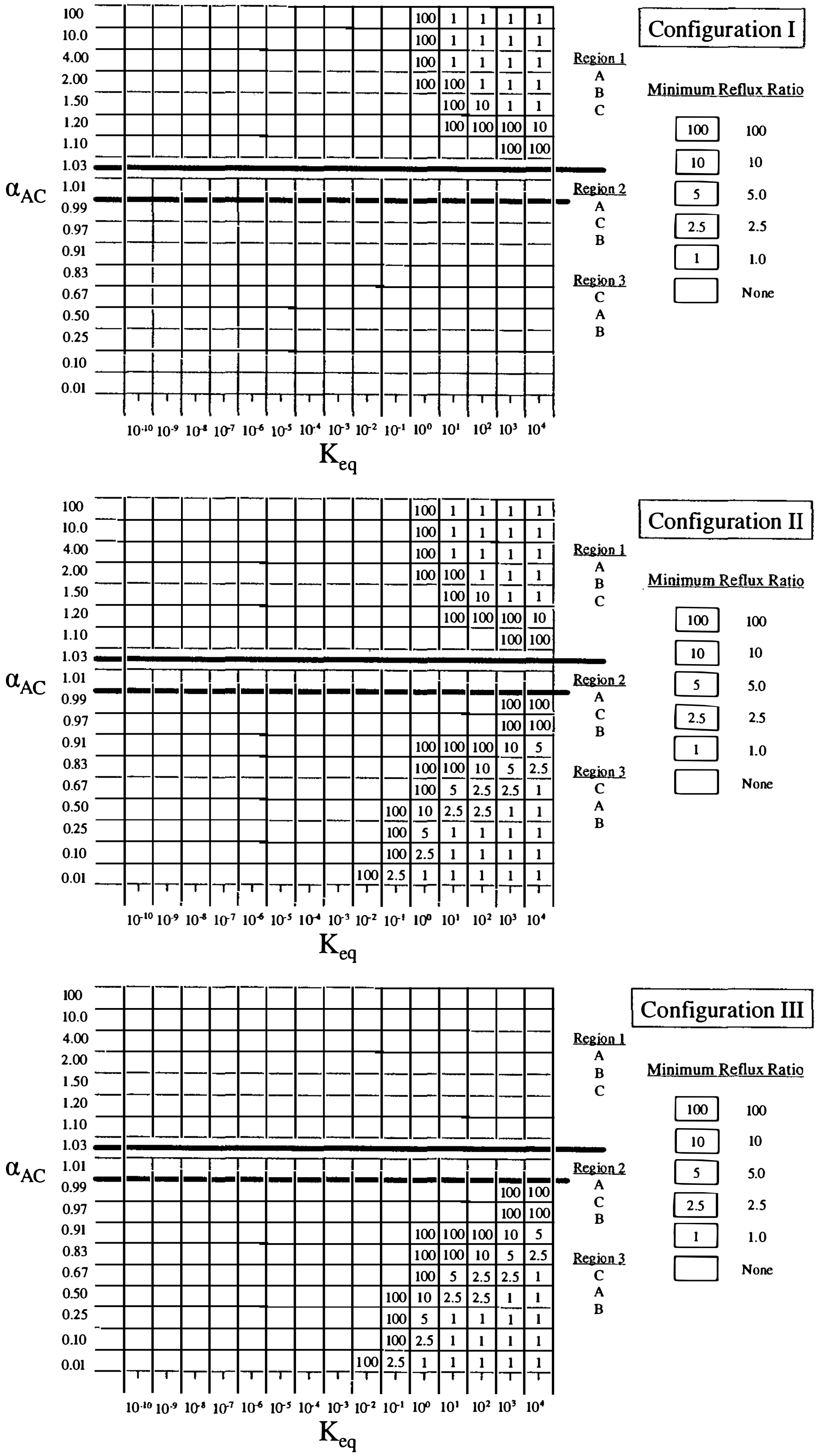
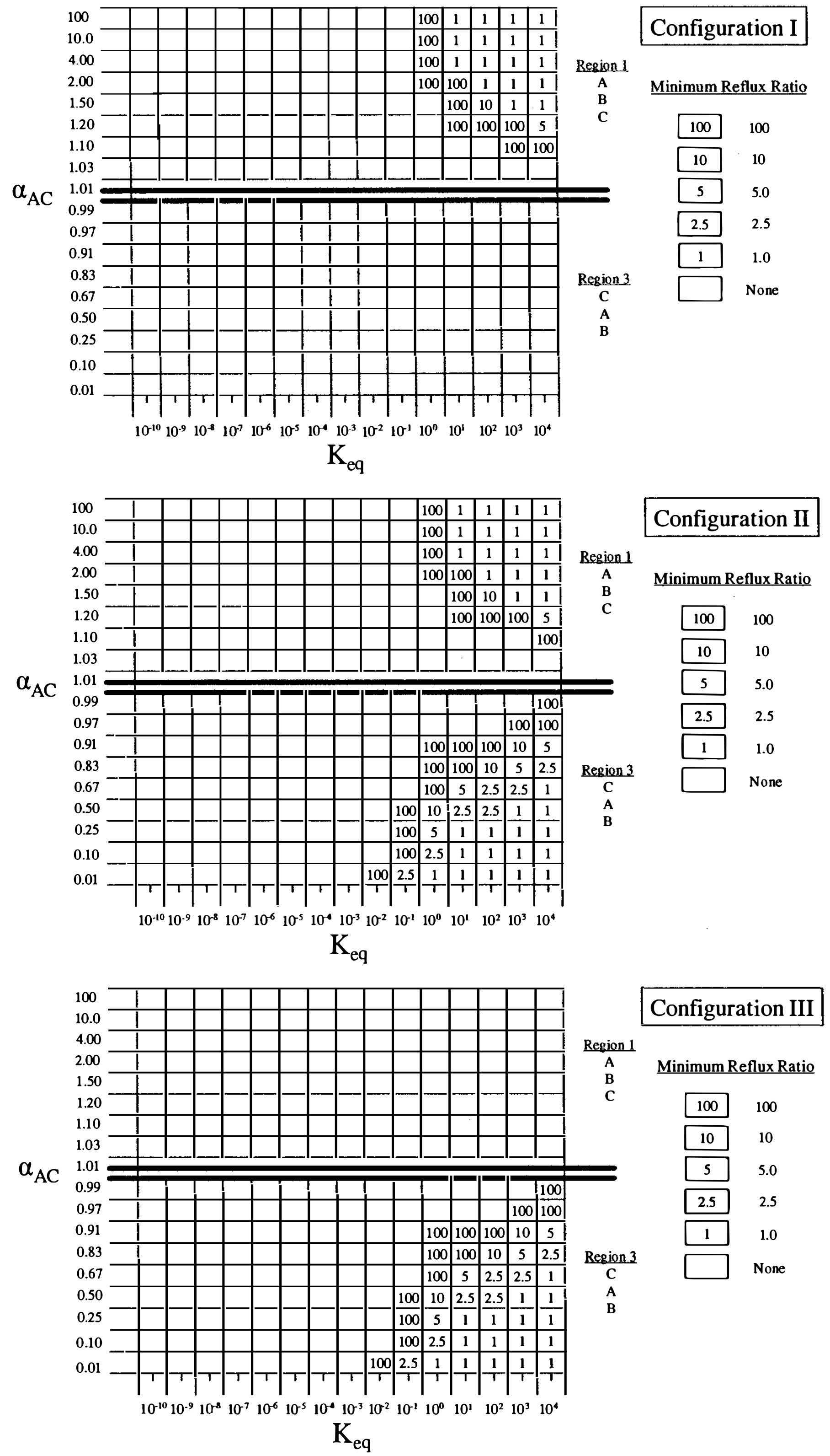


Figure 95. A+B↔C α_{AB} =1.03, Single Feed: Configuration I, II, III



Configuration I

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100											100	1	1	1	1
10.0											100	1	1	1	1
4.00											100	1	1	1	1
2.00											100	100	1	1	1
1.50												100	10	1	1
1.20												100	100	100	5
1.10														100	100
1.03															
1.01															
0.99															
0.97															
0.91															
0.83															
0.67															
0.50															
0.25															
0.10															
0.01															

Region 1
A
B
C

Region 3
C
A
B

Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
	None

Configuration II

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100											100	1	1	1	1
10.0											100	1	1	1	1
4.00											100	1	1	1	1
2.00											100	100	1	1	1
1.50												100	10	1	1
1.20												100	100	100	5
1.10															100
1.03															
1.01															
0.99															100
0.97														100	100
0.91											100	100	100	10	5
0.83											100	100	10	5	2.5
0.67											100	5	2.5	2.5	1
0.50										100	10	2.5	2.5	1	1
0.25										100	5	1	1	1	1
0.10										100	2.5	1	1	1	1
0.01									100	2.5	1	1	1	1	1

Region 1
A
B
C

Region 3
C
A
B

Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
	None

Configuration III

α_{AC}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100															
10.0															
4.00															
2.00															
1.50															
1.20															
1.10															
1.03															
1.01															
0.99															100
0.97														100	100
0.91											100	100	100	10	5
0.83											100	100	10	5	2.5
0.67											100	5	2.5	2.5	1
0.50										100	10	2.5	2.5	1	1
0.25										100	5	1	1	1	1
0.10										100	2.5	1	1	1	1
0.01									100	2.5	1	1	1	1	1

Region 1
A
B
C

Region 3
C
A
B

Minimum Reflux Ratio

100	100
10	10
5	5.0
2.5	2.5
1	1.0
	None

Figure 96. A+B↔C α_{AB} =1.01, Single Feed: Configuration I, II, III

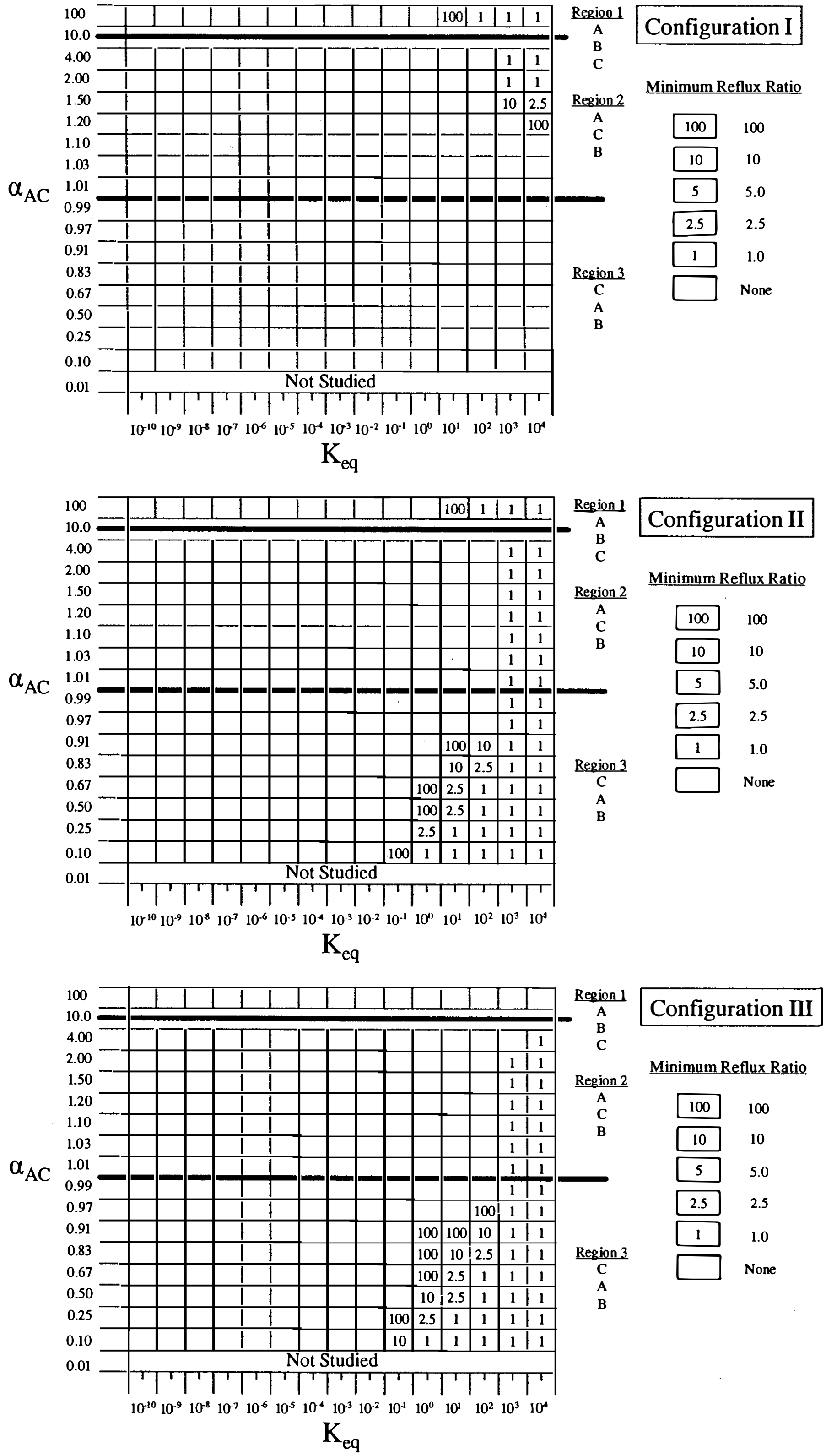


Figure 98. A+B↔C α_{AB} = 10, Double Feed: Configuration I, II, III

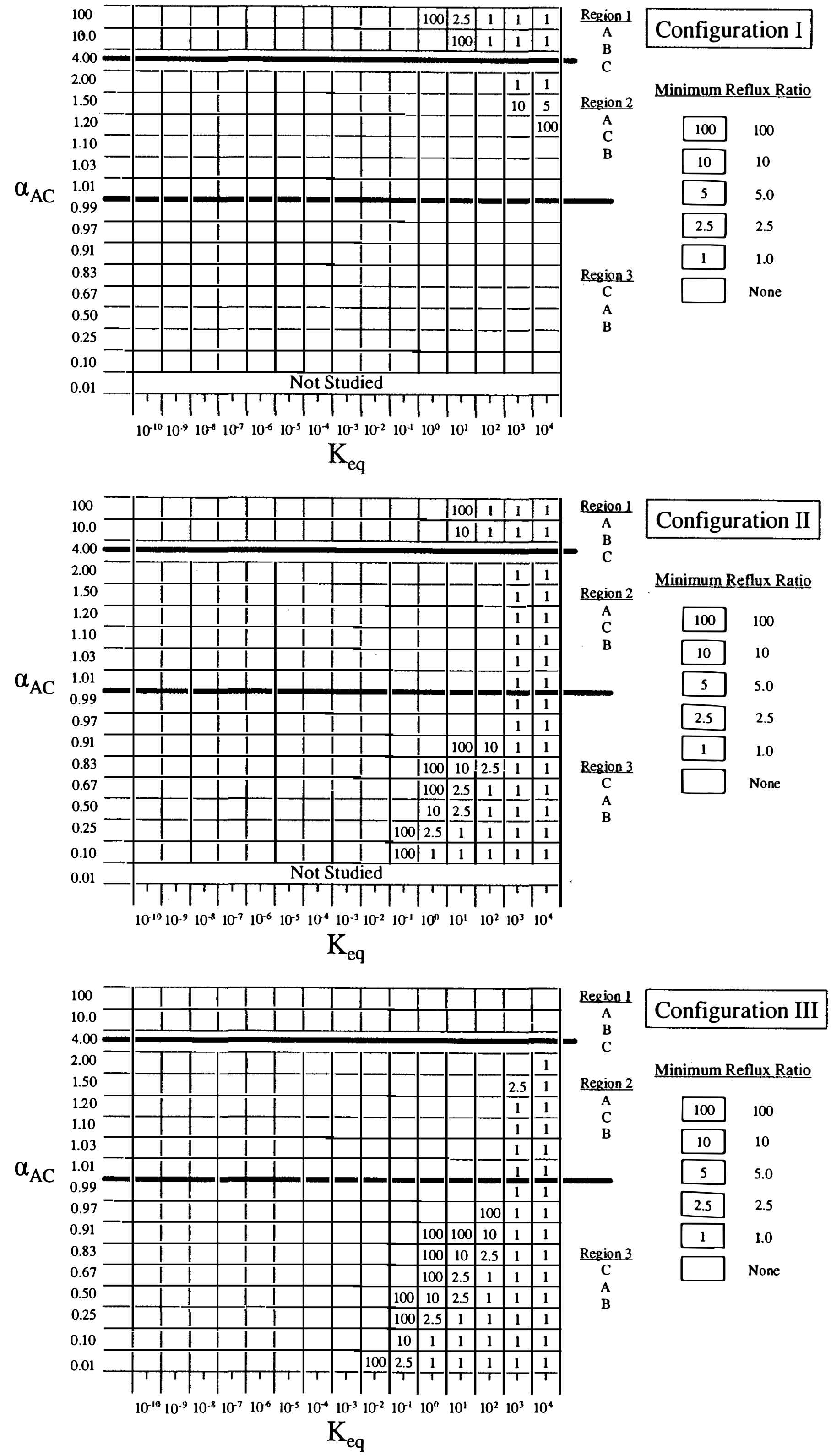


Figure 99. A+B↔C α_{AB} = 4.0, Double Feed: Configuration I, II, III

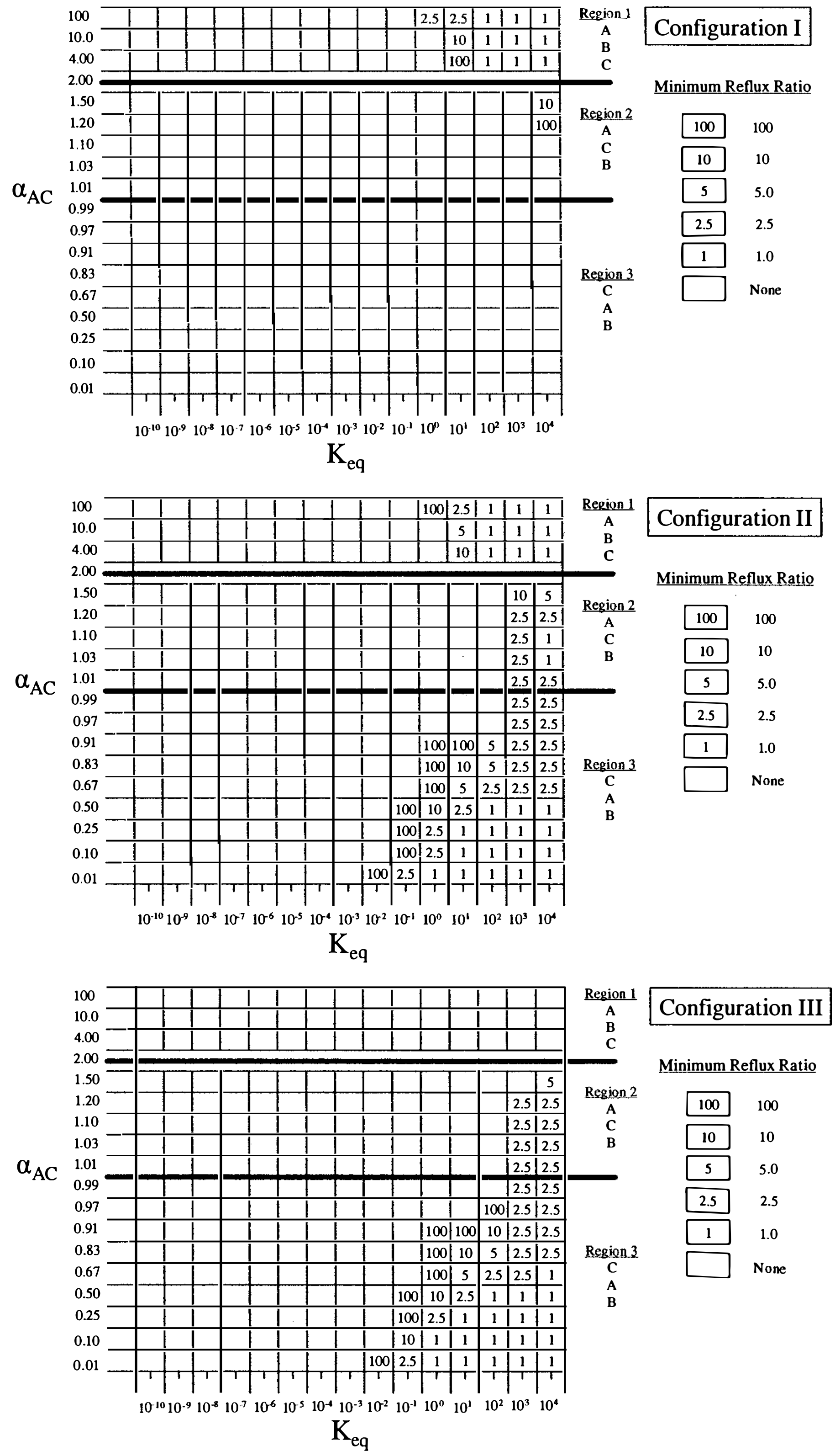


Figure 100. A+B↔C $\alpha_{AB} = 2.0$, Double Feed: Configuration I, II, III

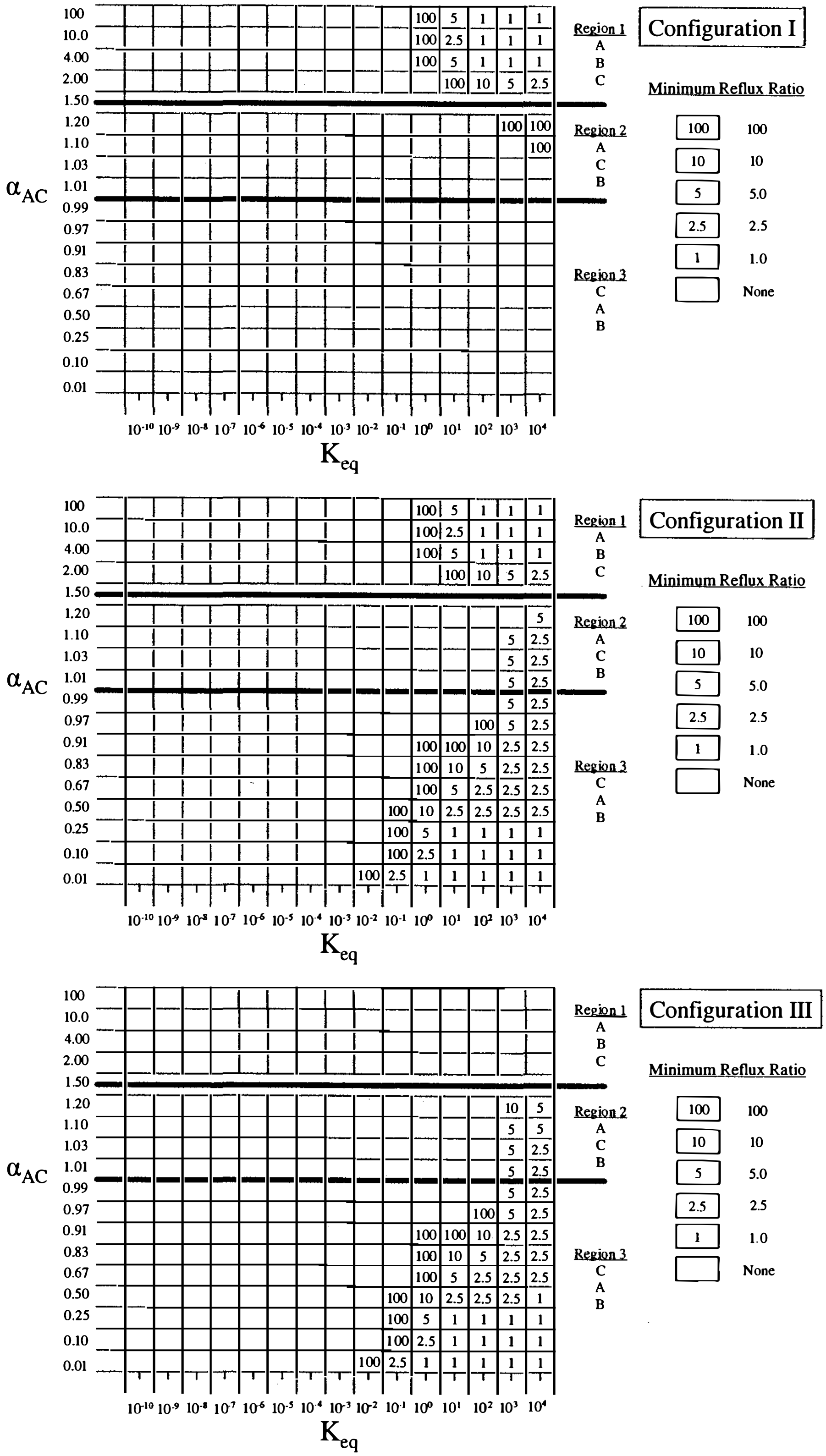


Figure 101. A+B↔C α_{AB} = 1.5, Double Feed: Configuration I, II, III

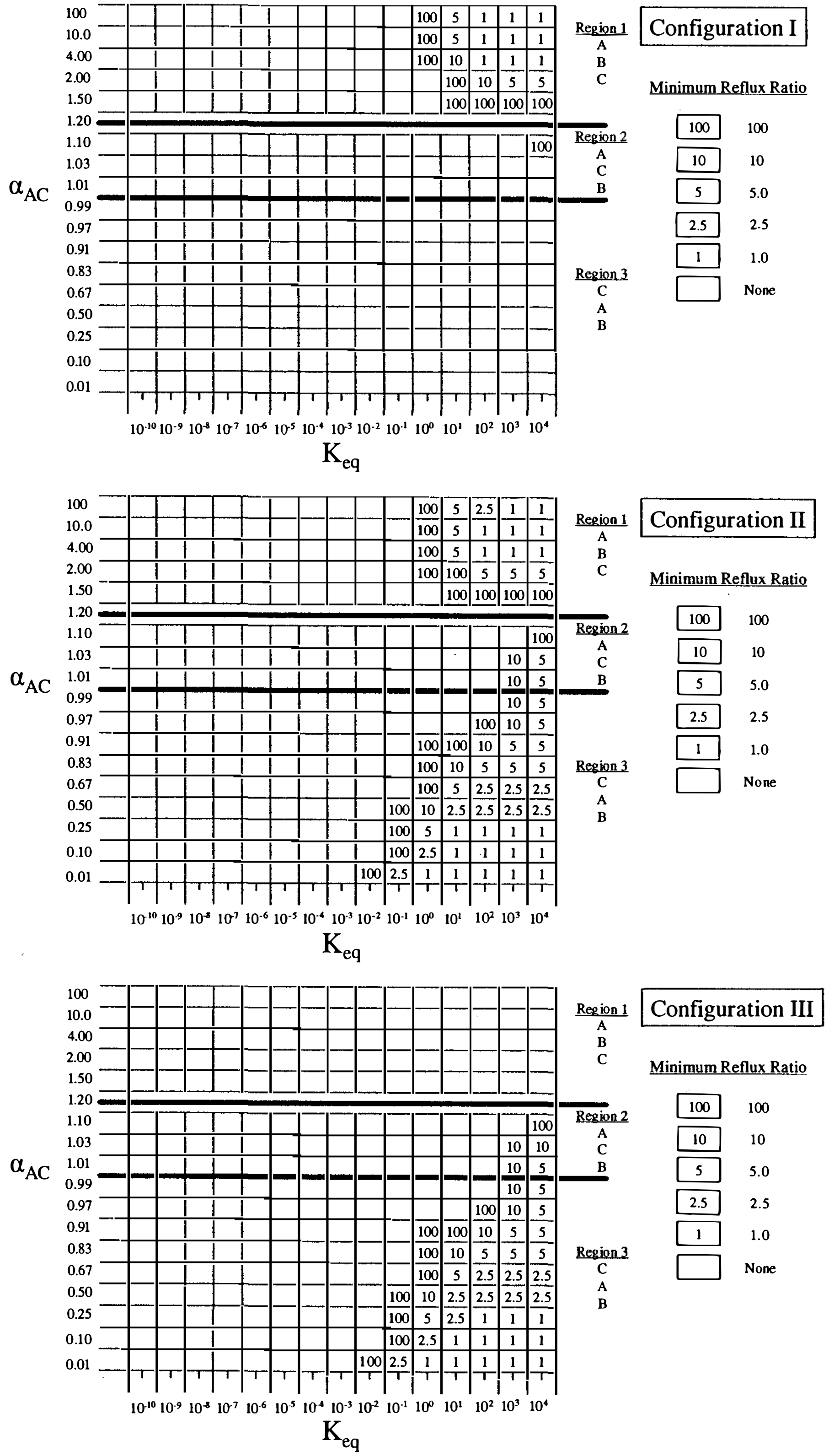


Figure 102. $A+B \leftrightarrow C$ $\alpha_{AB} = 1.2$, Double Feed: Configuration I, II, III

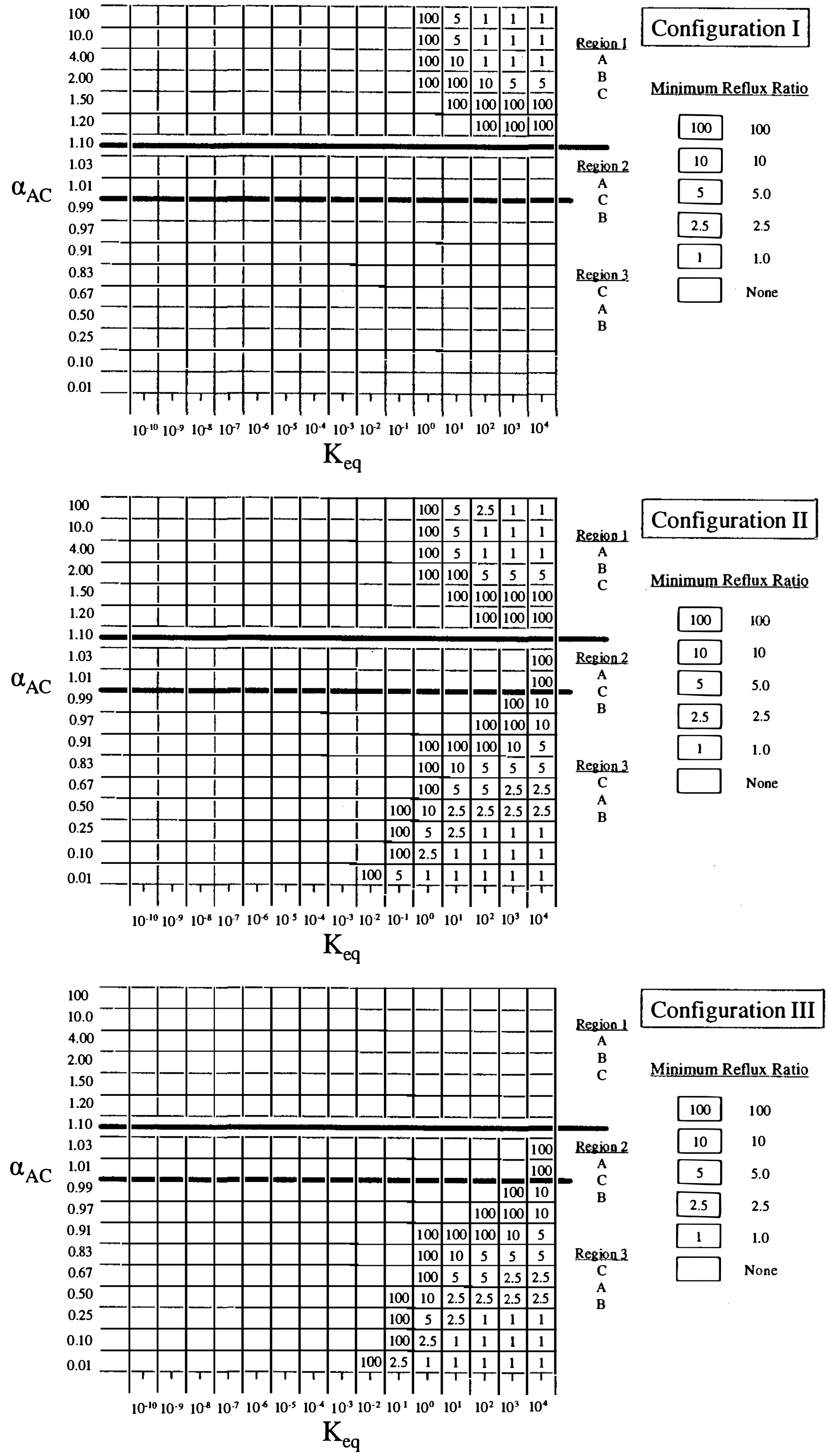


Figure 103. A+B↔C α_{AB} = 1.1, Double Feed: Configuration I, II, III

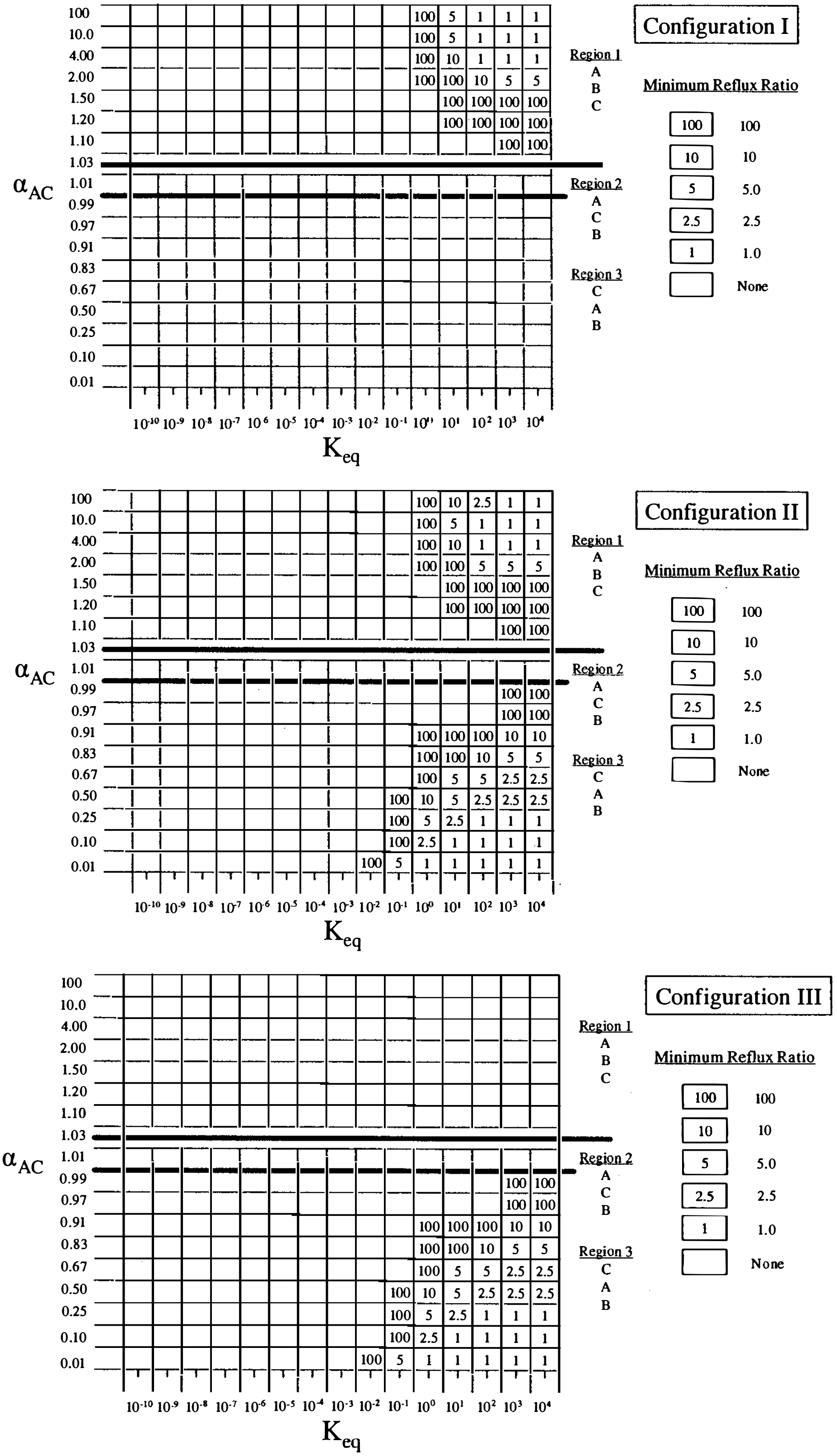


Figure 104. A+B↔C α_{AB} = 1.03, Double Feed: Configuration I, II, III

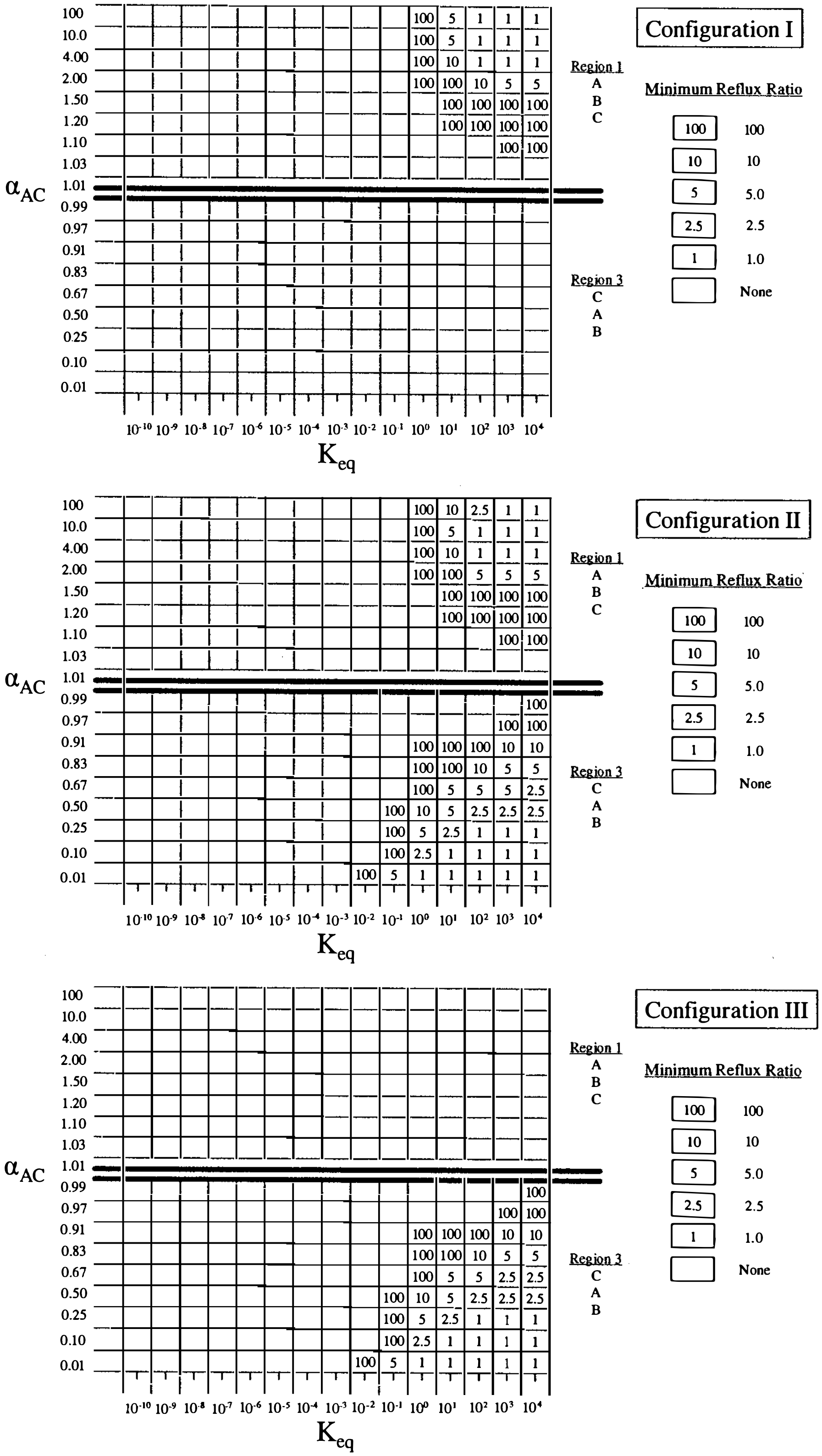
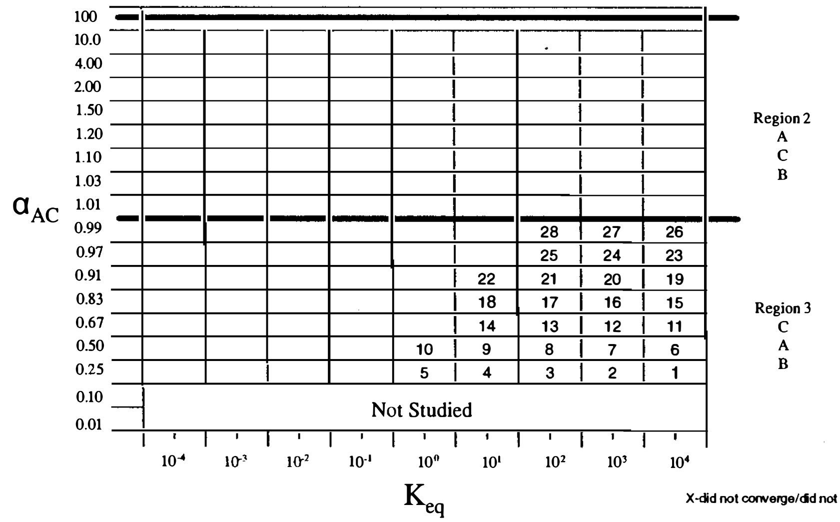


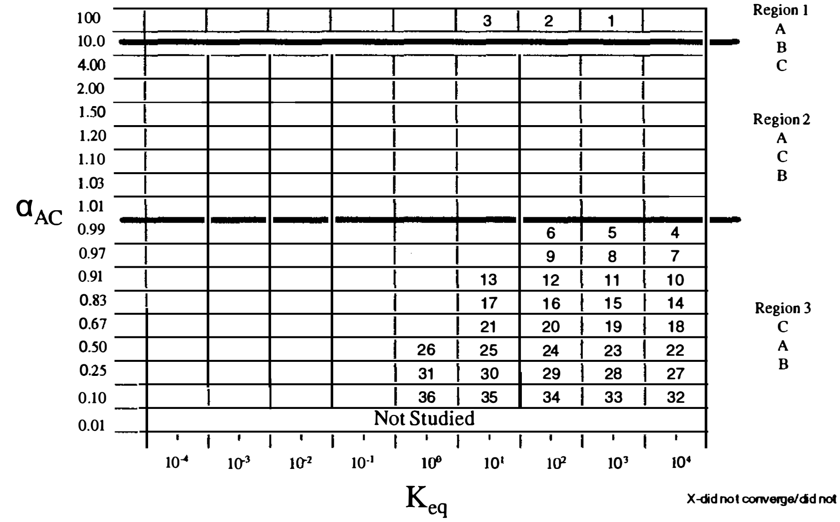
Figure 105. A+B↔C α_{AB} = 1.01, Double Feed: Configuration I, II, III



X-did not converge/did not analyze

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	6.1	122.4	-36.2	0.0107	0.0092	0.9801	-35.8	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
2	6.1	122.4	-36.2	0.0331	0.0284	0.9385	-34.9	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
3	6.1	122.4	-36.2	0.0985	0.0831	0.8184	-32.0	Unstable	Strip/Rect	0.504	0.496	0.50	0.50
4	6.1	122.4	-36.2	0.2614	0.2044	0.5342	-23.0	Unstable	Strip/Rect	0.519	0.481	0.50	0.50
5	6.1	122.4	-36.2	0.5751	0.2697	0.1552	-1.6	Unstable	Strip/Rect	0.632	0.368	0.50	0.50
6	2.8	122.4	-18.4	0.0128	0.0077	0.9795	-18.0	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
7	2.8	122.4	-18.4	0.0399	0.0235	0.9366	-17.2	Unstable	Strip/Rect	0.504	0.496	0.50	0.50
8	2.8	122.4	-18.4	0.1204	0.0674	0.8122	-14.8	Unstable	Strip/Rect	0.515	0.485	0.50	0.50
9	2.8	122.4	-18.4	0.3357	0.1525	0.5118	-7.8	Unstable	Strip/Rect	0.561	0.439	0.50	0.50
10	2.8	122.4	-18.4	0.8912	0.0575	0.0513	2.6	Unstable	Strip/Rect	0.897	0.103	0.50	0.50
11	1.4	122.4	-10.8	0.0157	0.0062	0.9781	-10.5	Unstable	Strip/Rect	0.502	0.498	0.50	0.50
12	1.4	122.4	-10.8	0.0491	0.0190	0.9319	-9.9	Unstable	Strip/Rect	0.508	0.492	0.50	0.50
13	1.4	122.4	-10.8	0.1498	0.0532	0.7970	-7.9	Unstable	Strip/Rect	0.527	0.473	0.50	0.50
14	1.4	122.4	-10.8	0.4330	0.1064	0.4606	-2.8	Unstable	Strip/Rect	0.612	0.388	0.50	0.50
15	0.5	122.4	-5.4	0.0216	0.0045	0.9739	-5.2	Unstable	Strip/Rect	0.504	0.496	0.50	0.50
16	0.5	122.4	-5.4	0.0677	0.0136	0.9187	-4.7	Unstable	Strip/Rect	0.514	0.486	0.50	0.50
17	0.5	122.4	-5.4	0.2089	0.0361	0.7550	-3.3	Unstable	Strip/Rect	0.549	0.451	0.50	0.50
18	0.5	122.4	-5.4	0.6277	0.0512	0.3211	-0.4	Unstable	Strip/Rect	0.718	0.282	0.50	0.50
19	-0.1	122.4	-2.9	0.0304	0.0032	0.9664	-2.8	Unstable	Strip/Rect	0.507	0.493	0.50	0.50
20	-0.1	122.4	-2.9	0.0956	0.0094	0.8950	-2.4	Unstable	Strip/Rect	0.523	0.477	0.50	0.50
21	-0.1	122.4	-2.9	0.2975	0.0228	0.6797	-1.5	Unstable	Strip/Rect	0.582	0.418	0.50	0.50
22	-0.1	122.4	-2.9	0.9183	0.0080	0.0737	-0.1	Unstable	Strip/Rect	0.924	0.076	0.50	0.50
23	-0.4	122.4	-1.3	0.0520	0.0018	0.9462	-1.2	Unstable	Strip/Rect	0.513	0.487	0.50	0.50
24	-0.4	122.4	-1.3	0.1639	0.0051	0.8310	-1.0	Unstable	Strip/Rect	0.543	0.457	0.50	0.50
25	-0.4	122.4	-1.3	0.5144	0.0093	0.4763	-0.6	Unstable	Strip/Rect	0.671	0.329	0.50	0.50
26	-4.7	122.4	-0.8	0.0850	0.0011	0.9139	-0.8	Unstable	Strip/Rect	0.522	0.478	0.50	0.50
27	-4.7	122.4	-0.8	0.2683	0.0027	0.7290	-0.7	Unstable	Strip/Rect	0.577	0.423	0.50	0.50
28	-4.7	122.4	-0.8	0.8459	0.0018	0.1523	-0.5	Unstable	Strip/Rect	0.866	0.134	0.50	0.50

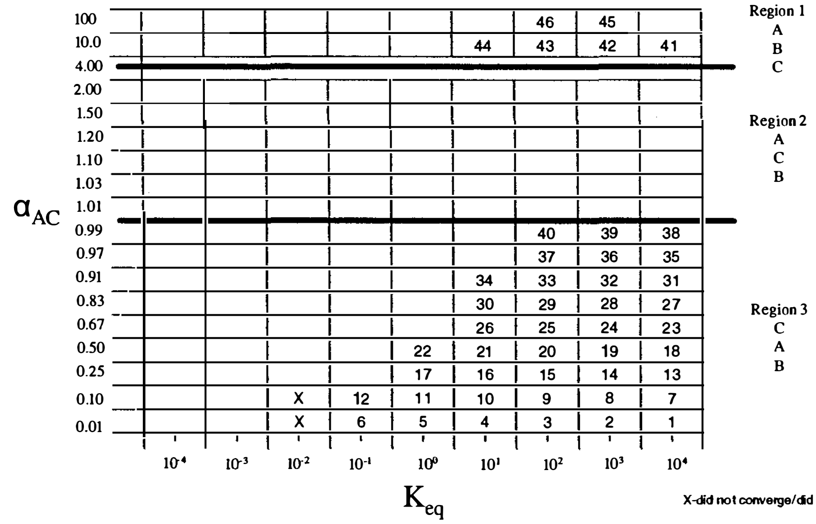
Figure 106. A+B↔C α_{AB} =100: Reactive Azeotropes



X-did not converge/did not analyze

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
1	-12.3	60.2	122.5	0.0103	0.0872	0.9025	103.7	Stable	Stripping	0.480	0.520	0.50	0.50
2	-12.3	60.2	122.5	0.0231	0.2948	0.6821	77.9	Stable	Strip/Rect	0.419	0.581	0.50	0.50
3	-12.3	60.2	122.5	0.0015	0.9839	0.0146	60.2	Stable	Strip/Rect	0.016	0.984	0.50	0.50
4	53.6	122.4	53.4	0.1076	0.0008	0.8916	53.5	Unstable	Strip/Rect	0.528	0.472	0.50	0.50
5	53.6	122.4	53.4	0.3398	0.0019	0.6583	53.6	Unstable	Strip/Rect	0.602	0.398	0.50	0.50
6	53.6	122.4	53.4	0.9987	0.0000	0.0013	53.7	Unstable	Rectifying	0.999	0.001	0.50	0.50
7	53.6	122.4	52.7	0.0546	0.0017	0.9437	52.8	Unstable	Strip/Rect	0.514	0.486	0.50	0.50
8	53.6	122.4	52.7	0.1720	0.0048	0.8232	53.0	Unstable	Strip/Rect	0.546	0.454	0.50	0.50
9	53.6	122.4	52.7	0.5399	0.0084	0.4517	53.6	Unstable	Strip/Rect	0.683	0.317	0.50	0.50
10	53.9	122.4	50.8	0.0303	0.0032	0.9665	51.0	Unstable	Strip/Rect	0.507	0.493	0.50	0.50
11	53.9	122.4	50.8	0.0953	0.0094	0.8953	51.4	Unstable	Strip/Rect	0.523	0.477	0.50	0.50
12	53.9	122.4	50.8	0.2964	0.0230	0.6806	52.3	Unstable	Strip/Rect	0.581	0.419	0.50	0.50
13	53.9	122.4	50.8	0.9140	0.0085	0.0775	54.0	Unstable	Strip/Rect	0.920	0.080	0.50	0.50
14	54.2	122.4	48.3	0.0223	0.0044	0.9733	48.6	Unstable	Strip/Rect	0.505	0.495	0.50	0.50
15	54.2	122.4	48.3	0.0701	0.0131	0.9168	49.1	Unstable	Strip/Rect	0.515	0.485	0.50	0.50
16	54.2	122.4	48.3	0.2163	0.0346	0.7491	50.5	Unstable	Strip/Rect	0.552	0.448	0.50	0.50
17	54.2	122.4	48.3	0.6506	0.0466	0.3028	53.5	Unstable	Strip/Rect	0.732	0.268	0.50	0.50
18	54.8	122.4	41.9	0.0160	0.0061	0.9779	42.3	Unstable	Strip/Rect	0.503	0.497	0.50	0.50
19	54.8	122.4	41.9	0.0500	0.0186	0.9314	43.0	Unstable	Strip/Rect	0.508	0.492	0.50	0.50
20	54.8	122.4	41.9	0.1525	0.0522	0.7953	45.1	Unstable	Strip/Rect	0.528	0.472	0.50	0.50
21	54.8	122.4	41.9	0.4406	0.1035	0.4559	50.6	Unstable	Strip/Rect	0.616	0.384	0.50	0.50
22	55.7	122.4	34.0	0.0132	0.0074	0.9794	34.4	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
23	55.7	122.4	34.0	0.0410	0.0228	0.9362	35.2	Unstable	Strip/Rect	0.505	0.495	0.50	0.50
24	55.7	122.4	34.0	0.1239	0.0655	0.8106	37.9	Unstable	Strip/Rect	0.516	0.484	0.50	0.50
25	55.7	122.4	34.0	0.3461	0.1466	0.5073	45.3	Unstable	Strip/Rect	0.566	0.434	0.50	0.50
26	55.7	122.4	34.0	0.9271	0.0378	0.0351	55.6	Unstable	Strip/Rect	0.930	0.070	0.50	0.50
27	57.6	122.4	14.0	0.0109	0.0090	0.9801	14.5	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
28	57.6	122.4	14.0	0.0337	0.0279	0.9384	15.5	Unstable	Stripping	0.501	0.499	0.50	0.50
29	57.6	122.4	14.0	0.1004	0.0814	0.8182	18.7	Unstable	Strip/Rect	0.505	0.495	0.50	0.50
30	57.6	122.4	14.0	0.2676	0.1992	0.5332	28.7	Unstable	Strip/Rect	0.522	0.478	0.50	0.50
31	57.6	122.4	14.0	0.5973	0.2521	0.1506	50.8	Unstable	Strip/Rect	0.650	0.350	0.50	0.50
32	60.1	122.4	-12.3	0.0101	0.0097	0.9802	-11.8	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
33	60.1	122.4	-12.3	0.0312	0.0300	0.9388	-10.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
34	60.1	122.4	-12.3	0.0926	0.0885	0.8189	-7.4	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
35	60.1	122.4	-12.3	0.2398	0.2237	0.5365	3.3	Unstable	Strip/Rect	0.505	0.495	0.50	0.50
36	60.1	122.4	-12.3	0.4676	0.3628	0.1696	33.5	Unstable	Strip/Rect	0.545	0.455	0.50	0.50

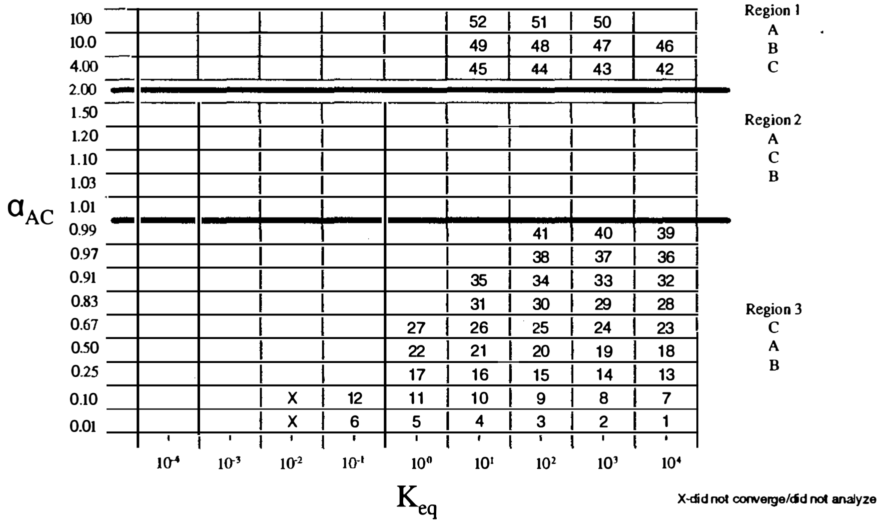
Figure 107. A+B↔C α_{AB} =10: Reactive Azeotropes



X-did not converge/did not analyze

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB,azeo	XC,azeo	XB,F	XC,F
1	86.1	122.4	-40.1	0.0099	0.0099	0.9802	-39.0	Unstable Strip/Rect	0.5	0.5	0.50	0.50
2	86.1	122.4	-40.1	0.0307	0.0306	0.9387	-38.3	Unstable Strip/Rect	0.500026	0.49997	0.50	0.50
3	86.1	122.4	-40.1	0.0906	0.0904	0.8190	-35.7	Unstable Rectifying	0.500055	0.49995	0.50	0.50
4	86.1	122.4	-40.1	0.2320	0.2314	0.5366	-25.5	Unstable Strip/Rect	0.500195	0.4998	0.50	0.50
5	86.1	122.4	-40.1	0.4177	0.4107	0.1716	7.2	Unstable Rectifying	0.502987	0.49701	0.50	0.50
6	86.1	122.4	-40.1	0.5761	0.4009	0.0230	70.5	Unstable Strip/Rect	0.58563	0.41437	0.50	0.50
7	78.9	117.9	6.0	0.0101	0.0097	0.9802	6.5	Unstable Strip/Rect	0.500101	0.4999	0.50	0.50
8	78.9	117.9	6.0	0.0313	0.0300	0.9387	7.6	Unstable Strip/Rect	0.500335	0.49966	0.50	0.50
9	78.9	117.9	6.0	0.0926	0.0884	0.8190	11.0	Unstable Strip/Rect	0.501154	0.49885	0.50	0.50
10	78.9	117.9	6.0	0.2399	0.2237	0.5364	22.2	Unstable Strip/Rect	0.505272	0.49473	0.50	0.50
11	78.9	117.9	6.0	0.4644	0.3658	0.1698	52.7	Unstable Strip/Rect	0.542144	0.45786	0.50	0.50
12	78.9	117.9	6.0	0.9610	0.0356	0.0034	78.9	Unstable Strip/Rect	0.961132	0.03887	0.50	0.50
13	78.9	119.7	34.0	0.0108	0.0091	0.9801	34.4	Unstable Strip/Rect	0.500429	0.49957	0.50	0.50
14	78.9	119.7	34.0	0.0334	0.0281	0.9385	35.5	Unstable Strip/Rect	0.501367	0.49863	0.50	0.50
15	78.9	119.7	34.0	0.0995	0.0822	0.8183	38.9	Unstable Strip/Rect	0.504757	0.49524	0.50	0.50
16	78.9	119.7	34.0	0.2639	0.2023	0.5338	49.1	Unstable Strip/Rect	0.520081	0.47992	0.50	0.50
17	78.9	119.7	34.0	0.5731	0.2714	0.1555	71.2	Unstable Stripping	0.63055	0.36945	0.50	0.50
18	78.9	120.7	56.6	0.0128	0.0076	0.9796	57.0	Unstable Strip/Rect	0.501313	0.49869	0.50	0.50
19	78.9	120.7	56.6	0.0399	0.0235	0.9366	57.9	Unstable Strip/Rect	0.504234	0.49577	0.50	0.50
20	78.9	120.7	56.6	0.1203	0.0675	0.8122	60.6	Unstable Strip/Rect	0.514568	0.48543	0.50	0.50
21	78.9	120.7	56.6	0.3331	0.1540	0.5129	68.0	Unstable Strip/Rect	0.559191	0.44081	0.50	0.50
22	78.9	120.7	56.6	0.8641	0.0729	0.0630	78.6	Unstable Strip/Rect	0.872154	0.12785	0.50	0.50
23	78.9	121.6	65.8	0.0154	0.0063	0.9783	66.2	Unstable Strip/Rect	0.5023	0.4977	0.50	0.50
24	78.9	121.6	65.8	0.0481	0.0194	0.9325	66.9	Unstable Strip/Rect	0.507426	0.49257	0.50	0.50
25	78.9	121.6	65.8	0.1465	0.0546	0.7989	68.96	Unstable Strip/Rect	0.525543	0.47446	0.50	0.50
26	78.9	121.6	65.8	0.4193	0.1118	0.4689	74.3	Unstable Strip/Rect	0.60467	0.39533	0.50	0.50
27	78.9	122.1	78.9	0.0209	0.0047	0.9744	72.885	Unstable Strip/Rect	0.504103	0.4959	0.50	0.50
28	78.9	121.6	65.8	0.0654	0.0141	0.9205	73.38	Unstable Strip/Rect	0.513356	0.48664	0.50	0.50
29	78.9	121.6	65.8	0.2012	0.0378	0.7610	74.81	Unstable Strip/Rect	0.546394	0.45361	0.50	0.50
30	78.9	121.6	65.8	0.5994	0.0573	0.3433	77.9	Unstable Strip/Rect	0.701779	0.29822	0.50	0.50
31	78.9	122.4	75.7	0.0281	0.0034	0.9685	75.8	Unstable Strip/Rect	0.506274	0.49373	0.50	0.50
32	78.9	122.4	65.8	0.0883	0.0102	0.9015	76.2	Unstable Strip/Rect	0.520536	0.47946	0.50	0.50
33	78.9	122.4	65.8	0.2738	0.0256	0.7006	77.2	Unstable Strip/Rect	0.572974	0.42703	0.50	0.50
34	78.9	122.4	65.8	0.8386	0.0172	0.1442	78.8	Unstable Strip/Rect	0.858941	0.14106	0.50	0.50
35	78.9	122.4	77.9	0.0493	0.0019	0.9488	78.0	Unstable Strip/Rect	0.512161	0.48784	0.50	0.50
36	78.9	122.4	77.9	0.1552	0.0054	0.8394	78.2	Unstable Strip/Rect	0.54072	0.45928	0.50	0.50
37	78.9	122.4	77.9	0.4863	0.0103	0.5034	78.6	Unstable Strip/Rect	0.658308	0.34169	0.50	0.50
38	78.9	122.4	78.4	0.073	0.0013	0.9257	78.5	Unstable Strip/Rect	0.518617	0.48138	0.50	0.50
39	78.9	122.4	78.4	0.2302	0.0033	0.7665	78.6	Unstable Strip/Rect	0.564223	0.43578	0.50	0.50
40	78.9	122.4	78.4	0.7245	0.0038	0.2717	78.9	Unstable Strip/Rect	0.783361	0.21664	0.50	0.50
41	-11.3	27.1	50.4	0.0042	0.0230	0.9728	48.8	Stable Strip/Rect	0.495235	0.50476	0.50	0.50
42	-11.3	27.1	50.4	0.0126	0.0727	0.9147	45.8	Stable Strip/Rect	0.484306	0.51569	0.50	0.50
43	-11.3	27.1	50.4	0.0325	0.2276	0.7399	38.6	Stable Strip/Rect	0.443934	0.55607	0.50	0.50
44	-11.3	27.1	50.4	0.0371	0.7023	0.2606	28.4	Stable Strip/Rect	0.236157	0.76384	0.50	0.50
45	-11.3	31.5	116.9	0.0416	0.1857	0.7727	62.0	Stable Stripping	0.459356	0.54064	0.50	0.50
46	-11.3	31.5	116.9	0.0581	0.5958	0.3461	35.9	Stable Strip/Rect	0.300275	0.69973	0.50	0.50

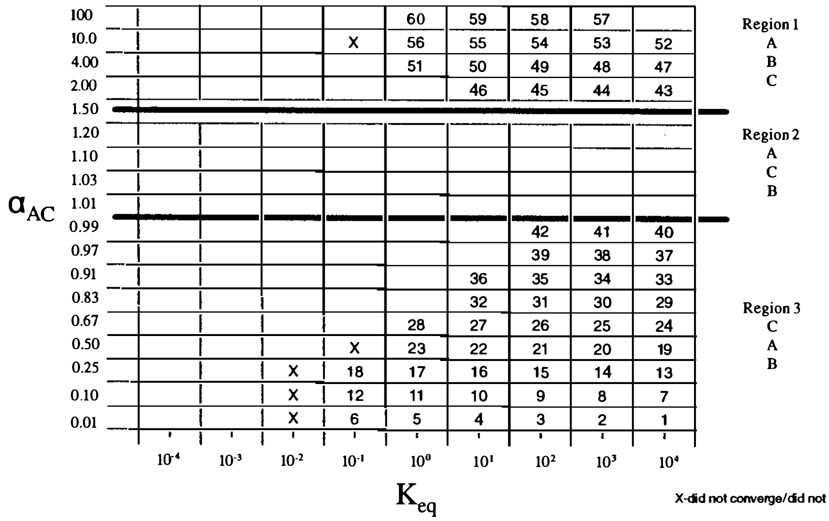
Figure 108. A+B↔C α_{AB} =4.0: Reactive Azeotropes



X-did not converge/did not analyze

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB.azeo	XC.azeo	XB.F	XC.F
1	99.0	117.9	-40.1	0.0099	0.0099	0.9802	-39.7	Unstable Strip/Rect	0.500	0.500	0.50	0.50
2	99.0	117.9	-40.1	0.0306	0.0306	0.9388	-38.7	Unstable Strip/Rect	0.500	0.500	0.50	0.50
3	99.0	117.9	-40.1	0.0905	0.0905	0.8190	-35.6	Unstable Strip/Rect	0.500	0.500	0.50	0.50
4	99.0	117.9	-40.1	0.2318	0.2316	0.5366	-25.4	Unstable Strip/Rect	0.500	0.500	0.50	0.50
5	99.0	117.9	-40.1	0.4156	0.4128	0.1716	7.4	Unstable Rectifying	0.501	0.499	0.50	0.50
6	99.0	117.9	-40.1	0.5286	0.4477	0.0237	74.7	Unstable Strip/Rect	0.540	0.460	0.50	0.50
7	99.0	119.7	26.0	0.0101	0.0097	0.9802	26.6	Unstable Strip/Rect	0.500	0.500	0.50	0.50
8	99.0	119.7	26.0	0.0312	0.0301	0.9387	27.7	Unstable Strip/Rect	0.500	0.500	0.50	0.50
9	99.0	119.7	26.0	0.0923	0.0887	0.8190	31.3	Unstable Strip/Rect	0.501	0.499	0.50	0.50
10	99.0	119.7	26.0	0.2384	0.2250	0.5366	42.8	Unstable Strip/Rect	0.504	0.496	0.50	0.50
11	99.0	119.7	26.0	0.4527	0.3768	0.1705	72.9	Unstable Strip/Rect	0.532	0.468	0.50	0.50
12	99.0	119.7	26.0	0.8330	0.1542	0.0128	98.4	Unstable Strip/Rect	0.835	0.165	0.50	0.50
13	99.0	119.7	53.6	0.0105	0.0093	0.9802	54.2	Unstable Strip/Rect	0.500	0.500	0.50	0.50
14	99.0	119.7	53.6	0.0327	0.0287	0.9386	55.2	Unstable Strip/Rect	0.501	0.499	0.50	0.50
15	99.0	119.7	53.6	0.0972	0.0842	0.8186	58.6	Unstable Strip/Rect	0.504	0.496	0.50	0.50
16	99.0	119.7	53.6	0.2550	0.2098	0.5352	68.7	Unstable Strip/Rect	0.515	0.485	0.50	0.50
17	99.0	119.7	53.6	0.5251	0.3113	0.1636	89.8	Unstable Strip/Rect	0.592	0.408	0.50	0.50
18	99.0	120.7	76.0	0.0120	0.0082	0.9798	76.4	Unstable Strip/Rect	0.501	0.499	0.50	0.50
19	99.0	120.7	76.0	0.0373	0.0252	0.9375	77.2	Unstable Strip/Rect	0.503	0.497	0.50	0.50
20	99.0	120.7	76.0	0.1117	0.0730	0.8153	79.8	Unstable Strip/Rect	0.511	0.489	0.50	0.50
21	99.0	120.7	76.0	0.3030	0.1729	0.5241	86.9	Unstable Rectifying	0.543	0.457	0.50	0.50
22	99.0	120.7	76.0	0.7276	0.1577	0.1147	97.8	Unstable Strip/Rect	0.756	0.244	0.50	0.50
23	99.0	120.7	85.7	0.0139	0.0070	0.9791	86.0	Unstable Strip/Rect	0.502	0.498	0.50	0.50
24	99.0	120.7	85.7	0.0433	0.0216	0.9351	86.6	Unstable Strip/Rect	0.506	0.494	0.50	0.50
25	99.0	120.7	85.7	0.1309	0.0617	0.8074	88.6	Unstable Strip/Rect	0.519	0.481	0.50	0.50
26	99.0	120.7	85.7	0.3662	0.1360	0.4978	93.5	Unstable Strip/Rect	0.577	0.423	0.50	0.50
27	99.0	120.7	85.7	0.9937	0.0032	0.0031	99.0	Unstable Strip/Rect	0.994	0.006	0.50	0.50
28	99.0	121.6	92.7	0.0183	0.0053	0.9764	92.9	Unstable Strip/Rect	0.503	0.497	0.50	0.50
29	99.0	121.6	92.7	0.0572	0.0162	0.9266	93.4	Unstable Strip/Rect	0.511	0.489	0.50	0.50
30	99.0	121.6	92.7	0.1749	0.0446	0.7805	94.6	Unstable Strip/Rect	0.537	0.463	0.50	0.50
31	99.0	121.6	92.7	0.5113	0.0800	0.4087	97.5	Unstable Strip/Rect	0.653	0.347	0.50	0.50
32	99.0	121.6	95.6	0.0235	0.0041	0.9724	95.7	Unstable Strip/Rect	0.505	0.495	0.50	0.50
33	99.0	121.6	95.6	0.0738	0.0124	0.9138	96.1	Unstable Strip/Rect	0.516	0.484	0.50	0.50
34	99.0	121.6	95.6	0.2278	0.0323	0.7399	96.9	Unstable Strip/Rect	0.556	0.444	0.50	0.50
35	99.0	121.6	95.6	0.6856	0.0400	0.2744	98.7	Unstable Strip/Rect	0.753	0.247	0.50	0.50
36	99.0	121.6	98.0	0.0419	0.0023	0.9558	98.1	Unstable Strip/Rect	0.510	0.490	0.50	0.50
37	99.0	121.6	98.0	0.1319	0.0065	0.8616	98.3	Unstable Strip/Rect	0.534	0.466	0.50	0.50
38	99.0	121.6	98.0	0.4123	0.0139	0.5738	98.7	Unstable Strip/Rect	0.627	0.373	0.50	0.50
39	99.0	121.6	98.4	0.0557	0.0017	0.9426	98.5	Unstable Strip/Rect	0.514	0.486	0.50	0.50
40	99.0	121.6	98.4	0.1754	0.0047	0.8199	98.6	Unstable Strip/Rect	0.547	0.453	0.50	0.50
41	99.0	121.6	98.4	0.5504	0.0080	0.4416	98.9	Unstable Strip/Rect	0.688	0.312	0.50	0.50
42	-11.3	7.0	24.1	0.0057	0.0171	0.9772	23.3	Stable Strip/Rect	0.497	0.503	0.50	0.50
43	-11.3	7.0	24.1	0.0174	0.0534	0.9292	21.7	Stable Strip/Rect	0.491	0.509	0.50	0.50
44	-11.3	7.0	24.1	0.0483	0.1634	0.7883	17.7	Stable Strip/Rect	0.468	0.532	0.50	0.50
45	-11.3	7.0	24.1	0.0907	0.4768	0.4325	10.4	Stable Strip/Rect	0.365	0.635	0.50	0.50
46	-11.3	7.5	48.3	0.0068	0.0143	0.9789	46.0	Stable Strip/Rect	0.498	0.502	0.50	0.50
47	-11.3	7.5	48.3	0.0208	0.0448	0.9344	41.6	Stable Strip/Rect	0.494	0.506	0.50	0.50
48	-11.3	7.5	48.3	0.0586	0.1373	0.8041	31.2	Stable Strip/Rect	0.478	0.522	0.50	0.50
49	-11.3	7.5	48.3	0.1220	0.3955	0.4825	15.7	Stable Strip/Rect	0.408	0.592	0.50	0.50
50	-11.3	10.0	112.2	0.0224	0.0417	0.9359	84.6	Stable Stripping	0.495	0.505	0.50	0.50
51	-11.3	10.0	112.2	0.0616	0.1310	0.8074	49.2	Stable Strip/Rect	0.481	0.519	0.50	0.50
52	-11.3	10.0	112.2	0.1260	0.3868	0.4872	21.2	Stable Strip/Rect	0.412	0.588	0.50	0.50

Figure 109. A+B↔C α_{AB} =2.0: Reactive Azeotropes



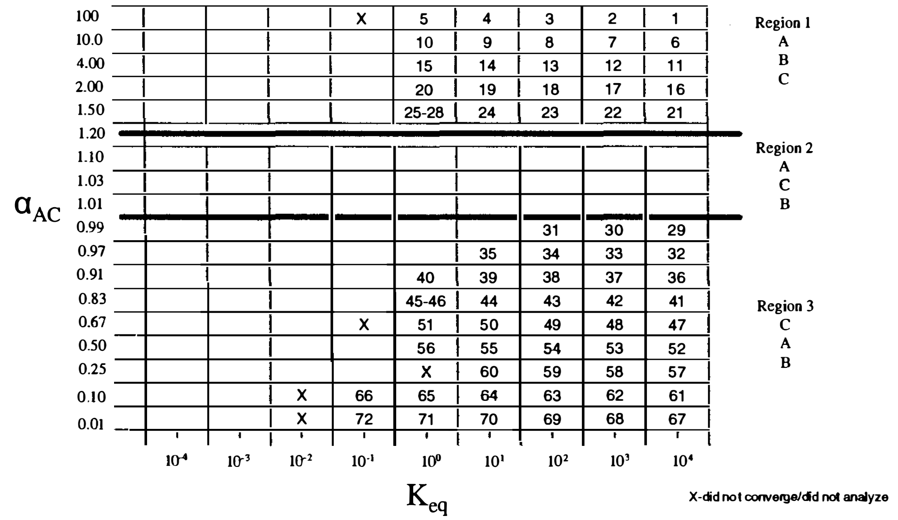
X-did not converge/did not analyze

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	102.7	113.1	-40.1	0.0099	0.0099	0.9802	-39.6	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
2	102.7	113.1	-40.1	0.0306	0.0306	0.9388	-38.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
3	102.7	113.1	-40.1	0.0905	0.0905	0.8190	-35.6	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
4	102.7	113.1	-40.1	0.2317	0.2316	0.5367	-25.4	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
5	102.7	113.1	-40.1	0.4150	0.4135	0.1715	7.5	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
6	102.7	113.1	-40.1	0.5106	0.4656	0.0238	74.9	Unstable	Rectifying	0.522	0.478	0.50	0.50
7	102.7	115.0	30.0	0.0100	0.0098	0.9802	30.6	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
8	102.7	115.0	30.0	0.0310	0.0303	0.9387	31.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
9	102.7	115.0	30.0	0.0918	0.0892	0.8190	35.3	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
10	102.7	115.0	30.0	0.2365	0.2269	0.5366	46.8	Unstable	Strip/Rect	0.503	0.497	0.50	0.50
11	102.7	115.0	30.0	0.4408	0.3881	0.1711	76.1	Unstable	Strip/Rect	0.523	0.477	0.50	0.50
12	102.7	115.0	30.0	0.7224	0.2589	0.0187	101.2	Unstable	Strip/Rect	0.727	0.273	0.50	0.50
13	102.7	115.0	58.6	0.0104	0.0094	0.9802	59.1	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
14	102.7	115.0	58.6	0.0322	0.0292	0.9386	60.2	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
15	102.7	115.0	58.6	0.0954	0.0858	0.8188	63.4	Unstable	Strip/Rect	0.503	0.497	0.50	0.50
16	102.7	115.0	58.6	0.2487	0.2155	0.5358	73.2	Unstable	Strip/Rect	0.511	0.489	0.50	0.50
17	102.7	115.0	58.6	0.4934	0.3392	0.1674	92.9	Unstable	Strip/Rect	0.566	0.434	0.50	0.50
18	102.7	115.0	58.6	0.9977	0.0021	0.0002	102.7	Unstable	Stripping	0.998	0.002	0.50	0.50
19	102.7	115.9	80.3	0.0114	0.0086	0.9800	80.7	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
20	102.7	115.9	80.3	0.0355	0.0264	0.9381	81.5	Unstable	Strip/Rect	0.502	0.498	0.50	0.50
21	102.7	115.9	80.3	0.1061	0.0770	0.8169	83.9	Unstable	Strip/Rect	0.508	0.492	0.50	0.50
22	102.7	115.9	80.3	0.2840	0.1864	0.5296	90.5	Unstable	Strip/Rect	0.532	0.468	0.50	0.50
23	102.7	115.9	80.3	0.6428	0.2174	0.1398	100.8	Unstable	Rectifying	0.687	0.313	0.50	0.50
24	102.7	115.9	90.0	0.0129	0.0076	0.9795	90.2	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
25	102.7	115.9	90.0	0.0402	0.0233	0.9365	90.8	Unstable	Strip/Rect	0.504	0.496	0.50	0.50
26	102.7	115.9	90.0	0.1210	0.0671	0.8119	92.6	Unstable	Strip/Rect	0.515	0.485	0.50	0.50
27	102.7	115.9	90.0	0.3332	0.1539	0.5129	97.0	Unstable	Strip/Rect	0.559	0.441	0.50	0.50
28	102.7	115.9	90.0	0.8506	0.0807	0.0687	102.6	Unstable	Strip/Rect	0.860	0.140	0.50	0.50
29	102.7	115.9	96.6	0.0161	0.0061	0.9778	96.8	Unstable	Strip/Rect	0.503	0.497	0.50	0.50
30	102.7	115.9	96.6	0.0502	0.0185	0.9313	97.1	Unstable	Strip/Rect	0.508	0.492	0.50	0.50
31	102.7	115.9	96.6	0.1528	0.0521	0.7951	98.2	Unstable	Strip/Rect	0.528	0.472	0.50	0.50
32	102.7	115.9	96.6	0.4376	0.1046	0.4578	100.8	Unstable	Strip/Rect	0.614	0.386	0.50	0.50
33	102.7	115.9	99.7	0.0209	0.0047	0.9744	99.8	Unstable	Strip/Rect	0.504	0.496	0.50	0.50
34	102.7	115.9	99.7	0.0654	0.0141	0.9205	100.0	Unstable	Strip/Rect	0.513	0.487	0.50	0.50
35	102.7	115.9	99.7	0.2009	0.0379	0.7612	100.8	Unstable	Strip/Rect	0.546	0.454	0.50	0.50
36	102.7	115.9	99.7	0.5965	0.0579	0.3456	102.3	Unstable	Strip/Rect	0.700	0.300	0.50	0.50
37	102.7	115.9	101.8	0.0363	0.0027	0.9610	101.9	Unstable	Strip/Rect	0.509	0.491	0.50	0.50
38	102.7	115.9	99.7	0.1141	0.0077	0.8782	102.0	Unstable	Strip/Rect	0.528	0.472	0.50	0.50
39	102.7	115.9	99.7	0.3555	0.0176	0.6269	102.4	Unstable	Strip/Rect	0.604	0.396	0.50	0.50
40	102.7	115.9	102.3	0.0504	0.0019	0.9477	102.3	Unstable	Strip/Rect	0.512	0.488	0.50	0.50
41	102.7	115.9	102.3	0.1589	0.0053	0.8358	102.4	Unstable	Strip/Rect	0.542	0.458	0.50	0.50
42	102.7	115.9	102.3	0.4978	0.0099	0.4923	102.6	Unstable	Rectifying	0.663	0.337	0.50	0.50
43	-11.3	-1.1	6.0	0.0057	0.0172	0.9771	5.7	Stable	Strip/Rect	0.497	0.503	0.50	0.50
44	-11.3	-1.1	6.0	0.0173	0.0537	0.9290	5.1	Stable	Strip/Rect	0.491	0.509	0.50	0.50
45	-11.3	-1.1	6.0	0.0480	0.1641	0.7879	3.6	Stable	Strip/Rect	0.468	0.532	0.50	0.50
46	-11.3	-1.1	6.0	0.0912	0.4755	0.4333	0.5	Stable	Strip/Rect	0.366	0.634	0.50	0.50
47	-11.3	-1.1	23.0	0.0075	0.0131	0.9794	22.1	Stable	Strip/Rect	0.499	0.501	0.50	0.50
48	-11.3	-1.1	23.0	0.0230	0.0407	0.9363	20.1	Stable	Strip/Rect	0.495	0.505	0.50	0.50
49	-11.3	-1.1	23.0	0.0659	0.1230	0.8111	15.2	Stable	Strip/Rect	0.484	0.516	0.50	0.50
50	-11.3	-1.1	23.0	0.1491	0.3415	0.5094	6.1	Stable	Strip/Rect	0.436	0.564	0.50	0.50

Figure 110. A+B↔C α_{AB} =1.5: Reactive Azeotropes

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
51	-11.3	-1.1	23.0	0.0570	0.8921	0.0509	-1.0	Stable	Strip/Rect	0.103	0.897	0.50	0.50
52	-11.3	-0.1	47.3	0.0080	0.0123	0.9797	44.7	Stable	Strip/Rect	0.499	0.501	0.50	0.50
53	-11.3	-0.1	47.3	0.0245	0.0382	0.9373	39.8	Stable	Strip/Rect	0.496	0.504	0.50	0.50
54	-11.3	-0.1	47.3	0.0704	0.1156	0.8140	28.3	Stable	Strip/Rect	0.488	0.512	0.50	0.50
55	-11.3	-0.1	47.3	0.1619	0.3200	0.5181	5.9	Stable	Strip/Rect	0.448	0.552	0.50	0.50
56	-11.3	-0.1	47.3	0.1057	0.8089	0.0854	0.3	Stable	Strip/Rect	0.176	0.824	0.50	0.50
57	-11.3	0.9	110.3	0.0256	0.0366	0.9378	90.9	Stable	Stripping	0.497	0.503	0.50	0.50
58	-11.3	0.9	110.3	0.0726	0.1123	0.8151	44.1	Stable	Strip/Rect	0.489	0.511	0.50	0.50
59	-11.3	0.9	110.3	0.1653	0.3146	0.5201	15.6	Stable	Strip/Rect	0.451	0.549	0.50	0.50
60	-11.3	0.9	110.3	0.1129	0.7971	0.0900	1.5	Stable	Strip/Rect	0.186	0.814	0.50	0.50

Figure 110. Continued.



α_{AC}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100				X	5	4	3	2	1
10.0					10	9	8	7	6
4.00					15	14	13	12	11
2.00					20	19	18	17	16
1.50					25-28	24	23	22	21
1.20									
1.10									
1.03									
1.01									
0.99							31	30	29
0.97						35	34	33	32
0.91					40	39	38	37	36
0.83					45-46	44	43	42	41
0.67				X	51	50	49	48	47
0.50					56	55	54	53	52
0.25					X	60	59	58	57
0.10			X	66	65	64	63	62	61
0.01			X	72	71	70	69	68	67

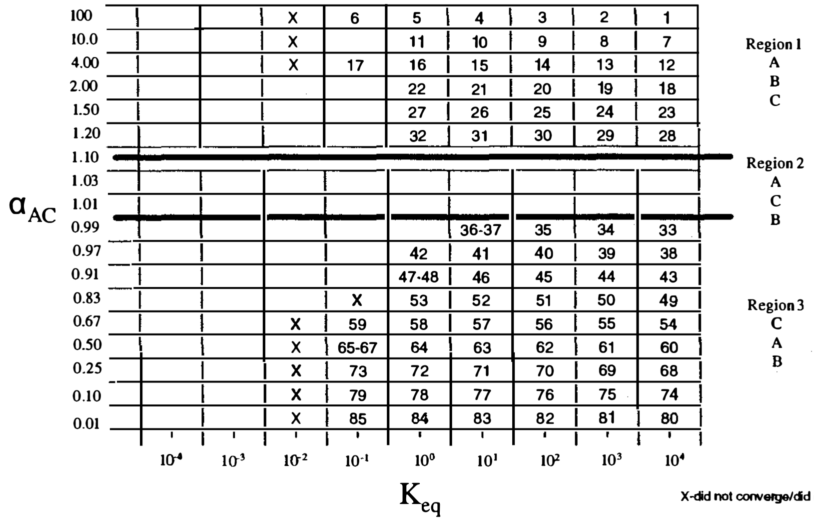
X-did not converge/did not analyze

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	-11.3	-5.6	109.4	0.0037	0.0043	0.9920	103.5	Stable	Stripping	0.500	0.500	0.50	0.50
2	-11.3	-5.6	109.4	0.0282	0.0330	0.9388	73.9	Stable	Strip/Rect	0.499	0.501	0.50	0.50
3	-11.3	-5.6	109.4	0.0817	0.1001	0.8182	40.6	Stable	Strip/Rect	0.495	0.505	0.50	0.50
4	-11.3	-5.6	109.4	0.1989	0.2681	0.5330	11.9	Stable	Strip/Rect	0.477	0.523	0.50	0.50
5	-11.3	-5.6	109.4	0.2636	0.5828	0.1536	-3.4	Stable	Strip/Rect	0.362	0.638	0.50	0.50
6	-11.3	-6.9	46.6	0.0091	0.0107	0.9802	43.7	Stable	Strip/Rect	0.500	0.500	0.50	0.50
7	-11.3	-6.9	46.6	0.0281	0.0334	0.9385	38.3	Stable	Strip/Rect	0.499	0.501	0.50	0.50
8	-11.3	-6.9	46.6	0.0822	0.0995	0.8183	25.9	Stable	Strip/Rect	0.495	0.505	0.50	0.50
9	-11.3	-6.9	46.6	0.2027	0.2634	0.5339	8.1	Stable	Strip/Rect	0.480	0.520	0.50	0.50
10	-11.3	-6.9	46.6	0.2848	0.5567	0.1585	-4.6	Stable	Strip/Rect	0.383	0.617	0.50	0.50
11	-11.3	-6.9	23.0	0.0089	0.0111	0.9800	21.9	Stable	Strip/Rect	0.499	0.501	0.50	0.50
12	-11.3	-6.9	23.0	0.0273	0.0344	0.9383	19.6	Stable	Strip/Rect	0.498	0.502	0.50	0.50
13	-11.3	-6.9	23.0	0.0798	0.1025	0.8177	13.9	Stable	Strip/Rect	0.494	0.506	0.50	0.50
14	-11.3	-6.9	23.0	0.1954	0.2724	0.5322	3.6	Stable	Strip/Rect	0.475	0.525	0.50	0.50
15	-11.3	-6.9	23.0	0.2560	0.5924	0.1516	-5.4	Stable	Strip/Rect	0.354	0.646	0.50	0.50
16	-11.3	-6.9	5.8	0.0082	0.0120	0.9798	5.5	Stable	Strip/Rect	0.499	0.501	0.50	0.50
17	-11.3	-6.9	5.8	0.0252	0.0373	0.9375	4.7	Stable	Strip/Rect	0.497	0.503	0.50	0.50
18	-11.3	-6.9	5.8	0.0731	0.1116	0.8153	2.5	Stable	Strip/Rect	0.489	0.511	0.50	0.50
19	-11.3	-6.9	5.8	0.1738	0.3017	0.5245	-2.0	Stable	Strip/Rect	0.458	0.542	0.50	0.50
20	-11.3	-6.9	5.8	0.1660	0.7152	0.1188	-6.5	Stable	Strip/Rect	0.255	0.745	0.50	0.50
21	-11.3	-6.9	-1.4	0.0071	0.0139	0.9790	-1.6	Stable	Strip/Rect	0.498	0.502	0.50	0.50
22	-11.3	-6.9	-1.4	0.0217	0.0432	0.9351	-1.9	Stable	Strip/Rect	0.494	0.506	0.50	0.50
23	-11.3	-6.9	-1.4	0.0619	0.1304	0.8077	-2.9	Stable	Strip/Rect	0.481	0.519	0.50	0.50
24	-11.3	-6.9	-1.4	0.1373	0.3636	0.4991	-5.0	Stable	Strip/Rect	0.425	0.575	0.50	0.50
25	-11.3	-6.9	-1.4	0.0113	0.9777	0.0110	-6.9	Stable	Strip/Rect	0.022	0.978	0.50	0.50
26	-11.3	-6.9	-1.4	0.0088	0.9826	0.0086	-6.9	Stable	Rectifying	0.017	0.983	0.50	0.50
27	-11.3	-6.9	-1.4	0.0059	0.9882	0.0059	-6.9	Stable	Stripping	0.012	0.988	0.50	0.50
28	-11.3	-6.9	-1.4	0.0051	0.9899	0.0050	-6.9	Unstable	Rectifying	0.010	0.990	0.50	0.50
29	102.7	107.7	102.3	0.0338	0.0029	0.9633	102.3	Unstable	Strip/Rect	0.508	0.492	0.50	0.50
30	102.7	107.7	102.3	0.1061	0.0083	0.8856	102.4	Unstable	Strip/Rect	0.526	0.474	0.50	0.50
31	102.7	107.7	102.3	0.3302	0.0197	0.6501	102.5	Unstable	Strip/Rect	0.594	0.406	0.50	0.50
32	102.7	107.7	101.8	0.0248	0.0039	0.9713	101.9	Unstable	Strip/Rect	0.505	0.495	0.50	0.50
33	102.7	107.7	101.8	0.0779	0.0117	0.9104	102.0	Unstable	Strip/Rect	0.517	0.483	0.50	0.50
34	102.7	107.7	101.8	0.2405	0.0303	0.7292	102.2	Unstable	Strip/Rect	0.561	0.439	0.50	0.50
35	102.7	107.7	101.8	0.7269	0.0330	0.2401	102.7	Unstable	Strip/Rect	0.780	0.220	0.50	0.50
36	102.7	107.7	99.7	0.0156	0.0063	0.9781	99.7	Unstable	Strip/Rect	0.502	0.498	0.50	0.50
37	102.7	107.7	99.7	0.0485	0.0192	0.9323	99.9	Unstable	Strip/Rect	0.508	0.492	0.50	0.50
38	102.7	107.7	99.7	0.1474	0.0542	0.7984	100.5	Unstable	Strip/Rect	0.526	0.474	0.50	0.50
39	102.7	107.7	99.7	0.4196	0.1117	0.4687	101.8	Unstable	Strip/Rect	0.605	0.395	0.50	0.50
40	102.7	107.7	99.7	0.9973	0.0014	0.0013	102.7	Unstable	Stripping	0.997	0.003	0.50	0.50
41	102.7	107.7	96.6	0.0129	0.0076	0.9795	96.7	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
42	102.7	107.7	96.6	0.0402	0.0233	0.9365	97.0	Unstable	Strip/Rect	0.504	0.496	0.50	0.50
43	102.7	107.7	96.6	0.1208	0.0672	0.8120	97.9	Unstable	Strip/Rect	0.515	0.485	0.50	0.50
44	102.7	107.7	96.6	0.3317	0.1548	0.5135	100.1	Unstable	Stripping	0.558	0.442	0.50	0.50
45	102.7	107.7	96.6	0.8415	0.0861	0.0724	102.6	Unstable	Strip/Rect	0.852	0.148	0.50	0.50
46	102.7	107.7	96.6	0.9973	0.0014	0.0013	102.7	Stable	Rectifying	0.997	0.003	0.50	0.50
47	102.7	107.7	90.0	0.0113	0.0087	0.9800	90.2	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
48	102.7	107.7	90.0	0.0351	0.0268	0.9381	90.7	Unstable	Strip/Rect	0.502	0.498	0.50	0.50
49	102.7	107.7	90.0	0.1046	0.0781	0.8173	92.2	Unstable	Strip/Rect	0.507	0.493	0.50	0.50
50	102.7	107.7	90.0	0.2784	0.1907	0.5309	96.1	Unstable	Strip/Rect	0.529	0.471	0.50	0.50

Figure 111. A+B↔C α_{AB} =1.2: Reactive Azeotropes

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope	Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node	XB,azeo	XC,azeo	XB,F	XC,F
51	102.7	107.7	90.0	0.6146	0.2387	0.1467	101.6	Unstable Strip/Rect	0.664	0.336	0.50	0.50
52	102.7	107.7	80.3	0.0106	0.0093	0.9801	80.7	Unstable Strip/Rect	0.500	0.500	0.50	0.50
53	102.7	107.7	80.3	0.0328	0.0286	0.9386	81.4	Unstable Strip/Rect	0.501	0.499	0.50	0.50
54	102.7	107.7	80.3	0.0975	0.0840	0.8185	83.6	Unstable Strip/Rect	0.504	0.496	0.50	0.50
55	102.7	107.7	80.3	0.2550	0.2098	0.5352	89.6	Unstable Strip/Rect	0.515	0.485	0.50	0.50
56	102.7	107.7	80.3	0.5157	0.3195	0.1648	99.2	Unstable Strip/Rect	0.584	0.416	0.50	0.50
57	102.7	107.7	58.6	0.0101	0.0097	0.9802	59.1	Unstable Strip/Rect	0.500	0.500	0.50	0.50
58	102.7	107.7	58.6	0.0313	0.0299	0.9388	60.1	Unstable Strip/Rect	0.500	0.500	0.50	0.50
59	102.7	107.7	58.6	0.0928	0.0883	0.8189	63.3	Unstable Strip/Rect	0.501	0.499	0.50	0.50
60	102.7	107.7	58.6	0.2395	0.2240	0.5365	72.7	Unstable Strip/Rect	0.505	0.495	0.50	0.50
61	102.7	107.7	30.0	0.0100	0.0098	0.9802	30.6	Unstable Strip/Rect	0.500	0.500	0.50	0.50
62	102.7	107.7	30.0	0.0308	0.0305	0.9387	31.7	Unstable Strip/Rect	0.500	0.500	0.50	0.50
63	102.7	107.7	30.0	0.0911	0.0899	0.8190	35.3	Unstable Strip/Rect	0.500	0.500	0.50	0.50
64	102.7	107.7	30.0	0.2339	0.2294	0.5367	46.6	Unstable Strip/Rect	0.501	0.499	0.50	0.50
65	102.7	107.7	30.0	0.4263	0.4022	0.1715	75.1	Unstable Strip/Rect	0.510	0.490	0.50	0.50
66	102.7	107.7	30.0	0.5935	0.3837	0.0228	99.4	Unstable Strip/Rect	0.603	0.397	0.50	0.50
67	102.7	107.7	-40.1	0.0099	0.0099	0.9802	-39.7	Unstable Strip/Rect	0.500	0.500	0.50	0.50
68	102.7	107.7	-40.1	0.0306	0.0306	0.9388	-38.7	Unstable Strip/Rect	0.500	0.500	0.50	0.50
69	102.7	107.7	-40.1	0.0905	0.0905	0.8190	-35.6	Unstable Strip/Rect	0.500	0.500	0.50	0.50
70	102.7	107.7	-40.1	0.2317	0.2316	0.5367	-25.4	Unstable Strip/Rect	0.500	0.500	0.50	0.50
71	102.7	107.7	-40.1	0.4146	0.4138	0.1716	7.5	Unstable Strip/Rect	0.500	0.500	0.50	0.50
72	102.7	107.7	-40.1	0.4998	0.4764	0.0238	74.0	Unstable Strip/Rect	0.511	0.489	0.50	0.50

Figure 111. Continued.



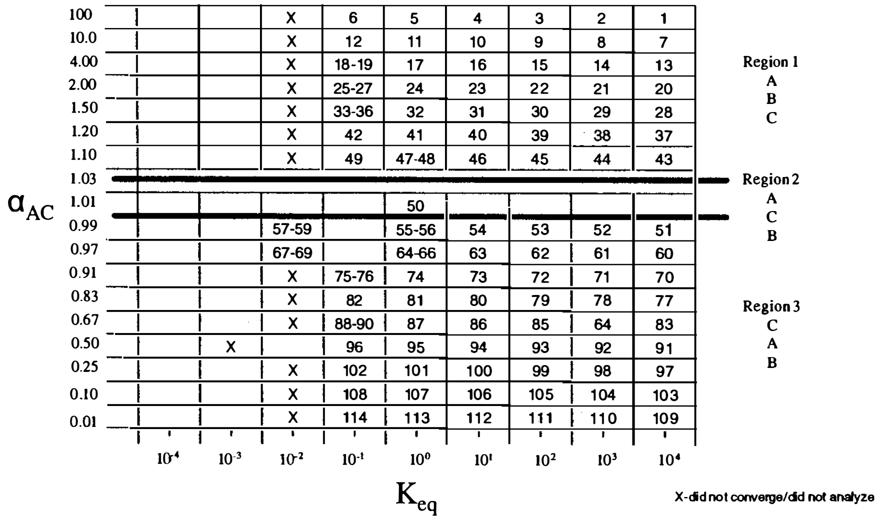
X-did not converge/did not analyze

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	-11.3	-8.4	108.4	0.0095	0.0103	0.9802	92.8	Stable	Strip/Rect	0.500	0.500	0.50	0.50
2	-11.3	-8.4	108.4	0.0293	0.0320	0.9387	72.5	Stable	Strip/Rect	0.499	0.501	0.50	0.50
3	-11.3	-8.4	108.4	0.0858	0.0954	0.8188	39.1	Stable	Strip/Rect	0.497	0.503	0.50	0.50
4	-11.3	-8.4	108.4	0.2141	0.2502	0.5357	10.4	Stable	Strip/Rect	0.488	0.512	0.50	0.50
5	-11.3	-8.4	108.4	0.3333	0.5001	0.1666	-5.3	Unstable	Strip/Rect	0.429	0.571	0.50	0.50
6	-11.3	-8.4	108.4	0.0021	0.9977	0.0002	-8.4	Unstable	Rectifying	0.002	0.998	0.50	0.50
7	-11.3	-8.7	46.6	0.0094	0.0104	0.9802	43.6	Stable	Strip/Rect	0.500	0.500	0.50	0.50
8	-11.3	-8.7	46.6	0.0291	0.0322	0.9387	38.0	Stable	Strip/Rect	0.499	0.501	0.50	0.50
9	-11.3	-8.7	46.6	0.0855	0.0957	0.8188	25.3	Stable	Strip/Rect	0.497	0.503	0.50	0.50
10	-11.3	-8.7	46.6	0.2142	0.2501	0.5357	7.2	Stable	Strip/Rect	0.488	0.512	0.50	0.50
11	-11.3	-8.7	46.6	0.3361	0.4969	0.1670	-5.7	Stable	Strip/Rect	0.431	0.569	0.50	0.50
12	-11.3	-8.8	23.0	0.0093	0.0105	0.9802	21.9	Stable	Strip/Rect	0.500	0.500	0.50	0.50
13	-11.3	-8.8	23.0	0.0287	0.0327	0.9386	19.5	Stable	Strip/Rect	0.499	0.501	0.50	0.50
14	-11.3	-8.8	23.0	0.0844	0.0970	0.8186	13.5	Stable	Strip/Rect	0.497	0.503	0.50	0.50
15	-11.3	-8.8	23.0	0.2109	0.2538	0.5353	2.8	Stable	Strip/Rect	0.486	0.514	0.50	0.50
16	-11.3	-8.8	23.0	0.3235	0.5111	0.1654	-6.5	Stable	Strip/Rect	0.420	0.580	0.50	0.50
17	-11.3	-8.8	23.0	0.0021	0.9977	0.0002	-8.8	Stable	Rectifying	0.002	0.998	0.50	0.50
18	-11.3	-8.8	5.8	0.0089	0.0110	0.9801	5.4	Stable	Strip/Rect	0.499	0.501	0.50	0.50
19	-11.3	-8.8	5.8	0.0276	0.0340	0.9384	4.6	Stable	Strip/Rect	0.498	0.502	0.50	0.50
20	-11.3	-8.8	5.8	0.0807	0.1014	0.8179	2.2	Stable	Strip/Rect	0.494	0.506	0.50	0.50
21	-11.3	-8.8	5.8	0.1991	0.2678	0.5331	-2.7	Stable	Strip/Rect	0.478	0.522	0.50	0.50
22	-11.3	-8.8	5.8	0.2744	0.5694	0.1562	-7.8	Stable	Strip/Rect	0.372	0.628	0.50	0.50
23	-11.3	-8.9	-1.4	0.0084	0.0116	0.9800	-1.6	Stable	Strip/Rect	0.499	0.501	0.50	0.50
24	-11.3	-8.9	5.8	0.0260	0.0361	0.9379	-2.0	Stable	Strip/Rect	0.497	0.503	0.50	0.50
25	-11.3	-8.9	5.8	0.0757	0.1078	0.8165	-3.2	Stable	Strip/Rect	0.491	0.509	0.50	0.50
26	-11.3	-8.9	5.8	0.1827	0.2891	0.5282	-5.7	Stable	Strip/Rect	0.465	0.535	0.50	0.50
27	-11.3	-8.9	5.8	0.2051	0.6596	0.1353	-8.6	Stable	Strip/Rect	0.300	0.700	0.50	0.50
28	-11.3	-8.9	-6.9	0.0065	0.0150	0.9785	-7.0	Stable	Strip/Rect	0.498	0.502	0.50	0.50
29	-11.3	-8.9	-6.9	0.0200	0.0467	0.9333	-7.1	Stable	Strip/Rect	0.493	0.507	0.50	0.50
30	-11.3	-8.9	-6.9	0.0567	0.1415	0.8018	-7.5	Stable	Strip/Rect	0.476	0.524	0.50	0.50
31	-11.3	-8.9	-6.9	0.1200	0.3999	0.4801	-8.3	Stable	Strip/Rect	0.405	0.595	0.50	0.50
32	-11.3	-8.9	-6.9	0.0014	0.9973	0.0013	-8.9	Stable	Rectifying	0.003	0.997	0.50	0.50
33	102.7	105.6	102.3	0.0266	0.0037	0.9697	102.3	Unstable	Strip/Rect	0.506	0.494	0.50	0.50
34	102.7	105.6	102.3	0.0833	0.0109	0.9058	102.4	Unstable	Strip/Rect	0.519	0.481	0.50	0.50
35	102.7	105.6	102.3	0.2579	0.0277	0.7144	102.5	Unstable	Strip/Rect	0.567	0.433	0.50	0.50
36	102.7	105.6	102.3	0.7840	0.0244	0.1916	102.7	Unstable	Strip/Rect	0.819	0.181	0.50	0.50
37	102.7	105.6	102.3	0.9866	0.0012	0.0122	102.7	Stable	Rectifying	0.987	0.013	0.50	0.50
38	102.7	105.6	101.8	0.0200	0.0049	0.9751	101.9	Unstable	Strip/Rect	0.504	0.496	0.50	0.50
39	102.7	105.6	101.8	0.0626	0.0147	0.9227	102.0	Unstable	Strip/Rect	0.512	0.488	0.50	0.50
40	102.7	105.6	101.8	0.1921	0.0400	0.7679	102.2	Unstable	Strip/Rect	0.543	0.457	0.50	0.50
41	102.7	105.6	101.8	0.5669	0.0649	0.3682	102.6	Unstable	Strip/Rect	0.683	0.317	0.50	0.50
42	102.7	105.6	101.8	0.9973	0.0014	0.0013	102.7	Unstable	Stripping	0.997	0.003	0.50	0.50
43	102.7	105.6	99.7	0.0135	0.0073	0.9792	99.7	Unstable	Strip/Rect	0.502	0.498	0.50	0.50
44	102.7	105.6	99.7	0.0420	0.0223	0.9357	99.9	Unstable	Strip/Rect	0.505	0.495	0.50	0.50
45	102.7	105.6	99.7	0.1266	0.0639	0.8095	100.4	Unstable	Strip/Rect	0.517	0.483	0.50	0.50
46	102.7	105.6	99.7	0.3509	0.1439	0.5052	101.5	Unstable	Strip/Rect	0.569	0.431	0.50	0.50
47	102.7	105.6	99.7	0.9230	0.0400	0.0370	102.7	Unstable	Strip/Rect	0.926	0.074	0.50	0.50
48	102.7	105.6	99.7	0.9879	0.0061	0.0060	102.7	Stable	Rectifying	0.988	0.012	0.50	0.50
49	102.7	105.6	96.6	0.0118	0.0083	0.9799	96.7	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
50	102.7	105.6	96.6	0.0365	0.0257	0.9378	97.0	Unstable	Strip/Rect	0.503	0.497	0.50	0.50

Figure 112. A+B↔C α_{AB} =1.1: Reactive Azeotropes

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
51	102.7	105.6	96.6	0.1091	0.0748	0.8161	97.8	Unstable	Strip/Rect	0.509	0.491	0.50	0.50
52	102.7	105.6	96.6	0.2932	0.1798	0.5270	99.8	Unstable	Strip/Rect	0.537	0.463	0.50	0.50
53	102.7	105.6	96.6	0.6768	0.1927	0.1305	102.4	Unstable	Strip/Rect	0.714	0.286	0.50	0.50
54	102.7	105.6	90.0	0.0107	0.0091	0.9802	90.2	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
55	102.7	105.6	90.0	0.0333	0.0282	0.9385	90.7	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
56	102.7	105.6	90.0	0.0990	0.0827	0.8183	92.1	Unstable	Strip/Rect	0.504	0.496	0.50	0.50
57	102.7	105.6	90.0	0.2597	0.2058	0.5345	95.8	Unstable	Strip/Rect	0.518	0.482	0.50	0.50
58	102.7	105.6	90.0	0.5343	0.3036	0.1621	101.1	Unstable	Strip/Rect	0.599	0.401	0.50	0.50
59	102.7	105.6	90.0	0.9977	0.0021	0.0002	102.7	Unstable	Stripping	0.998	0.002	0.50	0.50
60	102.7	105.6	80.3	0.0103	0.0095	0.9802	80.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
61	102.7	105.6	80.3	0.0319	0.0294	0.9387	81.4	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
62	102.7	105.6	80.3	0.0947	0.0865	0.8189	83.5	Unstable	Strip/Rect	0.502	0.498	0.50	0.50
63	102.7	105.6	80.3	0.2455	0.2184	0.5361	89.3	Unstable	Strip/Rect	0.509	0.491	0.50	0.50
64	102.7	105.6	80.3	0.4743	0.3566	0.1691	98.6	Unstable	Strip/Rect	0.550	0.450	0.50	0.50
65	102.7	105.6	80.3	0.9221	0.0713	0.0066	102.7	Unstable	Stripping	0.923	0.077	0.50	0.50
66	102.7	105.6	80.3	0.9881	0.0109	0.0010	102.7	Stable	Rectifying	0.988	0.012	0.50	0.50
67	102.7	105.6	80.3	0.9564	0.0398	0.0038	102.7	Unstable	Rectifying	0.957	0.043	0.50	0.50
68	102.7	105.6	58.6	0.0100	0.0098	0.9802	59.1	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
69	102.7	105.6	58.6	0.0311	0.0302	0.9387	60.1	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
70	102.7	105.6	58.6	0.0918	0.0892	0.8190	63.3	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
71	102.7	105.6	58.6	0.2363	0.2271	0.5366	72.5	Unstable	Strip/Rect	0.503	0.497	0.50	0.50
72	102.7	105.6	58.6	0.4355	0.3933	0.1712	90.8	Unstable	Strip/Rect	0.518	0.482	0.50	0.50
73	102.7	105.6	58.6	0.6517	0.3269	0.0214	101.8	Unstable	Strip/Rect	0.659	0.341	0.50	0.50
74	102.7	105.6	30.0	0.0099	0.0099	0.9802	30.6	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
75	102.7	105.6	30.0	0.0307	0.0305	0.9388	31.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
76	102.7	105.6	30.0	0.0909	0.0901	0.8190	35.3	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
77	102.7	105.6	30.0	0.2330	0.2303	0.5367	46.5	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
78	102.7	105.6	30.0	0.4213	0.4072	0.1715	74.8	Unstable	Strip/Rect	0.506	0.494	0.50	0.50
79	102.7	105.6	30.0	0.5495	0.4270	0.0235	98.7	Unstable	Strip/Rect	0.560	0.440	0.50	0.50
80	102.7	105.6	-40.1	0.0099	0.0099	0.9802	-39.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
81	102.7	105.6	-40.1	0.0306	0.0306	0.9388	-38.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
82	102.7	105.6	-40.1	0.0905	0.0905	0.8190	-35.6	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
83	102.7	105.6	-40.1	0.2317	0.2316	0.5367	-25.5	Unstable	Rectifying	0.500	0.500	0.50	0.50
84	102.7	105.6	-40.1	0.4145	0.4140	0.1715	7.4	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
85	102.7	105.6	-40.1	0.4949	0.4813	0.0238	73.5	Unstable	Strip/Rect	0.507	0.493	0.50	0.50

Figure 112. Continued.



α_{AC}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100			X	6	5	4	3	2	1
10.0			X	12	11	10	9	8	7
4.00			X	18-19	17	16	15	14	13
2.00			X	25-27	24	23	22	21	20
1.50			X	33-36	32	31	30	29	28
1.20			X	42	41	40	39	38	37
1.10			X	49	47-48	46	45	44	43
1.03									
1.01					50				
0.99			57-59		55-56	54	53	52	51
0.97			67-69		64-66	63	62	61	60
0.91			X	75-76	74	73	72	71	70
0.83			X	82	81	80	79	78	77
0.67			X	88-90	87	86	85	64	83
0.50		X		96	95	94	93	92	91
0.25			X	102	101	100	99	98	97
0.10			X	108	107	106	105	104	103
0.01			X	114	113	112	111	110	109

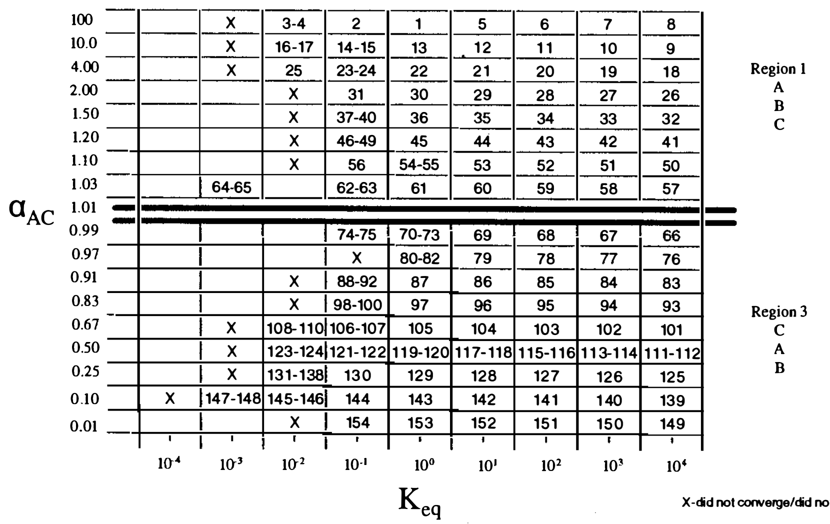
X-did not converge/did not analyze

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	-11.3	-10.6	108.4	0.0098	0.0100	0.9802	92.4	Stable	Strip/Rect	0.500	0.500	0.50	0.50
2	-11.3	-10.6	108.4	0.0303	0.0310	0.9387	71.7	Stable	Strip/Rect	0.500	0.500	0.50	0.50
3	-11.3	-10.6	108.4	0.0893	0.0917	0.8190	37.9	Stable	Strip/Rect	0.499	0.501	0.50	0.50
4	-11.3	-10.6	108.4	0.2273	0.2361	0.5366	9.2	Stable	Strip/Rect	0.497	0.503	0.50	0.50
5	-11.3	-10.6	108.4	0.3941	0.4346	0.1713	-6.3	Stable	Strip/Rect	0.483	0.517	0.50	0.50
6	-11.3	-10.6	108.4	0.3356	0.6428	0.0216	-10.3	Stable	Stripping	0.350	0.650	0.50	0.50
7	-11.3	-10.6	46.6	0.0098	0.0100	0.9802	43.5	Stable	Strip/Rect	0.500	0.500	0.50	0.50
8	-11.3	-10.6	46.6	0.0302	0.0311	0.9387	37.7	Stable	Strip/Rect	0.500	0.500	0.50	0.50
9	-11.3	-10.6	46.6	0.0891	0.0919	0.8190	24.7	Stable	Strip/Rect	0.499	0.501	0.50	0.50
10	-11.3	-10.6	46.6	0.2268	0.2366	0.5366	6.3	Stable	Strip/Rect	0.497	0.503	0.50	0.50
11	-11.3	-10.6	46.6	0.3923	0.4364	0.1713	-6.7	Stable	Strip/Rect	0.481	0.519	0.50	0.50
12	-11.3	-10.6	46.6	0.3232	0.6556	0.0212	-10.3	Stable	Strip/Rect	0.337	0.663	0.50	0.50
13	-11.3	-10.6	23.0	0.0097	0.0101	0.9802	21.8	Stable	Strip/Rect	0.500	0.500	0.50	0.50
14	-11.3	-10.6	23.0	0.0301	0.0312	0.9387	19.3	Stable	Strip/Rect	0.500	0.500	0.50	0.50
15	-11.3	-10.6	23.0	0.0887	0.0923	0.8190	13.1	Stable	Strip/Rect	0.499	0.501	0.50	0.50
16	-11.3	-10.6	23.0	0.2256	0.2378	0.5366	2.1	Stable	Strip/Rect	0.496	0.504	0.50	0.50
17	-11.3	-10.6	23.0	0.3878	0.4412	0.1710	-7.5	Stable	Strip/Rect	0.477	0.523	0.50	0.50
18	-11.3	-10.6	23.0	0.2902	0.6898	0.0200	-10.4	Stable	Strip/Rect	0.304	0.696	0.50	0.50
19	-11.3	-10.6	23.0	0.2897	0.6903	0.0200	-10.4	Stable	Rectifying	0.304	0.696	0.50	0.50
20	-11.3	-10.6	5.8	0.0096	0.0102	0.9802	5.4	Stable	Strip/Rect	0.500	0.500	0.50	0.50
21	-11.3	-10.6	5.8	0.0298	0.0315	0.9387	4.5	Stable	Strip/Rect	0.500	0.500	0.50	0.50
22	-11.3	-10.6	5.8	0.0877	0.0934	0.8189	1.9	Stable	Strip/Rect	0.498	0.502	0.50	0.50
23	-11.3	-10.6	5.8	0.2223	0.2413	0.5364	-3.3	Stable	Strip/Rect	0.494	0.506	0.50	0.50
24	-11.3	-10.6	5.8	0.3740	0.4556	0.1704	-8.7	Stable	Strip/Rect	0.465	0.535	0.50	0.50
25	-11.3	-10.6	5.8	0.1929	0.7918	0.0153	-10.5	Stable	Stripping	0.205	0.795	0.50	0.50
26	-11.3	-10.6	5.8	0.0096	0.9894	0.0010	-10.6	Unstable	Stripping	0.011	0.989	0.50	0.50
27	-11.3	-10.6	5.8	0.1950	0.7896	0.0154	-10.5	Stable	Rectifying	0.207	0.793	0.50	0.50
28	-11.3	-10.6	-1.41	0.0095	0.0104	0.9801	-1.6	Stable	Strip/Rect	0.500	0.500	0.50	0.50
29	-11.3	-10.6	-1.41	0.0293	0.0321	0.9386	-2.1	Stable	Strip/Rect	0.499	0.501	0.50	0.50
30	-11.3	-10.6	-1.41	0.0861	0.0951	0.8188	-3.4	Stable	Strip/Rect	0.498	0.502	0.50	0.50
31	-11.3	-10.6	-1.41	0.2172	0.2468	0.5360	-6.3	Stable	Strip/Rect	0.490	0.510	0.50	0.50
32	-11.3	-10.6	-1.41	0.3524	0.4788	0.1688	-9.5	Stable	Strip/Rect	0.446	0.554	0.50	0.50
33	-11.3	-10.6	-1.41	0.0086	0.9905	0.0009	-10.6	Unstable	Stripping	0.009	0.991	0.50	0.50
34	-11.3	-10.6	-1.41	0.0419	0.9541	0.0040	-10.6	Stable	Stripping	0.046	0.954	0.50	0.50
35	-11.3	-10.6	-1.41	0.0527	0.9423	0.0050	-10.6	Stable	Stripping	0.057	0.943	0.50	0.50
36	-11.3	-10.6	-1.41	0.9977	0.0021	0.0002	-11.3	Stable	Stripping	0.998	0.002	0.50	0.50
37	-11.3	-10.6	-6.928	0.0090	0.0109	0.9801	-7.0	Stable	Strip/Rect	0.500	0.500	0.50	0.50
38	-11.3	-10.6	-6.928	0.0277	0.0338	0.9385	-7.2	Stable	Strip/Rect	0.498	0.502	0.50	0.50
39	-11.3	-10.6	-6.928	0.0813	0.1006	0.8181	-7.7	Stable	Strip/Rect	0.495	0.505	0.50	0.50
40	-11.3	-10.6	-6.928	0.2013	0.2651	0.5336	-8.9	Stable	Strip/Rect	0.479	0.521	0.50	0.50
41	-11.3	-10.6	-6.928	0.2848	0.5567	0.1585	-10.3	Stable	Strip/Rect	0.383	0.617	0.50	0.50
42	-11.3	-10.6	-6.928	0.0091	0.9900	0.0009	-10.6	Stable	Rectifying	0.010	0.990	0.50	0.50
43	-11.3	-10.6	-8.941	0.0082	0.0120	0.9798	-9.0	Stable	Strip/Rect	0.499	0.501	0.50	0.50
44	-11.3	-10.6	-8.941	0.0252	0.0371	0.9377	-9.1	Stable	Strip/Rect	0.497	0.503	0.50	0.50
45	-11.3	-10.6	-8.941	0.0734	0.1112	0.8154	-9.3	Stable	Strip/Rect	0.490	0.510	0.50	0.50
46	-11.3	-10.6	-8.941	0.1751	0.2998	0.5251	-9.9	Stable	Strip/Rect	0.459	0.541	0.50	0.50
47	-11.3	-10.6	-8.941	0.1731	0.7049	0.1220	-10.5	Stable	Strip/Rect	0.263	0.737	0.50	0.50
48	-11.3	-10.6	-8.941	0.0014	0.9973	0.0013	-10.6	Unstable	Stripping	0.003	0.997	0.50	0.50
49	-11.3	-10.6	-8.941	0.9977	0.0021	0.0002	-11.3	Unstable	Stripping	0.998	0.002	0.50	0.50
50	-11.3	-10.6	-10.9	0.9973	0.0014	0.0013	-11.3	Unstable	Stripping	0.997	0.003	0.50	0.50

Figure 113. A+B↔C α_{AB} =1.03: Reactive Azeotropes

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
51	102.7	103.5	102.3	0.0163	0.0060	0.9777	102.3	Unstable	Strip/Rect	0.503	0.497	0.50	0.50
52	102.7	103.5	102.3	0.0510	0.0183	0.9307	102.3	Unstable	Strip/Rect	0.508	0.492	0.50	0.50
53	102.7	103.5	102.3	0.1550	0.0512	0.7938	102.4	Unstable	Strip/Rect	0.529	0.471	0.50	0.50
54	102.7	103.5	102.3	0.4445	0.1020	0.4535	102.6	Unstable	Strip/Rect	0.618	0.382	0.50	0.50
55	102.7	103.5	102.3	0.9973	0.0014	0.0013	102.7	Unstable	Strip	0.997	0.003	0.50	0.50
56	102.7	103.5	102.3	0.0014	0.9973	0.0013	103.5	Stable	Rectifying	0.003	0.997	0.50	0.50
57	102.7	103.5	102.3	0.9946	0.0054	0.0000	102.7	Unstable	Stripping	0.995	0.005	0.50	0.50
58	102.7	103.5	102.3	0.0022	0.9978	0.0000	103.5	Stable	Rectifying	0.002	0.998	0.50	0.50
59	102.7	103.5	102.3	0.0053	0.9947	0.0000	103.5	Stable	Rectifying	0.005	0.995	0.50	0.50
60	102.7	103.5	101.8	0.0135	0.0073	0.9792	101.9	Unstable	Strip/Rect	0.502	0.498	0.50	0.50
61	102.7	103.5	101.8	0.0420	0.0223	0.9357	101.9	Unstable	Strip/Rect	0.505	0.495	0.50	0.50
62	102.7	103.5	101.8	0.1265	0.0640	0.8095	102.1	Unstable	Strip/Rect	0.517	0.483	0.50	0.50
63	102.7	103.5	101.8	0.3505	0.1442	0.5053	102.4	Unstable	Strip/Rect	0.569	0.431	0.50	0.50
64	102.7	103.5	101.8	0.9184	0.0426	0.0390	102.7	Unstable	Stripping	0.921	0.079	0.50	0.50
65	102.7	103.5	101.8	0.9868	0.0067	0.0065	102.7	Unstable	Rectifying	0.987	0.013	0.50	0.50
66	102.7	103.5	101.8	0.9210	0.0411	0.0379	102.7	Unstable	Rectifying	0.924	0.076	0.50	0.50
67	102.7	103.5	101.8	0.9945	0.0054	0.0001	102.7	Unstable	Stripping	0.995	0.005	0.50	0.50
68	102.7	103.5	101.8	0.0023	0.9976	0.0001	103.5	Unstable	Rectifying	0.002	0.998	0.50	0.50
69	102.7	103.5	101.8	0.0052	0.9947	0.0001	103.5	Unstable	Rectifying	0.005	0.995	0.50	0.50
70	102.7	103.5	99.7	0.0110	0.0089	0.9801	99.7	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
71	102.7	103.5	101.8	0.0342	0.0275	0.9383	99.85	Unstable	Strip/Rect	0.502	0.498	0.50	0.50
72	102.7	103.5	101.8	0.1017	0.0804	0.8179	100.25	Unstable	Strip/Rect	0.506	0.494	0.50	0.50
73	102.7	103.5	101.8	0.2687	0.1984	0.5329	101.2	Unstable	Strip/Rect	0.523	0.477	0.50	0.50
74	102.7	103.5	101.8	0.5721	0.2722	0.1557	102.43	Unstable	Strip/Rect	0.630	0.370	0.50	0.50
75	102.7	103.5	101.8	0.9899	0.0092	0.0009	102.73	Unstable	Stripping	0.990	0.010	0.50	0.50
76	102.7	103.5	101.8	0.0021	0.9977	0.0002	103.49	Unstable	Rectifying	0.002	0.998	0.50	0.50
77	102.7	103.5	96.6	0.0104	0.0094	0.9802	96.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
78	102.7	103.5	96.6	0.0324	0.0290	0.9386	96.9	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
79	102.7	103.5	96.6	0.0960	0.0853	0.8187	97.7	Unstable	Strip/Rect	0.503	0.497	0.50	0.50
80	102.7	103.5	96.6	0.2498	0.2144	0.5358	88.4	Unstable	Strip/Rect	0.512	0.488	0.50	0.50
81	102.7	103.5	96.6	0.4918	0.3407	0.1675	101.9	Unstable	Strip/Rect	0.565	0.435	0.50	0.50
82	102.7	103.5	96.6	0.0021	0.9977	0.0002	103.5	Unstable	Rectifying	0.002	0.998	0.50	0.50
83	102.7	103.5	90.0	0.0101	0.0097	0.9802	90.2	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
84	102.7	103.5	90.0	0.0314	0.0299	0.9387	90.6	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
85	102.7	103.5	90.0	0.0929	0.0881	0.8190	92.0	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
86	102.7	103.5	90.0	0.2397	0.2238	0.5365	95.4	Unstable	Strip/Rect	0.505	0.495	0.50	0.50
87	102.7	103.5	90.0	0.4485	0.3807	0.1708	100.5	Unstable	Strip/Rect	0.529	0.471	0.50	0.50
88	102.7	103.5	90.0	0.7490	0.2335	0.0175	102.6	Unstable	Stripping	0.753	0.247	0.50	0.50
89	102.7	103.5	90.0	0.7434	0.2389	0.0177	102.6	Unstable	Stripping	0.748	0.252	0.50	0.50
90	102.7	103.5	90.0	0.7431	0.2391	0.0178	102.6	Unstable	Rectifying	0.748	0.252	0.50	0.50
91	102.7	103.5	80.3	0.0100	0.0098	0.9802	80.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
92	102.7	103.5	80.3	0.0310	0.0303	0.9387	81.4	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
93	102.7	103.5	80.3	0.0917	0.0893	0.8190	83.5	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
94	102.7	103.5	80.3	0.2356	0.2278	0.5366	89.0	Unstable	Strip/Rect	0.503	0.497	0.50	0.50
95	102.7	103.5	80.3	0.4311	0.3975	0.1714	98.0	Unstable	Strip/Rect	0.514	0.486	0.50	0.50
96	102.7	103.5	80.3	0.6144	0.3633	0.0223	102.3	Unstable	Strip/Rect	0.623	0.377	0.50	0.50
97	102.7	103.5	58.6	0.0099	0.0099	0.9802	59.1	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
98	102.7	103.5	58.6	0.0308	0.0305	0.9387	60.1	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
99	102.7	103.5	58.6	0.0909	0.0901	0.8190	63.2	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
100	102.7	103.5	58.6	0.2330	0.2304	0.5366	72.3	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
101	102.7	103.5	58.6	0.4201	0.4083	0.1716	90.2	Unstable	Strip/Rect	0.505	0.495	0.50	0.50
102	102.7	103.5	58.6	0.5337	0.4427	0.0236	101.1	Unstable	Strip/Rect	0.544	0.456	0.50	0.50
103	102.7	103.5	30.0	0.0099	0.0099	0.9802	30.6	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
104	102.7	103.5	30.0	0.0307	0.0306	0.9387	31.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
105	102.7	103.5	30.0	0.0906	0.0904	0.8190	35.3	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
106	102.7	103.5	30.0	0.2320	0.2313	0.5367	46.5	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
107	102.7	103.5	30.0	0.4162	0.4122	0.1716	74.4	Unstable	Strip/Rect	0.502	0.498	0.50	0.50
108	102.7	103.5	30.0	0.5051	0.4711	0.0238	97.9	Unstable	Strip/Rect	0.517	0.483	0.50	0.50
109	102.7	103.5	-40.1	0.0099	0.0099	0.9802	-39.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
110	102.7	103.5	-40.1	0.0306	0.0306	0.9388	-38.7	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
111	102.7	103.5	-40.1	0.0905	0.0905	0.8190	-35.6	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
112	102.7	103.5	-40.1	0.2317	0.2317	0.5366	-25.4	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
113	102.7	103.5	-40.1	0.4143	0.4141	0.1716	7.4	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
114	102.7	103.5	-40.1	0.4900	0.4862	0.0238	73.0	Unstable	Strip/Rect	0.502	0.498	0.50	0.50

Figure 113. Continued.



α_{AC}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
100		X	3-4	2	1	5	6	7	8
10.0		X	16-17	14-15	13	12	11	10	9
4.00		X	25	23-24	22	21	20	19	18
2.00			X	31	30	29	28	27	26
1.50			X	37-40	36	35	34	33	32
1.20			X	46-49	45	44	43	42	41
1.10			X	56	54-55	53	52	51	50
1.03		64-65		62-63	61	60	59	58	57
1.01									
0.99				74-75	70-73	69	68	67	66
0.97				X	80-82	79	78	77	76
0.91			X	88-92	87	86	85	84	83
0.83			X	98-100	97	96	95	94	93
0.67		X	108-110	106-107	105	104	103	102	101
0.50		X	123-124	121-122	119-120	117-118	115-116	113-114	111-112
0.25		X	131-138	130	129	128	127	126	125
0.10	X	147-148	145-146	144	143	142	141	140	139
0.01			X	154	153	152	151	150	149

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB,azeo	XC,azeo	XB,F	XC,F
1	-11.3	-10.9	108.4	0.404	0.424	0.172	-6.5	Stable	Strip/Rect	0.491	0.509	0.50	0.50
2	-11.3	-10.9	108.4	0.412	0.564	0.024	-10.5	Stable	Strip/Rect	0.426	0.574	0.50	0.50
3	-11.3	-10.9	108.4	0.010	0.990	0.000	-11.0	Stable	Rectifying	0.010	0.990	0.50	0.50
4	-11.3	-10.9	108.4	0.029	0.971	0.000	-11.0	Stable	Rectifying	0.029	0.971	0.50	0.50
5	-11.3	-10.9	108.4	0.229	0.234	0.537	9.0	Stable	Strip/Rect	0.498	0.502	0.50	0.50
6	-11.3	-10.9	108.4	0.090	0.091	0.819	37.7	Stable	Strip/Rect	0.500	0.500	0.50	0.50
7	-11.3	-10.9	108.4	0.030	0.031	0.939	71.5	Stable	Strip/Rect	0.500	0.500	0.50	0.50
8	-11.3	-10.9	108.4	0.010	0.010	0.980	92.3	Stable	Strip/Rect	0.500	0.500	0.50	0.50
9	-11.3	-10.9	46.6	0.010	0.010	0.980	43.5	Stable	Strip/Rect	0.500	0.500	0.50	0.50
10	-11.3	-10.9	46.6	0.030	0.031	0.939	37.7	Stable	Strip/Rect	0.500	0.500	0.50	0.50
11	-11.3	-10.9	46.6	0.090	0.091	0.819	24.6	Stable	Strip/Rect	0.500	0.500	0.50	0.50
12	-11.3	-10.9	46.6	0.229	0.234	0.537	6.2	Stable	Strip/Rect	0.498	0.502	0.50	0.50
13	-11.3	-10.9	46.6	0.403	0.425	0.172	-6.9	Stable	Strip/Rect	0.491	0.509	0.50	0.50
14	-11.3	-10.9	46.6	0.406	0.571	0.023	-10.6	Stable	Stripping	0.420	0.580	0.50	0.50
15	-11.3	-10.9	46.6	0.405	0.572	0.023	-10.6	Stable	Rectifying	0.419	0.581	0.50	0.50
16	-11.3	-10.9	46.6	0.990	0.010	0.000	-11.3	Stable	Stripping	0.990	0.010	0.50	0.50
17	-11.3	-10.9	46.6	0.037	0.963	0.000	-11.0	Stable	Rectifying	0.037	0.963	0.50	0.50
18	-11.3	-10.9	23.0	0.010	0.010	0.980	21.8	Stable	Strip/Rect	0.500	0.500	0.50	0.50
19	-11.3	-10.9	23.0	0.030	0.031	0.939	19.3	Stable	Strip/Rect	0.500	0.500	0.50	0.50
20	-11.3	-10.9	23.0	0.090	0.091	0.819	13.0	Stable	Strip/Rect	0.500	0.500	0.50	0.50
21	-11.3	-10.9	23.0	0.229	0.235	0.537	2.0	Stable	Strip/Rect	0.498	0.502	0.50	0.50
22	-11.3	-10.9	23.0	0.401	0.428	0.171	-7.7	Stable	Strip/Rect	0.489	0.511	0.50	0.50
23	-11.3	-10.9	23.0	0.390	0.587	0.023	-10.7	Stable	Strip/Rect	0.404	0.596	0.50	0.50
24	-11.3	-10.9	23.0	0.388	0.589	0.023	-10.7	Stable	Rectifying	0.402	0.598	0.50	0.50
25	-11.3	-10.9	23.0	0.990	0.010	0.000	-11.3	Stable	Stripping	0.990	0.010	0.50	0.50
26	-11.3	-10.9	5.8	0.010	0.010	0.980	5.4	Stable	Strip/Rect	0.500	0.500	0.50	0.50
27	-11.3	-10.9	5.8	0.030	0.031	0.939	4.4	Stable	Strip/Rect	0.500	0.500	0.50	0.50
28	-11.3	-10.9	5.8	0.089	0.092	0.819	1.9	Stable	Strip/Rect	0.499	0.501	0.50	0.50
29	-11.3	-10.9	5.8	0.227	0.236	0.537	-3.4	Stable	Strip/Rect	0.497	0.503	0.50	0.50
30	-11.3	-10.9	5.8	0.394	0.434	0.171	-8.9	Stable	Strip/Rect	0.483	0.517	0.50	0.50
31	-11.3	-10.9	5.8	0.340	0.638	0.022	-10.8	Stable	Strip/Rect	0.354	0.646	0.50	0.50
32	-11.3	-10.9	-1.4	0.010	0.010	0.980	-1.6	Stable	Strip/Rect	0.500	0.500	0.50	0.50
33	-11.3	-10.9	-1.4	0.030	0.031	0.939	-2.1	Stable	Strip/Rect	0.500	0.500	0.50	0.50
34	-11.3	-10.9	-1.4	0.088	0.093	0.819	-3.5	Stable	Strip/Rect	0.499	0.501	0.50	0.50
35	-11.3	-10.9	-1.4	0.225	0.239	0.537	-6.4	Stable	Strip/Rect	0.495	0.505	0.50	0.50
36	-11.3	-10.9	-1.4	0.384	0.445	0.171	-9.7	Stable	Stripping	0.474	0.526	0.50	0.50
37	-11.3	-10.9	-1.4	0.211	0.773	0.016	-10.9	Stable	Stripping	0.223	0.777	0.50	0.50
38	-11.3	-10.9	-1.4	0.009	0.990	0.001	-10.9	Unstable	Stripping	0.010	0.990	0.50	0.50
39	-11.3	-10.9	-1.4	0.261	0.720	0.019	-10.9	Stable	Rectifying	0.275	0.725	0.50	0.50
40	-11.3	-10.9	-1.4	0.274	0.707	0.019	-10.9	Stable	Rectifying	0.288	0.712	0.50	0.50
41	-11.3	-10.9	-6.9	0.010	0.010	0.980	-7.0	Stable	Strip/Rect	0.500	0.500	0.50	0.50
42	-11.3	-10.9	-6.9	0.029	0.032	0.939	-7.2	Stable	Strip/Rect	0.499	0.501	0.50	0.50
43	-11.3	-10.9	-6.9	0.086	0.095	0.819	-7.7	Stable	Strip/Rect	0.497	0.503	0.50	0.50
44	-11.3	-10.9	-6.9	0.217	0.247	0.536	-9.0	Stable	Strip/Rect	0.490	0.510	0.50	0.50
45	-11.3	-10.9	-6.9	0.351	0.480	0.169	-10.4	Stable	Strip/Rect	0.445	0.555	0.50	0.50
46	-11.3	-10.9	-6.9	0.011	0.988	0.001	-10.9	Stable	Stripping	0.012	0.988	0.50	0.50
47	-11.3	-10.9	-6.9	0.043	0.953	0.004	-10.9	Stable	Stripping	0.047	0.953	0.50	0.50
48	-11.3	-10.9	-6.9	0.068	0.926	0.006	-10.9	Stable	Rectifying	0.074	0.926	0.50	0.50
49	-11.3	-10.9	-6.9	0.088	0.904	0.008	-11.0	Stable	Rectifying	0.095	0.905	0.50	0.50
50	-11.3	-10.9	-8.9	0.009	0.011	0.980	-9.0	Stable	Strip/Rect	0.500	0.500	0.50	0.50

Figure 114. A+B↔C α_{AB} =1.01: Reactive Azeotropes

	Pure Boiling Points (°C)			Rxn Azeotrope Mol Frac			Tb,i (°C)	Rxn Azeotrope		Rxn Azeo Trans. Coordinates			
	A	B	C	A	B	C	Rxn Azeo	Node		XB.azeo	XC.azeo	XB.F	XC.F
51	-11.3	-10.9	-8.9	0.028	0.033	0.939	-9.1	Stable	Strip/Rect	0.499	0.501	0.50	0.50
52	-11.3	-10.9	-8.9	0.082	0.099	0.818	-9.4	Stable	Strip/Rect	0.495	0.505	0.50	0.50
53	-11.3	-10.9	-8.9	0.205	0.261	0.534	-10.0	Stable	Strip/Rect	0.482	0.518	0.50	0.50
54	-11.3	-10.9	-8.9	0.300	0.539	0.162	-10.7	Stable	Strip/Rect	0.397	0.603	0.50	0.50
55	-11.3	-10.9	-8.9	0.001	0.997	0.001	-10.9	Stable	Stripping	0.003	0.997	0.50	0.50
56	-11.3	-10.9	-8.9	0.009	0.990	0.001	-11.0	Stable	Rectifying	0.010	0.990	0.50	0.50
57	-11.3	-10.9	-10.6	0.007	0.014	0.979	-10.6	Stable	Strip/Rect	0.498	0.502	0.50	0.50
58	-11.3	-10.9	-10.6	0.021	0.044	0.935	-10.6	Stable	Strip/Rect	0.494	0.506	0.50	0.50
59	-11.3	-10.9	-10.6	0.061	0.132	0.807	-10.7	Stable	Strip/Rect	0.480	0.520	0.50	0.50
60	-11.3	-10.9	-10.6	0.135	0.368	0.497	-10.8	Stable	Strip/Rect	0.422	0.578	0.50	0.50
61	-11.3	-10.9	-10.6	0.997	0.001	0.001	-11.3	Unstable	Stripping	0.997	0.003	0.50	0.50
62	-11.3	-10.9	-10.6	0.990	0.009	0.001	-11.3	Unstable	Stripping	0.990	0.010	0.50	0.50
63	-11.3	-10.9	-10.6	0.009	0.990	0.001	-11.0	Stable	Rectifying	0.010	0.990	0.50	0.50
64	-11.3	-10.9	-10.6	0.991	0.009	0.000	-11.3	Unstable	Stripping	0.991	0.009	0.50	0.50
65	-11.3	-10.9	-10.6	0.009	0.991	0.000	-11.0	Stable	Rectifying	0.009	0.991	0.50	0.50
66	102.7	103.1	102.3	0.013	0.008	0.980	102.29	Unstable	Rectifying	0.501	0.499	0.50	0.50
67	102.7	103.1	102.3	0.041	0.023	0.936	102.32	Unstable	Rectifying	0.504	0.496	0.50	0.50
68	102.7	103.1	102.3	0.122	0.067	0.812	102.39	Unstable	Rectifying	0.515	0.485	0.50	0.50
69	102.7	103.1	102.3	0.336	0.153	0.512	102.55	Unstable	Strip/Rect	0.560	0.440	0.50	0.50
70	102.7	103.1	102.3	0.841	0.087	0.073	102.72	Unstable	Stripping	0.851	0.149	0.50	0.50
71	102.7	103.1	102.3	0.857	0.077	0.066	102.72	Unstable	Stripping	0.866	0.134	0.50	0.50
72	102.7	103.1	102.3	0.897	0.054	0.049	102.72	Unstable	Rectifying	0.902	0.098	0.50	0.50
73	102.7	103.1	102.3	0.001	0.997	0.001	103.05	Stable	Rectifying	0.003	0.997	0.50	0.50
74	102.7	103.1	102.3	0.990	0.009	0.001	102.73	Unstable	Stripping	0.990	0.010	0.50	0.50
75	102.7	103.1	102.3	0.009	0.990	0.001	103.05	Stable	Rectifying	0.010	0.990	0.50	0.50
76	102.7	103.1	101.8	0.012	0.010	0.979	101.86	Unstable	Rectifying	0.501	0.499	0.50	0.50
77	102.7	103.1	101.8	0.036	0.026	0.938	101.9	Unstable	Rectifying	0.503	0.497	0.50	0.50
78	102.7	103.1	101.8	0.107	0.076	0.817	102.03	Unstable	Rectifying	0.509	0.491	0.50	0.50
79	102.7	103.1	101.8	0.287	0.184	0.529	102.31	Unstable	Strip/Rect	0.534	0.466	0.50	0.50
80	102.7	103.1	101.8	0.650	0.212	0.138	102.67	Unstable	Strip/Rect	0.692	0.308	0.50	0.50
81	102.7	103.1	101.8	0.001	0.997	0.001	103.05	Stable	Rectifying	0.003	0.997	0.50	0.50
82	102.7	103.1	101.8	0.997	0.001	0.001	102.72	Stable	Rectifying	0.997	0.003	0.50	0.50
83	102.7	103.1	99.7	0.010	0.009	0.980	99.71	Unstable	Rectifying	0.500	0.500	0.50	0.50
84	102.7	103.1	99.7	0.032	0.029	0.939	99.84	Unstable	Rectifying	0.501	0.499	0.50	0.50
85	102.7	103.1	99.7	0.095	0.086	0.819	100.21	Unstable	Rectifying	0.503	0.497	0.50	0.50
86	102.7	103.1	99.7	0.248	0.216	0.536	101.11	Unstable	Rectifying	0.510	0.490	0.50	0.50
87	102.7	103.1	99.7	0.484	0.348	0.168	102.3	Unstable	Strip/Rect	0.558	0.442	0.50	0.50
88	102.7	103.1	99.7	0.009	0.990	0.001	103.4	Unstable	Rectifying	0.010	0.990	0.50	0.50
89	102.7	103.1	99.7	0.896	0.095	0.009	102.73	Unstable	Stripping	0.897	0.103	0.50	0.50
90	102.7	103.1	99.7	0.904	0.088	0.008	102.73	Unstable	Stripping	0.904	0.096	0.50	0.50
91	102.7	103.1	99.7	0.909	0.084	0.008	102.73	Unstable	Stripping	0.909	0.091	0.50	0.50
92	102.7	103.1	99.7	0.992	0.008	0.001	102.73	Unstable	Stripping	0.992	0.008	0.50	0.50
93	102.7	103.1	96.6	0.010	0.010	0.980	96.69	Unstable	Rectifying	0.500	0.500	0.50	0.50
94	102.7	103.1	96.6	0.031	0.030	0.939	96.93	Unstable	Rectifying	0.500	0.500	0.50	0.50
95	102.7	103.1	96.6	0.093	0.088	0.819	97.64	Unstable	Rectifying	0.501	0.499	0.50	0.50
96	102.7	103.1	96.6	0.240	0.224	0.537	99.36	Unstable	Rectifying	0.505	0.495	0.50	0.50
97	102.7	103.1	96.6	0.448	0.381	0.171	101.72	Unstable	Rectifying	0.528	0.472	0.50	0.50
98	102.7	103.1	96.6	0.736	0.246	0.018	102.68	Unstable	Stripping	0.741	0.259	0.50	0.50
99	102.7	103.1	96.6	0.989	0.010	0.001	102.72	Stable	Rectifying	0.989	0.011	0.50	0.50
100	102.7	103.1	96.6	0.719	0.262	0.019	102.68	Unstable	Rectifying	0.724	0.276	0.50	0.50
101	102.7	103.1	90.0	0.010	0.010	0.980	90.17	Unstable	Rectifying	0.500	0.500	0.50	0.50
102	102.7	103.1	90.0	0.031	0.030	0.939	90.62	Unstable	Rectifying	0.500	0.500	0.50	0.50
103	102.7	103.1	90.0	0.092	0.090	0.819	91.96	Unstable	Rectifying	0.501	0.499	0.50	0.50
104	102.7	103.1	90.0	0.235	0.228	0.537	95.35	Unstable	Rectifying	0.502	0.498	0.50	0.50
105	102.7	103.1	90.0	0.429	0.400	0.171	100.3	Unstable	Rectifying	0.513	0.487	0.50	0.50
106	102.7	103.1	90.0	0.598	0.380	0.023	102.5	Unstable	Strip/Rect	0.607	0.393	0.50	0.50
107	102.7	103.1	90.0	0.599	0.378	0.023	102.5	Unstable	Stripping	0.608	0.392	0.50	0.50
108	102.7	103.1	90.0	0.006	0.994	0.0000	103.05	Stable	Rectifying	0.006	0.994	0.50	0.50
109	102.7	103.1	90.0	0.007	0.993	0.0001	103.05	Stable	Rectifying	0.007	0.993	0.50	0.50
110	102.7	103.1	90.0	0.013	0.987	0.0001	103.04	Stable	Rectifying	0.013	0.987	0.50	0.50
111	102.7	103.1	80.3	0.010	0.010	0.980	80.64	Unstable	Rectifying	0.500	0.500	0.50	0.50
112	75.1	75.4	54.2	0.010	0.010	0.980	54.51	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
113	102.7	103.1	80.3	0.031	0.031	0.939	81.33	Unstable	Rectifying	0.500	0.500	0.50	0.50
114	75.1	75.4	54.2	0.031	0.031	0.939	55.16	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
115	102.7	103.1	80.3	0.091	0.090	0.819	83.42	Unstable	Rectifying	0.500	0.500	0.50	0.50
116	75.1	75.4	54.2	0.091	0.090	0.819	57.11	Unstable	Strip/Rect	0.500	0.500	0.50	0.50
117	102.7	103.1	80.3	0.233	0.230	0.537	88.96	Unstable	Rectifying	0.501	0.499	0.50	0.50
118	75.1	75.4	54.2	0.234	0.230	0.537	62.28	Unstable	Strip/Rect	0.501	0.499	0.50	0.50
119	102.7	103.1	80.3	0.422	0.407	0.172	97.82	Unstable	Rectifying	0.506	0.494	0.50	0.50
120	75.1	75.4	54.2	0.422	0.406	0.172	70.55	Unstable	Strip/Rect	0.507	0.493	0.50	0.50
121	102.7	103.1	80.3	0.542	0.434	0.024	102.14	Unstable	Strip/Rect	0.553	0.447	0.50	0.50
122	75.1	75.4	54.2	0.549	0.428	0.024	74.56	Unstable	Strip/Rect	0.559	0.441	0.50	0.50
123	102.7	103.1	80.3	0.946	0.054	0.001	102.73	Unstable	Stripping	0.946	0.054	0.50	0.50

Figure 114. Continued.

VITA

Craig Alan Hoyme was born in St. Paul, MN on November 3, 1967. He was raised in Luverne, MN and received his high school diploma from Luverne High School in 1986. From there, he went to the University of Minnesota, Twin Cities and received a B.S. in chemistry in 1991. He then went to work at Eastman Chemical Company in Kingsport, TN and worked as a chemist in the Environmental Services Laboratory. In 1999 he obtained his M.S. in chemical engineering as a distance student from the National Technological University in Minneapolis, MN. Under the direction of Dr. Jeff J. Siirola and Dr. Paul R. Bienkowski, he completed the requirements for a Ph.D. in chemical engineering from the University of Tennessee, Knoxville in May 2004.

Craig is currently working at Eastman Chemical Company as a chemical engineer in the Research Pilot Plant in Kingsport, TN.