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IMPROVEMENT OF BATCH DISTILLATION SEPARATION OF AZEOTROPIC MIXTURES

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Amélioration de la séparation distillation discontinue des mélanges azéotropiques

La distillation est le procédé de séparation le plus répandu dans l'industrie chimique. Pour la séparation des mélanges azéotropiques, une méthode spéciale de distillation doit être appliquée. Le but de mon travail était d'améliorer la séparation des mélanges azéotropiques par distillation discontinue (DD).
Un nouvel algorithme a été présenté pour la détermination de la séquence des produits de DD pour des mélanges multicomposants azéotropiques. Contrairement aux méthodes publiées précédemment, cet algorithme n'a pas besoin des paramètres d'équilibre.
Configurations non-conventionnelles de DD ont été étudiées par simulation rigoureuse avec un accent sur l'opération fermée. Nombreux modes d'opération fermés étaient proposés, lesquelles diffèrent en l'opération de réservoir supérieur.
Les effets du recyclage des fractions sur un procédé de séparation existant de 6 lots d'un mélange déchet azéotropique ont été étudiés. Les études ont été étendues pour un procédé de distillation extractive discontinue (DED). Un volume minimal de pré-fraction doit être incinéré. Le cas optimal de DED a donné un profit plus grand que celui de DD.
DED a été étudié pour la séparation des deux mélanges azéotropiques. La séparation a été infaisable ou le rendement a été bas par DD, mais DED et le procédé hybride ont donné des rendements élevés. Une nouvelle politique de DED a été aussi proposée.
Un modèle généralisé de la distillation hétéroazéotropique discontinue avec une rétention variable de décanteur a été développé. Dans une analyse de faisabilité, toutes les politiques opérationnelles possibles ont été identifiées. Ce modèle a été étendu pour la distillation extractive hétérogène discontinue.

Mots clés : distillation discontinue, azéotropes, séquence des produits, distillation extractive discontinue, opération fermée, distillation hétéroazéotropique discontinue

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Improvement of Batch Distillation Separation of Azeotropic Mixtures

Distillation is the most widespread method for separating liquid mixtures. The separation of azeotropic mixtures requires a special distillation method. My aim was to improve the batch distillation separation of azeotropic mixtures. A new algorithm was presented for the determination of product sequences of batch distillation of multicomponent azeotropic mixtures. Non-conventional configurations were studied by simulation with emphasis on closed operation. The effects of off-cut recycle on a six-batch separation process of a waste solvent mixture were also investigated. Batch extractive distillation was studied for the separation of two azeotropic mixtures. A new extractive policy was also proposed. A generalised model of batch heteroazeotropic distillation with variable decanter hold-up was developed. This model was extended for batch heterogeneous extractive distillation.

Keywords : batch distillation, azeotropes, product sequences, batch extractive distillation, closed operation, batch heteroazeotropic distillation

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Résumé en français

La distillation est la méthode appliquée la plus fréquemment pour la séparation des mélanges liquides, qui est basée sur la différence des volatilités des composants. Comme la distillation se compose d'étapes consécutives de vaporisation et condensation partielle, son besoin en énergie est très élevé. Pour cette raison, la conception et opération optimale des procédés de distillation est un enjeu important tant de point de vue de l'économie que d'environnement.

Si le mélange est fortement non-idéal, des azéotropes peuvent se produire. Au point azéotropique, les compositions de la phase vapeur et celle de liquide sont identiques, ce qui signifie qu'un mélange azéotropique ne peut pas être séparé par un procédé de distillation conventionnelle. Si la volatilité relative est très basse, la séparation est faisable en théorie, mais le taux de reflux et nombre des plateaux élevés rendent la distillation conventionnelle non rentable.

Pour la séparation des mélanges azéotropiques et à points d'ébullition voisins, des méthodes de distillation spéciales doivent être appliquées. Ces méthodes exploitent la sensibilité à la pression éventuelle de la composition azéotropique (distillation avec changement de pression), ou l'influence favorable d'un agent de séparation (entraîneur). L'effet de l'entraîneur est différent selon la technique de séparation. Dans le cas de la distillation homoazéotropique, un comportement azéotropique provoqué par l'entraîneur est exploité. Dans le cas de la distillation extractive, l'entraîneur, alimenté continuellement à la colonne, change les volatilités relatives favorablement. Dans le cas de la distillation hétéroazéotropique, l'entraîneur forme deux phases liquides avec un des composants originaux, et cette répartition liquide-liquide est exploitée par décantation pour séparer le mélange originel.

Dans certain industries, par exemple l'industrie pharmaceutique, la récupération des solvants, l'industrie chimique fine, la production d'alcool et de teinture, la distillation est effectuée en mode discontinu. L'avantage de distillation discontinue est que cela peut être appliqué pour la séparation des mélanges de quantité et composition variable. Dans les industries ci-dessus, des mélanges multicomposants azéotropiques sont fréquents. Dans le cas de la régénération des déchets mélanges des solvants, on cherche à récupérer un composant principal, ce qui est avantageux tant de point de vue de l'économie (une quantité du mélange plus faible doit être incinérée) que de l'environnement. L'existence des azéotropes peut limiter le rendement, ou même rendre la séparation infaisable, à moins qu'une méthode de distillation spéciale soit appliquée.

La possibilité d'économiser de l'énergie et la réglementation environnementale plus sévère ont provoqué un intérêt accru à la recherche de la distillation discontinue dans les dernières dizaines d'années, avec un accent sur les méthodes de distillation spécial et les configurations de colonne non-conventionnelles.

Le but de mes travaux de recherche est l'amélioration de la séparation des mélanges azéotropiques par distillation discontinue, notamment de :

- proposer un algorithme pour la détermination de la séquence des produits et leurs quantités maximales pour la distillation discontinue des mélanges multicomposants azéotropiques,
- comparer différents modes d'opération fermés des configurations de colonne discontinue (rectificateur discontinu, colonne avec bac intermédiaire, colonne multibac),
- étudier la séparation extractive discontinue des mélanges azéotropique des solvants pharmaceutiques par des expériences en laboratoire, des productions pilote de l'échelle industrielle et par simulation rigoureuse ; et examiner une nouvelle politique de conduite pour la distillation extractive discontinue,
- examiner l'effet du recyclage des fractions pour la séparation d'un mélange déchet de solvants pharmaceutique par distillation discontinue traditionnelle et extractive,
- construire un modèle général pour la distillation hétéroazéotropique discontinue avec une rétention variable de décanteur,
- étendre le modèle ci-dessus pour la distillation extractive hétérogène discontinue.

Dans le Chapitre 2, j'ai développé un nouvel algorithme pour la détermination de la séquence des produits de distillation discontinue avec l'hypothèse de séparation maximale (taux de reflux très élevé, nombre des plateaux infini) pour un nombre arbitraire de composants, basé seulement sur les points d'ébullition des composants purs et des azéotropes, et sur des compositions azéotropiques. C'est aussi approprié pour considérer le changement de pression et l'existence des hétéroazéotropes. Les algorithmes publiés auparavant ont eu besoin de l'emploi d'un modèle d'équilibre liquide-vapeur (ELV) ou ont pu être appliqués pour des mélanges ternaires.

La stabilité des points stationnaires est déterminée avec l'hypothèse que chaque sous-mélange ternaire appartient à une classe de Serafimov répertoriée en pratique. Sur la base des stabilités, toutes les séquences des produits faisables sont déterminées. Enfin, les quantités relatives des fractions sont déterminées pour la composition donnée de la charge. J'ai testé favorablement le nouvel algorithme en comparant les stabilités et l'ensemble des séquences des produits pour un mélange de cinq composants avec les résultats publiés à la littérature. Sur un exemple d'un deuxième mélange, j'ai montré que le nouvel algorithme est capable de traiter aussi des hétéroazéotropes. Ces résultats montrent que l'algorithme est approprié pour la détermination de la séquence des produits sans utiliser un modèle d'ELV.

Dans le Chapitre 3, j'ai étudié par simulation dynamique rigoureuse différents modes opératoires fermés et le mode opératoire habituel ouvert du rectificateur discontinu et de la colonne avec bac intermédiaire. J'ai aussi examiné quatre différents modes fermés de la colonne multibacs. J'ai comparé les rendements sous contrainte de pureté de produit et de consommation d'énergie constants.

J'ai suggéré une nouvelle définition du taux de reflux (R) pour les modes d'opération fermés. Comme aucun distillat n'est tiré, R est toujours infini selon la définition conventionnelle. Dans la nouvelle définition, le débit du distillat est remplacé par la différence des débits de vapeur et de liquide. De cette façon, le changement de la rétention au réservoir supérieur est pris en considération. R est infini dans le seul cas où la rétention est constante. Si l'accumulation a lieu au réservoir, R est un nombre fini et positif.

Dans le cas du rectificateur discontinu, l'opération fermée a donné des rendements plus élevés lorsque la rétention de liquide sur les plateaux est négligeable. Pour la colonne avec bac intermédiaire, le mode ouvert s'est révélé meilleur que les modes fermés dans tous les cas. Pour la colonne multibacs, les différences des rendements entre les modes ont été petites, ne permettant pas de conclure aussi catégoriquement ; mais la division de la charge parmi les réservoirs (au lieu de remplir toute la charge au bouilleur) a eu un effet défavorable sur la consommation d'énergie.

Dans le Chapitre 4, j'ai étudié par simulation l'influence du recyclage des fractions sur la régénération d'un mélange pharmaceutique de quatre composants (méthanol, THF, eau, toluène) par distillation homoazéotropique discontinue (DD) et distillation extractive discontinue (DED). J'ai examiné un procédé de distillation pour une campagne de 6 lots consécutifs, où la première pré-fraction a été incinérée, tandis que la deuxième pré-fraction, la post-fraction et la rétention de la colonne ont été recyclées. Pour le procédé DED, l'eau comme entraîneur a été alimentée à la tête de la colonne pendant le démarrage.

J'ai créé un programme pour la simulation du procédé de production avec recyclage des fractions. Le programme, écrit en Visual Basic for Applications dans Microsoft Excel, achève les calculs de bilan matériel du recyclage et appelle ChemCAD pour la simulation dynamique rigoureuse des productions. J'ai déterminé le volume optimal de la première pré-fraction quant au profit du procédé de régénération, et j'ai affirmé que sa valeur est légèrement plus basse pour DED. J'ai conclu qu'un volume minimum de la première pré-fraction est nécessaire pour éviter l'accumulation des polluants organiques à la charge ; ce qui rendrait le procédé de 6 lots infaisable. Ce volume est plus élevé pour DED. J'ai aussi trouvé que le procédé DED optimal a donné un profit considérablement plus élevé que la DD optimal.

Dans le Chapitre 5, l'application de DED et celui du procédé hybride (PH) a été étudiée pour deux mélanges pharmaceutiques de solvants. Leur séparation est impossible (Mélange 1 : méthanol, THF, acétonitrile, eau, pyridine) ou limitée par azéotropes (Mélange 2 : acétone, méthanol, THF, n-hexane, éthanol, eau, toluène) dans le cas d'une distillation conventionnelle.

J'ai étudié la performance de deux politiques de conduite (basique et modifiée) de DED et PH pour la récupération de THF du Mélange 1. J'ai conclu que l'eau ainsi que la pyridine sont appropriés comme entraîneurs, mais que l'emploi de l'eau est plus pratique. J'ai évalué des expériences réalisées sur une colonne laboratoire à garnissage par simulation rigoureuse. La tâche de séparation prescrite n'a pas été faisable par DD, mais c'était possible de produire THF de la qualité désirée par DED et PH. Le rendement et la vitesse de production plus élevés ont été obtenus par PH, tandis que le procédé le moins efficace a été la politique basique de DED. Les effets des paramètres opérationnels ont été aussi étudiés.

Dans le cas du Mélange 2, plusieurs azéotropes limitent le rendement du méthanol par DD en causant une perte considérable du méthanol. Nous avons suggéré une nouvelle politique de conduite de DED, où l'alimentation de l'eau (entraîneur) a été appliquée pendant le démarrage (DED1). À la fin du démarrage, la concentration des polluants organiques est augmentée (en comparaison avec DD) et la concentration du méthanol a diminué considérablement à la tête de la colonne. J'ai affirmé que l'alimentation de l'eau peut être maintenue pendant la pré-fraction (DED2), mais que cela augmente la quantité de la pré-fraction et dilue le mélange à partir duquel le méthanol est récupéré.

J'ai réalisé des expériences laboratoires pour comparer DD et les deux politiques de conduite DED. J'ai conclu que le rendement le plus élevé a été obtenu par DED1, le moins élevé par DD. J'ai aussi réalisé la simulation postérieure des expériences. Des productions pilote de l'échelle industrielle ont été aussi exécutées dans une colonne de 50 plateaux à calotte. En cas de DED1, le rendement a augmenté considérablement, qui est expliqué par la réduction considérable dans la concentration du méthanol au distillat à la fin du démarrage, et ainsi par la perte du méthanol réduite à la première pré-fraction. J'ai étudié les productions pilote aussi par simulation rigoureuse postérieure, et j'ai trouvé que la consommation d'énergie de DED a été significativement plus basse que celle de DD.

Dans la Chapitre 6, j'ai proposé un modèle général de la distillation hétéroazéotropique discontinue, où toutes les deux phases liquides peuvent être refluées ou tirées comme distillat. Ses rétentions au décanteur peuvent être augmentées, réduises ou maintenues constantes. J'ai suggéré deux nouveaux paramètres opérationnels (r_R et r_W) définissant le taux des débits des phases riche et pauvre en entraîneur refluées et condensées, respectivement.

En supposant la séparation maximale, j'ai dérivé l'équation du chemin du bouilleur qui décrit la variation de la composition de bouilleur en temps. Selon les valeurs de r_R et r_W, j'ai distingué 16 possibles politiques de conduite, plusieurs desquelles ont été proposées pour la première fois. J'ai affirmé que la direction du chemin de bouilleur peut se trouver dans huit zones différentes. Ces zones couvrent toutes les directions possibles, c'est-à-dire que la composition de bouilleur peut être changée dans n'importe quelle direction désirée. J'ai aussi conclu qu'il est possible de récupérer un composant pur dans le bouilleur en choisissant les politiques appropriées, et ainsi d'éliminer le besoin d'une étape de séparation suivante.

J'ai validé les directions du chemin du bouilleur pour trois nouvelles politiques de conduite par simulation rigoureuse pour le mélange eau – acide formique – propyl formiate. J'ai démontré l'avantage de l'emploi d'une politique non-traditionnelle avec la réduction de la rétention au décanteur.

Dans le Chapitre 7, j'ai étendu le modèle de la distillation hétéroazéotropique discontinue pour la distillation extractive hétérogène discontinue en prenant en considération l'alimentation d'entraîneur continuelle. J'ai distingué deux positions différentes de l'alimentation d'entraîneur : dans le Cas 1, l'entraîneur est alimenté dans la colonne, dans le Cas 2, il est ajouté au décanteur.

J'ai dérivé l'équation décrivant l'évolution de la composition de bouilleur pour les deux cas. En comparaison avec la distillation hétéroazéotropique discontinue, un nouveau terme lié à l'alimentation d'entraîneur continuelle est apparu, et dans le Cas 2, l'influence des termes existants, liés à l'opération du décanteur, a augmenté.

J'ai discuté l'applicabilité pratique des politiques de conduite possibles et j'ai étudié l'effet de l'alimentation d'entraîneur continûment sur le chemin du bouilleur. J'ai conclu que les huit zones de chemin du bouilleur originelles de la distillation hétéroazéotropique distillation sont modifiées : certaines d'entre eux disparaissent, et d'autres zones se superposent. J'ai aussi trouvé qu'il est possible de diriger la composition de bouilleur à n'importe quelle direction, pareillement à la distillation hétéroazéotropique discontinue. Toutefois l'influence de l'alimentation d'entraîneur est forte en pratique, et il est difficile de décaler le chemin de bouilleur de la direction de la composition d'entraîneur. Pour la même raison, la variation de la rétention des phases au décanteur n'a qu'un effet faible sur le chemin du bouilleur.

J'ai validé les directions du chemin du bouilleur par simulation rigoureuses pour la déshydratation du mélange eau – éthanol avec n-butanol comme entraîneur. J'ai trouvé qu‘en utilisant une nouvelle politique de conduite (reflux partiel de la phase riche en entraîneur seulement), il était possible de réduire la teneur en eau du résidu du bouilleur contenant principalement éthanol et butanol.

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Notations

Latin letters

A	most volatile original component
A	acetone (Chapter 2 and Section 5.2)
A	adjacency matrix
A	aniline (Section 6.3.4)
A	Antoine constant
A	element of the adjacency matrix
A	methanol (Chapter 4 and Section 5.1)
A	NRTL binary interaction parameter (Appendix 2)
A	n-hexane (Chapter 3)
A	UNIQUAC binary interaction parameter (Appendix 2)
A	water (Section 6.3.3 and Chapter 7)
a	accumulation ratio
a	vector of linear combination coefficients
Az, AZ	azeotrope
B	less volatile component
B	Antoine constant, °C
B	benzene (Chapter 2)
B	ethanol (Chapter 7)
B	ethylene glycol (Section 6.3.4)
B	formic acid (Section 6.3.3)
B	methanol (Section 5.2)
B	n-heptane (Chapter 3)
B	NRTL binary interaction parameter, K (Appendix 2)
B	tetrahydrofuran (Chapter 4 and Section 5.1)
b	vector for simplex checking
BD	batch distillation
BED	batch extractive distillation
BED1	batch extractive distillation with entrainer feeding during the heating-up only
BED2	batch extractive distillation with entrainer feeding during the heating-up and fore-cuts
BEDB	basic policy of batch extractive distillation
BEDM	modified policy of batch extractive distillation
BHD	batch heteroazeotropic distillation
BHED	batch heterogeneous extractive distillation
BR	batch rectifier
C	acetonitrile (Section 5.1)
C	Antoine constant, °C
C	chloroform (Chapter 2)
C	component
C	n-octane (Chapter 3)
C	NRTL binary interaction parameter (Appendix 2)
C	tetrahydrofuran (Section 5.2)
C	UNIQUAC binary interaction parameter (Appendix 2)
C	water (Chapter 4)
CAMD	computer-aided molecular design
Ch	charge
D	component
D	distillate
D	distillate molar flow rate, mol/h
D	n-decane (Chapter 3)
D	n-hexane (Section 5.2)
D	toluene (Chapter 4)
D	water (Section 5.1)

DoF	degree of freedom
E	entrainer
E	ethanol (Chapter 2 and Section 5.2)
E	n-butanol (Chapter 7)
E	propyl formate (Section 6.3.3)
E	pyridine (Section 5.1)
E	water (Section 6.3.4)
EtAc	ethyl acetate (Chapter 2)
F	feed
F	feed flow rate, mol/h or kg/h
F	water (Section 5.2)
f	feed plate location
f	fugacity, Pa
G	free enthalpy, J/mol
G	toluene (Section 5.2)
H	hold-up, mol or m^3
HP	hybrid process
i	component
IPA	isopropyl alcohol (Chapter 2)
j	component
K	vapour-liquid distribution ratio
k	component
L	liquid molar flow rate, mol/h
M	methanol (Chapter 2)
m	mass, kg
MuVC	multivessel column
MVC	middle-vessel column
N	number of plates
n	number of components
OF	objective function
p, P	pressure, bar
$\mathcal{P}$	Poynting correction
PSBD	pressure-swing batch distillation
PSD	pressure-swing distillation
Q	heat duty, MJ/h
QS	quaternary system
R	reflux ratio
R	universal gas constant, J/molK
r	the ratio of the flow rates of the refluxed and condensed streams
rs	reflux splitting ratio
S	reboil ratio
S	saddle
S	selectivity
SEC	specific energy consumption, MJ/kg
SN	stable node
SRK	Soave-Redlich-Kwong equation of state
SWC	specific water consumption, kg/kg
T	temperature, K or °C
T	tetrahydrofuran (Chapter 2)
t	time, min
Δt	operation time, min
THF	tetrahydrofuran
TS	ternary system
U	hold-up, mol or m^3
U	UNIQUAC parameter, cal/mol (Appendix)
UN	unstable node
V	vapour molar flow rate, mol/h
V	volume, m^3
VLE	vapour-liquid equilibrium
VLLE	vapour-liquid-liquid equilibrium
W	bottom product
W	liquid flow rate from the middle-vessel, dm^3/h
W	water (Chapter 2)
W	water feeding, dm^3/h
x	liquid mole fraction, mol/mol
y	vapour mole fraction, mol/mol

Greek letters

α	NRTL parameter (Appendix 2)
α	relative volatility

γ	activity coefficient
η	phase split ratio, mol/mol
τ	dimensionless time
ϕ	fugacity coefficient

Subscripts

0	condensate
0	end of total reflux period
1	heating-up (Section 5.1)
1a	first fore-cut (Chapter 4)
1b	second fore-cut (Chapter 4)
2	main cut (Chapter 4)
2	production (Section 5.1)
2	top vapour (Chapter 6)
3	after-cut (Chapter 4)
B	bottoms
BP	boiling point
ch	charge
D	distillate
E	entrainer
F	charge
final	final
i	component
j	component
k	component
naz	azeotrope containing all components
open	open operation mode
R	entrainer-rich phase
S	still
total	total
W	entrainer-lean phase

Superscripts

‘	Case 2 (Chapter 7)
0	pure component
I, II	phases
I, II, III	columns
L	liquid phase
R	residual
∞	infinite dilution

General Introduction

Distillation is the most widespread separation process in the chemical industry. The components of a liquid mixture are separated on the basis of the difference in their volatilities. In the course of successive partial vaporization and condensation steps, the more volatile components become enriched in the vapour phase and depleted in the liquid phase. As the energy demand of distillation is very high, the optimal design and operation of the process is an important question, both economically and environmentally.

In the case of a close-boiling (low relative volatility) mixture, however, the difference in the composition of the vapour and the liquid phase is small, and the separation requires a high number of plates and a high reflux ratio, which often render the conventional distillation process uneconomical. If the liquid phase solution of the components is highly non-ideal, azeotropes may occur. In the azeotropic point, the composition of the vapour and liquid phase is identical, and the separation is not possible by conventional distillation. For the separation of azeotropic and close-boiling mixtures a special distillation method must be applied.

Special distillation methods can exploit:

- the pressure-sensibility of the azeotrope composition (pressure-swing distillation),
- an azeotropic behaviour usually produced by a mass separating agent (entrainer) added to the mixture (homoazeotropic distillation),
- a change in the relative volatilities of the components due to the continuous feeding of an entrainer (extractive and salt distillation),
- a liquid-liquid split either occurring in the original mixture, or induced by the addition of an entrainer (heteroazeotropic distillation), or
- the combination of distillation with another separation technique (membrane distillation or adsorptive distillation).

Batch distillation is frequently applied in the pharmaceutical and fine chemical industries and in solvent recovery. The advantage of batch distillation is that it is capable of processing mixtures of varying (and often small) amount and changing composition. Moreover, more than two components can be produced (without side withdrawal) in a single equipment because the distillate composition changes in time. Azeotropic and close-boiling mixtures are often encountered in the industries mentioned above, and researchers devoted increased attention to special batch distillation methods in the recent decades.

The aim of this work is to improve the batch distillation separation of azeotropic mixtures, in particular to

- propose a new algorithm for the determination of product sequence of the batch distillation of multicomponent azeotropic mixtures,
- compare different closed operational modes of batch column configurations (batch rectifier, middle-vessel column, multivessel column),
- study the batch extractive separation of pharmaceutical azeotropic waste solvent mixtures by laboratory experiments, industrial-size pilot productions and rigorous simulation, and to investigate a new operational policy for batch extractive distillation,
- investigate the effect of off-cut recycle on the traditional batch and batch extractive distillation separation of a pharmaceutical waste solvent mixture,
- construct a general model for batch heteroazeotropic distillation with variable decanter hold-up, and
- extend the above model for batch heterogeneous extractive distillation.

Chapter 1 is a literature review addressing the principles of phase equilibria and the different special distillation methods. The approaches for equilibrium calculations, azeotropy, residue curve maps and their structure are introduced. The operational policies and non-conventional configurations of batch distillation are discussed, as well as the determination of the product sequence of azeotropic mixtures for batch distillation. Although the different special distillation methods are presented both for continuous and batch operations, emphasis is placed on batch distillation.

Chapter 2 presents a new algorithm for the determination of the product sequence of the batch distillation of multicomponent azeotropic mixtures. Unlike previously published methods, which were either applicable only to ternary mixtures (e.g. Foucher et al., 1991), or required the knowledge of vapour-liquid equilibria parameters (e.g. Ahmad et al., 1998), the new algorithm can be used for any number of components, and needs only the boiling points of components and azeotropes, and azeotropic compositions. The algorithm can also take pressure change and heteroazeotropy into account.

Chapter 3 deals with non-conventional batch distillation configurations, with an emphasis on closed operation. Several closed operation modes of batch rectifier are proposed, which differ in the operation of the top vessel. The recoveries achieved by these closed modes are compared with each other, and with that of the open operation mode of batch rectifier. The comparison is also performed for the open and different closed modes of middle-vessel column. In the case of the multi-vessel column, four different closed modes are compared.

In Chapter 4 the effects of off-cut recycle on an existing six-batch separation process of a multicomponent azeotropic waste solvent mixture are studied. The investigation is extended for a batch extractive distillation process.

In Chapter 5, the batch extractive distillation is studied for the separation of two multicomponent azeotropic mixtures. The recovery of the main component from the first mixture was not feasible with traditional batch distillation, but two different operational policies of batch extractive distillation, and a hybrid process, absorption+distillation, gave good recoveries. The posterior rigorous simulation of experiments is performed and the effects of operational parameters are studied. Although the separation of the second mixture is possible with traditional batch distillation, the recovery of the main component is limited because of the presence of several azeotropes. A new batch extractive distillation policy is proposed, entrainer feeding during the heating-up only, to reduce the loss of the main component. The new policy is compared with an existing batch extractive distillation policy, as well.

Chapter 6 presents a generalised model of batch heteroazeotropic distillation with variable decanter hold-up, as a combination and extension of the models of Rodriguez-Donis et al. (2002) and Lang and Modla (2006). In a feasibility analysis, the still path equation is derived, the vectors determining the still path directions are determined, and all possible operational policies, including several new ones, are identified. The results are validated by rigorous simulations.

Chapter 7 extends the model described in Chapter 6 for the batch heterogeneous extractive distillation. The effect of the continuous entrainer feeding on the still path directions and operational policies is discussed. The validity of the predicted still path directions is investigated by simulations.

CHAPTER 1

Literature Review

In this chapter, after the presentation of the foundations of vapour-liquid and liquid equilibria, a literature review on the different distillation methods for the separation of azeotropic mixtures is given, with an emphasis on batch processes.

1.1. Phase Equilibria

First a brief overview is given over the methods of phase equilibria calculations (Perry and Green, 2008), and then the non-ideal behaviour of mixtures, such as the occurrence of azeotropes and limited miscibility of liquid phases, is discussed both for binary and ternary systems.

1.1.1 Equilibrium relations

The condition of equilibrium of two phases (I and II) of a mixture is the simultaneous existence of thermal equilibrium (equality of temperatures), mechanical equilibrium (equality of pressures) and thermodynamic equilibrium of the phases. The latter is expressed by the equality of fugacities in phase I and II for every component *i*:

$$f_i^I = f_i^{II} \tag{1.1}$$

The definition of the fugacity coefficient is the following:

$$\phi_i = \frac{f_i}{p_i} \tag{1.2}$$

where p_i is the partial pressure of component *i*. The fugacity coefficient characterises the non-ideal behaviour of component *i* in the mixture and it is related to the residual free enthalpy G_i^R:

$$G_i^R = RT \ln \phi_i \tag{1.3}$$

For a pure component in ideal gas state, fugacity equals its pressure. The fugacity may be calculated on the basis of fugacity coefficient ϕ_i and partial pressure p_i, or for a liquid phase, on the basis of activity coefficient γ_i and pure component liquid fugacity f_i^0. Depending on the method of calculation applied to the two phases, three approaches can be distinguished:

- γ - ϕ approach
- ϕ - ϕ approach
- γ - γ approach

1.1.1.1. γ - ϕ Approach

This method can be applied both for vapour-liquid and liquid-liquid systems under pressure well below the critical pressure. The vapour phase fugacity of component *i* is calculated from its partial pressure by using the definition of fugacity coefficient:

$$f_i^V = \phi_i p_i \tag{1.4}$$

The partial pressure of component *i* can be calculated according to Dalton's law:

$$p_i = y_i P, \tag{1.5}$$

where y_i is the mole fraction of *i* and P is the total pressure of the system. Therefore the vapour phase fugacity is:

$$f_i^V = \phi_i y_i P \tag{1.6}$$

The non-ideality of the liquid phase is expressed by the activity coefficient, which is, by definition, the ratio of the fugacity of the component in the liquid phase and the product of its mole fraction in the liquid phase (x_i) and the pure component liquid fugacity:

$$\gamma_i = \frac{f_i^L}{X_I f_i^0} \tag{1.7}$$

That is, the liquid phase fugacity of component *i* is:

$$f_i^L = \gamma_i x_i f_i^0 \tag{1.8}$$

The pure component liquid fugacity is related to the vapour pressure by the following equation, with approximating the molar volume of component *i* in the mixture (V_i^L) with the molar volume in pure state (V_i^{0L}):

$$f_i^0 = \phi_i^0 p_i^0 e^{\frac{V_i^{0L} \ P - p_i^0}{RT}}, \tag{1.9}$$

where ϕ_i^0 is the pure component liquid fugacity coefficient, and p_i^0 is the vapour pressure of component *i*. The exponential term on the right hand side is called the Poynting correction:

$$\mathcal{P} = e^{\frac{V_i^{0L} \ P - p_i^0}{RT}} \tag{1.10}$$

In this way, Equation 1.1 can be written as:

$$\phi_i y_i P = \gamma_i x_i \phi_i^0 p_i^0 \mathcal{P} \tag{1.11}$$

For low pressures and non-associating vapour phase, the vapour phase can be regarded as a mixture of ideal gases, and the fugacity coefficient can be taken as unity. For the liquid phase, the pure component liquid fugacity coefficient and Poynting correction can be ignored at low pressure. With these simplifications, the modified Raoult-Dalton equation is obtained:

$$y_i P = \gamma_i x_i p_i^0 \tag{1.12}$$

For ideal liquid phase solutions, the activity coefficients equal unity, leading to the Raoult-Dalton's equation:

$$y_i P = x_i p_i^0 \tag{1.13}$$

However, the assumption of ideality of the liquid phase solution almost never holds, and so the Raoult-Dalton's equation usually does not give realistic results.

The vapour pressure can be calculated for a given temperature by data correlations, e.g. by the Antoine equation:

$$\log p_i^0 = A_i - \frac{B_i}{T + C_i} \tag{1.14}$$

The value of Antoine parameters can be found among others in the book of Ohe (1976).

The activity coefficients, which are functions of the temperature and liquid phase composition, can be calculated by different activity coefficient models (Stichlmair and Fair, 1998). These include the models van Laar, Margules, Wilson, NRTL (Non-Random Two Liquid) and UNIQUAC (UNIversial QUasi-Chemical). In the present work NRTL and UNIQUAC models are applied. Both of them can be used for vapour-liquid and liquid-liquid equilibrium calculations, as well. The activity coefficient models require a number of parameters (NRTL: 3, UNIQUAC: 2) specific to a particular pair of components, computed on the basis of experimental data, which can be found in the DECHEMA chemical book series data collection of Gmehling et al. (1977). If the binary interaction parameters are not available, the UNIFAC (UNIQUAC Functional-group Activity Coefficients) group-contribution method can be used, where activity coefficients are calculated based on the functional groups of the molecules present in the mixture.

1.1.1.2. ϕ – ϕ Approach

This is an alternative to the γ - ϕ approach, which can be used for vapour-liquid and liquid-liquid calculations, even for high pressures. Both phases are described by the same equation of state used to compute the fugacity of each phase, and Equation 1.1 can be written as:

$$\phi_i^V y_i = \phi_i^L x_i \tag{1.15}$$

The cubic equations of state Soave-Redlich-Kong (SRK) and Peng-Robinson (PR) are widely used, e.g. for the phase equilibrium calculations of hydrocarbon mixtures. In Chapter 3, the SRK equation is applied to the VLE calculations.

1.1.1.3. γ – γ Approach

If two liquid phases are in equilibrium, the same activity coefficient model can be applied to both phases, and the condition of thermodynamic equilibrium can be written from Equations 1.1 and 1.8 as:

$$\gamma_i^I y_i = \gamma_i^{II} x_i \tag{1.16}$$

A suitable activity coefficient model is required, which can predict the liquid-liquid phase split, e.g. UNIQUAC, NRTL or UNIFAC. The Wilson model is not applicable.

1.1.2. Azeotropic Binary Mixtures

Real liquid mixtures show a deviation from the Raoult’s law, as the activity coefficients of the components differ from unity. In a binary mixture, if the molecules of the two components repel each other, the components have a higher partial pressure than in the ideal case, that is, the boiling point of the mixture is lower. In this case, the activity coefficients are higher than unity, and this is called a positive deviation from the Raoult’s law.

In other cases, the molecules of different components attract each other more than the molecules of the same component, which results in a lower partial pressure, and therefore, a higher boiling point. The activity coefficients are lower than unity, and the phenomenon is called a negative deviation from Raoult’s law.

The difficulty of distillation separation of components *i* and *j* can be measured by their relative volatilities:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}}, \tag{1.17}$$

where K_i is the vapour-liquid distribution ratio of component i. The higher K_i, the more volatile is component i. If the difference between the volatilities (the distribution ratios) of the components is high, their relative volatility is high, as well, and the separation is easy. On the contrary, a low relative volatility indicates a difficult separation. If the relative volatility is very low, the mixture is called a close-boiling one. For nearly ideal mixtures, a constant relative volatility is a good approximation.

If the positive deviation from Raoult's law is sufficiently strong, the boiling and dew point temperature – composition curves will exhibit a minimum value. The two components are said to form a minimum boiling azeotrope. At the azeotropic point, the liquid and vapour phase compositions are equal:

$$y_i = x_i, \tag{1.18}$$

which means that an azeotrope cannot be separated by conventional distillation methods, whose driving force is the difference between y_i and x_i. At the azeotropic composition, both distribution coefficients and the relative volatility, as well, equal unity:

$$K_i = K_j = 1 \tag{1.19}$$

$$\alpha_{ij} = \frac{K_i}{K_j} = 1 \tag{1.20}$$

Mixtures that do not exhibit azeotropy are called zeotropic mixtures.

Ultimately, the positive deviation can be so strong that the two components become partially miscible, and two liquid phases appear. In most cases, the azeotrope point is in the immiscible region, and it is called a heteroazeotrope. Any overall liquid composition in the two liquid phase region is in vapour-liquid equilibrium with the vapour phase of azeotropic composition, which can however be separated by decantation of the two liquid phases in liquid-liquid equilibrium. Nevertheless, the azeotrope does not necessarily lie in the heterogeneous region, that is, a homoazeotrope can also occur, next to a partially miscible region.

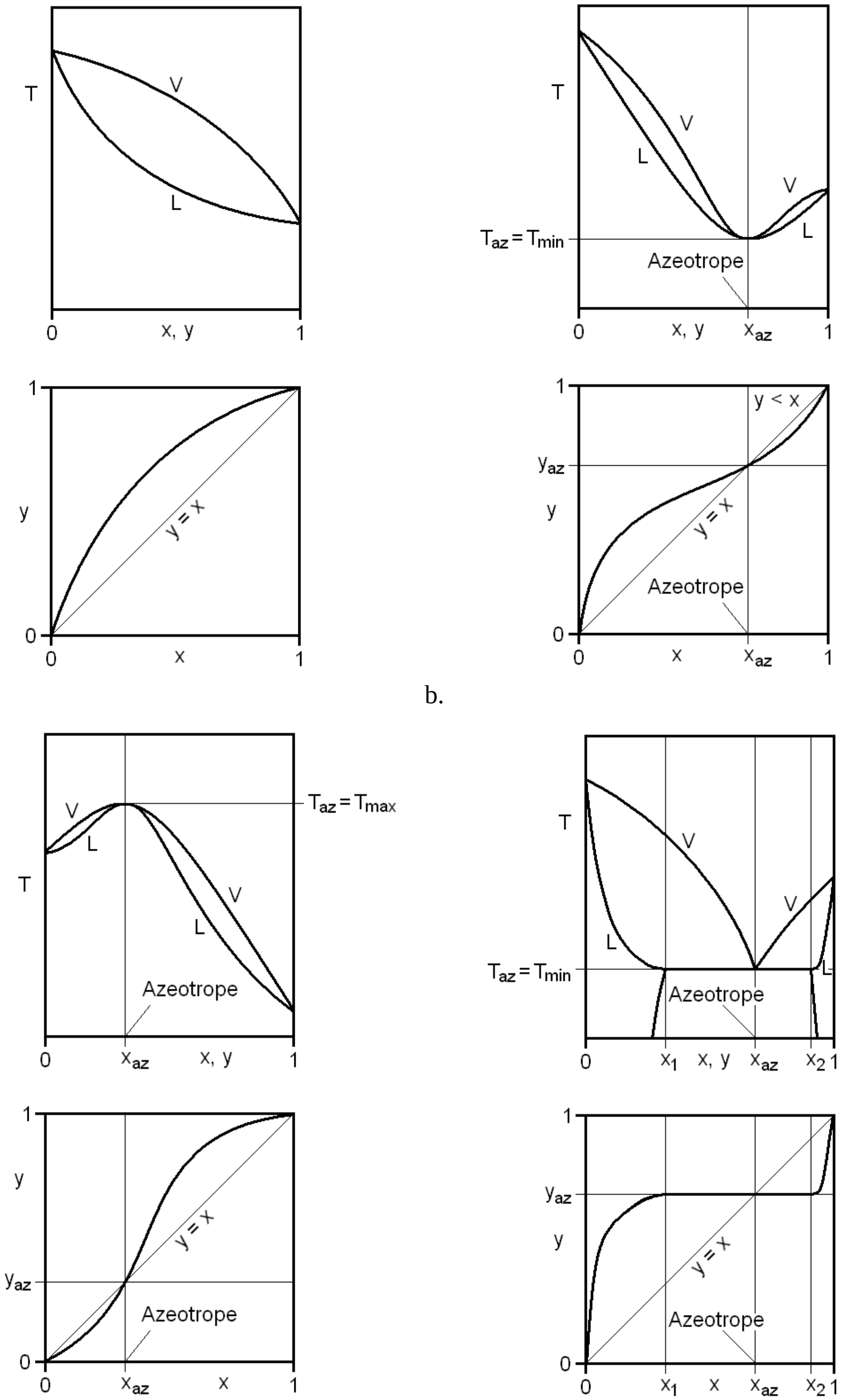
A maximum boiling point azeotrope can occur in the case of strong negative deviation from Raoult's law. The boiling and dew point temperature – composition curves exhibit a maximum value. In the simple batch distillation of the mixture, the composition of the residue always tends towards the azeotropic composition. A maximum boiling point azeotrope can never be heterogeneous, but it can occur in the homogeneous region of a partially miscible system.

An azeotrope may be formed in a nearly ideal mixture, as well, if the saturated vapour pressure curves of the two pure components cross each other. An example is the mixture of benzene and cyclohexane.

The types of binary azeotropes can be summarised in the following list:

1. Minimum boiling homogeneous azeotrope (e.g. ethanol – water)
2. Minimum boiling heteroazeotrope (e.g. benzene – water)
3. Minimum boiling homoazeotrope in a partially miscible system (e.g. tetrahydrofuran – water)
4. Maximum boiling homoazeotrope (e.g. acetone – chloroform)
5. Maximum boiling homoazeotrope in a partially miscible system (e.g. hydrogen chloride – water)
6. Double azeotrope (e.g. benzene – hexafluorobenzene)

Figure 1.1 shows the dew and boiling point curves (T-x,y) at constant pressure and vapour – liquid equilibrium curves (y-x) for zeotropic and the most important types of azeotropic mixtures, namely number 1, 2 and 4 in the above list.



a.

b.

c.

d.

Figure 1.1. The dew and boiling point curves and vapour – liquid equilibrium curves for (a) zeotropic (b) minimum boiling homoazeotropic (c) maximum boiling homoazeotropic and (d) heteroazeotropic mixtures.

The necessary azeotropic data (compositions and boiling points) can be found in the book of Horsley (1973), or in that of Gmehling et al. (2004), which is the most complete collection of azeotropic data.

1.1.3. Ternary Mixtures

In these sections, the vapour-liquid equilibrium (VLE) of ternary mixtures is discussed with an emphasis on residue curve maps, unidistribution and univolatility lines.

1.1.3.1. Residue Curve Maps and Their Classification

The VLE of ternary mixtures is frequently investigated and illustrated using residue curve maps. Residue curve map analysis is a crucial tool for the assessment of the feasibility of distillation processes, in particular azeotropic ones. The residue curves were first defined by Schreinemakers (1901), although they were called distillation lines at that time, and only received their present name from Doherty and Perkins (1978). A residue curve is a trajectory of the still composition (x) during the open evaporation of a mixture:

$$\frac{dx}{d\tau} = x - y, \tag{1.21}$$

where τ is dimensionless time, the relative loss of the still liquid ($d\tau = dV/L$). If this differential equation is integrated both towards infinity and minus infinity, the residue curve is obtained. Some important characteristics of residue curves are:

- The boiling point of the mixture increases along the residue curve.
- Residue curves never intersect each other.
- Residue curves give the composition profile of a packed distillation column operated under total reflux, and approximate that of a tray distillation column.

In the stationary points of Equation 1.21, the still composition remains constant:

$$\frac{dx}{d\tau} = 0, \tag{1.22}$$

which means that the composition of the vapour and liquid phase is equal. This occurs in the case of pure components and azeotropes (Equation 1.18). In ternary mixtures, azeotropes containing all the three components (ternary azeotropes) are frequently encountered. Similarly, higher order (quaternary, quinary, etc.) azeotropes are also possible in multicomponent mixtures, although they become less frequent with the increasing number of components. Only one quinary azeotrope is known to exist according to Horsley (1973), and no azeotropes of higher order are reported to exist.

The differential formulation of Equation 1.21 enables a topological analysis in the mathematical meaning, which led to the classification of the stationary points and of the multicomponent mixtures presented now. Depending on the eigenvalues of Equation 1.21, the stability of the stationary points may be:

- unstable node (UN): All residue curves start at an unstable node, and the still compositions move away from it. It is marked by an empty circle (○).
- saddle (S): Along a residue curve, the still composition approaches the saddle point to a certain degree, then starts to move away. A finite number of residue curves reach the saddle point, namely (batch) distillation region boundaries and residue curves located on an edge of the composition triangle. It is marked by an empty triangle pointing downwards (▽).
- stable node (SN): All residue curves end at a stable node, and the still compositions move towards it. It is marked by a full circle (●).

A set of residue curves, which have common initial and end points (unstable and stable nodes, respectively) is defined as a residue curve region (or basic distillation region by Safrit and Westerberg, 1997a). The residue curve regions are separated from each other by the residue curve boundaries, which can be either unstable (going from an unstable node to a saddle) or stable (going from a saddle to a stable node). The existence of multiple residue curve regions is the necessary condition of the existence of several nodes of the same type (Kiva et al., 2003). In addition to this, the number of residue curve regions equals the sum of the number of repeated unstable and stable nodes.

Figure 1.2 presents an example for a residue curve map: the mixture tetrahydrofuran-acetonitrile-water, calculated by using the UNIQUAC model. The system has a ternary and three binary azeotropes. Residue curve boundaries, shown as thicker lines, separate the composition space into three regions, as the residue curves, which all start from the single unstable node, can reach three different stable nodes.

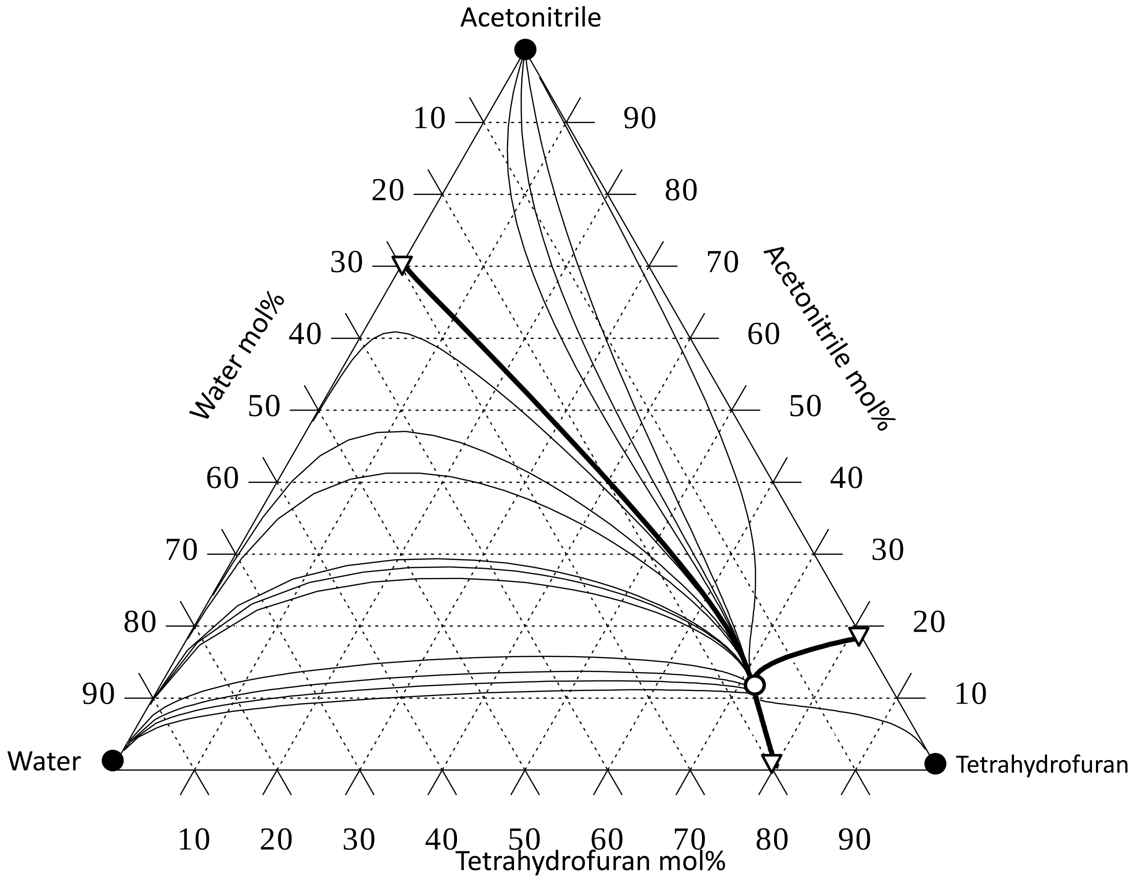


Figure 1.2. The residue curve map of the mixture tetrahydrofuran-acetonitrile-water.

Serafimov classified in the early 70's all the thermodynamically possible topological structures of residue curve maps for ternary mixtures into 26 classes (Serafimov, 1996, Hilmen et al., 2002, Kiva et al., 2003) presented in Figure 1.3, along with their occurrence among known ternary mixtures. The first number represents the number of binary azeotropes, the second number the number of ternary azeotropes, while the last one and the letter distinguish different sub-cases. The Serafimov classes do not distinguish the so-called antipodal structures, which are the exact opposite of each other. An antipodal structure can be obtained by changing the stabilities of nodes (from unstable to stable and vice versa), and reversing the directions of residue curves. The refined classification of Zharov and Serafimov (1975) takes into account the antipodal structures, as well, and comprises of 49 types of residue curve maps (ZS-types). These classifications do not take biazeotropy into account.

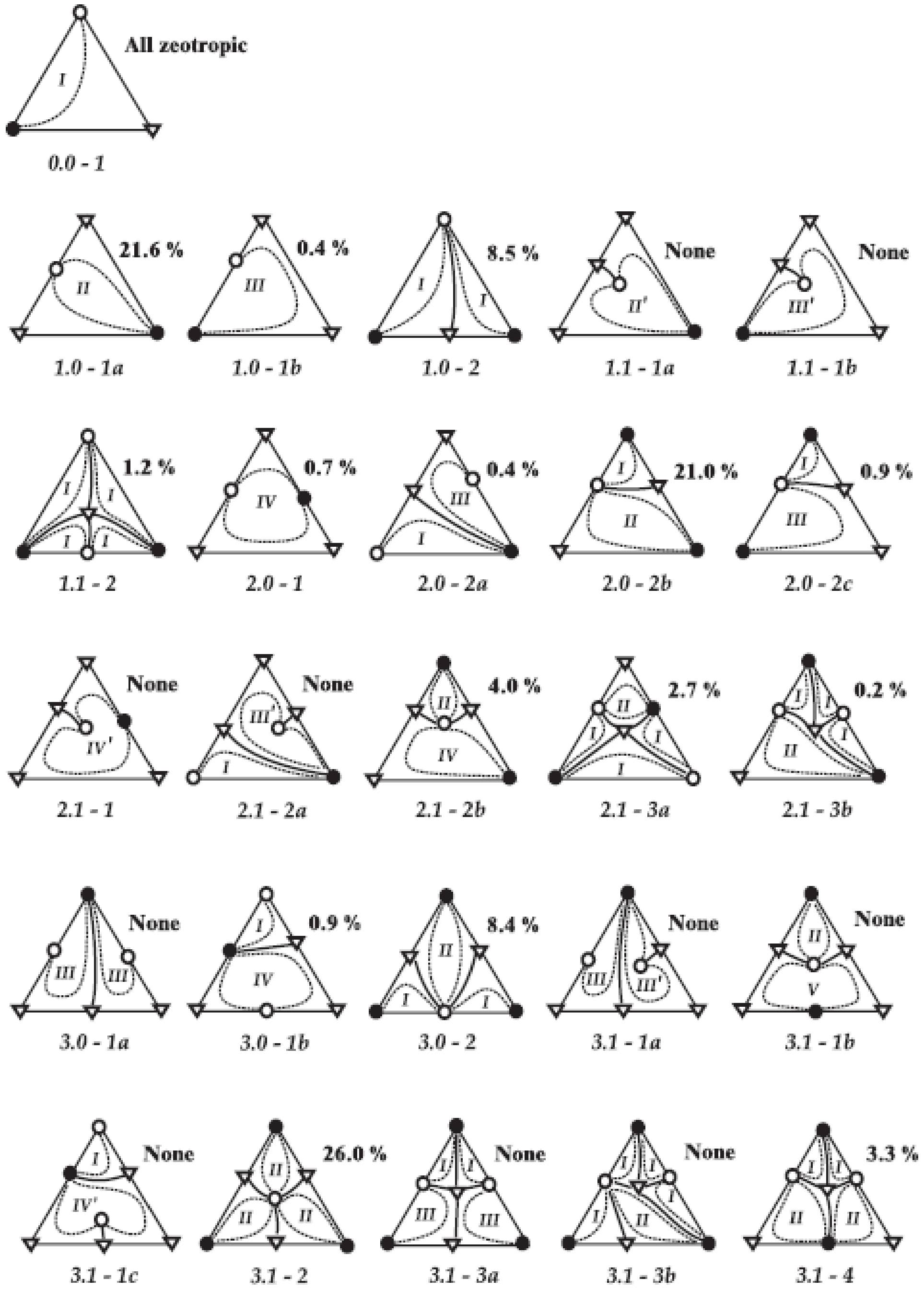


Figure 1.3. The Serafimov classes and their occurrence in Reshetov's statistics (Hilmen et al., 2002).

Matsuyama and Nishimura (1977) proposed another type of classification for ternary mixtures, with 113 classes. The Matsuyama & Nishimura (M&N) and the Serafimov classes describe the same set of residue curve maps, even though several M&N classes can correspond to the same Serafimov class, and one M&N may belong to more than one Serafimov classes. The M&N classes are denoted by three digits, which give the type and stability of the binary azeotropes. The first digit characterises the azeotrope of the light and the intermediate boiling component, the second one the azeotrope of the intermediate and heavy components, and the third one the azeotrope of the light and the heavy components, respectively. The digits can have the following values:

- 0: no azeotrope,
- 1: minimum boiling azeotrope, unstable node,
- 2: minimum boiling azeotrope, saddle,
- 3: maximum boiling azeotrope, stable node,
- 4: maximum boiling azeotrope, saddle.

The type of the eventual ternary azeotrope is denoted by a letter after the three digits, which may be:

- m: minimum boiling ternary azeotrope, unstable node,
- M: maximum boiling ternary azeotrope, stable node,
- S: intermediate boiling ternary azeotrope, saddle.

In order to estimate the natural occurrence of different Serafimov classes, Reshetov determined the Serafimov class of 1609 ternary mixtures based on thermodynamic data published between 1965 and 1988 (Reshetov and Kravchenko, 2007). The percentage distribution of the different classes is shown on Figure 1.3. Reshetov's statistics revealed that all mixture investigated belonged to 16 out of the 26 Serafimov classes, and 26 out of the 49 ZS-classes. This does not mean, however, that no mixtures may belong to these classes, but their occurrence is unlikely. It must also be noted that the majority (88.1 %) of the 371 ternary azeotropes reported by Horsley (1973) is minimum boiling, 40 are intermediate boiling (saddle) azeotropes, and only 4 are maximum boiling ones.

1.1.3.2. Unidistribution and Univolatility Lines

A unidistribution line can be defined as a set of points where the vapour-liquid distribution ratio of a component equals one (K_i=1). This obviously occurs in the pure components, which however, not necessarily gives rise to unidistribution lines. In the binary azeotrope of components *i* and *j*, the two unidistribution lines K_i and K_j intersect. Similarly, in the ternary azeotrope of components *i*, *j* and *k*, the three unidistribution lines K_i, K_j and K_k intersect each other.

A univolatility line comprises the points of composition space, where the relative volatility of a component pair equals one. The binary azeotrope of component *i* and *j* gives rise to the univolatility line α_{ij}=1, while a ternary azeotrope lies in the intersection of three univolatility lines. However, univolatility lines are not necessarily connected to azeotropic points, and may even occur in zeotropic mixtures (see Kiva et al., 2003).

The unidistribution and univolatility lines provide information on the individual behaviour of a mixture, not only on its class, and make it possible to sketch the residue curve maps of the mixture (Kiva et al. 2003). They are also useful tools along with residue curve analysis to predict the feasibility of extractive distillation processes (Rodriguez-Donis et al., 2009a).

1.2. Zeotropic and Homoazeotropic Distillation

Distillation can be performed both in continuous and batch processes. The coexistence of vapour and liquid on column interns, packings or trays, enables the mass transfer of the least volatile components from the liquid to the vapour, thanks to a driving force expressed as the difference between the vapour and the liquid phase compositions. The vapour rises from the column bottom where heat enables the liquid coming down to be vaporized. Some of the overhead vapour is removed as distillate and some is refluxed to the column, enabling to define R, the reflux ratio as the ratio of the distillate flow rate and flow returning the column.

In the continuous case, the mixture to be separated, the feed, is fed into the column continuously. For a binary zeotropic mixture of components A and B, where A is the most volatile one, A is obtained at the top of the column, while B is the bottom product. Both A and B belong to a residue curve, A, the distillate being the unstable node and B, the residue being the stable node. The column is operated in steady-state. By batch distillation, the mixture to be separated (charge) is filled into the still pot at the beginning of the operation, and A is withdrawn continuously as distillate, while B remains in the still. However, batch distillation is a dynamic process, as the variables (temperatures, compositions, etc.) change in time.

The notation of A as the most volatile, B the least volatile original component of a ternary mixture will be kept in the rest of the thesis, as well.

1.2.1. Continuous Homoazeotropic Distillation

In homoazeotropic distillation, an azeotropic behaviour is exploited to facilitate the separation. The component leading to this phenomenon is called entrainer. It may be already present in the mixture, but more frequently, it is added to the original mixture as a separating agent. A liquid-liquid split does not occur, or at least, it is not exploited in the separation process. The boiling point of the entrainer compared to that of the other components is very important in the separation synthesis.

For the separation of a binary mixture A-B forming a minimum boiling azeotrope, the entrainer (E) should be (Perry and Green, 2008):

- an intermediate boiling component that forms no azeotropes,
- a low or intermediate boiling component that forms a maximum boiling azeotrope with the lower boiling original component (A).

A separation sequence for the former case is presented in Figure 1.4. The mixture has only one distillation region. The unstable node of is the A-B azeotrope, the stable node is component B, while A and E are saddle points. The sequence consists of two columns, and applies indirect split, as in the first column the product is obtained in the bottom. The entrainer is introduced with the main feed into Column I that produces B as bottom product (W^I), and an A-E mixture as top product (D^I), which is fed into the Column II. A is obtained as the top product of Column II (D^{II}), whose bottom product (W^{II}), E is recycled to the original feed. If E formed azeotrope with A, the recycle stream would be the

A-E azeotope. In order to replace the E lost with the products, a make-up stream is mixed to the recycle stream.

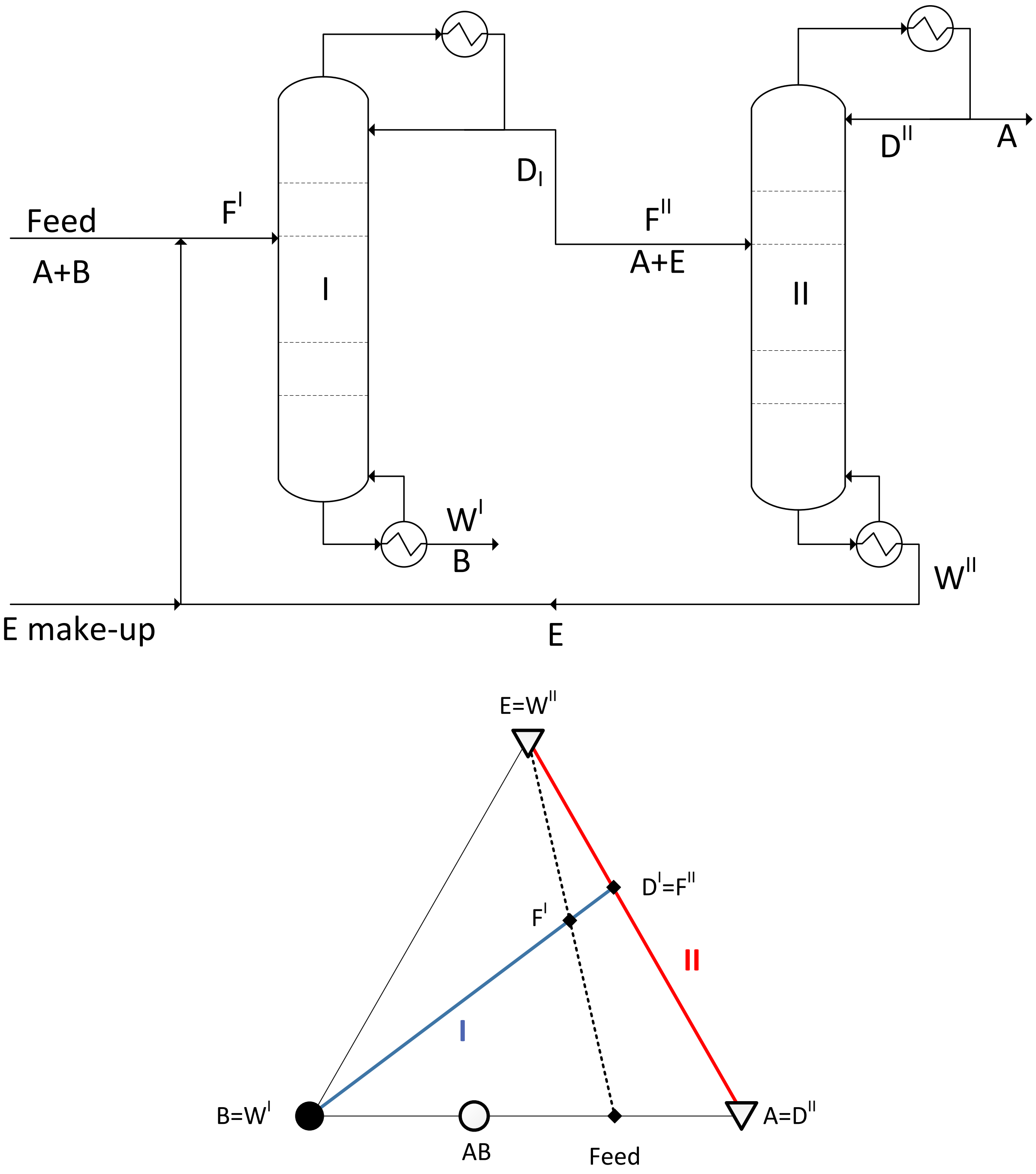


Figure 1.4. Separation of a minimum boiling azeotropic mixture by homoazeotropic distillation.

For the separation of a binary mixture forming a maximum boiling azeotrope, the entrainer can be either intermediate or high boiling. It must form a minimum boiling azeotrope with higher boiling original component (B), and either no azeotrope or a maximum boiling azeotrope with A.

Similarly to the former minimum boiling azeotrope separation, two columns are used for the separation of a maximum boiling azeotrope (Figure 1.5). The mixture has two distillation regions as there are two stable nodes: the A-B azeotrope and E. The only unstable node is component A. The columns operate in the region with A-B as stable node. Component B and the azeotrope B-E are saddle points. In this case, the direct split is applied, as in the first column the product is obtained as distillate. Column I produces A as top product (D^I) and a B-E mixture as bottom product (W^I), serving as feed for Column II (F^{II}), which produces B in the bottom (W^{II}). The B-E minimum boiling azeotrope is obtained from the top of Column II (D^{II}) and recycled to the feed.

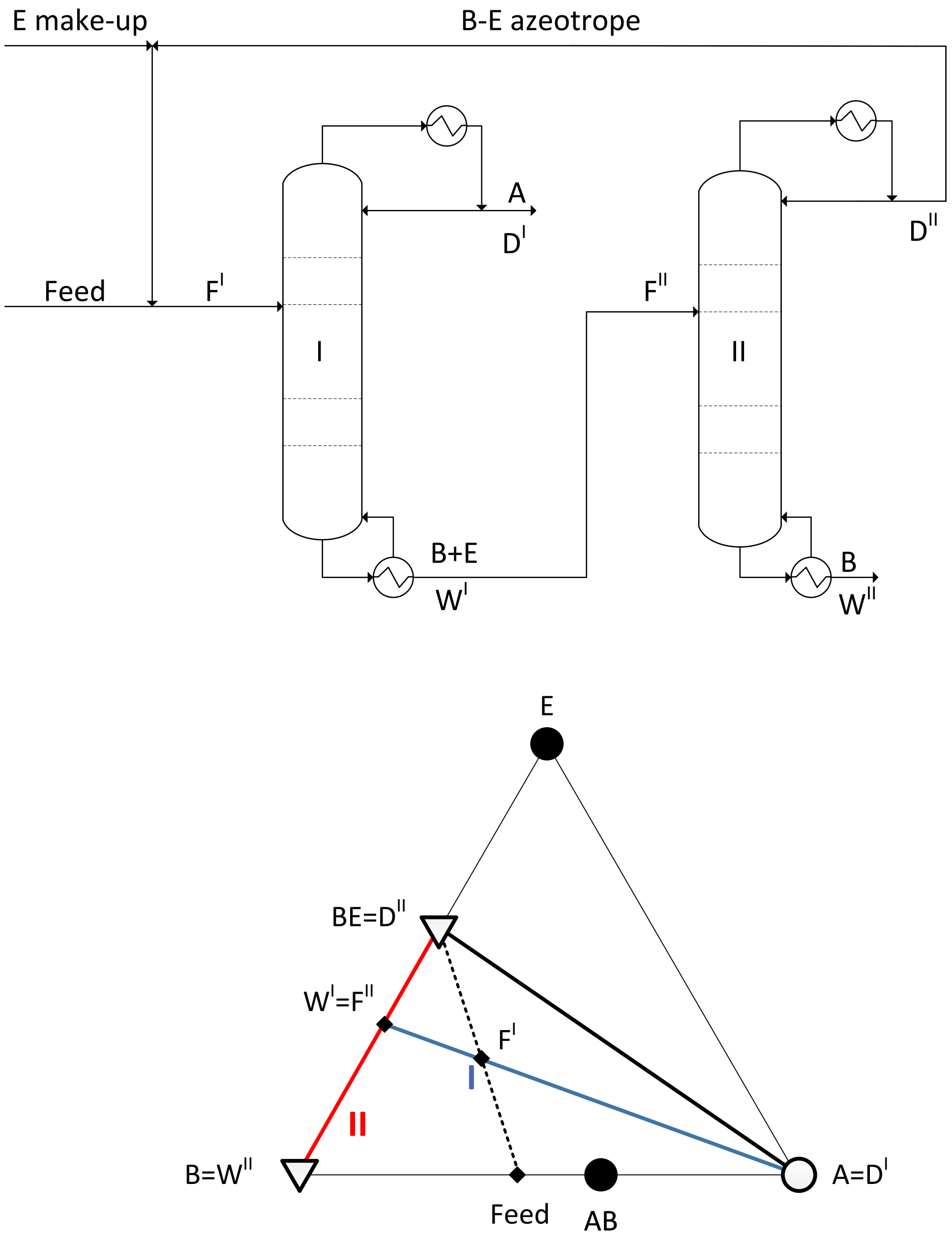


Figure 1.5. Separation of a maximum boiling azeotropic mixture by homoazeotropic distillation.

1.2.2. Homogeneous Batch Distillation

The advantage of batch distillation over the continuous one are well-known – primarily in the separation of mixtures produced in small, changing quantities and compositions. In the pharmaceutical industry, distilling industry, fine chemical production and solvent recovery distillation is mostly performed in batch mode (Mujtaba, 2004). Azeotropic and close-boiling mixtures are often encountered in these industries, and the separation of these mixtures requires the application of special distillation methods.

1.2.2.1. Operational Policies

A batch distillation column can be operated according to several different operational policies (Mujtaba, 2004, Perry and Green, 2008):

- Constant reflux ratio (R).

  This is the simplest and most frequently applied operational policy. For a binary mixture A-B, A is continuously removed from the column, its concentration in the distillate gradually decreases in time. When the accumulated distillate product falls down to its desired purity, an intermediate (slop) cut is started. If the separation is binary, the slop cut is ended, if component B reaches its purity requirement by the removal of a mixture of A and B. For multicomponent mixtures, a new product cut is started to withdraw the second most volatile component.
- Constant distillate composition.

  The composition of the distillate is kept constant during the operation for a binary separation. For multicomponent mixtures, the concentration of the main component of the actual cut is kept constant during the removal of that cut. In order to achieve a constant composition, the reflux ratio has to be increased continuously with the aid of a controller, reducing as a side effect the distillate flow rate. If the reflux ratio becomes uneconomically high, the withdrawal of the cut is stopped.
- Optimal reflux ratio.

  By this operational policy, neither the reflux ratio nor the distillate composition is constant, but a reflux ratio function is optimised to obtain the desired separation in minimum time. It is more economical than the two previous policies; however, the determination of the reflux ratio function, which is possible on the basis of optimal control theory, is a complicated task.
- Cyclic operation.

  By the cyclic operation, unlike the previously presented policies, the withdrawal of the distillate is not continuous. A cycle of two different periods are repeated throughout the operation. A total reflux ($R=\infty$) period is applied until reaching steady-state, then distillate is withdrawn without any reflux ($R=0$) for a short period of time.

  Sørensen and Skogestad (1994) studied a cyclic operation, where a cycle comprises three steps: filling up of the condenser (without reflux), total reflux period, and dumping of the condenser hold-up (withdrawal of product). They stated that the application of the cyclic operation is advantageous over the traditional one in the case of more difficult separations. Sørensen and Prenzler (1997) realised the above policy experimentally.

Watson et al. (1995) applied the cyclic operation for the separation of a four component mixture. A heteroazeotrope, which was unobtainable under finite reflux, was concentrated in the condenser during the total reflux periods.

1.2.2.2. Product Sequences for Azeotropic Distillation

In this subsection, first, the different distillation regions are discussed, and then the literature on the determination of distillation regions and product sequences for batch azeotropic distillation is reviewed. Some examples of the application of residue curve map analysis are also given.

Batch distillation is a common solvent recovery technology in the pharmaceutical and specialty chemical industries (Mujtaba, 2004). The components of waste solvents usually form multicomponent azeotropic mixtures, which form multiple batch distillation regions. Therefore, the sequence of distillate cuts and the maximum recovery of the components in each cut are highly dependent on the initial composition of the mixture. For the successful recovery of solvents the ability to predict the feasibility of recovering components with a very high purity from such a process stream is essential. Phase equilibrium diagrams (e.g. residue curve maps) are very useful tools in feasibility analysis.

Residue curve maps, and thus distillation regions can be usually determined solely from the boiling points of pure components and azeotropes. If this is not possible, we talk about indeterminacy, which may be local or global (Foucher et al., 1991). Local indeterminacy means that the same set of boiling points may occur for two different types of residue curve maps (two Serafimov-classes), but if the stability of stationary points are known, the Serafimov class of the mixture can be determined unambiguously. On the contrary, global indeterminacy means that even if the stabilities are known, the mixture can belong to two Serafimov classes. Global indeterminacy can only occur for Serafimov classes 3.1-3a and 3.1-3b, for which, fortunately no existing mixtures were reported. The classes could only be distinguished by investigating the position of actual residue curves.

Ewell and Welch (1945) defined a batch distillation region as a region in which the same product sequence can be obtained for every composition using traditional batch distillation. Safrit and Westerberg (1997a) define a continuous distillation region similarly, as a region with only one unstable and stable node, which has the same feasible products for any initial composition within this region. A basic distillation region (or residue curve region) can be always broken up into one or more continuous and batch distillation regions. For example, two batch distillation regions can have the same unstable and stable nodes, meaning that they are part of the same basic distillation region, but they can have different saddle points. Every batch distillation region is made up by *n* stationary points (making it an *n*-simplex), if *n* is the number of components, as *n* cuts can be taken from the mixture.

Bernot et al. (1990) determined the batch distillation regions and product sequences of a ternary mixture by the knowledge of the stable and unstable separatrices and the stabilities of the stationary points, which, in turn, can only be computed by applying VLE calculations. The batch distillation regions were determined for ternary mixtures on the basis of knowing only the temperatures of pure components and azeotropes, and azeotropic compositions by Foucher et al. (1991), though they state that their method is not applicable in the case of indeterminacy. According to these authors, indeterminacy occurs if the number of intermediate boiling azeotropes and binary saddles are different, or if, in the presence of a ternary saddle azeotrope, the total number of pure component nodes and binary azeotropes equal six. The algorithm is capable of screening for topologically and thermodynamically inconsistent data. Foucher et al. (1991) also applied their method to the screening of entrainers. This method was used also by Peterson and Partin (1997) to enumerate all the 382 ternary temperature sequence-distillation boundary map pair. The distillation boundary maps are simplified residue curve maps that show the basic pattern of the residue curve map temperature directions and the distillation boundaries when they exist. The number of possible ternary temperature sequences is 307, that of distillation boundary maps is 125. Distillation boundary maps are named according to an extended version of the M&N classification, as in some cases multiple distillation boundary maps are possible in the presence of a ternary saddle azeotrope. Different temperature sequences can yield the same distillation boundary map (and thus, the same batch distillation regions), while, in the case of indeterminacy, more than one distillation boundary map can correspond to a single temperature sequence. The relationship between temperature sequences and distillation boundary maps (called distillation regions diagrams or DRD in Perry and Green, 2008) are also given in Perry and Green (2008), whereas Kiva et al. (2003) give the correspondence between the distillation boundary maps and Serafimov's and Zharov's classifications.

Methods were suggested for mixtures with arbitrary number of components by Safrit and Westerberg (1997a), Rooks et al. (1998), and Ahmad et al. (1998). All these latter methods require the knowledge of the type of all stationary points demanding the application of a VLE model.

Safrit and Westerberg (1997a) identify the distillation boundaries of a *n*-component mixture, those of every submixture consisting of at least three components and of their maximum (MaxRS) and minimum residue surface (MinRS), if they exist. The MaxRS (respectively MinRS) is a boundary surface separating the unstable (respectively stable) nodes. MaxRS is the set of stationary points reachable from two unstable nodes, that is, those that form a boundary between the unstable nodes. The algorithm divides the mixture into *n*-2 dimension submixtures, which are on the one hand *n* mixtures formed by *n*-1 component and on the other hand, the MaxRS and MinRS of the *n*-component mixture. These steps are repeated for each submixture until ternary submixtures are reached. By removing the components while creating the submixtures, the stability of the stationary points in the new submixture may be different from its stability in the previous mixture. Through this process, connections are made between the stationary points located on boundaries. The basic distillation regions are found by following the boundaries and the edges of the composition simplex with increasing boiling temperature from each unstable node to the stable nodes. By adding additional batch boundaries through connecting the unstable node to every other stationary point in the basic distillation region, the batch distillation regions are determined, as well.

Safrit and Westerberg (1997b) presented a tool for the synthesis of azeotropic batch distillation. With the knowledge of batch distillation regions, product sequences can be determined, which makes possible to generate the network of all possible batch column sequences. The distillation regions were determined for four column configurations: rectifier, stripper, middle vessel column and extractive middle vessel column.

Rodriguez-Donis et al. (2001a) pointed out several cases, related to indeterminacy diagrams, where Safrit's method fails. They quoted Ahmad et al. (1998) that demonstrated that while Safrit and Westerberg (1997a) assumed that a saddle point involving all components is always in the unstable boundary limit set of all unstable nodes, and in the stable boundary limit set of all stable nodes in a system, this assumption does not always hold. It must be mentioned that the latter case occurs only in the case globally undetermined systems, which hasn't been found yet in the practice. Ahmad et al. (1998) assumed that the maximum number of both unstable and stable nodes is two, as they stated that global indeterminacy occurs, if the number of unstable nodes are two and the number of stable nodes is higher than two (or vice versa). Their algorithm used the concept of adjacency matrix to describe the structure of the mixture and to determine the batch distillation regions. It distinguishes 13 types of systems on the basis of the number of unstable and stable nodes, and the existence and type of the *n*-component azeotropes. By applying different rules for the different types of systems, it finds the boundary surfaces separating stable (respectively unstable) nodes, and creates the necessary connections between the stationary points.

Rooks et al. (1998) used not only the results of the stability analysis, but they also integrated the differential equations describing the VLE of the mixture in order to determine the boundaries and thus, they were able to fill out the adjacency matrix. The sequence of the cuts is determined by using the so-called reachability matrix, computed from the adjacency matrix.

Pöllmann et al. (1996) presents methods for determining the boundary surfaces of multicomponent mixtures both qualitatively and rigorously. By the qualitative method, the boundaries are identified by computing closed distillation profiles (with the aid of a VLE model), and analysing the reachability matrix, which is filled out based on the direction of the closed distillation profiles.

All the above methods assume that the distillation region boundaries are straight lines, and that no biazeotropy occurs.

Strongly curved distillation boundaries may strongly affect the product sequence even under the assumption of maximal separation. Pöpken and Gmehling (2004) proposed a simple method for determining the location of distillation boundaries in quaternary systems, by starting the integration from the points of ternary boundaries.

Espinosa et al. (2004) presented a software tool that integrated the steps of conceptual design of batch distillation, from the determination of distillation regions to the calculation of minimum reflux and stage number. To select among different separation alternatives, the maximum feasible separation of each task was calculated.

Gerbaud et al. (2006) applied residue curve map analysis (implanted in a software tool) in order to find a suitable batch process (pressure-swing or extractive distillation) for the separation of azeotropic or close-boiling mixtures, by using a complete set of entrainer selection rules for homoazeotropic distillation of ternary mixtures A-B-E published earlier (Rodriguez-Donis et al., 2001a).

1.2.2.3. Non-Conventional Configurations

The batch rectifier (Figure 1.6a) is the only widespread configuration in the industry, operated in open system (with continuous product withdrawal). The cuts are obtained in the order of decreasing volatility. In the batch distillation region where the initial feed lies, the distillate products sequence can be found by using the above methods. In order to reduce the energy requirement of batch distillation non-conventional configurations have received attention, as well. The non-conventional column configurations are (Kim and Diwekar, 2001):

- batch stripper,
- middle vessel column,
- multivessel column.

Similarly to batch rectifier, the bottommost vessel (reboiler) is heated, and heat is removed by condensing the vapour leaving the topmost column section in all non-conventional configurations. Their operation is presented for a ternary (batch stripper and middle vessel column) and a quaternary mixture (multivessel column), with components A, B, C and D in order of decreasing volatility.

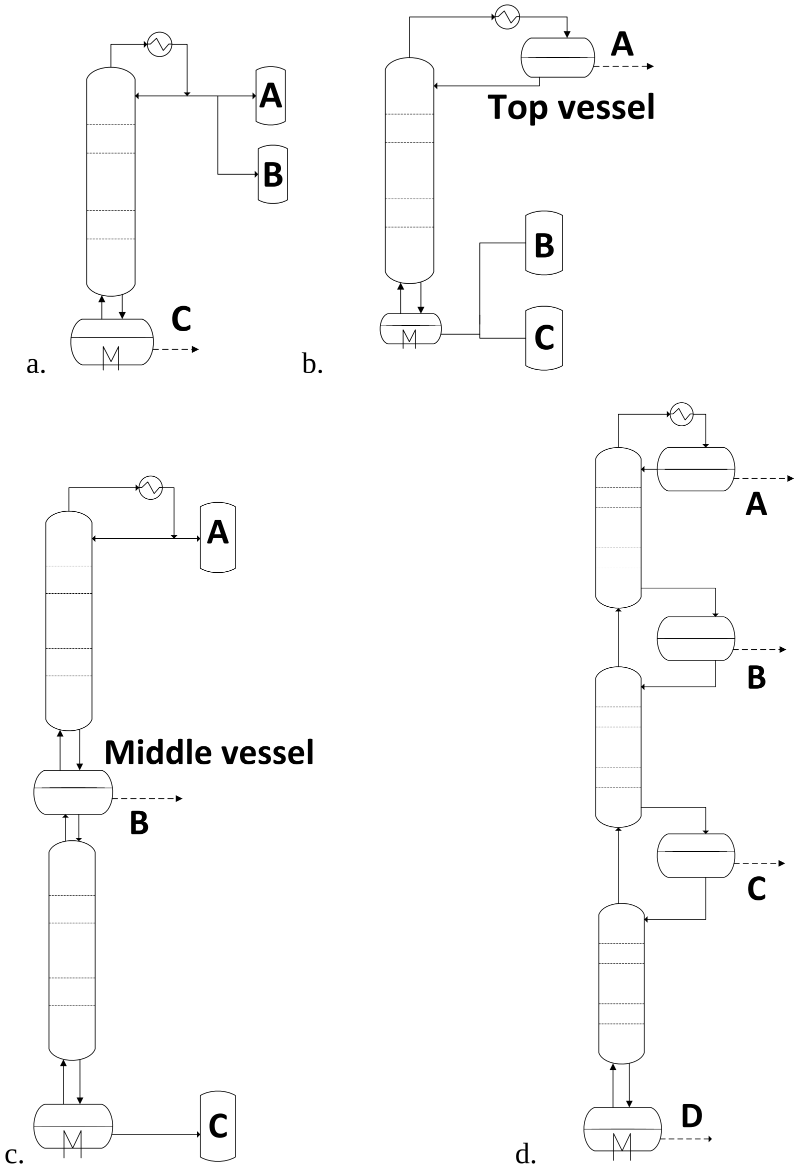


Figure 1.6. Batch distillation configurations: (a) batch rectifier, (b) batch stripper, (c) middle vessel column, (d) multivessel column

The batch stripper configuration (Figure 1.6b) was first mentioned by Robinson and Gilliland (1950). It can be considered as an inverted batch rectifier (Sørensen and Skogestad, 1996), with the charge filled into a top vessel, comprising only of a stripping section. The product, which is enriched in heavy components, is withdrawn either from a partial reboiler, or in the case of the total reboiler, from the bottom of the column. The cuts are obtained in the order of increasing volatility, that is, first C, the least volatile component, then B, while A is recovered in the top vessel. The operational parameters of the batch stripper are the reboil ratio (which is analogous to the reflux ratio of batch rectifier, being the ratio of the flow rates of the vapour leaving the reboiler and the product stream) and the liquid flow rate leaving the top vessel. The reboil ratio is connected to the heat duty of the reboiler. The operational policies of batch stripper are: constant reboil ratio, constant bottom product composition, optimal reboil ratio. The operation of the batch stripper is more complicated than that of the batch rectifier, since while in the latter case the flow rate of the mixture entering the column is fixed by the heat duty, for the batch stripper, the liquid flow rate entering the column and the heat duty have to be adjusted separately. If the reboil ratio is constant, the heat duty has to be determined by taking into account the liquid feed rate. A too high reboil ratio leads to the drying of the heat transfer surface; a too low value can cause the draining of the column.

A middle-vessel column (Figure 1.6c; Bortolini and Guarise, 1970; Hasebe at al., 1992) consists of a rectifier and a stripper column section connected through a middle vessel, and can produce three products simultaneously. The charge is filled into the middle vessel. The liquid leaving the rectifier section and the vapour leaving the stripping section are led into the middle vessel. However, a variant of middle vessel column uses a vapour by-pass, that is, the middle vessel is connected to the column sections only with liquid streams, and the vapour coming from the stripping section is led directly into rectifying one. Component A is withdrawn as distillate, C as bottom product, while the intermediate component B is accumulated in the middle vessel, in a continuously increasing purity. The configuration has three operational parameters: the reflux ratio, the flow rate of the liquid leaving the middle vessel, and the reboil ratio. The operation is more flexible, as the two column sections can be operated independently according to the operational policies of batch rectifier and stripper, respectively. The operational problems described by the batch stripper can also occur by the middle vessel column. A possible solution is applying level control in the bottom of the column (Phimister and Seider, 2000a), however, this requires a considerable liquid hold-up, which is disadvantageous for the separation. The middle vessel column was experimentally investigated by Barolo et al. (1998) and also by Warter et al. (2004), who performed a batch extractive distillation separation in the middle-vessel column, as well. Cheong and Barton (1999a) developed a mathematical model of middle-vessel column and determined the obtainable product sequences with the assumption of maximum separation (infinite number of trays, very high reflux and reboil ratios). In the continuation of the above work, the effects of curved separation boundaries were also investigated (Cheong and Barton, 1999b). Their model was validated by simulation, as well (Cheong and Barton, 1999c). Stéger et al. (2006) studied reactive distillation in middle-vessel column by feasibility analysis and rigorous simulation.

The generalisation of the middle-vessel column is the multivessel column (Figure 1.6d) proposed by Hasebe et al. (1995), which is built up from more column sections and intermediate vessels. The multivessel column is operated in a closed way, that is, without continuous product withdrawal. The charge can be divided between the vessels at the start of the operation, and each component is enriched during operation in the hold-up of a corresponding vessel. The most volatile component is obtained in the top vessel, the least volatile one in the bottom vessel (reboiler). Based on the number of vessels, several components can be separated simultaneously. The operational parameters are the heat duty and the liquid flow rates leaving the vessels, or equivalently, the hold-up of the vessels. The operation is possible both with constant and variable vessel hold-up (Hasebe et al. 1997). In the latter case, the temperature at a point in the column section is controlled by the flow rate of liquid leaving the vessel above the section (Wittgens et al., 1996; Skogestad et al., 1997). Wittgens and Skogestad (2000) investigated experimentally the multivessel column, where they applied the control strategy described above. The authors above also mentioned that it is frequently more advantageous to fill the whole amount of charge into the reboiler.

All the non-conventional configurations and batch rectifier, as well, can be operated in closed mode, with the accumulation of the products in the vessels, first proposed by Treybal (1970) and Bortolini and Guarise (1970). The closed operation mode of a batch rectifier can be considered as the simplest case of multi-vessel column, and can be called a two-vessel column (Lang, 2005). The benefits of closed operation are the infinite reflux and reboil ratios, and the simplicity of operation, while its drawback is the large hold-up of the vessels, slowing down the composition change.

Hasebe et al. (1999) stated that the optimization of the reboiler hold-up has a much greater effect on the performance in the case of the two-vessel column than with the batch rectifier. After optimization, the closed mode provided shorter operation times. The charge should be filled into the reboiler, except if the purification of the light component is much easier than that of the heavy one in the lower section. With a variant of the multivessel column realized as a series of sequentially connected batch rectifiers with vapour by-pass around the still pots, where only the reboiler of the first column and the condenser of the last one are operating, the energy demand of the separation was much lower than with a batch rectifier.

Skouras and Skogestad (2004a) compared the total batch time of the two-vessel column, and the multivessel column with and without vapour by-pass for the same separation task. All of them were operated with temperature control. The shortest times were achieved by the multivessel column operation without vapour by-pass, while the two-vessel column gave the worst results. The same investigations were also performed for batch heteroazeotropic distillation by Skouras and Skogestad (2004b). The top vessel of the two-vessel column and either the top or the middle vessel (depending on the mixture) of the middle vessel column were used as a decanter. The organic phase was completely refluxed, and the aqueous phase was accumulated in the decanter. The multivessel columns always provided a shorter operation time than the two-vessel column. The elimination of the vapour by-pass was not recommended.

1.2.2.4. Off-Cut Recycle

A synonym of batch distillation is fractional distillation which refers to the possibility of taking arbitrary number of fractions (cuts). The main component to be recovered with the highest possible recovery is produced in specified purity in the main cut(s). The polluting components and azeotropes having

- lower boiling point than that of the main component are removed in the fore-cuts (light off-cuts) before the main cut,

- higher boiling point than that of the main component are withdrawn in the after-cuts (heavy off-cuts) after the main cut.

Both types of off-cut may contain the main component in considerable quantity because of the occurrence of minimum and maximum azeotropes containing the main component and/or the limited sharpness of the separation. The off-cuts can either be disposed of safely (meeting environmental constraints) by incineration or can be recycled to the next batch in order to reduce the loss of the main component. Recycle of the final hold-up serves the same goal. However the cuts recycled

- diminish the amount of the fresh feed in the next batch since the (mixed) charge will also contain the cuts recycled, and
- vary the composition of the charge.

In the book of Mujtaba (2004), an entire chapter deals with the question of off-cut recycles, both in the case of binary and multicomponent mixtures, with a particular emphasis on the optimization of the recycle policy. Mayur et al. (1970) was the first to perform the dynamic optimization of the periodic operation (with the off-cuts recycled to consecutive batches) of a binary separation. Mujtaba (1989), Mujtaba and Macchietto (1992) and Bonny et al. (1996) investigated the dynamic optimization of multicomponent separation with off-cut recycle. Miladi and Mujtaba (2005) also considered a fixed product demand for their optimization of binary batch distillation with recycles, and stated that the storage cost can be a deciding factor for the production and recycling of off-cuts. The majority of the works cited are not dealing with azeotropic multicomponent mixtures.

1.3. Homoextractive Distillation

In extractive distillation, a new component called entrainer or solvent is added to the original mixture. The entrainer is usually considered in the literature to be a high-boiling, non-volatile component forming no new azeotropes but other types of entrainers work as well. The process differs from homoazeotropic distillation in that the entrainer is fed to the column at a point other than the original mixture (continuous process), or that the entrainer is added continuously to the column, instead of being filled into the still with the charge (batch).

1.3.1. The Role and Selection of the Entrainer

The entrainer selectively interacts with one of the original components, which usually contain one or more different functional groups (Perry and Green, 2008), while being similar to the other components with which it displays a near ideal VLE behaviour. The entrainer enhances the non-ideality of the other, dissimilar original component, changing its activity coefficient. The relative volatility of the original mixture is usually increased, but there exist many examples where the volatility order of the components is reversed. To be able to exploit the favourable effect of the entrainer on the relative volatility, usually a high solvent concentration is necessary in the column.

As the entrainer determines the feasibility and effectiveness of the extractive separation process to a great extent, its choice is of crucial importance. The most important characteristic of the entrainer is the selectivity. The effect of the entrainer can be studied with the aid of different graphic methods, as well. The binary phase diagram of the original components (using entrainer-free concentrations) can be plotted for different entrainer concentrations. At a certain entrainer concentration, the azeotrope disappears.

Another method is to plot the change the relative volatility of the azeotropic mixture with the addition of entrainer. Plotting of equivolatility lines in the ternary composition space is also applied. The A-B univolatility line α_{AB}=1 is especially important. For a heavy entrainer used to separate a minimum boiling azeotrope, if this line reaches the A-E edge, A is obtained as distillate (Laroche et al., 1991). If it reaches the B-E edge, B will be the distillate. The amount of entrainer at which the α_{AB}=1 crosses the triangle edge correspond to the amount necessary for the azeotrope to disappear, as in entrainer-free binary diagrams. The process feasibility when using a light, an intermediate or a heavy entrainer for the separation of minimum or maximum boiling azeotrope or of low relative volatility mixtures can also be predicted from residue curve map analysis combined with the A-B univolatility line information (Rodriguez-Donis et al. 2009a, 2009b, 2012a, 2012b, Shen et al., 2012, Shen and Gerbaud, 2012).

Another important choice criterion to consider is the separability of the entrainer from the remaining original component, as the product has to be purified from the entrainer and the entrainer has to be regenerated for reuse. Entrainers with much higher boiling point than the original components are easier to separate, but they may require more energy in the regeneration column.

The entrainers should preferably also be thermally stable, cheap, with low melting point and viscosity. It should not be corrosive, toxic or react with the original components. The molar volume of the entrainer is not important in the continuous process, but in the batch one, a low molar volume is needed (Lang et al., 1994), so that the liquid volume in the still does not increase exceedingly.

For heavy entrainer choices, which represents the most industrial cases, two methods of entrainer selection have been proposed (a) the use of chemical heuristics combined with the checking of quantities such as the entrainer selectivity and (b) a multi-objective search with computer-aided molecular design (CAMD) tools. In the heuristic methods, the entrainer selection is often divided into two steps (Perry and Green, 2008). First, the functional groups or chemical families are identified, where favourable molecular interactions with the original components are likely to occur. The possibility of hydrogen bonding with one of the components and the polarity characteristics of the components are useful to be investigated. It is often possible to find good entrainer candidates in the homologous series of one of the components (preferably that of the heavy one). In the second step, individual entrainer candidates are evaluated according to different criteria, such as

- boiling point: the entrainer should have a boiling point by 30-40 °C above that of the high boiling original component, in order to avoid azeotrope formation and to ensure the non-volatility of the entrainer.
- selectivity at infinite dilution, which is defined as the ratio of the activity coefficients of the original components infinitely diluted in the entrainer:

$$S_{AB}^{\infty} = \frac{\gamma_A^{\infty}}{\gamma_B^{\infty}} \tag{1.22}$$

This value is the upper limit of the selectivity, as the effect of the entrainer increases with its concentration.

- the increase of the A-B relative volatility with the addition of the entrainer.

CAMD is a systematic way for designing an entrainer by combining structural groups in order to satisfy a set of predefined target property specifications, such as high selectivity for one component, together with other criteria. The problem of entrainer design can be regarded as an optimization problem, with the objective of maximizing selectivity, subject to a set of structural, pure component property and mixture property constraints (Karunanithi et al., 2005). Generate-and-test is another approach of CAMD (Harper and Gani, 2000). After defining the desired and undesired properties of the entrainer to be designed, a generation algorithm creates a set of feasible molecules, which are later ranked and tested according to selected properties, such as selectivity at infinite dilution. Kossack et al. (2008) described a complete and systematic framework for heavy entrainer selection using CAMD, which evaluated entrainer candidates by using thermodynamic based criteria like their selectivity at infinite dilution and by evaluating the process feasibility by the rectification body method, as well. An MINLP optimization of the resulting processes was also performed.

1.3.2. Continuous Homoextractive Distillation

In continuous homoextractive distillation, the separation is performed in a two column sequence (Figure 1.7). The entrainer is fed into Column I at a stage above the feed. In this way, the column is divided into three sections. The uppermost, the rectifying section, separates one of the original components (here A) from the entrainer. This task usually requires only a few stages, as the entrainer is non-volatile. The section below the feed is the stripping section removing A from the bottom product, a mixture of B and E. These two sections are joined by the extractive one, in which the A-B azeotropic composition is crossed, making the separation of the original components possible. The bottom product is fed into Column II, entrainer regeneration column, where B is separated from the entrainer, which is led back to the first column. The make-up E is mixed to this recycle stream.

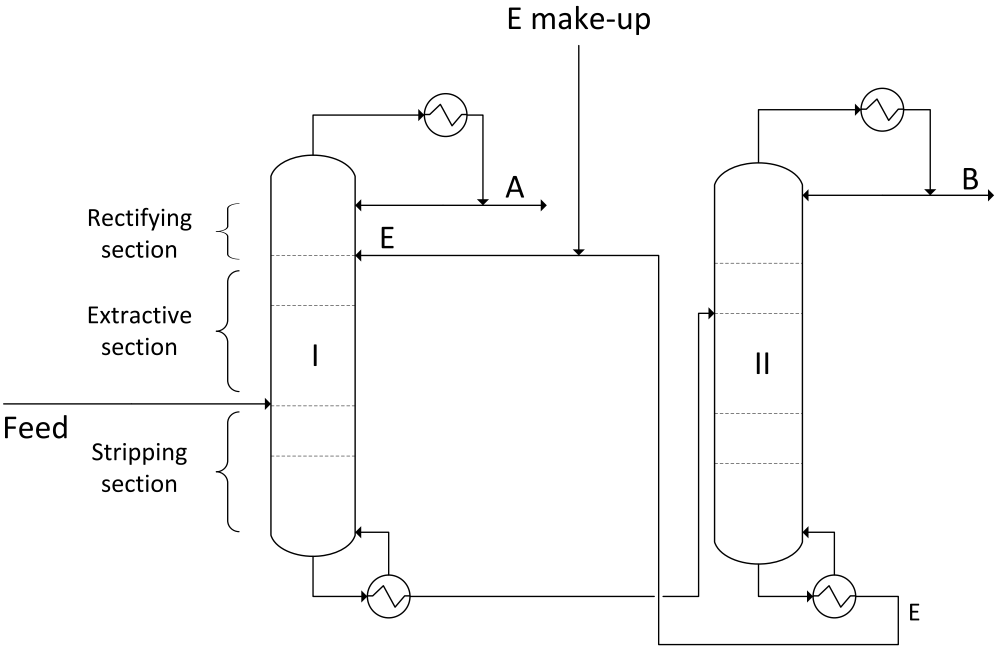


Figure 1.7. Continuous homoextractive distillation scheme.

The entrainer to feed ratio F_E/F is a very important parameter of continuous homoazeotropic distillation (Stéger at al., 2005). For azeotropic mixtures, a minimum value is necessary for the feasibility of the separation, and the increase of the parameter reduces the necessary stage number. Unlike traditional distillation, the separation performance does not necessarily increase with the reflux ratio. Laroche et al. (1992) stated that a maximum reflux ratio occurs, as a greater reflux dilutes the entrainer in the column. However, the maximum reflux ratio usually occurs at very high values of F_E/F.

Before the two column sequence, a preconcentrator column can be applied, in order to approach the azeotropic composition (Stichlmair and Fair, 1998). In this way, a lower amount of (more concentrated) feed is separated in the extractive column, and the amount of entrainer can be reduced, although investment costs are higher.

1.3.3. Batch Homoextractive Distillation

In batch extractive distillation (BED), the entrainer is fed continuously to the column, instead of prefilling it into the still pot with the charge. The term is usually applied to processes where the components do not form heteroazeotropes or even if a heteroazeotrope is present, its existence is not exploited. Contrary to batch homoazeotropic distillation, the feasibility study of batch extractive distillation requires also the knowledge of volatility order regions implied from the calculation of the univolatility lines, in addition to residue curve map analysis. The first to investigate batch extractive distillation, both experimentally and by simulation, were Yatim et al. (1993) and Lang et al. (1994).

The entrainer is conventionally chosen in industrial practice as a heavy component (Lang et al., 1994; Lelkes et al., 1998a; Seader and Henley, 1998; Lang et al., 2006; Rodriguez-Donis et al., 2009a; Lang et al., 2010; Luyben and Chien, 2010) and performed in a batch rectifier. However, there are some cases when the use of a high boiling entrainer is not recommended (e.g. heat sensitive mixtures or inconveniently high boiling point in the still). As demonstrated by the feasibility studies of Rodriguez-Donis et al. (2012a,b), it is indeed possible to use light or intermediate entrainers, as well.

Lelkes et al. (1998b) developed a method for studying the feasibility of batch extractive distillation. They determined the feasibility and limiting values of the most important operational parameters by the means of calculating feasible profiles of different column sections. Rodriguez-Donis et al. (2009a) published the following general feasibility criterion for batch extractive distillation: “homogeneous batch extractive distillation of a A−B mixture with entrainer (E) feeding is feasible if there exists a residue curve connecting E to A or B following a decreasing (a) or increasing (b) temperature direction inside the region where A or B is the most volatile (a) or the heaviest (b) component of the mixture”. The authors demonstrated the application of this criterion in the feasibility analysis of batch extractive distillation of azeotropic mixtures using a heavy entrainer. Their method was also applied to the light or intermediate entrainers (Rodriguez-Donis et al., 2012a,b) and for the separation of low relative volatility mixtures (Rodriguez-Donis et al., 2009b), as well.

Stéger et al. (2005) studied the limiting parameters of batch extractive distillation. As by traditional batch distillation, reflux ratio has a minimum value for feasible separations. The rectifying section may require a minimum number of stages, but in some cases the separation is also feasible with the extractive section only. Unlike traditional batch distillation, the number of rectifying stages can have a maximum value, as well, at separating minimum boiling azeotropes, or at separation tasks with light entrainer. Both reflux ratio and the number of the extractive stages may have limiting maximal values.

The batch extractive distillation was also studied in non-conventional configurations, as in middle vessel column, among others by Safrit et al. (1995), Warter and Stichlmair (1999), and Cui et al. (2002). Low and Sorensen (2002) performed the optimisation of middle vessel extractive distillation, while Warter et al. (2004) presented experimental results of the process. Hua et al. (2007) proposed a two-reboiler batch rectifier configuration for batch extractive distillation. Based on industrial experiences of batch extractive distillation in a rectifier, where a very long start-up phase was observed, Lang et al. (2006) suggested a new operational policy, where entrainer feeding is started already during start-up, when the vapour reaches the entrainer feeding stage of the column. Acosta-Esquijarosa et al. (2006) studied the sequential combination of a crosscurrent liquid extraction process and batch distillation both experimentally and by simulation. Steger et al. (2006) proposed a new variant of batch extractive distillation, the inverse-fed batch extractive distillation, where the total amount of the entrainer is pre-loaded to the still, and the mixture to be separated is continuously fed to the column.

The book of Luyben and Chien (2010) devotes a whole chapter to the batch distillation of azeotropes, including batch extractive distillation. They studied the separation of two mixtures by batch extractive distillation, using different operational policies. In most of the extractive distillation processes, the component withdrawn is a saddle point of the residue curve map, namely an intermediate boiling of the distillation region.

1.4. Heteroazeotropic Distillation

In heteroazeotropic distillation, either the original components form a heteroazeotrope, or a heteroazeotrope is introduced by adding an entrainer to the mixture, leading to the formation of two liquid phases. By separating the two liquid phases with a decanter, it is possible to get through the original azeotropic composition. The method has been applied as early as 1902 (Young, 1902) for the dehydration of ethanol using benzene as entrainer.

1.4.1. Continuous Heteroazeotropic Distillation

A separation scheme for binary heteroazeotropic distillation, where the two components A and B form a heteroazeotrope, is shown on Figure 1.8. The homogeneous feed is separated Column I into the original component, whose concentration is higher in the feed than in the azeotrope (here: A), in the bottom, and the heteroazeotrope in the distillate. The distillate of both columns is led into the decanter, where the phase separation occurs. The A-rich phase is recycled into Column I, the B-rich phase into Column II, which produces B and the heteroazeotrope. If the feed is richer in B than the azeotrope, it is fed into Column II. In the case of a heterogeneous column, feeding into the decanter is also possible.

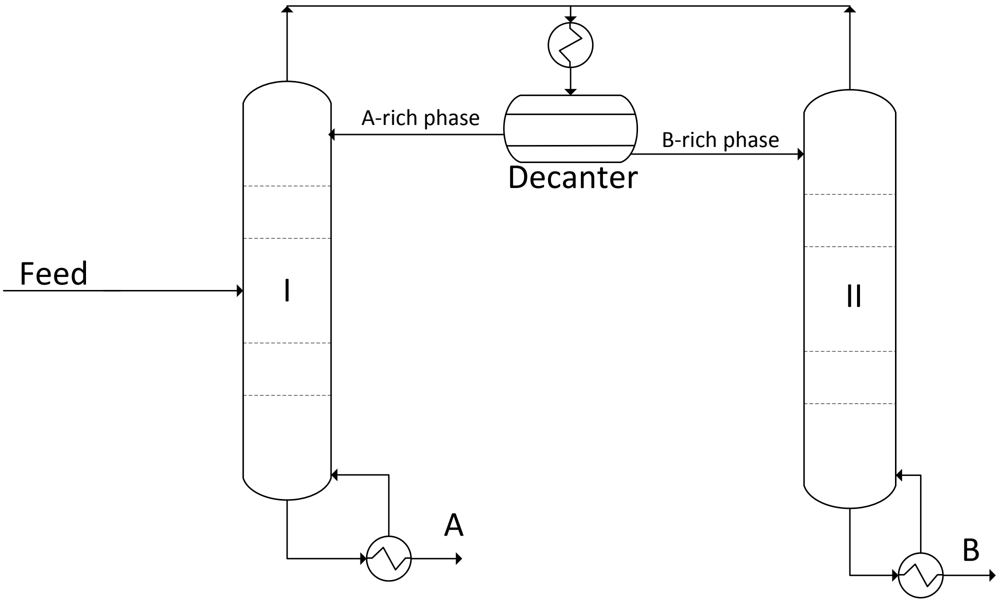


Figure 1.8. Column sequence for binary continuous heteroazeotropic distillation.

For the separation of a binary homoazeotropic mixture with the aid of heteroazeotropic distillation, the example of ethanol dehydration using cyclohexane as entrainer in a three column sequence is presented (Figure 1.9). Other column sequences than this one are also possible (Doherty and Knapp, 2004). The aqueous ethanol feed is led into a preconcentrator column (Column I), where water is removed as bottom product, and the ethanol-water azeotrope is obtained as distillate, which than serves as the feed of Column II. This column produces the dehydrated ethanol as bottoms, and the ternary heteroazeotrope ethanol-water-cyclohexane, which is separated into two liquid phases in the decanter. The cyclohexane-rich phase is refluxed to Column II; the cyclohexane-lean phase is fed to Column III, the entrainer retaining column. The distillate of Column III is the B-E heteroazeotrope, its bottom product is aqueous ethanol fed into the water-producing column.

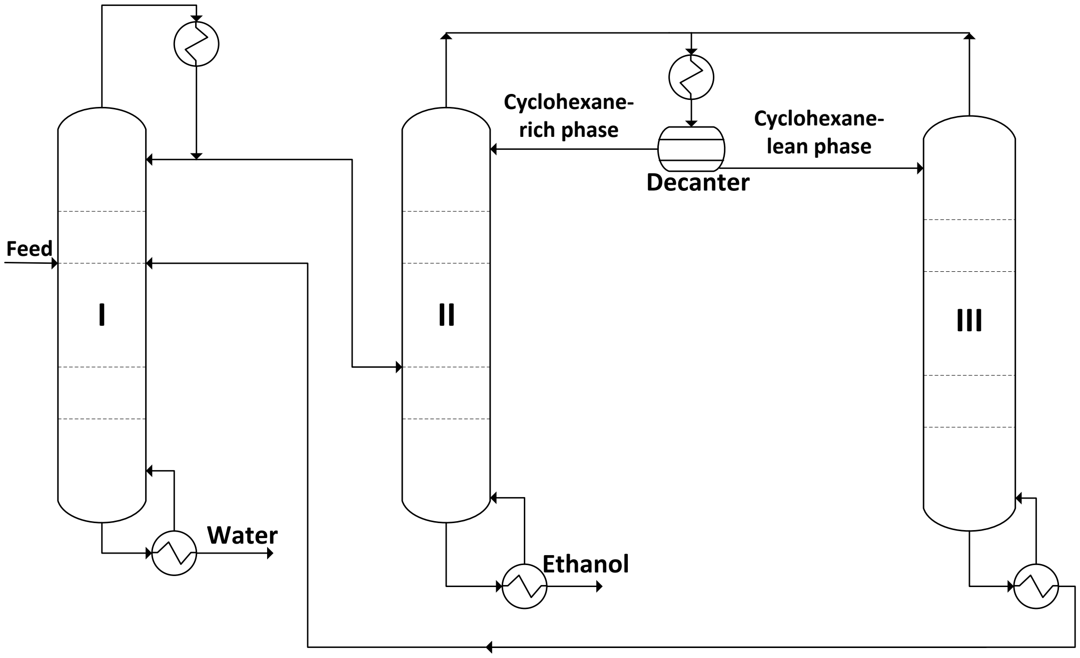


Figure 1.9. Three column sequence for the continuous heteroazeotropic distillation of aqueous ethanol using cyclohexane as entrainer.

1.4.2. Batch Heteroazeotropic Distillation

The batch heteroazeotropic distillation (BHD) is used frequently in the industry, however, to our best knowledge, only in batch rectifiers (equipped with a decanter) with continuous distillate withdrawal (open operation mode). In this configuration the heteroazeotrope has to be the unstable node of the residue curve map, so that the top vapour composition to be decanted after condensation should lie in the two liquid phase region, near the heteroazeotropic composition.

Pham and Doherty (1990) described the structure and properties of residue curve maps for ternary heterogeneous azeotropic mixtures and pointed out the differences between heterogeneous and homogeneous mixtures. Extending their previous work for homoazeotropic distillation (Rodriguez-

Donis et al., 2001a), Rodriguez-Donis et al. (2001b) presented a complete set of rules for the selection of entrainers for batch heteroazeotropic distillation of minimum or maximum temperature azeotropic mixtures or close boiling mixtures.

Different modes of batch heteroazeotropic distillation exist in the literature. Two main types can be distinguished, on the basis of whether distillation and the decantation of the two liquid phases occur sequentially (Mode I) or simultaneously (Mode II; Skouras et al., 2005a,b). By Mode I, distillation and the liquid-liquid phase split are applied sequentially, that is the composition of the reflux (and the distillate) equals that of the heterogeneous condensate (as by Pham and Doherty, 1990), and the existence of two liquid phases is only exploited at subsequent separation of the distillate. Düssel and Stichlmair (1995) presented a batch rectifying process operated by Mode I for the separation of water and pyridine using toluene as entrainer. By Mode II, distillation and phase separation occurs simultaneously and the reflux has a different composition than that of the condensate, unlike homoazeotropic distillation. Koehler et al. (1995) and Skouras et al. (2005a,b) distinguished two strategies for Mode II, on the basis of the reflux of the entrainer-rich phase. The entrainer-rich phase is totally refluxed by Strategy A, and only partially refluxed by Strategy B. Obviously more entrainer is required for Strategy B since a considerable part of it is removed from the column. Therefore it proves to be a competitive alternative to Strategy A only in the cases where the original mixture already contains the entrainer in sufficient quantity.

Rodriguez-Donis et al. (2002) investigated the batch heteroazeotropic distillation with variable entrainer-rich phase decanter hold-up. The entrainer-lean phase had a constant decanter hold-up, and distillate was withdrawn only from this phase. The partial reflux of the entrainer-lean phase is also allowed, as it can increase the main product recovery by maintaining the phase split longer.

By extending the method of Pham and Doherty (1990) Lang and Modla (2006) suggested a general method for the calculation of the residue curves and for the determination of batch distillation regions relevant for the heteroazeotropic distillation. The method considers not only the VLLE, but operating parameters like reflux ratio, as well. Any fraction of either liquid phase can be refluxed (and withdrawn as distillate), while the hold-up of both phases is constant. The authors suggested distinguishing two versions for both strategies of Mode II. The E-lean phase is not refluxed in Version 1 and partially refluxed in Version 2, which may be necessary in order to increase the reflux ratio.

The operation modes and strategies presented above are also discussed by Luyben and Chien (2010) dealing with the design and control of distillation systems for separating azeotropes. They studied the dehydration of acetic acid via batch heteroazeotropic distillation by using isobutyl acetate and vinyl acetate as entrainer. They also suggested an overall control strategy for this process.

Pommier et al. (2008) developed a specific software architecture, which uses sequential quadratic programming and genetic algorithm to optimise batch columns. The efficiency of this tool was also demonstrated on the batch heteroazeotropic distillation separation of the azeotrope toluene – pyridine with water. The batch heteroazeotropic distillation process was conducted according to Mode

II Strategy A Version 1 (entrainer-rich phase totally refluxed). The authors observed that due to the change of top vapour composition (and thus that of the phase split ratio in the decanter) with time, the process behaviour was similar to Mode II Strategy B Version 1 (partial reflux of entrainer-rich phase and its accumulation in the decanter).

Skouras et al. (2005a,b) extensively studied the closed operation mode of the batch rectifier configuration and multivessel columns for batch heteroazeotropic distillation. Denes et al. (2009) suggested a new double-column system operated in closed mode for heterogeneous batch distillation, which can produce both original components at the same time. The charge is divided between the two reboilers, where the two products are accumulated at the end of the process, that is, the system is operated in closed mode. The system is operated according to Mode II, Strategy A, Version 1. For ternary mixtures, Denes et al. (2012) proposed a generalised configuration of the above double-column system, which has more operational parameters and thus greater flexibility.

The behaviour of rectifying profiles and overlapping of distillation regions in heterogeneous mixtures were studied by Krolikowski et al. (2011). This paper contains a very comprehensive and detailed literature review about all aspects of the synthesis of distillation systems for the separation of homo- and heteroazeotropic mixtures, too.

1.5. Heterogeneous Extractive Distillation

Heterogeneous extractive distillation can be considered as the combination of heteroazeotropic and extractive distillation (Skouras, 2004). The process was called heteroextractive distillation by Petlyuk (2004). The batch realization of the process was first proposed by Modla et al. (2001, 2003), although they called it batch heteroazeotropic distillation with continuous entrainer feeding. The entrainer forms a heteroazeotrope with one of the original components. However, it is a high boiling component, and unlike in heteroazeotropic distillation, it is present in significant concentration in the column, also exerting a favourable influence on the relative volatilities. Finally, the entrainer appears in the bottom product of the column, as well.

1.5.1. Continuous Heterogeneous Extractive Distillation

In the continuous process, the entrainer is obtained in the bottom product along with the original component not forming a heteroazeotrope with it. From the top of the column, a mixture close to the heteroazeotrope is removed, which is subsequently separated in the decanter. The entrainer-rich phase is refluxed, while the entrainer-lean phase containing one of the original components is withdrawn as distillate. It can be partially refluxed, as well. Szanyi et al. (2004) successfully developed separation systems based on continuous heteroextractive distillation for the separation of quaternary mixtures with water as entrainer. The heteroextractive column was also realized experimentally.

A three column sequence of the heterogeneous extractive process from Rodriguez-Donis et al. (2007) is shown on Figure 1.10. The original mixture to be separated is acetonitrile (A) and water (B). Butyl acetate (E) is applied as heterogeneous entrainer. B and E form a saddle heteroazeotrope, which, however, can be obtained as top product if E is recycled to the column at a specific location. A preconcentrator column (I) produces the azeotropic feed for the heterogeneous extractive column (II). The B-rich (E-lean) phase is withdrawn from the decanter, while the bottom product (A and E) is led to entrainer regenerator column (III). A is obtained as distillate, and the bottom product, the entrainer is recycled to the top tray of column II.

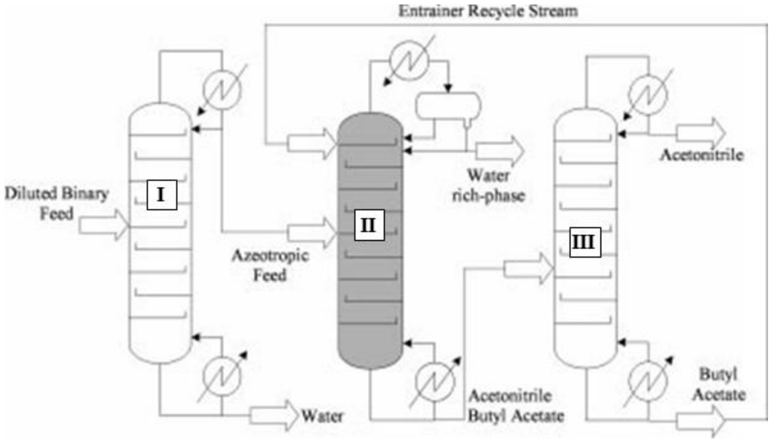


Figure 1.10. Continuous heterogeneous extractive process for the separation of acetonitrile and water using butyl acetate as entrainer (Rodriguez-Donis et al., 2007).

Rodriguez-Donis et al. (2007) investigated the feasibility of continuous heterogeneous extractive distillation with several feed point strategies for the entrainer stream and the main azeotropic feed. A stripping section is always present, and depending on the feeding locations the column might contain a rectifying or an extractive section, both or none.

1.5.2. Batch Heterogeneous Extractive Distillation

In batch heteroextractive distillation (BHED) or batch heterogeneous extractive distillation, the entrainer forms a heteroazeotrope with one of the original components, similarly to batch heteroazeotropic distillation, but it is fed continuously into the column.

Koehler et al. (1995) was the first to mention batch heterogeneous extractive distillation. They described the industrial application of the process for the separation of two unspecified organic components using water as heterogeneous entrainer, where the top vapour was the binary heteroazeotrope. However, the authors did not present any theoretical analysis. Modla et al. (2001, 2003) extended the feasibility of Lelkes et al. (1998b) to heterogeneous extractive distillation, and also performed rigorous simulations for the separation of dichloromethane (A) and acetone (B) using water as entrainer (E). The authors stated that the mixed addition (continuous feeding, and mixing to the charge) provided the best results. Two-phase reflux was applied, as the benefits of phase separation were found to be lost because of the increased hold-up caused by decanter. Rodriguez-Donis et al.

(2003) stated that BHED is particularly useful for mixtures where the entrainer forms a saddle azeotrope with one of the original components. By analysing the isovolatility curves and the volatility order diagram, it is possible to predict the distillate, which can either be an original component (as in the case of BED), or a heterogeneous saddle azeotrope of E and A or B. In the latter case a rectification section is not required for the feasibility if the extractive stable node (and thus the overhead composition) lies in the VLLE region. Van Kaam et al. (2008) presented the experimental validation of the BHED process, where the saddle binary heterogeneous azeotrope A-E was taken as distillate. Barreto et al. (2011) performed the optimization of heterogeneous batch extractive distillation using a genetic algorithm, with the optimization parameters entrainer flow rate, reflux policy and, the portion of the distillate-rich phase refluxed to the column.

1.6. Pressure Swing Distillation

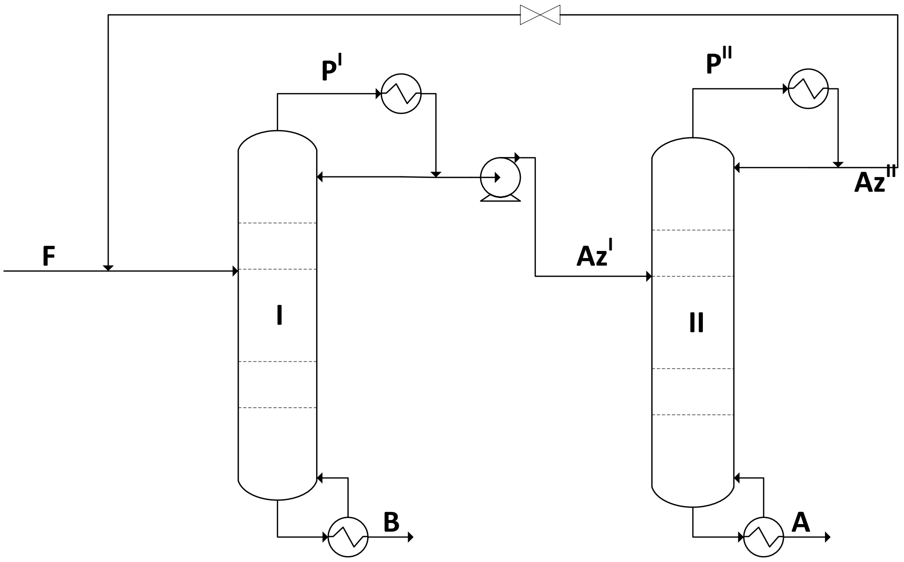
For many mixtures the composition of the azeotrope varies significantly with the pressure (pressure sensitive azeotropes), and the azeotrope might even disappear. This effect can be used to separate azeotropic mixtures by the pressure swing distillation (PSD) without the addition of a separating agent. A pressure sensitive azeotrope in a ternary mixture changes the location of the distillation boundary, that is, it can be crossed at a different pressure.

Lewis (1928) appears to be the first one to exploit the pressure sensibility for separating azeotropic mixtures. Knapp and Doherty (1992) listed 36 pressure sensitive binary azeotropes. They presented a method by which non-pressure-sensitive binary azeotropes can be separated by using entrainers that form pressure-sensitive distillation boundaries. Wasylkiewicz et al. (2003) developed an algorithm which allows the variation of compositions of azeotropes with pressure to be tracked, and all new azeotropes that appear within specified pressure range to be found.

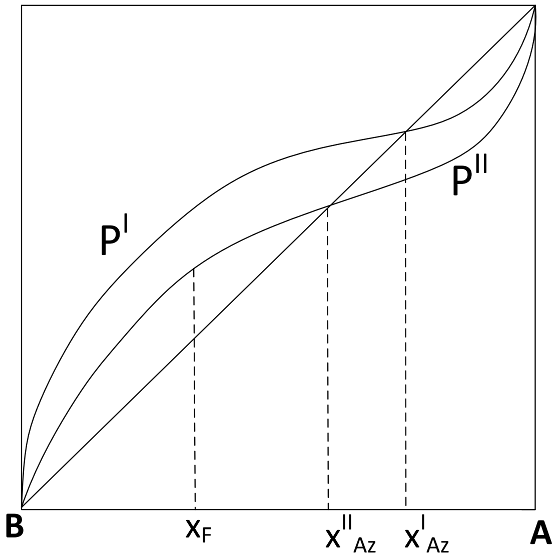
1.6.1. Continuous Pressure Swing Distillation

A pressure sensitive binary azeotrope can be separated by a two column sequence. The process is illustrated (Figure 1.11) for a minimum boiling azeotrope. Column I operating at P^I produces component B as bottoms, and the azeotrope at P^I (Az^I) as top product, respectively. This azeotropic stream is fed into Column II working at P^{II}. In this example P^I is lower than P^{II}. Column II produces A as bottom, and the azeotrope at P^{II} (Az^{II}) as top product. The pressure of Az^I is reduced through a throttling valve, and the stream is recycled to the original feed.

If the components form a maximum boiling point azeotrope, they are recovered as the distillates of the two columns working at different pressures.



a.



b.

Figure 1.11. Pressure-swing distillation process for the separation of a minimum boiling azeotropic mixture: a. column sequence, b. vapour-liquid equilibrium diagram.

1.6.2. Batch Pressure Swing Distillation

In the last decade several teams studied the realization of the PSD in batch. Unlike in the case of continuous distillation, the pressure switch takes place in time, and the operation is performed in two steps at different pressures. Phimister and Seider (2000b) were the first who studied the application of binary PSD in a batch stripper and in a semi-continuous configuration by simulation, for the separation of the pressure sensitive minimum boiling azeotrope acetonitrile – water. Repke et al. (2007) were the first to investigate experimentally the application of the pressure swing batch distillation (PSBD). Modla and Lang (2008) studied the feasibility of PSBD of binary mixtures in different column configurations assuming maximal separation. They suggested two novel configurations containing two rectifying (double column batch rectifier for maximum azeotropes) or two stripping sections (double column batch stripper for minimum azeotropes) as modifications of the middle vessel column. With the double column configurations, the two column sections are operated at different pressures, and it is possible to separate the mixture in one operation step.

Based on the analysis of batch stripping/batch rectifying distillation regions, assuming maximal separation, Modla et al. (2010) studied the feasibility of the separation of ternary homoazeotropic mixtures with pressure swing batch distillation in different column configurations: single column (batch stripper and rectifier) and double column configurations (double column batch stripper and rectifier). The separation steps were also determined for the corresponding column configurations. Modla and Lang (2010) presented the benefit of the thermal integration on the separation of an acetone-methanol mixture in a double column batch stripper. Two versions of closed double-column systems for batch pressure swing distillation of binary homoazeotropic mixtures were investigated by Modla (2010) with rigorous simulations. Recently, Modla (2011a) suggested a reactive PSBD process in a double column configuration for the production of ethyl acetate. Modla (2011b) proposed a triple-column configuration for the PSBD separation of a chloroform-acetone-toluene mixture. This novel configuration is the combination of a double column batch rectifier and a middle-vessel column.

1.7. Other Distillation Methods

Beyond the special distillation processes presented above, other methods exist, as well, for the separation of azeotropic and closed-boiling mixtures. These include the hybrid process, salt-effect collection and adsorptive distillation, the first two of them will be briefly discussed below. In adsorptive distillation, a solid separating agent is added to the mixture, which adsorbs selectively one of the components (Marple and Foecking, 1956).

1.7.1. Hybrid (Distillation+Absorption) Process

The hybrid process (Düssel and Stichlmair, 1995) is a border-line case of batch extractive distillation, where no external reflux is applied, and the column consists only of an extractive section. It can be considered as a hybrid of absorption and distillation. By the hybrid process, contrary to batch extractive distillation, the entrainer is fed as a highly sub-cooled liquid, always onto the top plate of the column. Comparing the performance of batch extractive distillation and the hybrid process in the separation of acetone-methanol and ethanol-water mixtures using water and ethylene glycol as entrainers, respectively, Kotai et al. (2007) concluded that batch extractive distillation is more flexible than the hybrid process. However the hybrid process can be competitive if there is no strict requirement for the separation of the light component and the entrainer.

1.7.2. Salt-Effect Distillation

In salt-effect distillation, a non-volatile, solid salt is added to the mixture, as an extractive agent. The salt is usually mixed to the hot reflux stream, where it is dissolved. It changes the VLE conditions favourably throughout the liquid phase of the column, and leaves the column in the bottom stream, from which it must be recovered by evaporation (or drying). As it is completely non-volatile, the column requires no rectifying section. Salts are usually more effective in changing the VLE conditions than liquid entrainers, therefore a lower entrainer/feed ratio can be applied. On the other hand, operational difficulties can be encountered, such as the feeding and transporting of the solid salt, corrosion problems, and eventual problems of solubility. (The salt should be soluble in both components in the composition ranges likely to exist in the column.) If, however, salt-effect distillation can be applied, significant energy and equipment cost can be saved (Furter, 1992). An example of salt-effect distillation is the dehydration of ethanol using potassium acetate solution (Furter, 1968).

CHAPTER 2

Algorithm and Program for the Determination of Product Sequences in Azeotropic Batch Distillation

Related publications: Hegely and Lang (2011c, 2011d, 2011e)

In multicomponent azeotropic mixtures, the products obtainable by batch distillation and their maximal amount is highly dependent on the charge composition. The algorithms published previously for the determination of product sequences, are either suitable only for ternary mixtures (Foucher et al., 1991), or require the application of a VLE model (e.g. Ahmad et al., 1998).

Here, a new, rapid and automatic method is presented (Hegely and Lang, 2011e):

- for generating product sequences for batch distillation of a mixture containing any number of components,
- based only on the knowledge of the temperatures of pure components and azeotropes, and azeotropic compositions (including the compositions of the two liquid phases in the case of heteroazeotropes),
- making unnecessary the knowledge of further VLE data (e.g. binary interaction parameters), test runs in pilot columns and detailed dynamic simulations,
- suitable also for mixtures containing heteroazeotropes and operations with pressure change after an arbitrary cut.

The algorithm was implemented in Visual Basic for Applications. Microsoft Excel was used as an interface for input and output data. Calculations were performed among others for the systems acetone-chloroform-methanol-ethanol-benzene (Mixture 1) studied by Ahmad et al. (1998) and methanol-tetrahydrofuran-ethyl acetate-ethanol-isopropyl alcohol-water (Mixture 2).

2.1. Description of the Algorithm

The following simplifying assumptions are applied:

- Maximal separation: very high reflux ratio, infinite number of plates.
- The distillation boundaries are straight lines.
- In an *n*-component mixture there is maximum one azeotrope of *n*-component (exclusion of biazeotropy).
- The quaternary azeotrope cannot be a stable node and is the common point of all distillation regions in a quaternary mixture. (According to Kurtyka (1988) eight minimum boiling and one saddle quaternary azeotrope exists).
- The mixture does not contain quinary or higher order azeotrope. (Only one quinary azeotrope is reported to exist according to Horsley, 1973).
- The ternary submixtures have at least one occurrence in practice (present in Reshetov’s statistics, Kiva et al., 2003). Every ternary submixture is supposed to be of such a Serafimov topological class for which physical mixtures were reported in Reshetov’s statistics to exist.

In this way, it is possible to avoid complex mixtures, which are, however, highly unlikely to be encountered in the practice.

- In any submixture, the number of unstable and stable nodes does not exceed two at the same time. This latter assumption of Ahmad et al. (1998) is necessary for Step 2, where their method is utilized. For globally undetermined mixtures, this assumption does not hold (e.g. in the case of mixtures of Serafimov classes 3.1-3a and 3.1-3b), and the product sequence can only be determined by calculating the locations of the distillation boundaries (the knowledge of the stability of the fixed points is insufficient). However, such a mixture has not been reported yet in Reshetov's statistics.

The input data of the algorithm are as follows:

- Number of components.
- Boiling point of pure components.
- Boiling point and composition of azeotropes.
- In the case of heteroazeotropes: the composition of both liquid phases, selection of the distillate phase.
- Composition of the charge.
- In the case of pressure change: the cut after which the change of pressure occurs.

The overall structure of the algorithm is presented in Figure 2.1. The main steps are the following ones:

1. Determination of the type of all stationary points.
2. Completing the adjacency matrix of stationary points which represent the topological structure of the composition simplex by the method of Ahmad et al. (1998).
3. Determination of all product sequences and the relative amount of cuts for the given charge composition.

Step 1, which is the new part of the algorithm, consists of the following steps:

a. Determination of the type of stationary points in each ternary submixture.

b. Unification of ternary submixtures to quaternary ones.

c. Unification of quaternary submixtures to quinary one(s), the quinary ones to six-component one(s) etc.

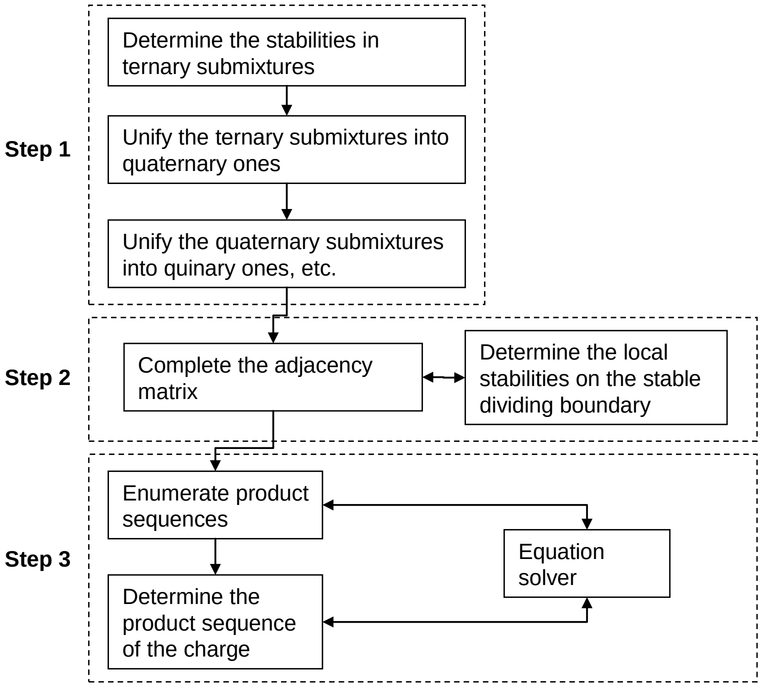


Figure 2.1. The overall structure of the algorithm

The main steps of the algorithm are described with more details below. Some of the steps and concepts are illustrated for the five-component system acetone (A) – chloroform (C) – methanol (M) – ethanol (E) – benzene (B) (Mixture 1).

2.1.1. Step 1: Determination of the Type of All Stationary Points

In this step, the stabilities of fixed points in all ternary submixtures are determined, then these stabilities are revised as the ternary submixtures are unified into quaternary ones, then the quaternary submixture into quinary ones, etc.

2.1.1.1. Step 1a: Determination of the Type of Stationary Points in Each Ternary Submixture

From the pure components, all ternary submixtures are created, and the azeotropes are assigned to the corresponding ternary submixtures. After that, the stability of all fixed points is determined within the ternary submixtures. This procedure is illustrated in Figure 2.2, with the indication of the respective Serafimov (and where necessary Zharov) topological classes. Every one of the 16 topological class reported in Reshetov’s statistics is displayed, proving that no mixture occurring in the practice is ignored in this part of the algorithm. In some of the branches more than one topological class can be seen, without any further distinction. The reason is that the algorithm does not determine the topological class, but the stabilities of the stationary points, which can be determined without the complete identification of the Serafimov classes.

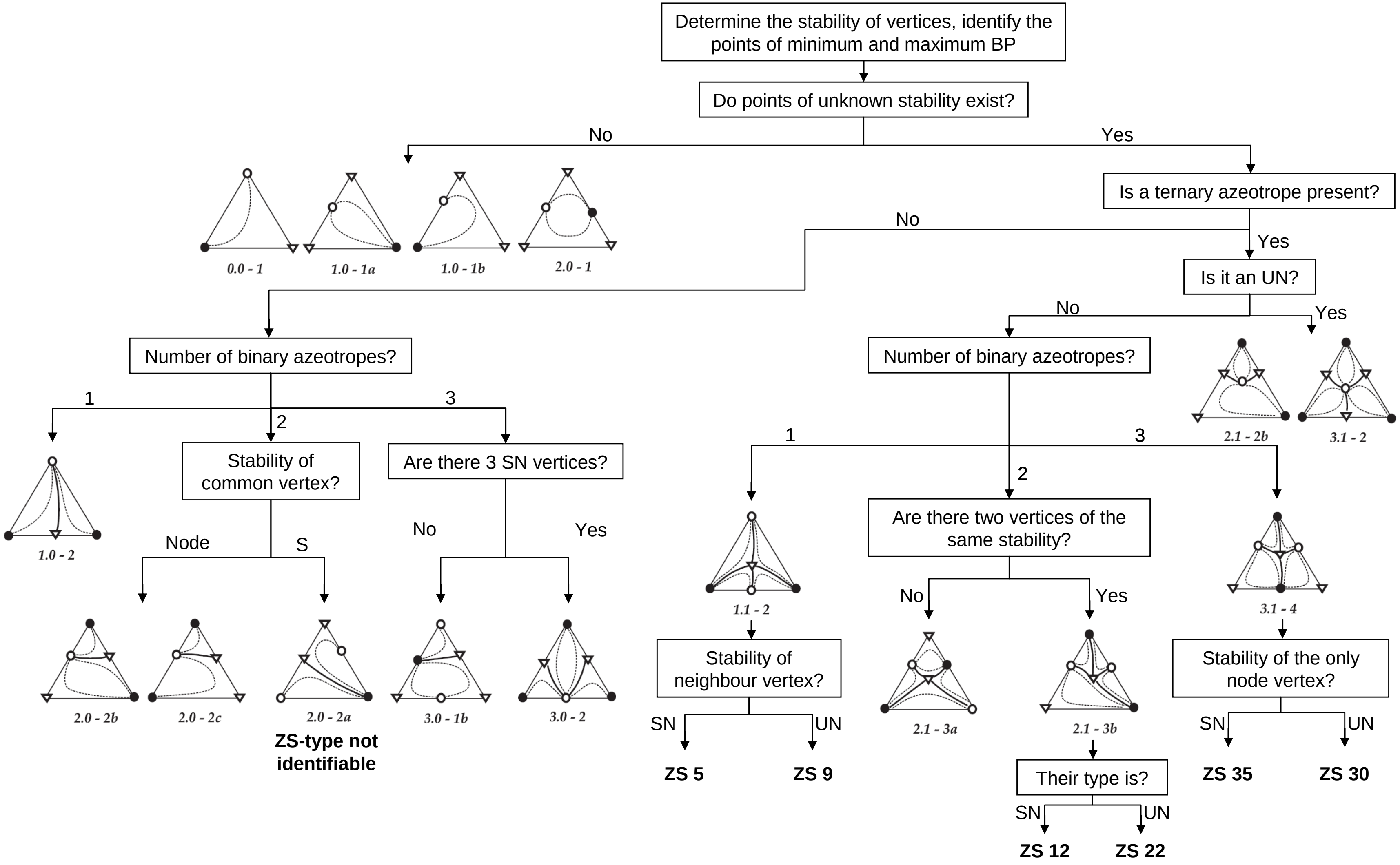


Figure 2.2. Determination of the type of stationary points in ternary submixtures (**O**: unstable node, ▽: saddle, ●: stable node).

The stability of pure component vertices are obtained by comparing their boiling point with those of the neighbour fixed points on the edges, which can be either pure components or binary azeotropes. If after the identification of the fixed points with minimum and maximum boiling point, there is no point with unknown stability, this step is ended for the given ternary submixture.

The next step depends on the presence and the stability of a ternary azeotrope. The determination of the stability of the ternary azeotrope is straightforward: if it has the lowest boiling point in the submixture, it is the only unstable node; otherwise, it is a saddle. (A second unstable node beside the ternary azeotrope exists in non-reported topological classes only. Reshetov's statistics reports no ternary maximum boiling azeotrope either which would have been a stable node, although four maximum boiling ternary azeotropes can be found in the book of Horsley, 1973.)

If there is a ternary azeotrope in the submixture, which is an unstable node, the binary ones are saddles.

If the ternary azeotrope is a saddle, the type of binary azeotropes depends on their number. If it is:

- 1: If any of the neighbour vertices is unstable (stable) node, the binary azeotrope will be a stable (unstable) node.
- 2: If there are two vertices, which are unstable (stable) nodes, both binary azeotropes will be stable (unstable) nodes, in the opposite case, one of the azeotropes is an unstable, and the other one is a stable node depending on their boiling points.
- 3: In this case there is only one vertex which is a node, whose stability determines that of the binary azeotropes. Two of the azeotropes will have the same stability as the vertex, the third one will be a node with opposite stability, depending on their boiling points.

If there is no ternary azeotrope, the stability of the binary azeotropes depends again on their number:

- 1: It is a saddle.
- 2: The stability of the two azeotropes depends on the stability of their common (pure) component. If it is:
  - an unstable node, the azeotrope with lower boiling point is a saddle, the other one is a stable node,
  - a stable node, the azeotrope with lower boiling point is an unstable node, the other one is a saddle,
  - a saddle (Serafimov-class: 2.0-2a), the stability of binary azeotropes cannot be determined, the system is locally undetermined.

On the basis of temperatures only, the two antipodes (Zharov types 17 and 18) cannot be distinguished, therefore the stability of the two azeotropes can be exchanged. However, Reshetov only reported 2 mixtures of Zharov type 17 and 3 mixtures of type 18, which amount to the 0.36 % of the total number of mixtures. Even if a ternary submixture belongs to the Serafimov class 2.0-2a, it does not necessarily mean that the stabilities in the complete mixture cannot be determined. Namely, if the two binary azeotropes are saddles in any other ternary submixture, they are saddles in the complete mixture, as well.

- 3: The stability depends on that of the pure components. If all vertices are stable nodes, the azeotrope with the lowest boiling point is an unstable node, the other ones are saddles, otherwise, the binary azeotropes form an unstable node, a saddle and a stable node, respectively.

2.1.1.2. Step 1b: Unification of Ternary Submixtures to Quaternary Ones

From the ternary mixtures all quaternary submixtures are created. The stability of all pure components and binary azeotropes are revised and if necessary updated. This procedure is illustrated in Figure 2.3, for one of the quaternary submixtures of Mixture 1.If a point is a saddle in any ternary mixtures unified, like point M, it will be a saddle otherwise it will remain a node, like point E.

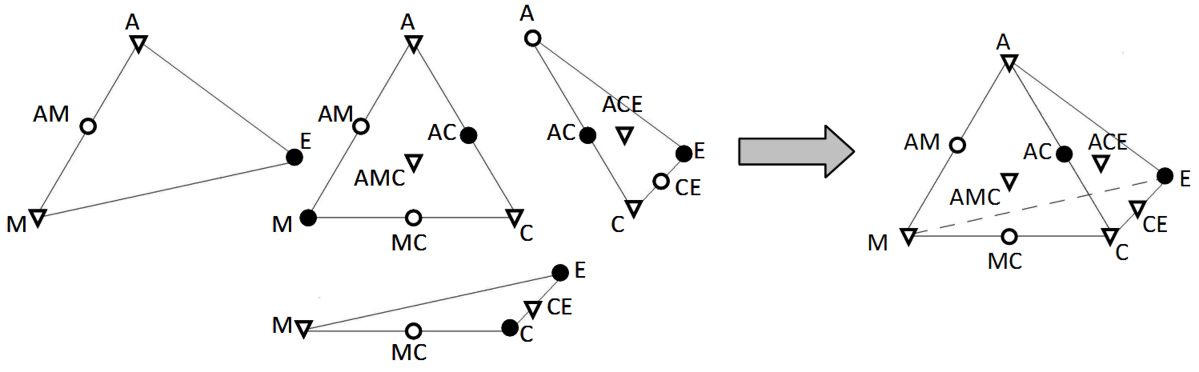


Figure 2.3. Unification of ternary submixtures to a quaternary one (Step 1b) illustrated for the mixture acetone (A) – chloroform (C) – methanol (M) – ethanol (E).

The stability of fixed points A, C, M, and CE is not uniform in the four ternary submixtures, and therefore these points become saddles.

The next step depends on the presence of the quaternary azeotrope. If there is a quaternary azeotrope, it is:

- the single unstable node (the other unstable nodes become saddles), if it has the lowest boiling point of the submixture, as we assume that the quaternary azeotrope is the common point of every distillation regions,
- a saddle, if it does not have the lowest boiling point.

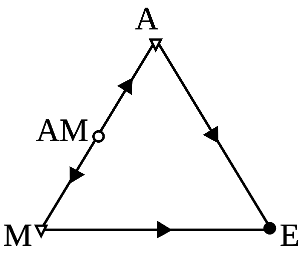
If there is no quaternary azeotrope, but there is an unstable ternary azeotrope and still another unstable node, Step 1b is continued (otherwise it is ended for this quaternary submixture), as two unstable nodes may exist simultaneously in a quaternary mixture only in this case. We investigate whether this other unstable node is a pure component (or not), and if there are boundaries on all the three ternary submixtures not containing the ternary unstable node. A boundary surface separating the two stationary points exists, only if both above conditions are satisfied. In this case, the two points are located in separate distillation regions, and thus it is possible for both to be unstable nodes. If these conditions are not fulfilled, they are located in the same distillation region, and the unstable node with higher boiling point becomes a saddle. The existence of the boundaries is investigated in the following way: if in a ternary submixture one of the stationary points on the edge, which is opposite to the pure component unstable node, was an unstable node (before the unification of the four submixtures into the quaternary one), a boundary is present in the ternary submixture.

2.1.1.3. Step 1c: Unification to Submixtures of Higher Dimension

The *n*-component mixture is decomposed into submixtures of *n*-1 components by omitting one component for each submixture. This procedure is continued until we have a set of five component submixtures, then to all submixtures of each level, the stationary points are assigned. The stability of the stationary points in the quinary submixtures are determined by comparing their stabilities in all (5) quaternary submixtures. If a point is a saddle in any quaternary mixture, it will be a saddle otherwise it will remain a node. If in the quaternary submixtures to be unified, there is more than one quaternary azeotrope, which are unstable nodes, the azeotrope with the lowest boiling point remains an unstable node, while the other(s) become(s) saddle. This comparison is repeated at every higher level until the stabilities in the n-component mixture are determined.

2.1.2. Step 2: Completion of Adjacency Matrix

In Step 2 the adjacency matrix is completed for every submixture and later on for the complete mixture, as well. It is based on the procedures OmegaAll and Omega by Ahmad et al., 1998. The adjacency matrix **A** represents the topological structure of the mixture. If the element A_{ij} equals 1, it means that a residue curve connects the stationary point *i* with the point *j*. An equivalent definition is that the stationary point *j* is in the unstable boundary limit set of the point *i*. The unstable boundary limit set of the stationary point *i* is the set of all the stationary points which can be reached from *i* by following residue curves in the direction of increasing temperature. Figure 2.4 shows the structure of residue curve map and the adjacency matrix of a ternary submixture A-M-E acetone-methanol-ethanol of Mixture 1. If it is possible from one of the four stationary points (e.g. from AM) to reach another one (A, M or E) following the directions indicated by the arrows, the value of the element in the crossing of the row of the initial point and the column of the end point of this imaginary path will be one (e.g. the element AM-E), otherwise it will be zero. For example, the unstable boundary limit set of point AM is (A, M, E); for point A it is (E). Now, AM is an unstable node, meaning that there is no point from where it can be reached (AM is not an element of any of the unstable boundary limit sets), therefore its *column* consists entirely of zeros. On the other hand, no points can be reached from the stable node E (its unstable boundary limit set is empty), therefore its *row* consists entirely of zeros.



$$\begin{array}{c|cccc} & AM & A & M & E \\ AM & 0 & 1 & 1 & 1 \\ A & 0 & 0 & 0 & 1 \\ M & 0 & 0 & 0 & 1 \\ E & 0 & 0 & 0 & 0 \end{array}$$

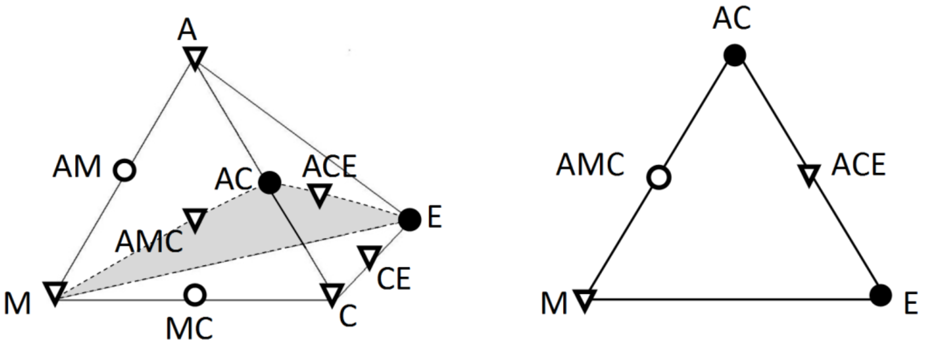
a. b.

Figure 2.4. The structure of residue curve map (a) and the adjacency matrix (b) of the mixture A-M-E acetone-methanol-ethanol.

Since we assume that there are no ternary (not reported in Reshetov's statistics) and quaternary stable node azeotropes, the number of topological structures to be considered decreases from the 13 distinguished by Ahmad et al. (1998) to 9. Therefore the steps of their algorithm related to the topological structures not considered were omitted. In addition to this, their algorithm had to be modified at two points. The first modification was the omission of an improper condition of smaller significance (namely that only those pure component pairs are considered where the corresponding element of the adjacency matrix was -1) in Step 2 of their procedure OmegaAll. The second more essential modification concerns the evaluation of the stabilities of fixed points in the common unstable boundary limit set. The common unstable boundary limit set of two unstable nodes is the intersection of their unstable boundary limit sets, that is, the set of stationary points connected to both unstable nodes by residue curves. These stationary points are the ones located on the stable dividing boundary separating the two unstable nodes For example in the mixture A-C-M-E (Figure 2.3) two unstable nodes are present: AM and MC. The unstable boundary limit sets are (A, AMC, AC, M, ACE, E) for AM and (AMC, AC, M, C, CE, ACE, E) for MC. The common unstable boundary limit set is obtained as the intersection of the two boundary limit sets: (AMC, M, AC, ACE, E). The elements of this set are the stationary points of the stable dividing boundary (Figure 2.5a) of AM and MC. For the completion of the adjacency matrix it is necessary to determine the local stability of the points of the common unstable boundary limit set, that is, their stability on the stable dividing boundary. The method of Ahmad et al. (1998) requires the knowledge of not only the stability of the stationary points in the complete mixture, but that of the number of positive and negative eigenvalues, as well. The number of positive and negative eigenvalues of a fixed point determines unambiguously its stability, however this is not valid in the reverse direction. Ahmad et al. (1998) determine the stability on the stable dividing boundary by subtracting one from the number of the negative eigenvalues. If all the eigenvalues are

- positive: the point is an unstable node,
- negative: the point is a stable node,
- otherwise it is a saddle.

Because our methods performs no VLE calculations necessary for the determination of the eigenvalues, it cannot follow this procedure, and we have to use the same method as in Step 1 of our algorithm, treating the stable dividing boundary as a fictive submixture (Figure 2.5), that is determining the stability of the stationary points with the aid of Figure 2.2.



a. b.

Figure 2.5. The stable dividing boundary (a) and its treatment as a fictive submixture (b).

The common unstable boundary limit set most probably does not form a simplex because the stable dividing boundary consists of several not necessarily parallel (hyper)surfaces. Therefore the azeotropic compositions have to be transformed, replacing the non-zero values with the reciprocal of the order (2 for a binary, 3 or 4) of the azeotrope, so that the common unstable boundary limit set forms a simplex and it can be treated as a fictive submixture. These arbitrary concentrations can be used because only the topological and not the precise geometrical structure of the residue curve map has to be known for the determination of the stabilities. The ternary submixtures of the fictive submixture are created, and by following the procedure described in Step 1, the local stabilities of the stationary points are determined. In the example shown in Figure 2.5, the common unstable boundary limit set is (AMC, M, AC, ACE, E). In the figure, the azeotropes are shown as containing the same amount from all of their components (e.g. AM contains the same amount of A and M) for the sake of simplicity, and therefore the stable dividing boundary is a triangle. In reality, the azeotropic compositions are different and the stable dividing boundary is made up from several non-parallel planes. By the change of azeotropic compositions described above, a transformation into a simplex (in this case a triangle) is possible. For example, AC is considered as a vertex that has a composition of 50% A and 50% C. If the composition of ACE is changed to 33.3% A, 33.3% C and 33.3% E, it can be treated as a binary azeotrope of the (fictive) components AC and E, as the composition of ACE is the linear combination of those of AC and E.

2.1.3. Step 3: Determination of Product Sequences

All possible sequences of cuts satisfying the criteria 1 and 2 of Ahmad et al. (1998), must be enumerated that is, a sequence consists of *n* fixed points (criterion 1), and each subsequent product cut has to be an element of the unstable boundary limit sets of all the preceding product cuts (criterion 2).

The latter criterion is tested by using the adjacency matrix. The list of possible sequences of cuts created in this way has to be checked whether they fulfil criterion 3, too, that is, the fixed points form an *n*-1 simplex (criterion 3). If the first point is a linear combination of the other ones (in which case the points are pointwise independent), we have an *n*-1 simplex. This check is performed by solving Equation 2.1 for vector **b**. If **b** is a null vector, the stationary points form an *n*-1 simplex.

$$\sum_{i=2}^{n} b_i \, x_i - x_1 \; = 0 \tag{2.1}$$

where $\mathbf{x}_i$ is the composition vector of the stationary point *i*.

As mentioned above, all batch distillation regions comprise of *n* stationary points. If a residue curve region contains more than *n* stationary points (e.g. Serafimov class 1.0-1b), one or more batch distillation regions arise, which do not have a stable node. In this way, the final residue of batch distillation can be a saddle, as well.

In the case of ternary and quaternary mixtures, it may occur that some of the batch distillation regions overlap. This may happen if an azeotrope containing all components is present in the mixture. If *n* is greater than four, this cannot occur, since there is no azeotrope containing all components, by the assumption of our method. It must be checked whether this azeotrope is located in the interior of a batch distillation region (Figure 2.6). If so, the region, which is a subset of another one, is not a real batch distillation region and it must be omitted. By this omission, the region which contains the non-real region becomes concave, therefore if the charge happens to lie in the omitted, non-real region, it will actually lie in a third, convex region. It must be also noted that the ternary saddle azeotrope is never obtained as a cut from the concave distillation region.

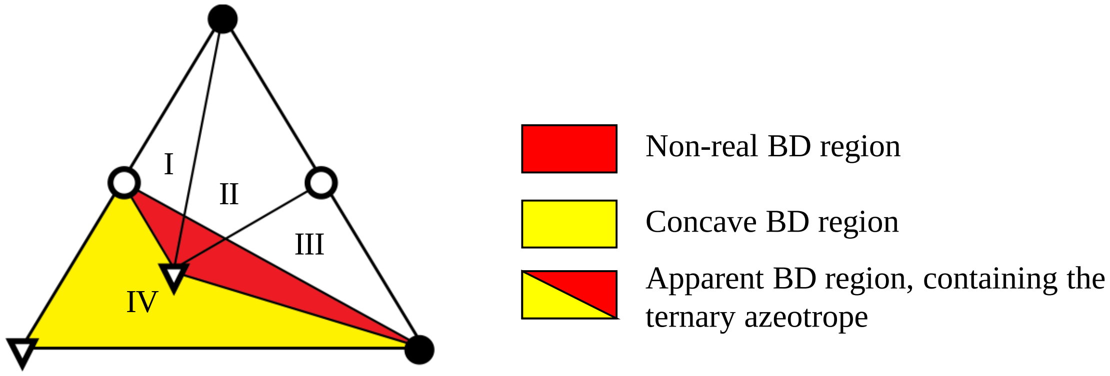


Figure 2.6. The overlapping of apparent batch distillation region.

The composition of the charge is the linear combination of those of the fixed points of its corresponding batch distillation region.

$$\sum_{i=1}^{n} a_i x_i = x_{naz} \tag{2.2}$$

where $\mathbf{x}_{naz}$ is the composition vector of the azeotrope containing all (*n*) components.

If Equation 2.2 is solved for vector **a**, for all regions, and the coefficients obtained are between 0 and 1, the charge is located in the corresponding region, and the coefficients give the relative amount of the cuts.

2.1.4. Managing Heteroazeotropes and Pressure Change

The algorithm can handle both Mode I and Mode II of heteroazeotropic distillation. In the case of Mode II, the composition of at least the liquid phase of the heteroazeotrope which is withdrawn as product must be given. Instead of the overall composition of the heteroazeotrope, the composition of the specified product phase is taken into consideration before Step 1. In this way, the area and shape of the distillation regions change and heterogeneous batch distillation must be considered (Lang and Modla, 2006).

It is possible to take into account pressure change during the process. In this case the necessary data for the new (modified) pressure (P_2) must be given, and we have to specify the cut, after which the pressure change occurs. The cut(s) obtained for P_1 are withdrawn from the original charge, and the algorithm is repeated for the modified charge using the data for P_2.

2.2. Results

Calculations are presented for a five- and a six-component mixture.

Mixture 1 is the system acetone (A) – chloroform (C) – methanol (M) – ethanol (E) – benzene (B), studied by Ahmad et al. (1998). By comparing the list of product sequences with their results, it is possible to validate the correct operation of our algorithm. The pressure change option was also tested for this mixture.

Mixture 2 is the system methanol (M) – tetrahydrofuran (T) – ethyl acetate (EtAc) – ethanol (E) – isopropyl alcohol (IPA) – water (W), a pharmaceutical waste solvent mixture, on which the operability of the heteroazeotropic distillation is demonstrated.

2.2.1. Calculations for Mixture 1

We have used the boiling points and azeotropic compositions (Table 2.1) for P_1=1.013 bar published by Ahmad el al. (1998). The only exception is the boiling point of the acetone-chloroform (AC) azeotrope, which was taken from the CRC Handbook of Chemistry and Physics (1963). In this way, the order of boiling points of AC and M corresponds to the one used by Ahmad et al. (1998) and predicted by Fidkowski et al. (1993), which is contrary to the order presented in their Table 5.

The boiling points and azeotropic compositions used for P_2=10 bar are also given in Table 2.1.

Fixed point	A	C	M	E	B	T_{BP} (°C)
CMB	-/0	-/0.340	-/0.522	-/0	-/0.138	-/127.7
CM	0/0	0.658/0.455	0.342/0.545	0/0	0/0	53.4/128.8
AM	0.778/0.38	0/0	0.222/0.62	0/0	0/0	54.9/133.9
A	1	0	0	0	0	55.8/143
ACMB	0.316/-	0.228/-	0.436/-	0/-	0.020/-	56.8/-
ACM	0.340/-	0.232/-	0.428/-	0/-	0/-	56.81/-
MB	0/0	0/0	0.607/0.728	0/0	0.393/0.272	57.7/134.1
AE	-/0.711	-/0	-/0	-/0.289	-/0	-/141.2
CE	0/0	0.845/0.57	0/0	0.155/0.43	0/0	59/142.5
C	0	1	0	0	0	60.8/153.7
ACE	0.357/0.215	0.464/0.274	0/0	0.179/0.511	0/0	62.4/144.2
M	0	0	1	0	0	64.2/136.8
AC	0.346/0.278	0.654/0.722	0/0	0/0	0/0	64.8/156.41
CEB	-/0	-/0.09	-/0	-/0.63	-/0.28	-/145.8
EB	0/0	0/0	0/0	0.444/0.647	0.556/0.353	67.4/145.7
E	0	0	0	1	0	78/150.8
B	0	0	0	0	1	79.8/178.7

Table 2.1. Boiling points and azeotropic compositions (mole fractions) for Mixture 1 (P=1.013/10 bar)

Due to the pressure change:

- Azeotropes may disappear (in our case: ACMB, ACM).
- New azeotropes may appear (CMB, AE, CEB).
- The volatility order of the components may change (to M, A, E, C, B from A, C, M, E, B, that is, the volatility order is reversed between A and M, C and M, C and E).

First, the calculations were done without pressure change for P_1. The stabilities calculated without using a VLE model (Table 2.2) agree with the ones obtained by Ahmad et al. (1998) requiring the knowledge of VLE parameters.

System	CM	AM	A	ACMB	ACM	MB	CE	C	ACE	M	AC	EB	E	B
TS 1	UN	UN	S		S			S		SN	SN			
TS 2			UN				UN	S	S		SN		SN	
TS 3			UN					UN			S			SN
TS 4		UN	S							S			SN	
TS 5		UN	S			S				SN				SN
TS 6			UN									S	SN	
TS 7	UN						S	SN		S			SN	
TS 8	UN					S		S		SN				SN
TS 9							UN	S				S	SN	SN
TS 10						UN				S		S	SN	SN
QS 1	UN	UN	S		S		S	S	S	S	SN		SN	
QS 2	UN	UN	S	S	S	S		S		SN	S			SN
QS 3			UN				UN	S	S		S	S	SN	SN
QS 4		UN	S			S				S		S	SN	SN
QS 5	UN					S	S	S		S		S	SN	SN
Whole mixture	UN	UN	S	S	S	S	S	S	S	S	S	S	SN	SN

Table 2.2. The stabilities of fixed points in the different submixtures.

(UN: unstable node, SN: stable node, S: saddle, TS: ternary system, QS: quaternary system)

For testing Steps 2 and 3, we determined all the 25 feasible product sequences (Figure 2.7).

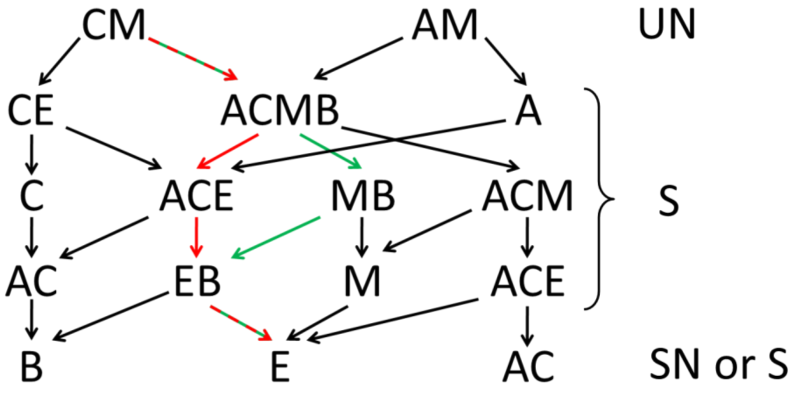


Figure 2.7. The feasible product sequences at P_1=1.013 bar (Mixture 1), with two sequences marked by red and green.

Every path following the direction of the arrows from an unstable node (UN), through saddles (S) to a stable node (SN) or a final saddle is a possible product sequence. The actual path is determined by the charge composition. If one of the components is missing, the quantity of one of the cuts will be zero (e.g. if $x_{ch,A}$=0, the possible product sequences are: CM, CE, C, AC=0, B and CM, CE, ACE=0, EB, B/E).

At P_2=10 bar, there are 31 possible product sequences (Figure 2.8). The number of unstable nodes is reduced to one (CMB), while the stable nodes (E, B) are the same as at P_1=1.013 bar.

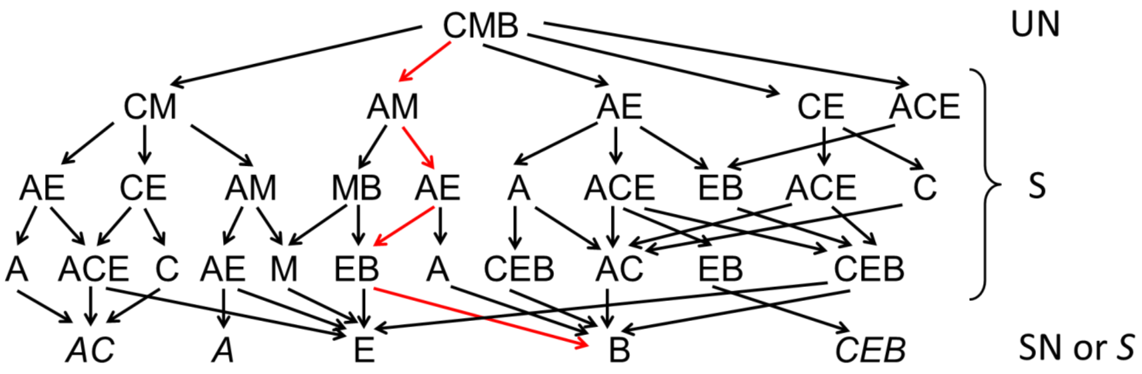


Figure 2.8. The feasible product sequences at P_2=10 bar (Mixture 1), with one sequence marked by red.

The relative amounts of the cuts were determined for two different charge compositions located in different batch distillation regions (Table 2.3). Due to the increased amount of methanol in the charge, not only the relative amounts of the cuts are altered, but the third cut is changed from ACE to MB. The product sequences calculated are shown in Figures 2.7 in red (first composition) and green (second composition).

Pressure (bar)	Charge composition (mole fraction; A,C,M,E,B)	Cuts (mol% of charge)					
		1st	2nd	3rd	4th	5th	6th
1.01	0.2, 0.2, 0.2, 0.2, 0.2	CM: 3.0	ACMB: 43.5	ACE: 17.5	EB: 34.5	E: 1.6	
1.01	0.15, 0.15, 0.4, 0.15, 0.15	CM: 6.4	ACMB: 47.4	MB: 28.2	EB: 5.4	E: 12.6	
1.01 (1st cut)	0.15, 0.15, 0.4, 0.15, 0.15	CM: 6.4					
10			CMB: 31.7	AM: 34.3	AE: 2.8	EB: 21.9	B: 2.9

Table 2.3. The sequence and relative amounts of products for different charge compositions.

The 25 product sequences calculated agree with the ones obtained by the method of Ahmad et al. (1998). The above results verify that our algorithm is suitable for the determination of the sequence of the cuts without using a VLE model.

For the second charge composition presented in Table 2.3, the results are also given for pressure change from P_1 to P_2 after the first cut (Table 2.3, 3rd row). The first cut and its relative amount is naturally identical, but the following cuts (Figure 2.8, red path) differ from those obtained without pressure change, due to the change of the mixture's topological structure. It must be also noted that by applying pressure change, six cuts are obtained. Unlike in the case without pressure change where the still composition after the first cut is located on a batch distillation boundary, here the pressure change moves the batch distillation boundaries and leaves the still composition in the inside of a batch distillation region, making it possible to obtain five further cuts.

2.2.2. Calculations for Mixture 2

Mixture 2 consists of methanol (M) – tetrahydrofuran (T) – ethyl acetate (EtAc) – ethanol (E) – isopropyl alcohol (IPA) – water (W). The azeotropic compositions and boiling points (Table 2.4) were taken from Gmehling et al. (1994). The six components form 10 azeotropes, one of which (ethyl acetate – water) is heterogeneous.

Fixed point	M	T	EtAc	E	IPA	W	T_{BP} (°C)
MT	0.5	0.5	0	0	0	0	59.5
MEtAc	0.71	0	0.29	0	0	0	62.5
TW	0	0.947	0	0	0	0.053	63.89
M	1	0	0	0	0	0	64.7
TE	0	0.905	0	0.095	0	0	65.7
T	0	1	0	0	0	0	65.97
EtAcEW	0	0	0.6005	0.1242	0	0.2753	70.3
EtAcW (het.)	0	0	0.705	0	0	0.295	70.5
org. phase	0	0	0.7753	0	0	0.2247	
aq. phase	0	0	0.0247	0	0	0.9753	
EtAcE	0	0	0.53	0.47	0	0	70.9
EtAcIPA	0	0	0.73	0	0.27	0	75.95
EtAc	0	0	1	0	0	0	77.2
EW	0	0	0	0.894	0	0.116	78.15
E	0	0	0	1	0	0	78.3
IPAW	0	0	0	0	0.674	0.326	80.3
IPA	0	0	0	0	1	0	82.47
W	0	0	0	0	0	1	100

Table 2.4. Measured boiling points and azeotropic compositions (mole fractions) for Mixture 2 at P=1.013 bar.

The mixture contains one unstable node (MT) and three stable nodes (EtAc, IPA, W). If the heteroazeotrope EtAcW is withdrawn without the decantation of the liquid phases (by Mode I), there are 28 possible product sequences (Figure 2.9).

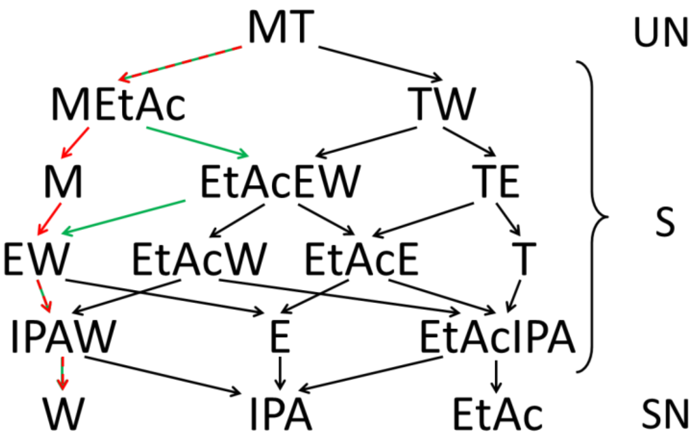


Figure 2.9. The feasible product sequences for Mixture 2 (Mode I), with two sequences marked by red and green.

By Mode II, two further cuts with different compositions can be obtained (the organic and the aqueous phase of EtAcW). If we take into consideration this difference in the composition of the cut EtAcW, this results in 16 new possible product sequences, that is, the total number of product sequences increases to 44. (The number of possible product sequences containing the cut EtAcW is 8, which has to be multiplied by 3, and from the 24 sequences, 16 are the new ones.) However, the difference in the composition of the three possible EtAcW cuts does not change the quality of the last two cuts. (The existence of the batch distillation regions is not affected, only their size varies.) Hence, the product sequence graph shown in Figure 2.9 remains valid for the withdrawal of any of the three EtAcW cuts of different compositions.

The relative amounts of the cuts were determined for three different charge compositions located in different batch distillation regions (Table 2.5). The product sequences for the first two sequences, for which Mode I is applied, are shown in Figure 2.9 in red (first composition) and green (second composition).

Charge composition (mole fraction; M, T, EtAc, E, IPA, W)	Phase withdrawn as distillate	Cuts (mol% of charge)					
		1st	2nd	3rd	4th	5th	6th
0.7644, 0.0038, 0.032, 0.0523, 0.0579, 0.0896	-	MT: 0.8	MEtAc: 11.0	M: 68.2	EW: 5.9	IPAW: 8.6	W: 5.5
0.167, 0.167, 0.167, 0.167, 0.167, 0.167	-	MT: 33.3	MEtAc: 0.0	EtAcEW: 27.8	EW: 14.8	IPAW: 22.4	IPA: 1.6
0.1, 0.12, 0.4, 0.05, 0.12, 0.21	organic	MT: 20.0	TW: 2.1	EtAcEW: 40.3	EtAcW (organic): 20.5	IPAW: 15.7	IPA: 1.4
	aqueous	MT: 20.0	TW: 2.1	EtAcEW: 40.3	EtAcW (aqueous): 9.9	EtAcIPA: 21.5	IPA: 6.2

Table 2.5. The sequence and relative amounts (%) of products for different charge compositions.

The first composition is that of a real, industrial waste solvent mixture, containing mainly methanol, which appears as a pure component in the third cut.

For the second composition (equimolar charge) another product sequence is obtained. As the concentrations of M and T are equal in both the azeotrope MT and the charge, both components are removed completely in the first cut, and therefore the amount of the second cut (MEtAc) is zero. For the first two compositions, the heteroazeotrope EtAcW was not obtained as a cut.

However, for the third charge composition, the fourth cut is the heteroazeotrope ethyl acetate – water (EtAcW). Mode II is applied, where one of the liquid phases is chosen as distillate. This choice influences the relative amounts, and it may influence the quality (composition) of the next cuts. Such a change in the quality of these cuts arises only at certain charge compositions. In our example, if the organic phase is withdrawn as distillate, the fifth cut is the azeotrope isopropyl alcohol – water (IPAW), if the aqueous phase is withdrawn, the fifth cut is the azeotrope ethyl acetate – isopropyl alcohol (EtAcIPA).

The algorithm was successfully tested on more mixtures including the five-component waste solvent mixture methanol – tetrahydrofuran – acetonitrile – water – pyridine, as well.

2.3 Conclusion

A method is presented for the determination of product sequences of batch distillation for any number of components based only on the boiling points of pure components and azeotropes, and azeotropic compositions. Algorithms published previously required the use of a VLE model for more than three components. The method is suitable for heteroazeotropes and for taking pressure change into consideration, as well. The stabilities of fixed points are determined in every ternary submixture assuming they occur in Reshetov's statistics (Kiva et al., 2003). The stabilities are updated as the ternary submixtures are unified into quaternary ones, quaternary submixtures into quinary ones, etc. On the basis of the stabilities, all feasible product sequences are enumerated using the algorithm of Ahmad et al. (1998). Finally, the relative amount of cuts are determined assuming maximal separation for the given charge composition. The algorithm was tested for the systems acetone-chloroform-methanol-ethanol-benzene (Mixture 1) and methanol-tetrahydrofuran-ethyl acetate-ethanol-isopropyl alcohol-water (Mixture 2). For Mixture 1, the stabilities and the set of product sequences calculated by the new algorithm without using a VLE model agree with the ones obtained by Ahmad et al. (1998) with the knowledge of the stabilities of stationary points, which however require VLE calculations. The product sequence was also calculated for one charge composition by applying pressure change after the first cut. The results for Mixture 2 demonstrated that our algorithm is able to handle heteroazeotropes as well. By changing the phase withdrawn as distillate, it is possible to influence the amount and the quality of the following cuts. These results verify that the new algorithm is suitable for the determination of the sequence of the cuts without using a VLE model.

CHAPTER 3

Closed Batch Distillation

Related publications: Hegely and Lang (2010a, 2011a, 2011b), Hegely et al. (2010)

In this chapter, open and non-conventional closed batch column operation modes are compared by rigorous simulation with the aim of studying the competitiveness of non-conventional operation modes of batch distillation (Hegely and Lang, 2011a,b).

3.1. Configurations and Operation Modes Studied

Three configurations are investigated:

- the batch rectifier ("two-vessel column", a reboiler and a product tank),
- middle-vessel column and, ("three-vessel column" with an additional middle vessel).
- multivessel column ("four-vessel column" with another middle vessel).

The calculations are performed for the open mode and for several closed operation modes. For the closed operation mode, six different variants are proposed, which differ in the operation of the vessels. The calculations are made for a binary (n-hexane (A) – n-heptane (B)), a ternary (A–B–n-octane (C)) and a quaternary (A–B–C–n-decane (D)) mixture with the dynamic module (CC-DCOLUMN) of the ChemCAD flow-sheet simulator (Chemstations, 2012). The recoveries obtained with the different operational modes for the same product purities are compared under constant energy consumption and process duration. The effects of the operational parameters are also studied.

The following simplifying assumptions are used:

- theoretical plates,
- constant volumetric liquid hold-up on the plates,
- negligible vapour hold-up.

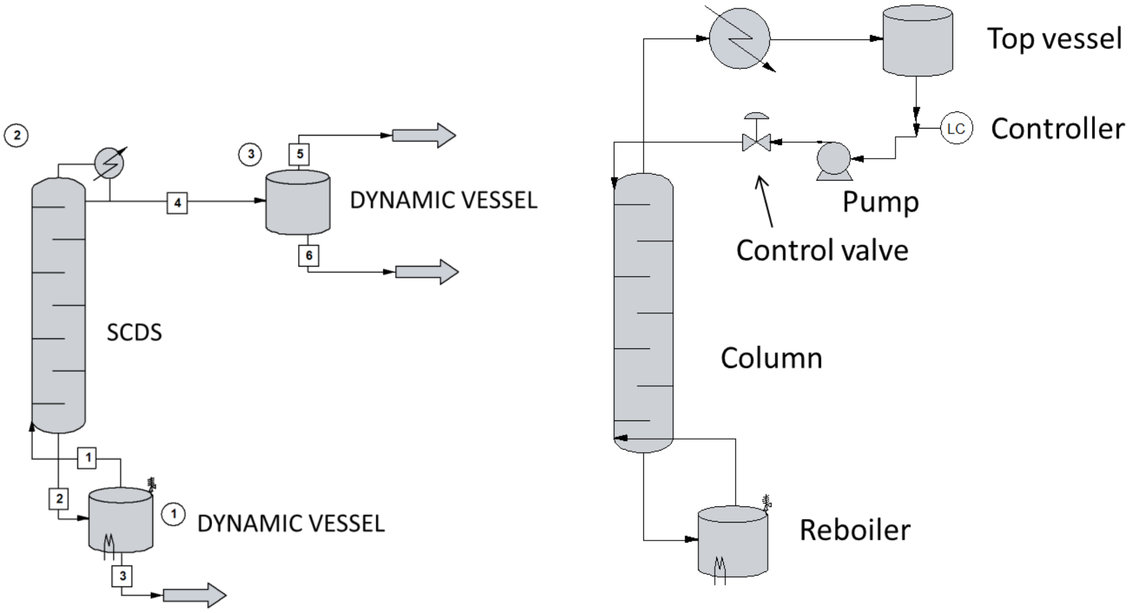
The Soave-Redlich-Kwong (SRK) equation of state is applied for the calculation of vapour-liquid equilibria and enthalpies.

3.1.1. Batch Rectifier (Two-Vessel Column)

The open and different closed operation modes of batch rectifier (BR) are compared for the recovery of A. The charge is an equimolar mixture of A and B, its volume is 10 dm^3. The prescribed purity of A is 99 mol%. The column has a total condenser and operates with a heat duty of 500 W. Calculations were performed for different values of the number of theoretical plates (8, 10 and 12).

3.1.1.1. Open Operation Mode

First, the batch rectifier is operated in open mode, with continuous distillate withdrawal. The ChemCAD model of the open operation mode (Figure 3.1a) consists of a SCDS column, and two Dynamic Vessels (reboiler, product tank). The reflux ratio is constant during the process. (The operation policy of constant distillate composition was also investigated, but as in the case studied it proved to be less efficient than this simpler policy, it is not presented here.) The operation is stopped when the A content of the accumulated product decreases to 99 mol%. The duration (Δt_{total}) obtained in this way is prescribed for the closed operation modes.



a. b.

Figure 3.1. (a) The ChemCAD model of the open operation mode of batch rectifier, (b) The scheme of the closed operation mode of the batch rectifier.

3.1.1.2. Closed Operation Modes

By the closed operation mode the A-rich product is accumulated in the top vessel. The process duration and the energy consumption are the same as those of the open mode. Six different closed modes are presented for the BR in Table 3.1, which differ in the operation of the top vessel, that is, in the method of varying the liquid flow rate from this vessel. For closed modes each (further) vessel provides one new degree of freedom (DoF).

The models of the closed modes are very similar to each other; the only difference is the presence or lack of the control equipment. Figure 3.1b shows the scheme of the configuration. The control equipment consists of a PID controller, a control valve, and a pump, creating pressure difference between the two sides of the valve.

The conventional reflux ratio, namely the ratio of reflux vs distillate flow rates, is always infinite during a closed operation, as there is no distillate withdrawal. However, if we take into consideration that the hold-up of the top vessel may vary and we define the reflux ratio with the following equation by replacing the distillate flow rate with the difference between the vapour (V) and liquid (L) flow rates:

$$R = \frac{L}{V-L} \tag{3.1}$$

then R is only infinite when the vapour and liquid flow rates are equal.

Mode	Principle of operation	Additional DoF	Advantage	Disadvantage
Mode 1	Constant volumetric flow rate from the top vessel	Liquid flow rate leaving the vessel	Existence of initial reflux (contrary to Mode 2a)	R is always finite
Mode 2a	Constant level, vessel empty at start	Liquid level	$R=\infty$ after initial period	$R=0$ initially (accumulation of liquid)
Mode 2b	Constant level, charge is distributed between the vessels	Liquid level (same as the initial level)	$R=\infty$ during the whole operation	Slower dynamics, low purity of initial reflux
Mode 3	Constant flow rate, then constant level (combn. of 1 & 2a)	Flow rate (1st part), liquid level (2nd part)	Faster dynamics at the beginning	Decreased duration of $R=\infty$
Mode 4a	Temperature control, empty vessel at start	Temperature of the 4th plate (from the top)	$R\approx\infty$ in the 2nd half of operation	R is finite in the 1st half of operation
Mode 4b	Temperature control, charge is distributed	Temperature of the 4th plate, initial level	The results are virtually the same as those of Mode 4a	

Table 3.1. The closed operation modes of batch rectifier.

3.1.1.2.1. Mode 1: constant volumetric flow rate

The constant value of the liquid flow rate from the top vessel provides an additional degree of freedom. However, this specified value can only be ensured when the flow rate of the condensate becomes sufficiently large. As the flow rate of the condensate is almost constant after the initial part of the operation, the level in the top vessel increases almost linearly. In this mode no controller is applied. The advantage of this operation mode is the initial existence of the reflux (contrary to Mode 2a). However, R always has a finite value.

3.1.1.2.2. Mode 2: constant level

The level of the top vessel is controlled. Two variants are considered. In both cases, the additional degree of freedom is the set-point of the level controller.

Mode 2a: top vessel empty at the start

The operation is started with empty top vessel. The drawback of this mode is the initial lack of reflux, as the liquid must accumulate in the vessel. After this period, however, the reflux ratio is infinite.

Mode 2b: top vessel filled up at the start

The charge is distributed between the top vessel and the reboiler, and the initial liquid level is maintained by the controller. *R* is infinite during the whole operation, but the purity of the initial reflux is much lower than that of the condensate, and the dynamics of the top vessel is shown below to be slower at the beginning than by the other operation modes.

3.1.1.2.3. Mode 3: constant liquid flow rate, then constant level

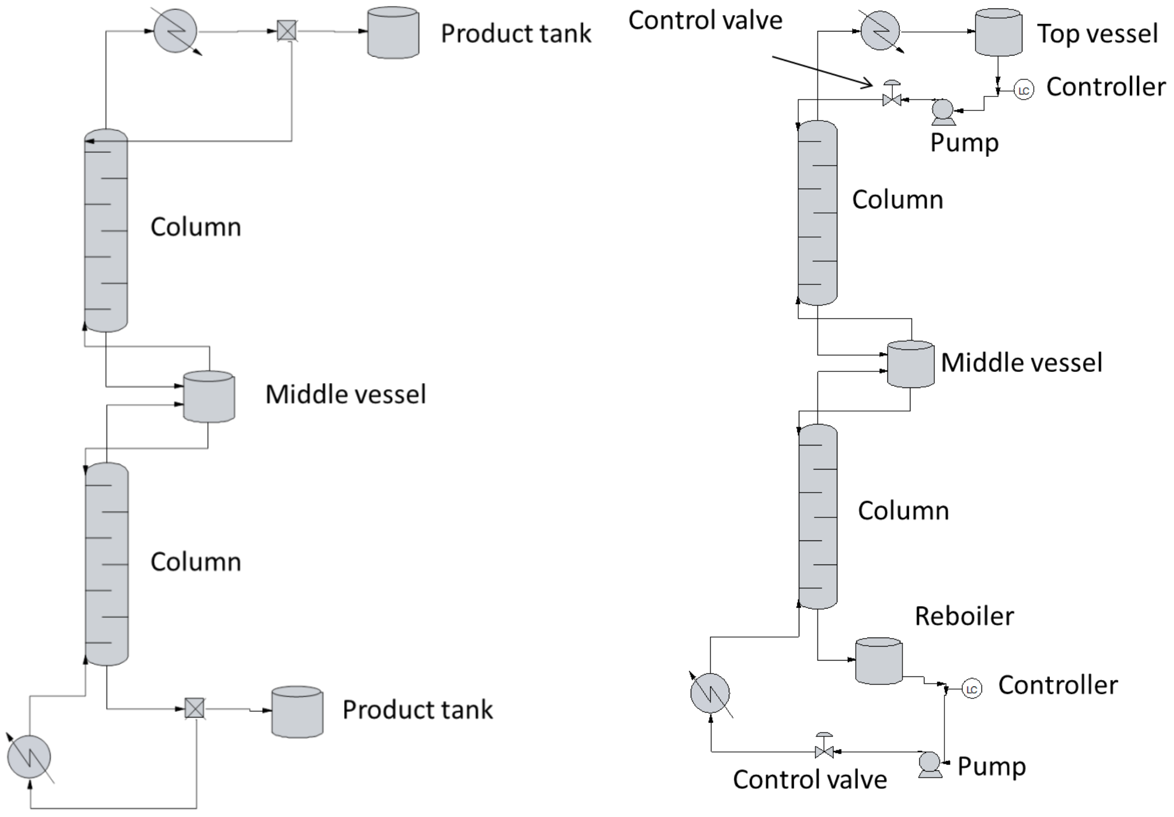
This mode can be considered as a combination of Modes 1 and 2a. In the first part of the operation the liquid flow rate is specified, and after the level reaches its specified value (which is the set-point of the controller), the level controller is activated. The additional degree of freedom is the liquid flow rate in the first part of the operation, and the liquid level in the vessel in the second one. Though the dynamics of the vessel is faster at the beginning than by Mode 2b, this decreases the duration of the period with infinite reflux.

3.1.1.2.4. Mode 4: temperature control

The temperature on one of the plates is controlled to maintain a constant distillate composition in the top vessel. The temperature change on the plate should be great enough to ensure sensitivity, but the plate should not be too far from the top. In the calculations, the plate chosen was the fourth from the top. The set point of the controller is the additional degree of freedom. The level in the vessel (and also *R*) begins to increase after an initial period, and finally becomes almost constant. On the basis of the possible division of the charge, two variants are proposed: at the beginning, the upper vessel is empty (Mode 4a) or filled up (Mode 4b). In the case of Mode 4b, the initial liquid level provides another degree of freedom, the optimal value of which has to be determined.

3.1.2. Middle Vessel (Three-Vessel) Column

The recoveries of open and different closed modes of the middle-vessel column are compared under constant energy consumption. The different modes of the middle-vessel column (MVC) without vapour by-pass are investigated for the separation of an equimolar mixture (20 dm^3) of A, B and C. Both column sections have 10 theoretical plates (Figure 3.2). In Figure 3.2b, the column is equipped with level controllers, and it is operated by either Mode 2 or Mode 3. The open operation mode of MVC is also compared to that of the batch rectifier (Hegely and Lang, 2009).



a. b.

Figure 3.2 The ChemCAD model of the (a) open, (b) closed operation mode (level control) of middle-vessel column.

3.1.2.1. Comparison of the Open Mode of Batch Rectifier and of Middle-Vessel Column

First, the recoveries obtained by the middle-vessel column are compared with those of the batch rectifier for the same product purities and energy consumption (process duration). Both configurations have the same number of trays and the same column liquid hold-up (40 cm^3/tray). The purity prescribed for A and C were 98 mol%. For B, the purity prescribed in the batch rectifier equals the purity reached with the middle-vessel column. In order to be able to compare the two configurations, their operational parameters are optimised. For the middle-vessel column the well-known downhill simplex optimising algorithm (Nelder and Mead, 1965) is applied. The optimization variables are the volumetric liquid flow rate from the middle vessel (W), the reflux (R) and the reboil (S) ratios. The objective function (OF) to be minimised is the sum of the deviations of the product purities from 98 mol% (instead of the sum of recoveries):

$$OF = 3 \cdot 0.98 - \sum_{i=1}^{3} x_{i,final} \qquad (3.2)$$

In the case of the middle-vessel column, the charge is filled into the middle vessel, and the operation begins with total reflux and reboil.

3.1.2.2. Comparison of the Operation Modes of the Middle-Vessel Column

The open operation mode of the middle-vessel column is also compared with the different closed ones. The flow rate of the liquid stream leaving the middle vessel is constant (40 dm^3/h) for both type of operation. By the open operation mode, the reflux and reboil ratios are chosen so that not only the purity of the top and bottom products but that of the B-rich product also reaches 98 mol% at the same time. The duration obtained in this way is prescribed for the closed operation modes, and the recoveries of A and C are compared. For the closed operation modes, the top and lower vessels are operated according to one of the modes presented by the closed modes of batch rectifier. The operation modes are not mixed, that is, the two vessels are operated by the same mode. The advantages and drawbacks of the different modes listed for BR (Table 3.1) are true for MVC as well, substituting R with the reboil ratio for the bottom vessel. By Modes 4a and 4b the temperatures of the third (upper column) and the eighth plate (lower one) are controlled. The operation mode applied by Skouras and Skogestad (2004a) is also studied, in order to compare the closed modes proposed here to a mode suggested in the literature. The mode of Skouras and Skogestad (2004a) is similar to Mode 4b, but the modified variables are the flow rate of the liquid leaving the top and middle vessels. The temperature of the middle (fifth) stage of each column sections is controlled; the set-points are the averages of the boiling points of the two components separated in this section. Choosing the set point in this way does not require preliminary calculations in the case of an industrial production. In the calculations presented, the values of the set points were 83.58 °C and 112.06 °C. At the start, 94 vol% of the charge is filled into the bottom, 5 % into the middle, 1 % into the top vessel, respectively, according to Skouras and Skogestad (2004a).

3.1.3. Multivessel (Four-Vessel) Column

The recoveries of A, B, C and D are compared for four closed modes (2a, 2b with constant level, 4a and 4b with temperature control) of the multivessel column (MuVC, Figure 3.3). As the multivessel column is usually not operated in open mode, the open mode is not studied here. The charge (31.42 dm^3) is equimolar, the purity requirements are 96 mol% for each product. The configuration consists of four vessels, and three column sections, each of them has 8 trays. The hold-up is 40 cm^3/tray. By Modes 4a and b, the temperature of the third plate of each section is controlled. For Mode 4b, the initial liquid level is 0.25 m (7.85 dm^3) in every vessel.

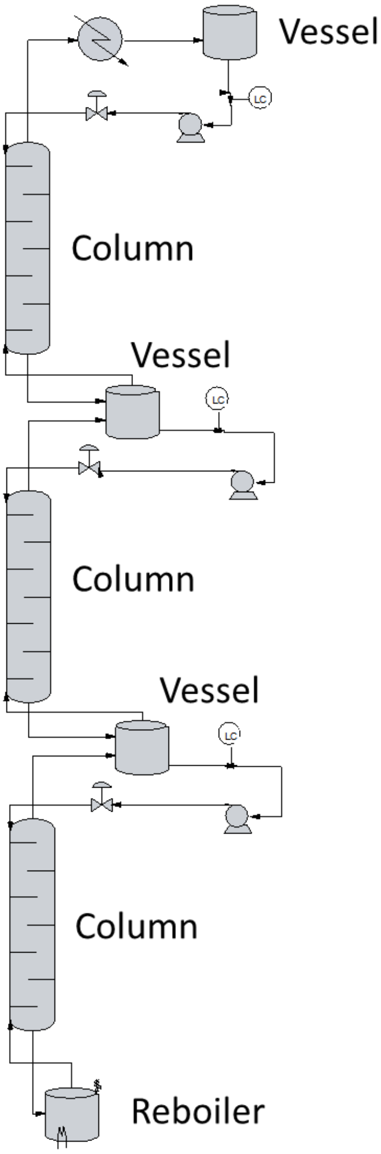


Figure 3.3. The scheme of the multivessel column with level control (Mode 2).

3.2. Calculation Results

The recoveries obtained with the open (only BR and MVC) and different closed modes are compared for the same product qualities. In the case of closed modes the value of at least one operation parameter has to be adjusted in order to maximise the recovery. The PI controllers for the closed modes are tuned by using the Ziegler-Nichols method. In a few cases, the quality of control was not satisfactory with gains calculated by the Ziegler-Nichols method, and even an exponential filter (Seborg et al., 1989) had to be applied.

The results of Mode 4b are only presented for the multivessel column, as the division of charge did not have significant effect on the recoveries in the cases of batch rectifier and middle-vessel column. The difference between the set-point and the tray temperatures, and therefore the error is so great initially, that the controller almost completely empties the vessel. In this way, the division of the charge is useless. This phenomenon can be avoided with a loose tuning, but the results are nevertheless very close to those of Mode 4a.

3.2.1. Batch Rectifier

The effects of three operational parameters on the recovery of A are studied for the open and six different closed modes of batch rectifier. The reflux ratio of the open mode (R_{open}, which determines the process duration) and the number of theoretical plates (N) have only slight effects, while the influence of the plate hold-up is very significant. Some of the recoveries reached with the different operation modes under different operation parameters are presented in Table 3.2.

N	8	10			12
Plate hold-up (ml)	0	0	50	100	0
Open	92.2%	93.3%	95.2%	94.4%	93.6%
Mode 1	88.7%	92.0%	91.7%	89.8%	92.5%
Mode 2a	93.0%	97.1%	92.8%	88.4%	97.9%
Mode 2b	93.9%	97.7%	93.3%	88.9%	98.5%
Mode 3	93.3%	97.1%	92.8%	88.4%	98.0%
Mode 4a	94.1%	97.4%	93.2%	88.8%	98.0%

Table 3.2. The effect of N and the hold-up on the recoveries of A (R_{open}=9).

The hold-up of the column is a very important parameter: in case of zero hold-up, the closed operation modes (except Mode 1) give better results than the open one. However, when the hold-up is greater, namely 50 or 100 ml, the open operation mode provides better recoveries (Figure 3.4). The recovery of A has a maximum with the hold-up by the open mode, while it decreases monotonously by the closed modes.

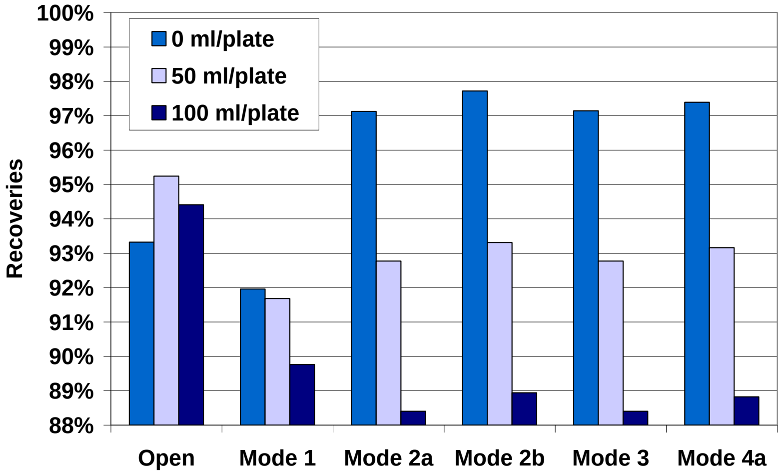
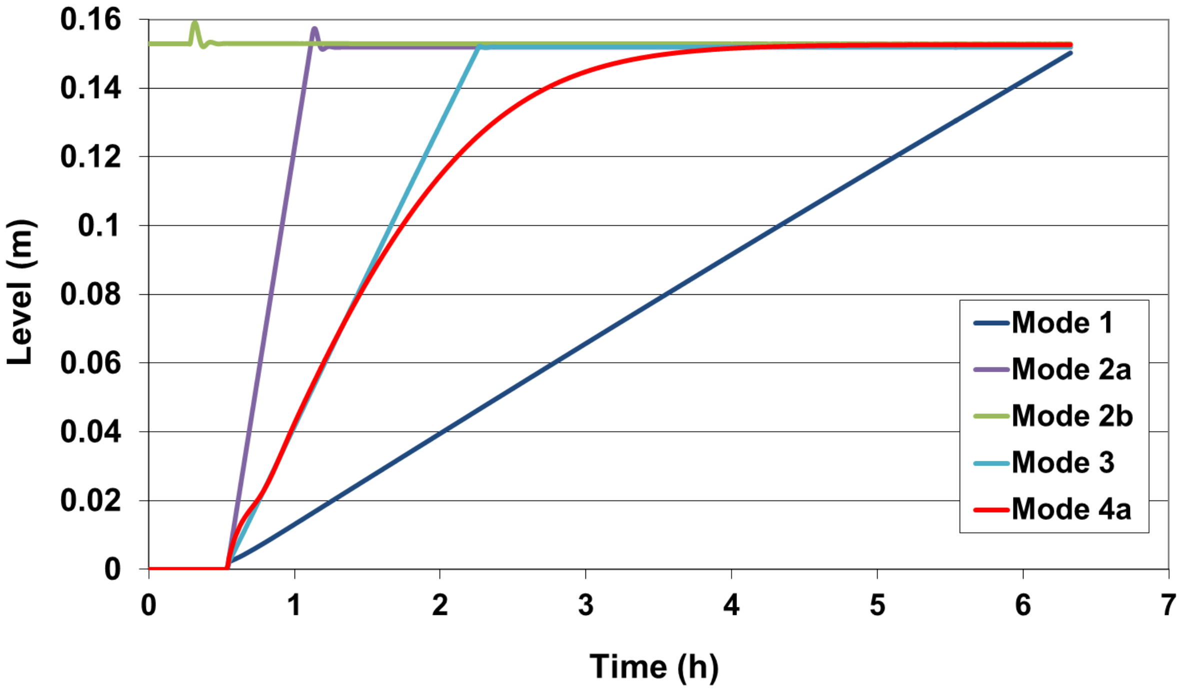


Figure 3.4. The recoveries of A by batch rectifier at different levels of hold-up (N=10, R_{open}=9)

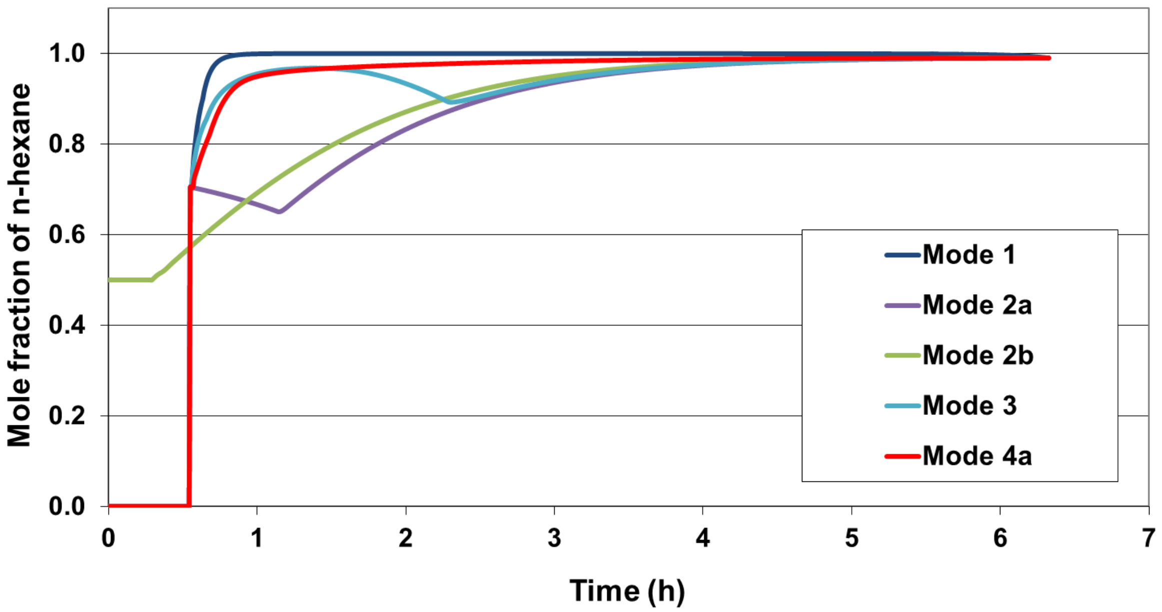
The advantage of the closed operation modes over the open one is also affected by R_{open}, (that is the total time Δt_{total}) and N, though to a smaller extent. The gain in recovery increases with increasing N, and decreasing R_{open}. More calculation results can be found in Appendix 1.

The closed operation modes can be ordered by the recoveries (with one exception). Mode 1 proved to be always worse than the open mode, and generally worse than the other closed modes. The order of the other closed operation modes (with decreasing recoveries): 2b, 4a, 3, 2a. Therefore Mode 2b (level control with initially filled up vessel) gives the best recovery with the exception of one case (R_{open}=7), in which it is preceded by Mode 4a.

The operation of closed modes is illustrated in Figures 3.5 and 3.6 (under N=10, R_{open}=9, hold-up: 50 ml/plate). The evolution of the liquid level in the top vessel (Figure 3.5) presents very clearly the behaviour of the different close operation modes. A constant level corresponds to infinite reflux ratio, as the total amount of condensate is refluxed to the column. If the flow rate of reflux, and thus R, is lower, some of the condensate is accumulated in the top vessel and the liquid level increases. The lower R, the faster the increase is. For instance, in the initial period of Mode 2a, R=0, which results in a steep increase in the level. Figure 3.6 shows the evolution of A concentration in the top vessel. The effect of the reflux and the top vessel hold-up can be observed, e.g. the slow change in the composition by Mode 2b is explained by the high top vessel hold-up.

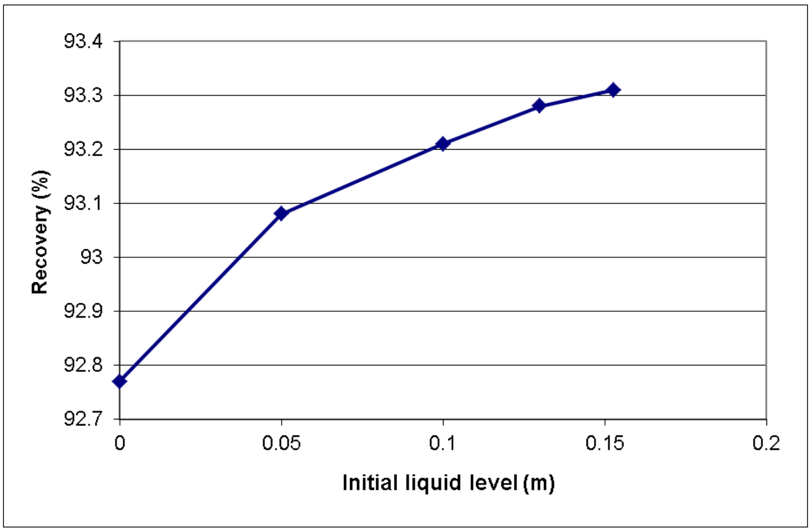


Figures 3.5. Evolution of the level in the top vessel (closed operation modes of a batch rectifier N=10, R_{open}=9, hold-up: 50 ml/plate).



Figures 3.6. Evolution of product compositions (closed operation modes of a batch rectifier N=10, R_{open}=9, hold-up: 50 ml/plate).

Modes 2a and 2b are extreme cases of the possible operation modes with a control of the top vessel level (Mode 2). The recovery of a number of intermediate cases, with initial liquid levels between zero (Mode 2a) and 0.1529 m (Mode 2b), were also investigated (Figure 3.7) under the parameters N=10, R_{open}=9 (Δt_{total}=379.5 min), hold-up=50 ml/plate. In each case, the level set point was adjusted to maximise recovery while satisfying the quality requirement. We can conclude that the recovery monotonously increases with the increase of initial liquid level.



Figures 3.7. The recoveries of Mode 2 for different initial liquid levels (N=10, R_{open}=9, hold-up: 50 ml/plate).

3.2.2. Middle-Vessel Column

First, the comparison of batch rectifier and middle-vessel column is presented, than the comparison of the open and six closed operation modes of middle-vessel.

3.2.2.1. Comparison of the Open Mode of Batch Rectifier and of Middle-Vessel Column

First, the optimal values of the operational parameters *W*, *R* and *S* of the middle-vessel column are determined. Table 3.3 contains the coordinates of the point, from which the initial simplex was generated in the direction of increasing values. The initial step size was 2 for *R* and *S*, and 2 dm^3/h for *W*, respectively. The results of this initial run are also presented.

W (dm^3/h)	40	Purities	
R	9	Hexane	0.9813
S	12	Heptane	0.7969
Time (min)	110.5	Octane	0.9938
OF	0.1982		

Table 3.3. The coordinates and results of the initial point for the optimization of MVC.

Due to convergence problems, the method of calculation was modified several times. First, the reflux and the reboil ratios were specified to be equal, and then step size of *W* was doubled, as the results are much more sensible for *R* and *S*. Finally, the original method with three independent variables was used from a later point, but with a step size four times higher than that of *R* or *S*. The characteristic data of the final point of the optimization are given in Table 3.4. *Q* is the average heat duty. (The heat duty is not constant, as the middle-vessel column has a total reboiler and a bottom stream of changing composition).

W (dm^3/h)	42.88	Purities		Recoveries
R	13.81	Hexane	0.9830	0.9541
S	13.25	Heptane	0.9309	0.7367
Time (min)	157	Octane	0.9802	0.9000
OF	0.052			
Q (MJ/h)	8.721			

Table 3.4. Optimal operating parameters and results of the MVC.

The batch rectifier is operated for the same duration (which was adjusted by changing the reflux ratio of the batch rectifier), and with the same heat duty as the average heat duty of the middle-vessel column. The evolution of the compositions is presented in Figure 3.8. The prescribed purity for B (heptane) was 93 mol%. Comparing the results of the two configurations, it can be seen in Tables 3.4 and 3.5 that the recoveries of A and C are higher in the middle-vessel column, while the recovery of B is higher in the batch rectifier. The largest difference occurs for C. These results can be explained by the different composition of the hold-ups: that of the middle- vessel column contains mostly B, while the batch rectifier's one is mostly C, respectively. In the batch rectifier, the recoveries of A and C are further decreased since some of these components is lost in the intermediate fractions (Figure 3.8a). The average recoveries (0.8636 for MVC, 0.8164 for BR) show more definitely the better performance of the middle-vessel column.

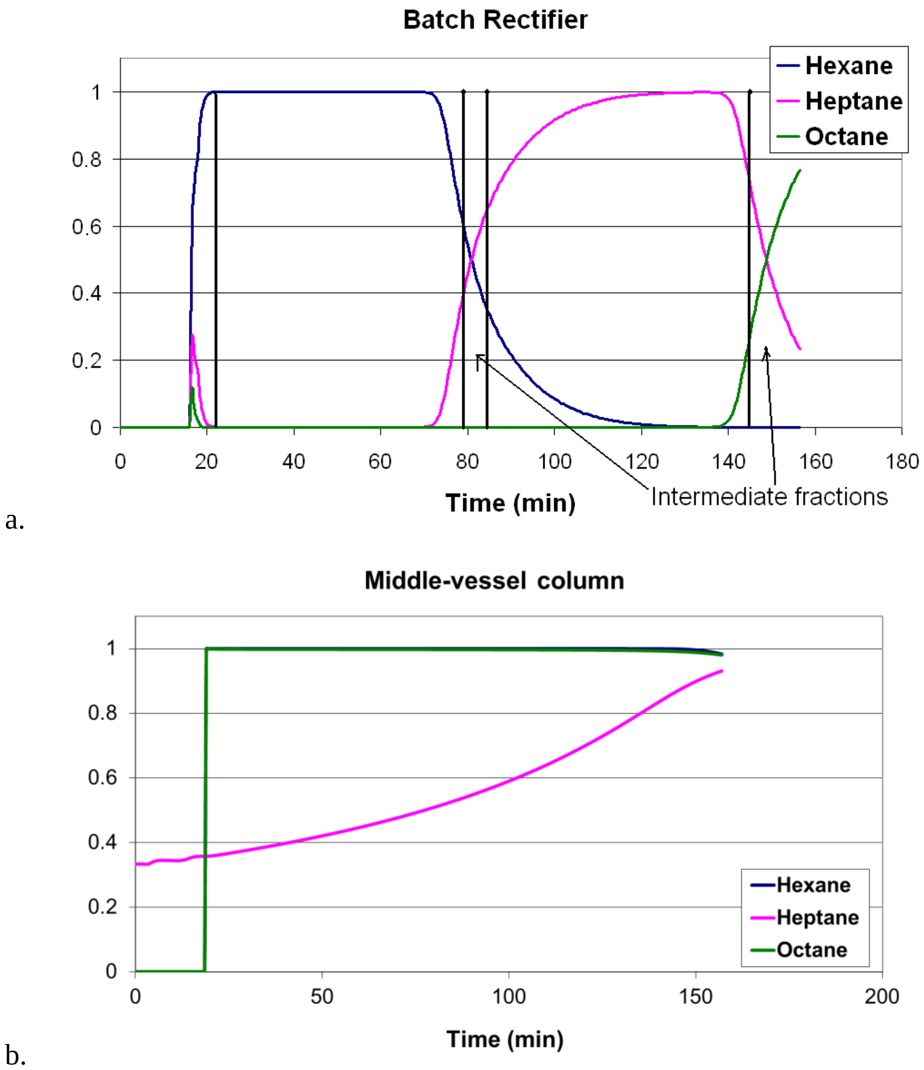


Figure 3.8. The evolution of compositions (a) in the distillate of BR, (b) of the products of MVC.

R	5.51	Purities		Recoveries
		Hexane	0.982	0.8996
Time (min)	157	Heptane	0.930	0.8357
		Octane	0.981	0.7138

Table 3.5. Results for the ternary separation in BR.

Another advantage of the middle-vessel column is that only one operation step is needed, as all three components can be recovered simultaneously. This also means that there is no need for intermediate fractions, which must be processed later. However, the operation of the middle-vessel column is more complicated because of the higher degree of freedom.

3.2.2.2. Comparison of the Operation Modes of the Middle-Vessel Column

Different operation modes are compared for the MVC with negligible or 40 cm^3/plate hold-up (4 % of the charge). The recoveries for 40 cm^3/plate hold-up are presented in Table 3.6 with the purity of B. Unlike the BR, the open mode always proved to be better overall than the closed ones (Figure 3.9) even at negligible hold-up. The order of the operation modes with respect to the recoveries is different not only for zero and non-zero hold-ups, but also for A and C. The recovery of A is greater than that of C (with one exception). The recovery of B is the highest by Mode 3. Mode 1 is very good in recovering A but its C-recovery is the lowest. While Mode 2b is the best closed operation mode of the BR, it is not very favourable for MVC. For low hold-up, Modes 3 or 4a, in the case of 40 cm^3/plate hold-up, Mode 2a and 3 can be suggested. The operation mode of Skouras and Skogestad (2004a) gives very similar results to those of Mode 4a, though the purity of A is slightly higher (98.4 mol%).

Hold-up: 40 cm^3/p.	Recovery (%)			Purity of B (mol%)
	Hexane (A)	Heptane (B)	Octane (C)	
Open	99.2	73.14	96.94	98.03
Mode 1	96.34	85.63	90.48	94.37
Mode 2a	96.55	84.03	94.15	96.63
Mode 2b	95.25	85.39	92.88	96.66
Mode 3	95.56	86.09	92.96	96.75
Mode 4a	93.61	80.94	91.83	96.69
Skouras	93.7	83.4	92.2	96.62

Table 3.6. The calculated results of MVC (hold-up: 40 cm^3/plate).

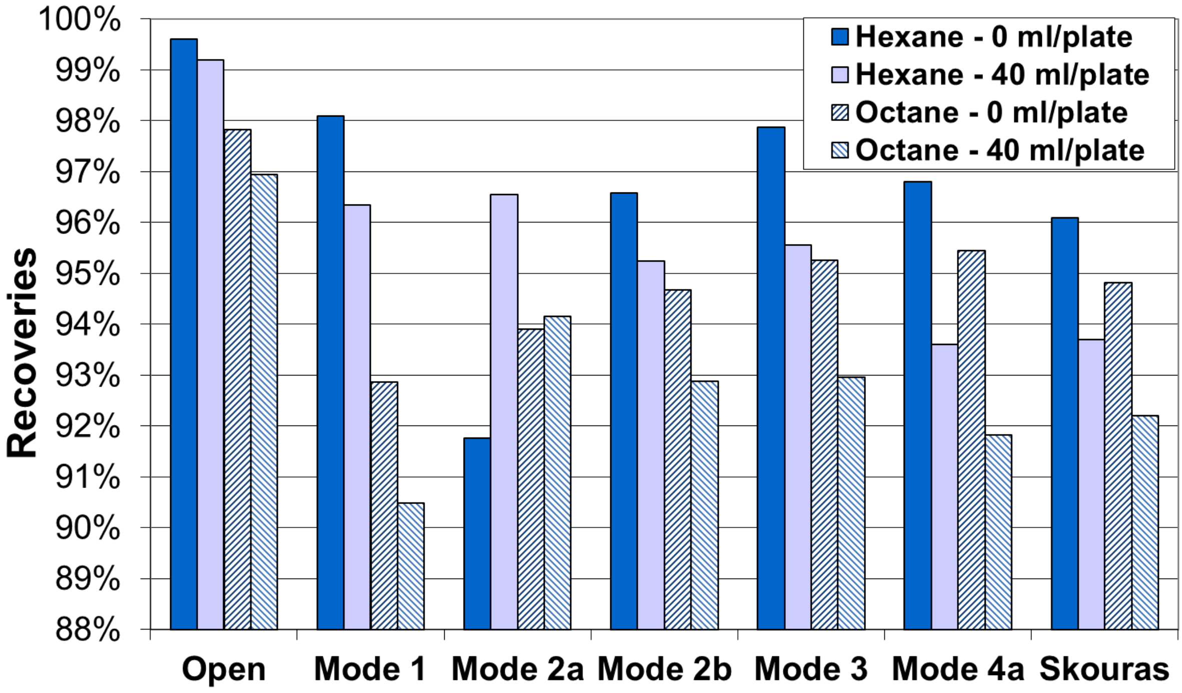


Figure 3.9. The recoveries of the different MVC operation modes.

The increase of the column hold-up has a detrimental effect on the recoveries of every operation mode, even the open one, except Mode 2a, where the recovery of A increases greatly, and even the recovery of C shows a slight increment.

3.2.3. Multivessel Column

The average recoveries (Table 3.7.) of the different closed modes do not show significant differences. However the energy consumption (proportional to the total time Δt_{total}) is the lowest by Mode 2a. The division of charge (Mode 2b and 4b) increases Δt_{total}, while the average recovery increases only slightly. The recoveries of the components always follow the same decreasing order: D, A, C, B. The operation modes with level control (Mode 2) are better for recovering B and D, those with temperature control (Mode 4) could be suggested for recovering A and C.

	Δt_{total} (min)		A	B	C	D	Average
Mode 2a	16.55	Recovery (%) Purity (%)	94.77 96.01	80.57 96.01	82.60 96.00	97.62 96.17	88.89 96.05
Mode 2b	25.85	Recovery (%) Purity (%)	95.38 96.07	80.16 96.06	82.60 96.00	98.63 96.07	89.19 96.05
Mode 4a	18.25	Recovery (%) Purity (%)	95.38 96.01	79.76 96.01	83.82 96.00	96.19 96.98	88.79 96.25
Mode 4b	22.75	Recovery (%) Purity (%)	95.59 96.01	79.55 96.00	84.02 96.00	97.21 97.13	89.09 96.29

Table 3.7. Calculated results for the multivessel column.

3.3. Conclusion

The open and non-conventional closed batch column operation modes were compared in order to study the competitiveness of non-conventional operation modes. The open and six different closed operation modes of batch rectifier and middle-vessel column were studied by rigorous dynamic simulation with ChemCAD. Four closed modes (Modes 2a, 2b, 4a, 4b) of the multivessel column were also investigated. The calculations were made for a binary (n-hexane – n-heptane), a ternary (n-hexane – n-heptane – n-octane) and a quaternary (n-hexane – n-heptane – n-octane – n-decane) mixture. The recoveries were compared under constant product quality and energy consumption. The closed modes differ from each other in the operation of the vessels.

For the batch rectifier, closed operation provided significantly better recoveries in case of negligible liquid hold-up. Modes 2b (level control with initially filled up top vessel) and 4a (composition control with initially empty top vessel) proved to be the best closed modes. The decrease of the process duration and increase of number of stages improved further the advantage of closed modes. But for higher hold-ups, the open operation mode gave the highest recovery.

Batch rectifier and middle-vessel column were also compared for a ternary mixture. Middle-vessel column provided much greater recoveries for n-hexane and n-octane, but smaller for n-heptane. The average recovery was higher for the middle-vessel column. In the middle-vessel column, all three components can be simultaneously recovered, and no intermediate fractions are needed contrary to batch rectifier. However, its operation is more complicated, since it has more operational parameters to be adjusted.

For the middle-vessel column the open operation mode proved to be better than the closed ones in every case. It was not possible to choose the best closed mode, as the order of the closed modes with respect to the recoveries was not the same for the two products (n-hexane and n-octane) or for the two different hold-ups considered. For negligible liquid hold-up, Modes 4a or 3 (constant flow rate then level control), for higher hold-ups Mode 2a (level control with initially empty top and bottom vessels) can be recommended.

For the multivessel column the energy consumption of Mode 2a was the lowest, while the recoveries were similar for all modes. The division of the charge between the vessels had adverse effect on energy consumption (proportional to the process duration).

The results show that the closed operation mode may produce higher recoveries than the open one, depending on the value of the liquid hold-up in the column. At low hold-ups, the closed batch rectifier (two-vessel column) can be recommended. Moreover, its operation is simpler than that of the open mode, as the product purity can only increase in time. By the open operation mode, the distillate composition has to be observed, so that the taking the off-cut(s) could be started at the right moment, as otherwise the product purity would fall below its specified value.

CHAPTER 4

The Effect of Off-Cut Recycle on the Solvent Recovery with Batch and Batch Extractive Distillation

Related publications: Hegely and Lang (2012), Lang et al. (2012a,b)

The influence of recycling off-cuts for the batch and batch extractive distillation separation of a four component (methanol (A) – THF (B) – water (C) – toluene (D)) waste solvent mixture of a pharmaceutical plant is studied by rigorous dynamic simulation (Hegely and Lang, 2012). The aim of the separation process is the recovery of the main component, methanol. The evolution of the charge composition, of the amount of fresh feed and that of methanol product are determined for six consecutive productions of the batch rectification process. Since tetrahydrofuran and toluene form minimum boiling azeotropes with methanol, these organic pollutant components have to be removed in the fore-cuts. The first fore-cut is incinerated to prevent the accumulation of the organic pollutants, whilst the second fore-cut, the after-cut and the hold-up are recycled to the next batch, in order to reduce the methanol loss.

As an alternative to the traditional batch distillation, batch extractive distillation by using water as entrainer is also studied. Water feeding is applied during the heating-up phase, in order to decrease the methanol concentration in the column top, in this way reducing methanol loss with the fore-cuts. The new BED policy applied here is described in Section 5.2 in more detail.

The profit of the productions is calculated on the basis of the operational and incineration costs and the price of the methanol. The influence of the volume of the first fore-cut on the profit of the whole production process is also investigated and its optimal amount is determined for both separation methods.

The program for the mass balance calculations is written in Visual Basic for Applications under Microsoft Excel. It calls the built-in dynamic simulator (CC-DCOLUMN) of ChemCAD 6 flow-sheet simulator for the rigorous calculations and the module MIXER of ChemCAD for calculating the volume after mixing recycled and fresh material.

4.1. Vapour-Liquid Equilibrium Conditions

The vapour-liquid conditions of this multicomponent, azeotropic mixture is presented. The presence of some of the azeotropes limit the recovery of methanol, but the addition of water has a favourable effect on relative volatilities.

4.1.1. Pure Components and Azeotropes

For the calculation of vapour-liquid equilibria, the UNIQUAC model is used. The UNIQUAC parameters can be found in Appendix 2. Table 4.1 shows the boiling points and compositions of the components and of the 5 minimum boiling azeotropes (including the heteroazeotrope C-D). Figure 4.1 shows the structure of the mixture and the stabilities of the stationary points. The azeotrope A-B is the only unstable node, components C and D are stable nodes.

Component(s)	T_{BP} (°C)	Composition (mass%)			
		A	B	C	D
A-B	59.5	30.0	70.0	-	-
A-D	63.6	71.5	-	-	28.5
B-C	63.9	-	94.7	5.3	-
A	64.7	100	-	-	-
B	65.97	-	100	-	-
C-D	84.4	-	-	19.7	80.3
C	100.0	-	-	100	-
D	110.6	-	-	-	100

Table 4.1. The boiling point and compositions of pure components and azeotropes for the methanol (A) – THF (B) – water (C) – toluene (D) mixture

Homoazeotropes A-B, A-D and B-C have lower boiling point than component A. The batch distillation region of the typical composition of the fresh feed is marked by red in Figure 4.1. The recovery of A is limited by the occurrence of azeotropes A-B and A-D, however the azeotrope B-C does not render the production of A more difficult as B is distilled off with the azeotrope A-B. Pure A can be produced only after the removal of components B and D in the azeotropes A-B and A-D, respectively.

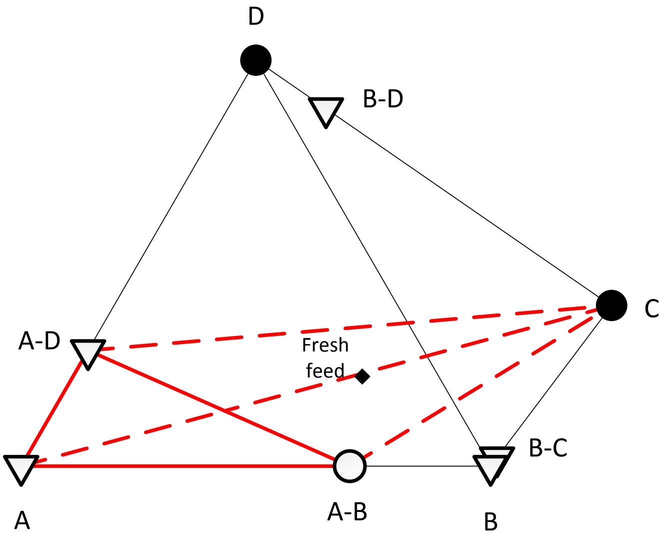


Figure 4.1. The structure of the methanol (A) – THF (B) – water (C) – toluene (D) mixture and the batch distillation region of the fresh feed marked by red.

4.1.2. The Influence of Water on Relative Volatilities

The addition of moderate amount of water changes the relative volatilities of the azeotropic mixtures A-B and A-D favourably (Figure 4.2). For example, by adding 25 kg water to 100 kg of A-B and A-D mixtures of azeotropic composition (corresponding to 42.1 mol% and 35.3 mol% water, respectively), the relative volatilities decrease from 1 to 0.535 and 0.430, respectively. This also means that the volatility order of components is reversed, as B and D become more volatile than A, the desired product.

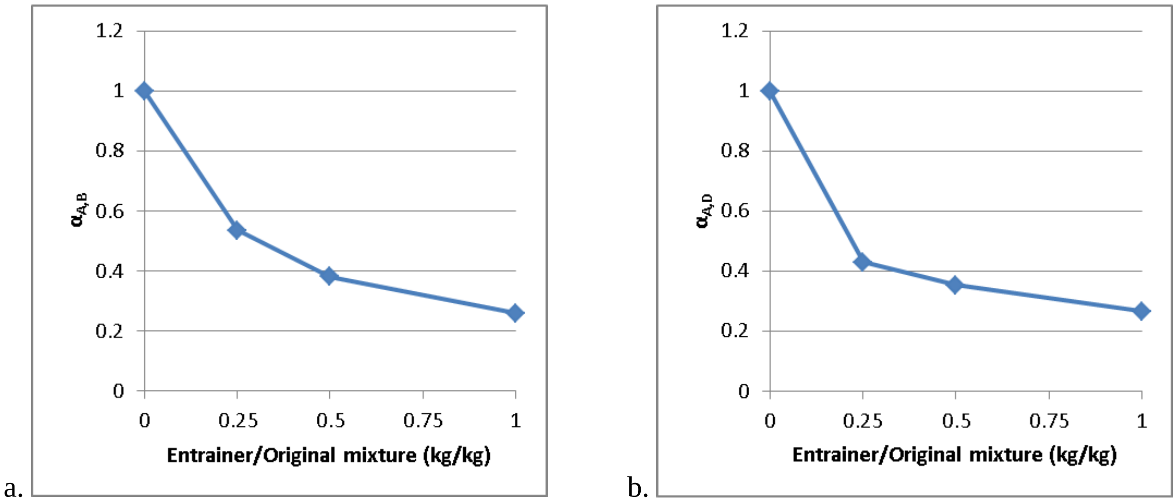


Figure 4.2. The change in relative volatilities with the addition of water:
a. A-B azeotropic mixture, b. A-D azeotropic mixture.

Even though water is present in the charge in a relatively high concentration, its favourable effect on the relative volatility can only be exploited by batch extractive distillation, that is, by continuously feeding it into the column, as the component to be recovered is a saddle point. Another advantage of choosing water as entrainer is that no new component is introduced into the system.

Unlike the traditional applications of BED, where pollutants are removed from beside the main component, the aim here is to wash out A, the main component from the column top, and to increase the concentration of organic pollutants B and D in the distillate. Therefore a new BED policy is applied (see Section 5.2), where water feeding starts as the vapour reaches the location of the feed and it is maintained during the total reflux start-up of the column only. The increased B and decreased A concentration at the top of the column at the end of the start-up period reduces the loss of A in the fore-cuts.

4.2. Rigorous Simulation

First, the calculation method for the six-batch process is presented, then the input data are given, and finally the simulation results are shown.

4.2.1. Calculation Method

The calculations are performed by using the following algorithm (Figure 4.3). First, the rigorous dynamic simulation is carried out with CC-DCOLUMN for the fresh charge composition. On the basis of the simulation results, the mass and composition of the recycled material is calculated by the code in EXCEL. These data are then used to compute the mass of the fresh charge needed for the prescribed charge volume, in the following way. ChemCAD calculates the volume of the mixture of the recycled material with an estimated amount of fresh feed. The mass of the fresh feed is varied with the bisection algorithm, until the new charge volume calculated is equal to the prescribed one. The new charge composition is calculated from the compositions and amounts of the recycled material and the fresh charge, and the rigorous dynamic simulation is repeated. The calculation cycle is performed for the given number of batches.

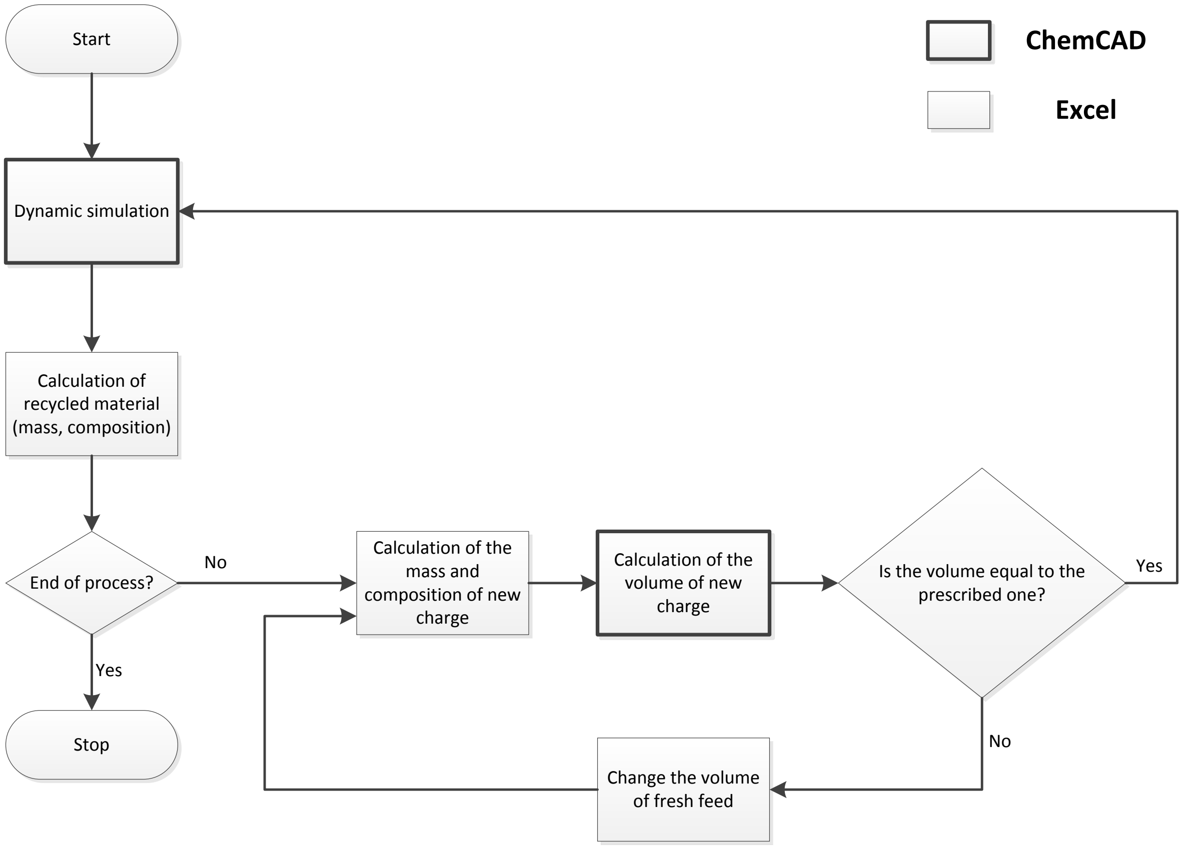


Figure 4.3. The algorithm of calculation for the methanol regeneration process with off-cut recycle.

4.2.2. Input Data

The state-task-network (Mujtaba, 2004) of the methanol regeneration process in the pharmaceutical plant is shown in Figure 4.4. Six consecutive batches are processed in two cycles (1-3 and 4-6). The bottoms (B) of each batch and the final hold-up of a cycle are withdrawn and sent to biological treatment (done in the plant itself). The second fore-cut and the after-cut are always recycled to the next charge. The hold-up (U) within a cycle remains in the column, that is, it is recycled to the next charge, as well. The regeneration process is the same for BED production, as well, the only difference is the water feeding (E) during the heating-up period.

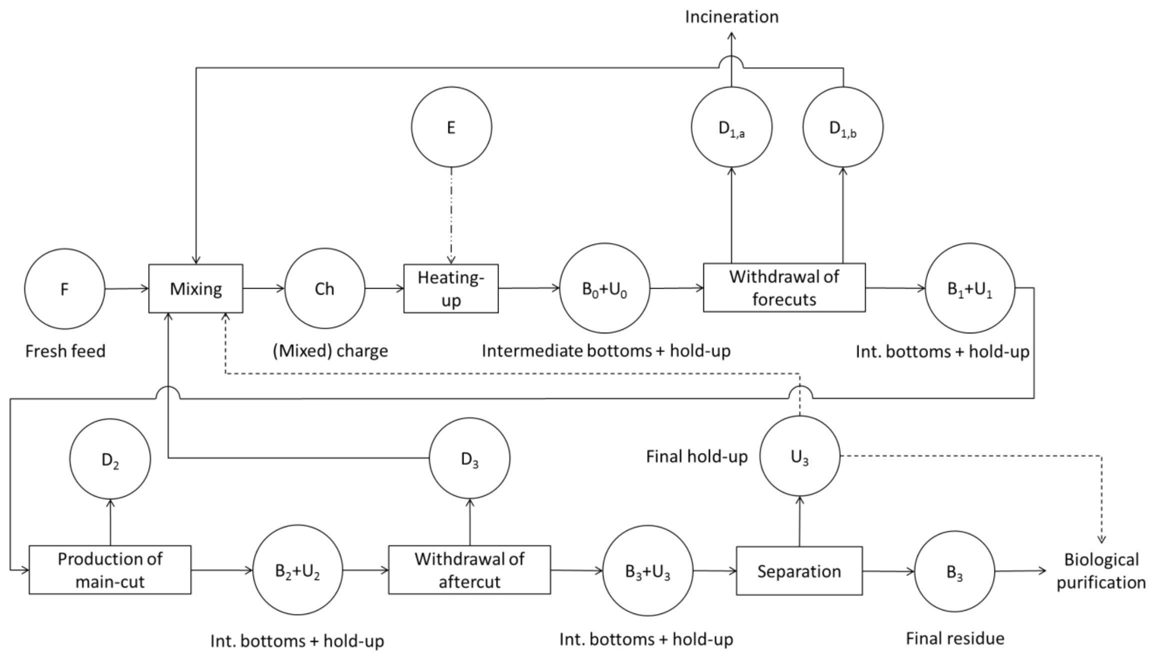


Figure 4.4. The state-task-network of methanol regeneration process (----: depends on the serial number of batch; —··—: for BED only).

During the simulation the following input data were fixed:

- the composition of the fresh feed: 40 wt% methanol (A), 6.5 % THF (B), 52 % water(C), 1.5 % toluene (D),
- number of theoretical stages: 25 (excluding the reboiler and the total condenser),
- volume of the charge: 25 m^3 (T= 20 °C),
- purity of methanol product: 99.5 wt%,
- top pressure=1.013 bar (atmospheric pressure), pressure drop=0.25 bar
- volumetric hold-ups: condenser: 0.45 m^3, column: 1.25 m^3
- reflux ratios (R): start-up: ∞, fore-cuts: 6, main-cut: 2, after-cut: 6

The stopping criteria applied were the following ones:

- the end of start-up: 300 min of operation,
- the end of taking the first fore-cut: $x_{D,B}$<20 wt% (distillate composition of B) for the base case, or a specified fore-cut volume ($V_{D,1a}$),
- the end of taking fore-cuts: $x_{D,B}$<2 wt%,
- the end of taking after-cut: $x_{B,A}$<0.25 wt% (bottoms composition of A).

The ratio of the first fore-cut ($V_{D,1a}/V_{D,1}$) to be incinerated is varied between 0 (no incineration) and 100 vol% (no fore-cut recycled: $V_{D,1b}$=0).

The operational costs and the profit of methanol regeneration were calculated for every batch. The data used for the operational cost calculations were given by the solvent recovery plant in the first quarter of 2013:

- steam: 57.6 US$/t (with a pressure of *P* = 3 bar),
- price of methanol: 0.46 $/kg, fee of incineration (for water contents below 20 wt%): 0.21 $/kg.

The capital cost, the costs of cooling water and electricity and also the cost of the biological purification of the final residue and hold-up can be neglected.

In the BED process, the water is fed into the top of the column with a flow rate of 1100 kg/h and a temperature of 20 °C. Water feeding is started after 100 min of operation.

4.2.3. Results

The results are presented first for the traditional batch distillation process applied in the pharmaceutical plant, and then for the suggested batch extractive distillation process.

4.2.3.1. Traditional Batch Distillation

First the variations of the charge composition (Figure 4.5), the volume of fresh feed and the mass of methanol product (Figure 4.6) and the profit (Table 4.2) during six consecutive batches were studied for the base case of a traditional batch distillation.

In the base case the charge composition varies only slightly (Figure 4.5). The concentration of methanol (A) at the beginning rises, it shows greater increase at Batch 4, and then it slightly decreases but still remains above that of the fresh feed. What is more important, B (THF) and D (toluene) do not accumulate in the subsequent charges.

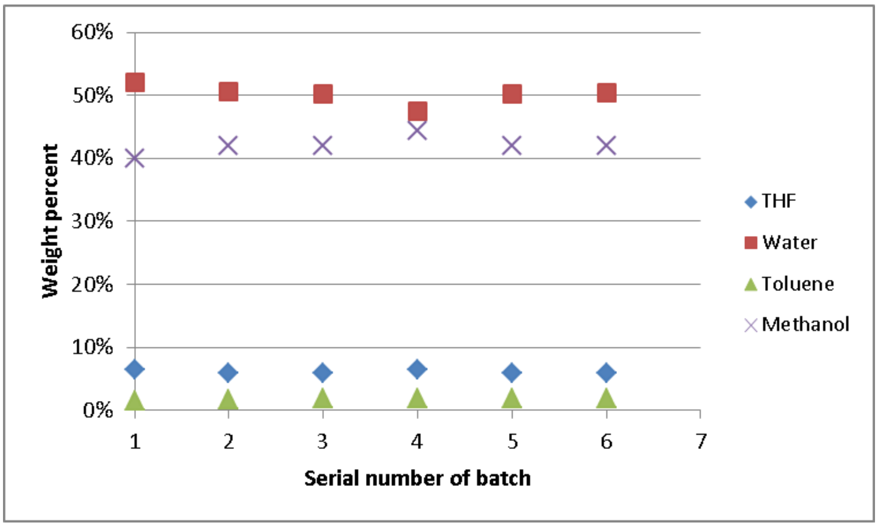


Figure 4.5. The variation of the charge composition as a function of the serial number (1-6) of batch for the base case of batch distillation regeneration of methanol (A). (B: THF, C: water, D: toluene)

The volume of fresh feed (Figure 4.6) considerably decreases for Batch 2, as the material recycled from Batch 1 is mixed with the fresh feed. Due to the fact that the recycled cuts occupy the place of fresh feed, the capacity of the production is reduced. After that it remains practically constant except for a temporary increase for Batch 4, which is due to the fact, that the final hold-up of Batch 3 is not recycled.

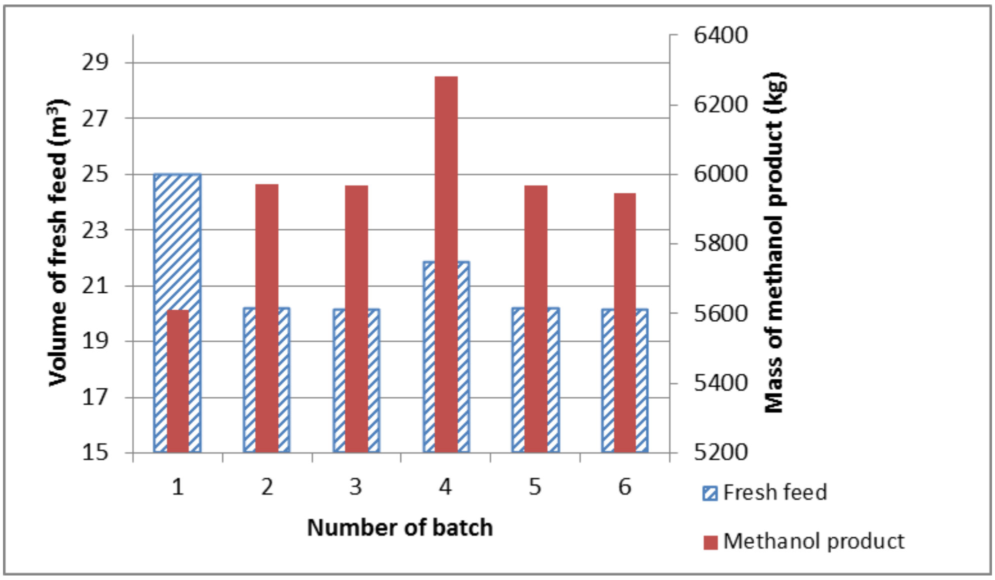


Figure 4.6. Evolution of the volume of fresh feed processed and mass of methanol product (base case)

The effect of the recycle of methanol-rich material can be seen on the increase of the mass of methanol product. The amount of methanol product considerably increases for Batch 2. After that it remains almost constant except for a temporary increase for Batch 4. (It shows a very slight decrease for the last batch but it still remains much above that of Batch 1.)

Both the incineration and operational costs vary in a narrow region except a temporary increase for Batch 4 (Table 4.2). The evolution of the income obviously follows that of the amount of methanol product. The trend of the evolution of the profit is very similar to that of the income. It considerably increases for Batch 2, and it is maximal for Batch 4, in spite of the fact that the costs are also the highest for this batch.

No. batch	1	2	3	4	5	6	**Total**
Incineration	578	547	560	613	566	562	3426
Operation	1733	1753	1759	1806	1761	1759	10571
Income	2585	2752	2750	2895	2750	2740	16472
Profit	275	452	431	476	423	418	2475

Table 4.2. The evolution of costs and that of the income (in $, base case) for the batch distillation regeneration of methanol.

The influence of the amount of fore-cut incinerated ($V_{D,1a}$) on the profit was also investigated (Table 4.3). The highest profit is achieved by the base case (based on industrial experiences, $V_{D,1a}$ varies between 3.3 and 3.7 m^3). When nothing ($V_{D,1a}=0$) or only 1 m^3 is incinerated from the fore-cut, the concentration of THF and toluene in the charge considerably increases therefore methanol of prescribed purity cannot be produced (under the given parameters) after Batch 3 or 4, respectively. In these cases all the fore-cut of the last (6th) batch still producing methanol of prescribed purity must be incinerated, which drastically diminishes the profit. These results show that there is a minimum volume of fore-cut to be incinerated, below which the 6-batch process is infeasible. The production process is considered feasible if it is possible to obtain methanol of prescribed purity from all the six batches under the given parameters. It must be still noted that in all other cases both the second fore-cut and after-cut of the last (6th) batch have compositions appropriate for recycling to a later production and therefore they need not be incinerated. In the cases where the 6-batch process is feasible, incineration cost increases, while operation cost slightly decreases with increasing $V_{D,1a}$. The income has a maximum value at the base case.

Case	$V_{D,1a}$ =0 m^3	$V_{D,1a}$ =1 m^3	$V_{D,1a}$ =2 m^3	$V_{D,1a}$ =3 m^3	Base	$V_{D,1a}$ =4 m^3	No recycle
Incineration cost	1674	2171	2009	2990	3426	3954	4994
Operation cost	5654	7602	11332	10807	10571	10385	10243
Income	7176	9914	15061	16081	16472	16451	15532
Profit	-153	141	1722	2285	2475	2112	295

Table 4.3. The influence of the amount of fore-cut incinerated on the profit (in $) for the batch distillation regeneration of methanol.

4.2.3.2. Batch Extractive Distillation

The same investigation concerning the effect of taking different amounts of first fore-cut was performed for batch extractive distillation, as well (Table 4.4). By the BED production, the base case means a first fore-cut between 2.65-2.97 m^3, which is lower than that of the traditional BD. Another important difference is that the minimum volume of the first fore-cut is higher, the 6-batch process is not feasible with $V_{D,1a} = 2\ m^3$, that is, the BED process is more sensitive to the accumulation of organic pollutants in the charge.

Case	$V_{D,1a}$ =0 m^3	$V_{D,1a}$ =1 m^3	$V_{D,1a}$ =2 m^3	Base	$V_{D,1a}$ =3 m^3	$V_{D,1a}$ =4 m^3	No recycle
Incineration cost	1236	1215	2120	2798	3018	3963	4431
Operation cost	3797	3746	7602	11145	11033	10819	10756
Income	5040	5291	10865	16812	16972	16524	16098
Profit	7	330	1142	2869	2921	1743	911

Table 4.4. The influence of the amount of fore-cut incinerated on the profit (in $) for the batch extractive distillation regeneration of methanol.

For the cases with feasible 6-batch process ($V_{D,1a} > 2\ m^3$), the incineration cost increases and the operation cost decreases monotonously with the increase of $V_{D,1a}$, while the income and the profit have maximal values, similarly by the traditional batch distillation. However, the two optima do not coincide, as the optimum of income is at the base case, that of the profit is when $V_{D,1a}$ =3 m^3.

If the cases with a feasible 6-batch process are compared, it can be seen that both operational costs and incomes are higher by BED than by BD, except for the value $V_{D,1a}$ = 4 m^3, but the stronger increase in incomes results in higher profits. The higher average A recovery of BED (Table 4.5), defined as the average of the recoveries of the batches for the 6-batch process, is explained by the fact that the methanol content of the first fore-cut is lower, that is, the methanol loss with the first fore-cut is reduced. The optimal case of BED shows a profit increase of 18 % compared to that of the traditional batch distillation. At the same time, the volume of material incinerated decreases from 20.7 to 18 m^3 (-13.1 %), contributing to pollution reduction. The water fed into the column causes a slight increase of water concentration in the first fore-cut compared to the BD production, but the majority of the water increases the amount of the final residue, subject to biological purification.

Case	$V_{D,1a}$ =0 m^3	$V_{D,1a}$ =1 m^3	$V_{D,1a}$ =2 m^3	Base	$V_{D,1a}$ =3 m^3	$V_{D,1a}$ =4 m^3	No recycle
BD	55.95	59.72	60.48	63.41	61.37	64.16	62.36
BED	59.70	61.84	61.35	63.91	64.74	64.90	64.40

Table 4.5. The influence of the amount of fore-cut incinerated on the average recovery (%) of methanol.

4.3. Conclusions

The influence of recycling off-cuts for the batch distillation and batch extractive distillation regeneration of a four component (methanol - THF - water - toluene) waste solvent mixture of a pharmaceutical plant was studied by rigorous dynamic simulation with the CC-DCOLUMN simulator. The variations of the charge composition, of the amount of fresh feed and that of the methanol product were determined for 6 consecutive productions of batch rectification, where the first fore-cut is incinerated, whilst the second fore-cut, the after-cut and (except batches 3 and 6) the (column and condenser) hold-up are recycled. In the batch extractive distillation separation process, fresh water as entrainer was fed into the top of the column during the heating-up period. The profit of the production was calculated on the basis of operational and incineration costs and the price of methanol. The influence of the amount of the first fore-cut on the profit of the whole production process was also investigated. For the traditional batch distillation, the highest profit was achieved when taking of the first fore-cut was continued until the THF concentration in the distillate fell below 20 wt% (incineration of cca. 14 vol% of the charge). By using batch extractive distillation the optimal incinerated volume was 12 vol% of the charge. For both separation processes, a minimum volume of first fore-cut must be taken to avoid the accumulation of THF and toluene in the charge, which would render the 6-batch process infeasible in terms of product purity, although this volume is higher for the batch extractive distillation. In the case of feasible 6-batch processes, the batch extractive distillation provided higher profits than the traditional one, except for one case. The optimal case of the batch extractive distillation process gives a higher profit by 18 % than the optimal case of the traditional process, moreover, the volume of incinerated material is also lower by 12 %, leading to a considerable reduction in air pollution. Although the exact place of the optimum may change with the actual steam and methanol prices, but the general results, as the higher recovery of BED or the existence of minimum first fore-cut volume, do not lose their validity.

CHAPTER 5

The Application of Batch Extractive Distillation for Pharmaceutical Waste Solvent Mixtures

Related publications: Lang et al. (2010, 2011), Hegely et al. (2010b)

In this chapter, the separation of two multicomponent, azeotropic waste solvent mixtures by batch extractive distillation (BED) and a hybrid process (HP) is investigated. Both mixtures contain a main component, which has to be recovered, organic pollutants and water. Some of the azeotropes make the separation infeasible (Section 5.1) or limit the recovery of the main component (Section 5.2). However, water as an entrainer can be successfully applied to solve these problems.

In Section 5.1, posterior simulation of previously performed experiments of traditional batch distillation, BED (a basic and a modified policy), and HP is described (Lang et al., 2010). The effects of operational parameters are also studied.

In Section 5.2, a new BED operational policy is suggested, where entrainer feeding is only applied during the heating-up (Research report, 2012). It is compared to the modified operational policy of BED (entrainer feeding during heating-up and fore-cut) and to traditional batch distillation by laboratory experiments and industrial-size pilot productions. Posterior simulation results are presented, as well.

5.1. Tetrahydrofuran Recovery from a Five-Component Mixture

The performance of the basic and of a modified operational policy of batch extractive distillation and hybrid process for the recovery of tetrahydrofuran (THF) from a five-component waste solvent mixture (methanol, THF, acetonitrile, water, pyridine) was investigated. The hybrid process is a combination of absorption and distillation, and can be considered as a special case of batch extractive distillation. No external reflux is applied, and the highly subcooled entrainer is fed onto the top plate of the column. Therefore, the column comprises only of an extractive section.

The composition of the mixture is methanol (A): 1.5 mass%, THF (B): 86%, acetonitrile (C): 9%, water (D): 1.5% and pyridine (E): 2%. The production of THF with limited content (0.5 mass%) of organic pollutants was infeasible with batch rectification, because of the presence of azeotropes, but it was feasible by BED and HP by using water as entrainer. The goal of the work presented in this section was to simulate and evaluate laboratory experiments of the two policies of BED and HP, and to compare their performance (recovery of THF, energy and entrainer consumption, water content of the product).

5.1.1. Vapour-Liquid Equilibrium Conditions

The vapour-liquid equilibrium conditions of the five-component azeotropic mixture are presented, and the influence of two possible entrainers (water and pyridine) on the relative volatilities is discussed.

5.1.1.1. VLE Data of Components and Azeotropes

For the calculation of vapour-liquid equilibria, the UNIQUAC model was used. The UNIQUAC parameters can be found in Appendix 2. In the case of mixture B-C, which is crucial for the appropriate description of the equilibrium, the literature was contradictive: Gmehling and Bölts (1996) gives the composition of an azeotrope, while the experimental data published by Darwish and Abdallah (2000) indicated that the components do not form azeotrope. Parameters regressed from aforementioned experimental data were used for describing the experimental results. Even though this resulted in a zeotropic B-C mixture, the description of the experimental results became more accurate. Table 5.1 shows the boiling points and compositions of the components and of the seven azeotropes.

Component(s)	T_{BP} (°C)	Composition (mass%)				
		A	B	C	D	E
A-B	59.5	25.9	74.1	-	-	-
A-C	63.6	77.4	-	22.6	-	-
B-C-D	63.7	-	87.8	7.1	5.1	-
B-D	63.89	-	94.7	-	5.3	-
A	64.7	100	-	-	-	-
B-C	65.8	-	88.4	11.6	-	-
B	65.97	-	100	-	-	-
C-D	76.5	-	-	84.2	15.8	-
C	81.6	-	-	100	-	-
D-E	92.6	-	-	-	43	57
D	100	-	-	-	100	-
E	115.2	-	-	-	-	100

Table 5.1. The boiling point and compositions of pure components and azeotropes of the methanol (A), THF (B), acetonitrile (C), water (D), pyridine (E) mixture.

5.1.1.2. The Effect of Entrainers on the Relative Volatilities

The azeotropes A-B, B-C-D, and B-C disturb the production of THF, as the charge composition is located in the batch distillation region (A-B, B-C-D, B-C, B, E), where THF is a saddle point. If maximal separation is assumed, A is removed with A-B unstable node, D with ternary saddle B-C-D, while C with the azeotrope B-C, all of which cause the loss of B. During real operation, the azeotropic compositions are not reached, especially because the boiling points of the azeotropes B-C-D, B-D and B-C are very close to each other. D is not completely removed in the beginning of the operation, and it will appear in the distillate during the production of B (THF), thus it is only possible to produce aqueous B. One possible method for breaking these azeotropes is extractive distillation, in particular because THF is a saddle point in the distillation region where the charge is located. The influence of the addition of water (D) and pyridine (E) – both of which are already present in the mixture and have high boiling points – on the relative volatilities of A-B (α_{AB}) and B-C (α_{BC}) mixtures of azeotropic compositions were studied by VLE calculations. The subsequent separation of either of the entrainers does not pose an additional problem. As it is possible to produce aqueous THF only, a drying step is necessary whether water is used as an entrainer or not. In the case of pyridine, the difference of the boiling point of the entrainer and that of THF is high enough to allow a very easy separation by distillation, if the pyridine content of the product is too high.

Figure 5.1 shows α_{AB} and α_{BC} versus the amount of entrainer added. Both solvents have favourable effects. Both reverse the volatility order in the mixture A-B, rendering B more volatile, and increase α_{BC}. Water has a stronger effect on α_{AB} whereas pyridine has a stronger effect on α_{BC}. However, using water is more practical, as it has a lower molar volume, ensuring a slower accumulation in the reboiler for the same molar amount of entrainer introduced, it is more available, cheaper, and non-toxic. Thus, further investigations are performed only for water.

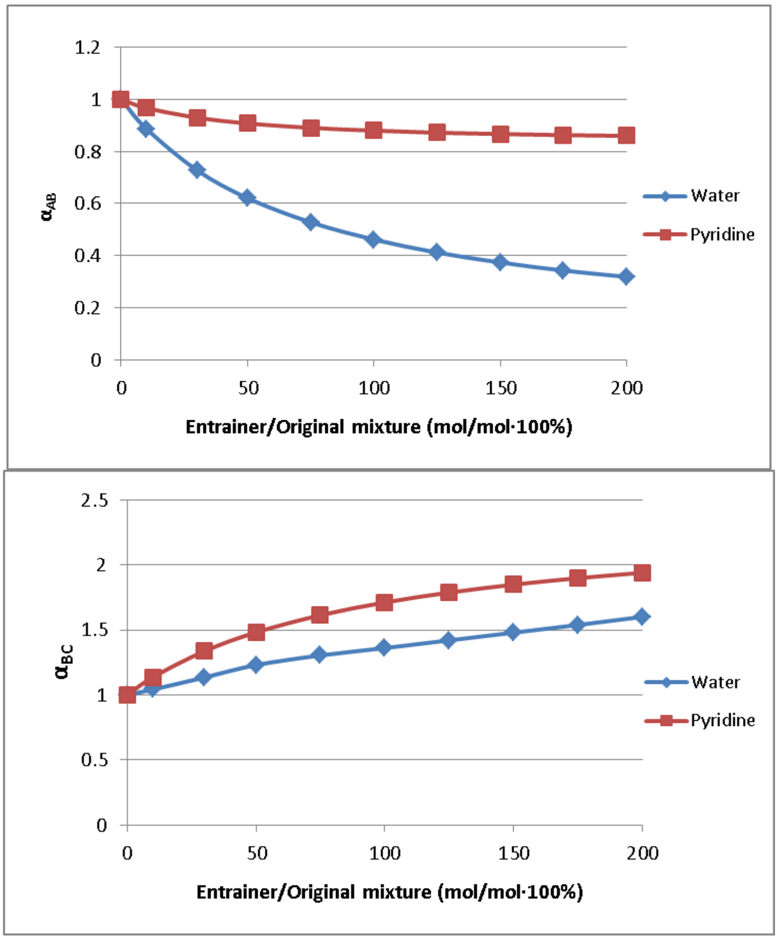


Figure 5.1. The influence of the entrainer on the relative volatilities of A-B and B-C mixtures

5.1.2. The Operation Modes Studied

For the recovery of THF, the basic and a modified policy of BED, as well as the HP were investigated. The operation steps of the basic policy of BED (BEDB) are:

- Step 1: start-up, including

a. warming-up of the charge onto its boiling point,

b. heating-up of the column.

- Step 2: purification step. Components A and C are washed out of the top product by continuous water feeding under infinite reflux ratio (R=∞).
- Step 3: production of aqueous THF under finite reflux ratio and water feeding.
- Step 4: the organic pollutants are stripped off from the reboiler, without water feeding. The aim is to reduce the organic content of the residue, so that it could be sent to biological purification.

The possible ending criteria of the respective steps are:

- Step 1: reaching steady-state operation (constant temperatures).
- Step 2: the sum of the concentrations of A and C at the top of the column falls below the prescribed value.
- Step 3: the concentration of organic impurities (A and C) in the distillate reaches the maximal allowed value.
- Step 4: the organic content of the distillate falls below a low given value (the top temperature is close to 100 °C). This criterion guarantees the prescribed low organic content of the residue.

By the BED modified operation policy (BEDM), suggested by Lang et al. (2006), water feeding is already started during the start-up. In this way, it is possible to extract impurities before their concentration reaches its high, steady-state value, and to decrease the duration of the heating-up. In this case, Step 1 is the heating-up without water feeding; Step 2 is the heating-up with water feeding. Step 1 is ended when the vapour reaches the water feed stage, while Step 2 finishes when the vapour reaches the top of the column.

The hybrid process can also be applied, as no strict limit is prescribed for the water content of the product (Kotai et al., 2007). If water feeding is already started – similarly to the BEDM – during start-up, then Steps 1, 2 and 4 are identical with those of the BEDM. Step 3, the production step of aqueous THF with absorption (R=0) is significantly shorter than the production step of either of the two BED processes. The ending criteria are the same as those for the BEDM.

5.1.3. Experimental Part

In this section, the experiments, which are evaluated with rigorous simulations, are briefly presented (Research report, 2005).

5.1.3.1. Preliminary Simulations

Before starting the experiments, preliminary calculations were done with CC-BATCH dynamic simulator of ChemCAD for BD, basic BED (BEDB) and basic HP. On the basis of the results, the values of the main operational parameters (*R*, flow rate of water) were selected for the experiments. The separation proved to be feasible with the two extractive distillation methods.

5.1.3.2. Experimental Apparatus

The experiments were carried out in a laboratory glass distillation column (Figure 5.2; diameter: 5 cm. The column was filled with PROPAK packing of 0.16 in (0.41 cm) diameter in a height of 153 cm. The still – a round bottom flask of 2 dm^3 – can be heated with a heating basket (nominal heat duty: 400 W). Temperatures were measured at four different column heights, at the top and in the still. In the BED experiments, one of the thermometers was removed during water feeding, and the stub was used as the water inlet point. The analysis was performed by gas chromatography (CHROMPAK with FFAB CB25 mx column). The water content was determined by Karl-Fischer method.

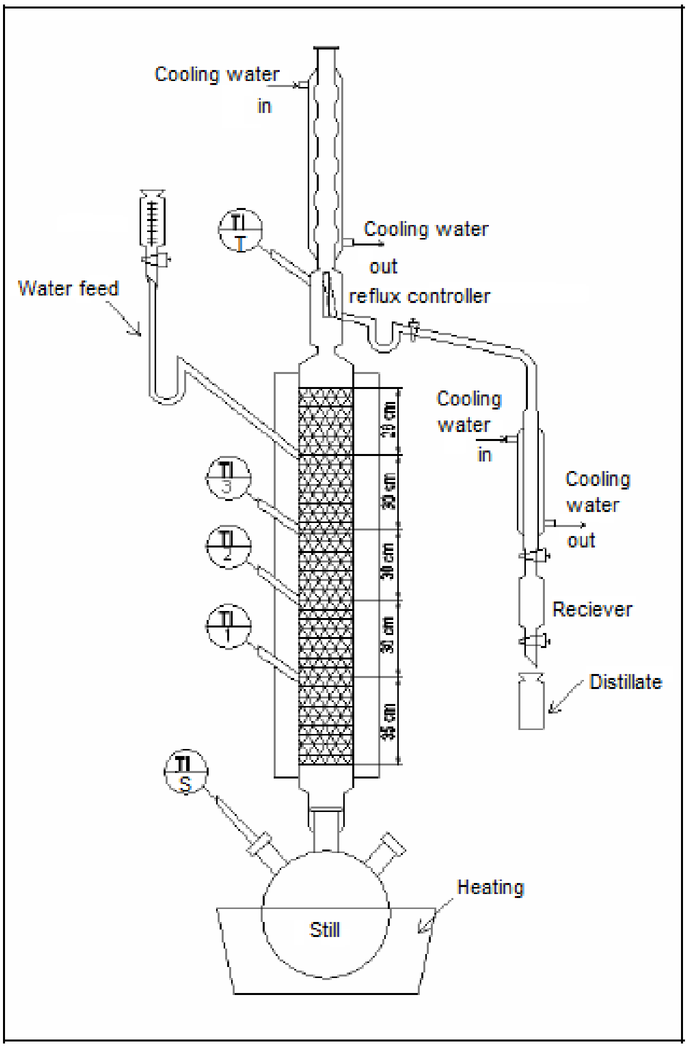


Figure 5.2. The sketch of the laboratory distillation column (BED and HP).

5.1.3.3. Experimental Results

Four experiments were performed. The mass and composition of the charge is shown in Table 5.2. The amount of charge (1 dm^3) and the reflux ratio (R=5) were the same, with the exception of HP. The temperature of the entrainer was approximately 60 °C in the BED experiments, and 18 °C in the HP experiment, respectively. The most important results of the experiments are presented in Table 5.3.

Method	Mass (g)	Composition (mass%)				
		A	B	C	D	E
BD	847.1	1.5	86	9	1.5	2
BEDB	875.2					
BEDM	878.4	0.99	87.28	7.2	1.56	2.81
HP	657.2	1.27	87.34	6.97	1.55	2.86

Table 5.2. The mass and composition of the charge in the laboratory experiments for THF recovery.

Method	Time (min)	Product composition (mass%)			Recovery (%)	*SWC* (kg water/kg product)	Water feeding (dm^3/h)	
		A+C+E	B	D			Step 2	Step 3
BD	535	2.88	91.96	5.15	-	-	-	-
BEDB	363	0.33	94	5.67	70.1	2.23	0.46	0.37
BEDM	310	0.06	93.66	6.11	80.6	1.96	0.44	0.39
HP	168	0.21	92.55	7.01	92	2.32	0.42	0.93

Table 5.3. The most important data of the laboratory experiments for THF recovery.
(BD: traditional batch distillation, BEDB: basic operational policy of BED, BEDM: modified operational policy of BED, HP: hybrid process)

A conventional batch distillation (reference) experiment was carried out to prove that the separation is infeasible with this method. Acceptable product was not obtained at all.

To investigate the applicability of BED, its basic policy (BEDB) was experimentally realized. It produced THF of the prescribed quality with acceptable recovery (70.1 %) under moderate *R* and specific water consumption (*SWC*). *SWC* is defined as the ratio of the mass of the water fed into column and that of the product B.

In the third experiment (BEDM) water feeding was already started during start-up. The concentration of organic impurities in the product was well below the limiting value. The recovery was higher (80.6 %) and the specific water consumption was smaller than by the basic policy.

The fourth experiment was carried out in order to study the HP. During the production the flow rate of water was much higher than that for the BED, as the reflux stream is also provided by the water feeding. THF was produced with very good recovery (92.0 %), with a slightly higher water consumption. The water content of the product was also higher (7 %), which could mean higher drying costs. It was possible to considerably decrease the duration of the separation process (from 310 to 168 minutes). It must be still mentioned, that under the given experimental conditions it was possible to feed water only through the first temperature stub, instead of the top of the column. Hence the number of theoretical stages was reduced by cca. 20 %.

5.1.4. Simulation Results

Posterior calculations were performed with the CC-DCOLUMN dynamic professional flow-sheet simulator. Contrary to CC-BATCH by this module the heating-up of the column (with continuous water-feeding) can be also simulated.

5.1.4.1. Simulation Method

The following simplifying assumptions were used:

- theoretical plates,
- constant liquid hold-up on the plates,
- negligible vapour hold-up,
- negligible pressure drop,
- perfect mixing on the plates and in the vessels.

The model of the HP is presented in Figure 5.3. The only difference between the models of BED and HP is that in the case of BED reflux and water streams are fed separately into the column. The encircled numbers identify the respective unit operations. The model consists of the column (SCDS, 1), the condenser (Heat Exchanger, 8), four Dynamic Vessels (2: still, 3-5: receivers), two Mixers (10, 11), two Time Switches (6, 7) and a Divider (9), in which reflux ratio can be set. For HP, the Divider is used only to change between total reflux and no reflux operation. Stream No. 19 is the water feeding.

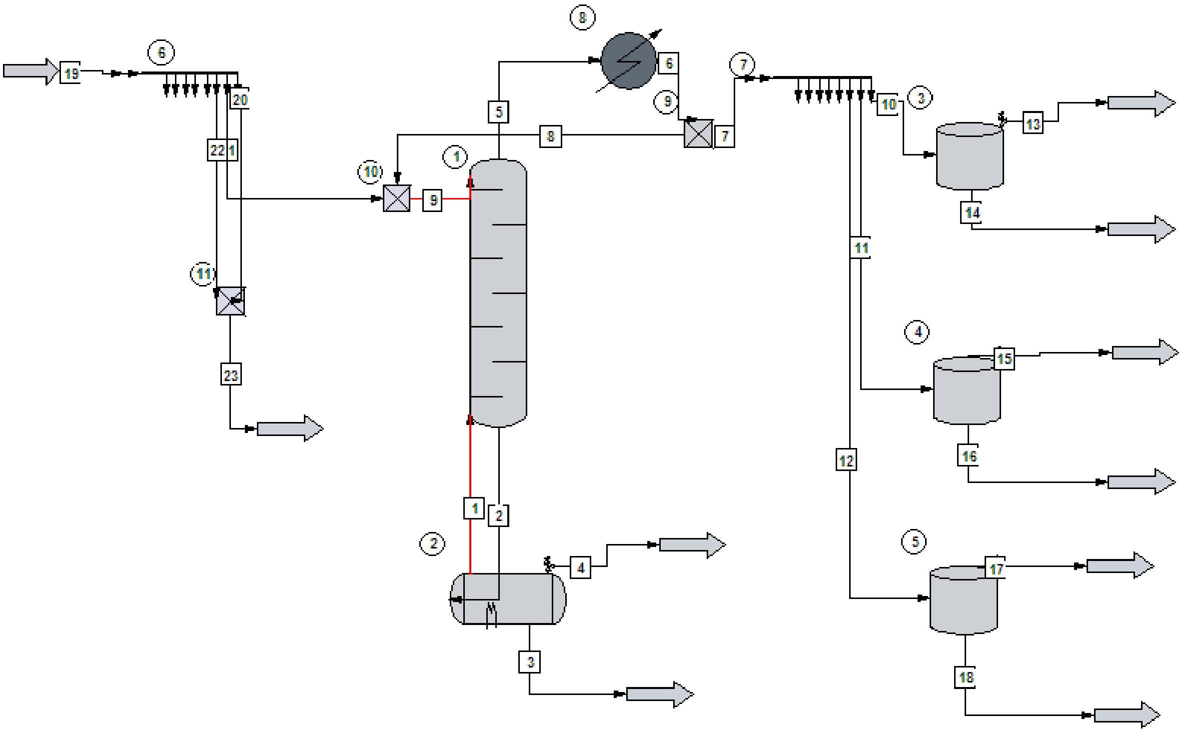


Figure 5.3. The CC-DCOLUMN model of hybrid process.

5.1.4.2. Posterior Simulation Results

The posterior simulation of BED and HP experiments were performed on the basis of the distillate's measured mass flow rate. The number of theoretical plates was estimated at 22 (BED) and 17 (HP), respectively, on the basis of previous experiments. The feed stage of the water was considered to be the seventh (BED) and first (HP) plate from the top. At the beginning of the simulation the plates were dry. The value of the estimated liquid hold-up was 15 cm^3 per theoretical plate. The experiments were divided into phases with similar magnitude of distillate flow rate. Average heat duties were estimated for each phase with CC-BATCH, and were thereafter used in the CC-DCOLUMN simulations. The cut volumes calculated were in good agreement with the measured ones. Description of the experiments was made more difficult by several factors: the approximate description of VLE conditions, the varying water flow rate, and the uncertainty in the number of theoretical plates.

The recoveries calculated (Table 5.4) are in good agreement with the experimental ones. The total organic impurity content is slightly higher than the measured value in the case of BED experiments, which allows a safe estimation of the experimental quality. However, in the case of HP, the measured impurity concentration (0.21 %) was found to be higher. The specific energy consumption (*SEC*), defined as the ratio of the total heat transferred in the reboiler and the mass of the product, is the highest by HP. Figure 5.4-5.6 shows the evolution of the measured and calculated distillate composition (without Step 4) for the BED and HP experiments, which are in good agreement, especially for Step 3.

	Recovery (%)	Organic impurities in the THF (mass%)	SEC (MJ/ kg product)
BED basic	69.4	0.73	8.66
BED modified	79.4	0.65	5.85
HP	89.1	0.09	2.61

Table 5.4. The results of posterior simulations of the laboratory experiments for THF recovery from a five-component THF rich waste solvent mixture by using the experimental values of the operational parameters and the same step durations.

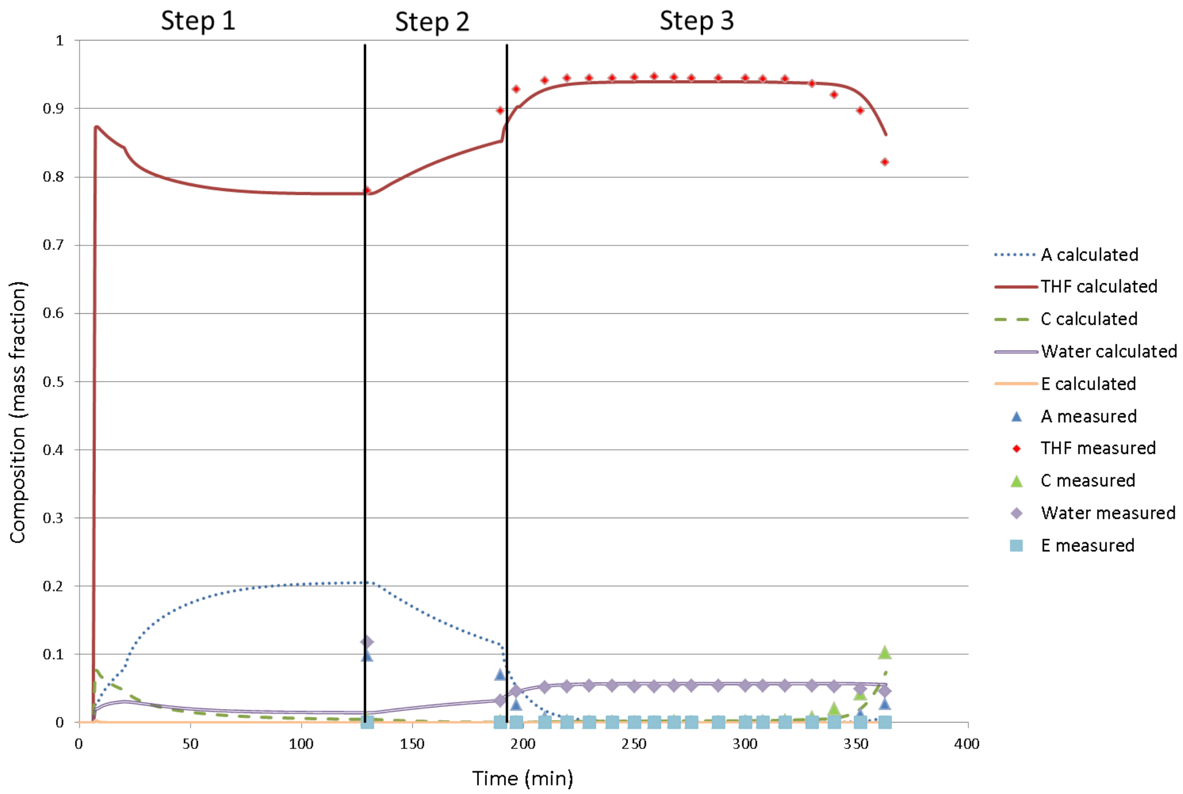


Figure 5.4. Evolution of the measured and calculated distillate composition for the regeneration of THF from a five-component waste solvent mixture using BEDB.

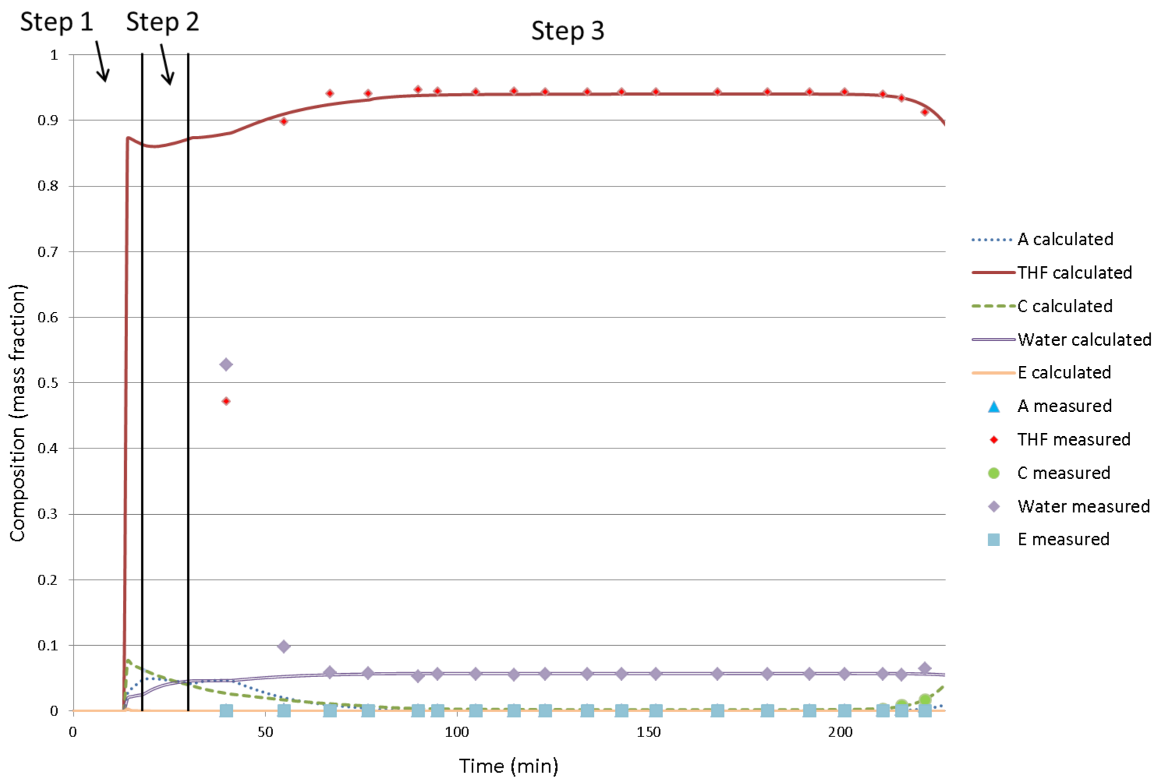


Figure 5.5. Evolution of the measured and calculated distillate composition for the regeneration of THF from a five-component waste solvent mixture using BEDM.

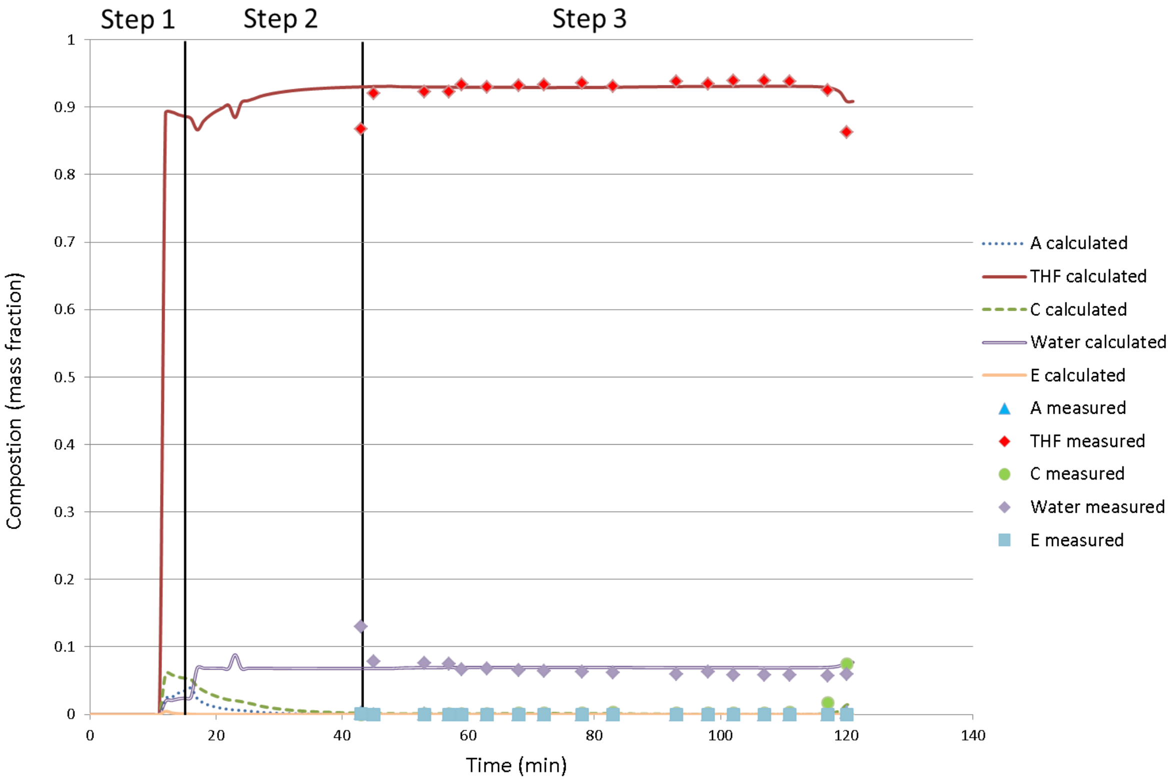


Figure 5.6. Evolution of the measured and calculated distillate composition for the regeneration of THF from a five-component waste solvent mixture using HP.

5.1.4.3. The Effect of Operational Parameters

The effect of operational parameters on the recovery, specific energy (*SEC*) and water consumption (*SWC*) were investigated for the BEDM and HP. The parameters studied were: the location of feed stage (*f*), the reflux ratio (only in the case of BEDM), and the water flow rate during heating-up (W_1) and production (W_2). The basic value of the parameters was the experimental one. The consumptions are calculated until the end of the main cut. The calculations were performed with constant heat duties in the reboiler. The detailed numerical results of the calculations can be found in Appendix 3.

By BED, the maximal allowed concentration of organic impurities was 0.65 mass% that corresponds to an acceptable experimental purity. The duration of heating-up was 40 minutes. The main-cut is started when impurity content of the distillate has fallen below the limiting value. The results using the base parameters: recovery: 72.8 %, *SEC*=5.1 MJ/kg, *SWC*=2.7 kg/kg. The effects of the increase of parameters are summarized in Table 5.5. The effect of the parameters is expressed in the case of the location of feed (*f*) as the relative change (in %) caused by the increase of *f* by one; in the case of the other variables, as the relative change (in %) caused by the increase of the parameter by 100 %. The location of feed plate (*f*) has the greatest effect (Figure 5.7): if water is fed to the top plate, the recovery increases to 90.9 %, though the water content of the product is also higher. *R* has an optimal value (4.0), where recovery is maximal and *SWC* is minimal, however its influence is slight. The recovery increases with both flow rates, but its growth is relatively small compared to that of the *SWC*. *SEC* has a shallow optimum at a flow rate of W_2=0.5 dm^3/h.

Parameter	Recovery	*SEC*	*SWC*
f	-3.0% – -4.8%	2.6% – 3.2%	2.8% – 3.9%
R	maximum	35.0% - 73.1%	minimum
W_1	0.2% – 5.9%	minimum	3.3% - 18.2%
W_2	2.4% - 25.8%	minimum	69.4% - 99.0%

Table 5.5. The effect of the increase of parameters for the BED process of a five-component THF rich waste solvent mixture (*f*: the relative change caused by the increase of *f* by one; *R*, W_1, W_2: the relative change caused by the increase of the parameter by 100 %).

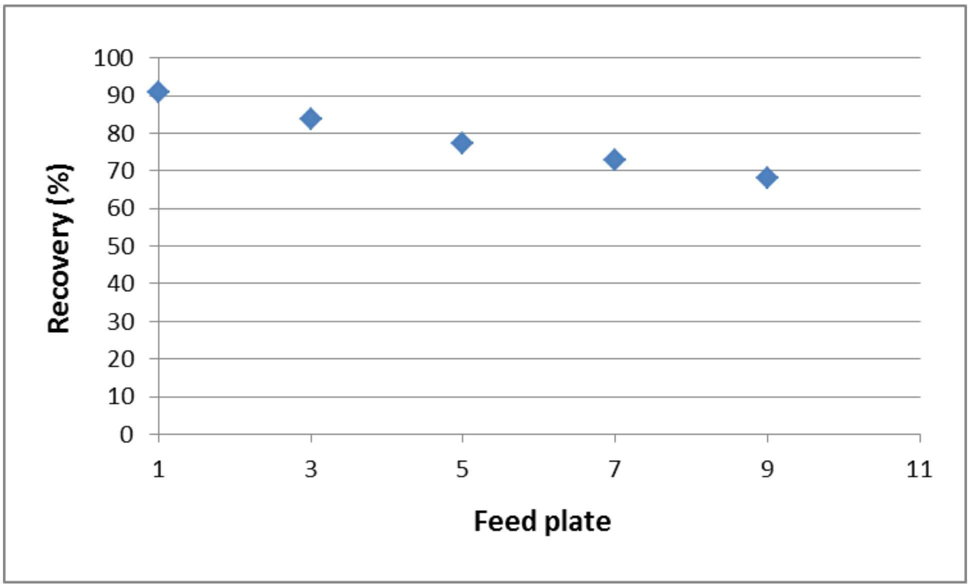


Figure 5.7. The effect of water feeding plate on the recovery of THF in the BED process of a five-component THF-rich waste solvent mixture (W_1=0.44 dm^3/h, W_2=0.39 dm^3/h).

On the basis of the above investigation, modifications in the values of operational parameters were suggested. For *f*=1 and *R*=4, recovery increases considerably (to 96.1 %). At the same time, both specific consumptions are reduced: *SEC*=3.7 MJ/kg, *SWC*=1.9 kg/kg. The water content of the product (6.8 %), however, is almost as high as in the case of HP (6.9 %).

Since under the experimental conditions available in the plant, it is not possible to feed the water higher than plate 7, we can state that the experimental parameters were well chosen.

In the case of HP, the total concentration of organic impurities was limited to 0.5 mass%. The duration of heating-up was 43 minutes. Fore-cut was unnecessary. The results of the base case: recovery is 98.1 %, *SEC*=2.0 MJ/kg, *SWC*=2.8 kg/kg. With the increase of the flow rates, the specific consumptions increase, while the change in recovery is very small (Table 5.6). The effect of the parameters is expressed as the relative change (in %) caused by the increase of the parameter by 100 %. As a function of W_1, both recovery and *SEC* have an optimum at the value of 0.25 dm^3/h, but the change in recovery is so small, that it can almost be considered as constant. Recovery slightly increases with W_2, but the growth of *SEC* and *SWC* is much higher. At the expense of a small decrease in recovery, it is possible to decrease the specific consumptions. It can be concluded that the experimental parameters were well chosen, only a slight decrease of W_1 would be advisable.

Parameter	Recovery	*SEC*	*SWC*
W_1	maximum	minimum	5.3% - 46.4%
W_2	1.3% - 6.5%	93% - 269%	239% - 572%

Table 5.6. The effect of the increase of parameters for the HP process of a five-component THF rich waste solvent mixture (the relative change caused by the increase of the parameter by 100 %).

5.1.4.4. Comparison of Batch Extractive Distillation and Hybrid Distillation

Comparing the modified policy of BED (which proved to be the better of the two BED policies) and HP (Table 5.7), using the modified operational parameters, we found that the recoveries of the two methods are very close. At the expense of higher specific water consumption and the higher water content of the product, HP is capable of considerably faster production, and thus much lower specific energy consumption.

Method	Recovery (%)	*SEC* (MJ/kg product)	*SWC* (kg water/ kg product)	Time consumption (min)
BEDM	96.1	3.7	1.9	244
HP	98.1	2.0	2.7	144

Table 5.7. The comparison of BED (modified policy) and HP for the regeneration of THF from a five-component THF rich waste solvent mixture.

5.2. Methanol Recovery from a Seven-Component Mixture

The recovery of methanol from a multicomponent aqueous waste solvent mixture containing acetone (A), methanol (B), tetrahydrofuran (C), n-hexane (D), ethanol (E), water (F) and toluene (G) was studied. The separation of this mixture was already discussed in Chapter 4, from the point of view of off-cut recycling, without considering then the acetone, the n-hexane and the ethanol content. The methanol purity required is 99.5 mass%. The components form several minimum azeotropes, which limit the recovery of methanol by traditional batch distillation (BD).

The addition of water decreases the relative volatility of both methanol-THF and methanol-toluene. Therefore by feeding water as entrainer, the methanol loss can be decreased. The usual application of BED is to extract pollutants of moderate concentration from beside the main component to be recovered. In some cases, the effect of the entrainer is the contrary, as it reduces the volatility of the main component, which is extracted from beside the pollutants of low concentration forming minimum azeotropes with it. These pollutants must then be removed in fore-cuts. The loss of the main component in the fore-cuts can be decreased by BED. However, the high amount of entrainer fed renders the separation of the main component from it more difficult. Thus, the application of BED can be even uneconomical.

The feeding of the entrainer can be started after the start-up of the column, or during the heating-up, as early as the vapour reaches the location of the feed, as suggested by Lang et al. (2006).

The aim of this chapter is to present a new batch extractive distillation policy (BED1, Lang et al., 2012b), where the entrainer feeding is only applied during the heating-up of the column, and the entrainer extracts the main component from beside the polluting components, removed in the fore-cuts. Another BED policy (BED2) is also investigated, where water feeding is started during the heating-up, but it continues during the fore-cut, as well. This is identical to BEDM described in Section 5.1.

Laboratory experiments were carried out in a packed column in order to compare the BD and the two BED operational policies. Industrial-size pilot productions of BD and BED1 in a 50 bubble cap tray column were also performed. The rigorous dynamic simulation of the laboratory experiments and pilot productions was made with CC-DCOLUMN dynamic module of the flowsheet simulator ChemCAD.

5.2.1. Vapour-Liquid Equilibrium Conditions

The vapour-liquid equilibrium conditions of the seven-component azeotropic mixture are presented. For the calculation of vapour-liquid equilibria, the UNIQUAC model is used, the parameters can be found in Appendix 2. First, the boiling points of pure components and azeotropes are given, and then the influence of water on the relative volatilities B-C and B-G is investigated.

5.2.1.1. VLE Data of Components and Azeotropes

The mixture contains methanol (B) as main component, two organic pollutants in moderate concentrations (THF (C) and toluene (G)), water (F), and three organic pollutants (acetone (A), n-hexane (D) and ethanol (E)) in very low concentration (less than 0.5 mass% together). Though the latter three components form azeotropes, they do not cause a notable loss of B. Therefore, we will focus on the four components with higher concentration, although all the components are included in the simulation. The boiling points of these components and their azeotropes, together with the azeotropic compositions are given in Table 5.8. The azeotrope F-G is heterogeneous.

Component	T_{BP} (°C)	Composition (mass%)			
		B	C	F	G
B – C	59.5	30.0	70.0	-	-
B – G	63.6	71.5	-	-	28.5
C – F	63.9	-	94.3	5.7	-
B	64.7	100	-	-	-
C	65.97	-	100	-	-
F – G	84.4	-	-	19.7	80.3
F	100.0	-	-	100	-
G	110.6	-	-	-	100

Table 5.8. Boiling points and compositions of the four most important components and their azeotropes in the acetone (A), methanol (B), tetrahydrofuran (C), n-hexane (D), ethanol (E), water (F) and toluene (G) mixture.

The recovery of B is decreased by the azeotropes B–C and B–G. C and G are removed in the fore-cut, causing a significant loss of methanol. Although the boiling point of the azeotrope C–F is also lower than that of B, C is entirely removed with the first azeotrope (B-C).

5.2.1.2. The Influence of Water on the VLE Conditions

The influence of water (F) as a potential entrainer on the relative volatilities of azeotropic B–C ($\alpha_{B,C}$) and B–G ($\alpha_{B,G}$) mixtures was investigated (Tables 5.9a-b). Water is readily available as a fresh feed, and as it is already present in the mixture at high concentration, no new component is introduced into the system.

a.

m_B (kg)	m_C (kg)	m_F (kg)	$\alpha_{B,C}$
30	70	-	1
“	“	25	0.535
“	“	50	0.380
“	“	100	0.259

b.

m_B (kg)	m_F (kg)	m_G (kg)	$\alpha_{B,G}$
71.5	-	28.5	1
“	25	“	0.430
“	50	“	0.354
“	100	“	0.266

Table 5.9. The influence of water on the relative volatility of azeotropic methanol (B) – THF (C) (a) and methanol (B) – toluene (G) (b) mixtures.

The addition of a moderate amount of water moves both relative volatilities away from 1.0 considerably. The B–C volatility order is reversed, and the azeotrope B-C disappears at a moderate water concentration (Figure 5.8, x_F≈45 mol%). It can be also noted that the effect of water on the A–B and B–D equilibria is favourable, as well: $\alpha_{A,B}$ increases and $\alpha_{B,D}$ decreases.

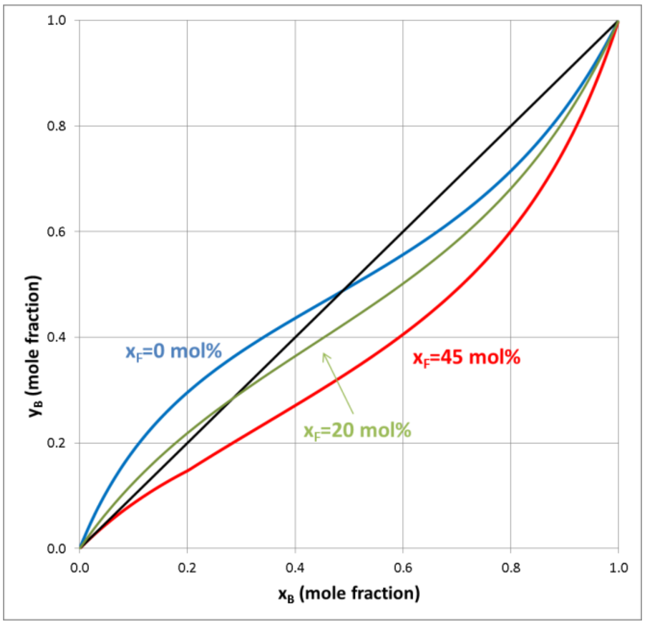


Figure 5.8. The effect of water (F) on the vapour-liquid equilibrium line of the mixture B-C.

Based on the above results, the BED using water as entrainer seemed to be suitable for removing C and G in the fore-cuts more efficiently (with lower loss of B) than the BD.

5.2.2. Separation Methods

Three separations methods were studied:

1. Traditional batch distillation (reference experiment based on the actual technology)
2. BED with entrainer fed only during the heating-up of the column, then traditional rectification (BED1)
3. BED with entrainer fed during both the heating-up of the column and fore-cuts, then traditional rectification (BED2)

The steps and their stopping criteria are shown in Table 5.10, where F_F denotes the flow rate of water, x_D the condensate composition, respectively. The aim of taking fore-cuts is the removal of C and G. Two fore-cuts are taken, the first one is incinerated, and the second one, whose C and G content is lower, is recycled to the next batch in order to reduce the loss of B. During the main-cut, B of high purity is obtained. The goal of taking an after-cut is to reduce the loss of B, as it is recycled to the next batch, and to decrease the organic content of the bottom, respectively. The production process is described in more details in Chapter 4.

Step	Batch distillation	BED 1	BED2
1.	Heating-up of the column $R=\infty$	Heating-up with water feeding $R=\infty$, $F_F > 0$ after vapour reaches the feed plate	
Stop. crit.	Reaching steady state	$x_{D,B}$ stops decreasing	
2.	Fore-cuts High R	Fore-cuts without water feeding High R, $F_F = 0$	Fore-cuts with water feeding High R, $F_F > 0$
Stop. crit.	$x_{D,C}$ decreases to a prescribed value		
3.	Main-cut Moderate R		
Stop crit.	$x_{D,F}$ increases (top temperature increases)		
4.	After-cut High R		
Stop crit.	Bottom temperature approaches the boiling point of water		

Table 5.10. The steps and the stopping criteria of the steps for the separation methods studied for methanol (B) regeneration from a waste solvent mixture (C: THF, F: water).

By using the two BED policies, $x_{D,B}$ gradually decreases during the heating-up (Step 1), while $x_{D,C}$ increases. When the C concentration hardly changes, Step 2 is started (t_1). Contrary to BD where steady state (constant temperatures and compositions in the column) is reached at the end of Step 1 because of the total reflux and the lack of external feed, there is no steady state at the end of Step 1, but the decrease and stabilisation of the temperatures in the middle section of column indicates the change in the composition. At the end of Step 2, $x_{D,C}$ decreases to its prescribed value, which is indicated by the increase of the top temperature onto a value close to the boiling point of B, except BED2, where it is slightly higher due to the water content of the distillate. By BED2, water feeding further dilutes the mixture from which B will be recovered in Step 3, and can also increase the amount of the fore-cut. It is possible to introduce an additional step for BED2, between Steps 2 and 3, in order to reduce the water content of the distillate. In this additional step, total reflux operation without water feeding is applied until the water concentration decreases to an acceptable level, indicated by the decrease of top temperature.

5.2.3. Laboratory Experiments

For each separation method, one laboratory experiment was performed at atmospheric pressure in the laboratory glass column described in Section 5.1.3. Temperatures were measured at four different column heights, at the top and in the still. In the BED experiments, one of the thermometers was removed during water feeding, and the stub was used as the water inlet point. The flow rate of the water feeding (T≈25 °C) was determined by preliminary simulations. The analysis of the organic compounds was performed by gas-chromatograph (Varian CP3800, column: CP-Sil-5CB; length: 30 m, diameter: 0.32 mm). The water content was determined by Karl-Fischer method.

5.2.3.1. Batch Distillation Experiment

The first experiment was made by running a traditional batch distillation, without after-cut. The amount of the charge was 886.4 g, its composition: 0.04 mass% A, 58.2 % B, 1.82 % C, 0.14 % D, 0.11 % E, 38.8 % F, 0.88 % G. The heating-up lasted 154 min. The reflux ratios were 5.5 during the fore-cut (102 min) and 2.2 during the main-cut (84 min). The cuts were taken in the form of fractions. Based on the results of the chemical analysis, many fractions of the fore-cut were considered to be already part of the main-cut due to their high B content. The recovery of B was 67.4 % with a purity of 99.8 mass%. At the end of the experiment, the still level decreased drastically, a great part of the heating surface became dry, and the experiment was stopped, because of the steep temperature increase in the still.

5.2.3.2. BED1 Experiment

The second experiment was made by BED1. The charge had the same composition as in the previous experiment, but its mass was higher (1332.0 g). Water feeding was started after 31 min of operation and lasted for 61 min with a flow rate of 274 cm^3/h. The reflux ratios were 5.6 during the fore-cut (69 min), 2.2 during the main-cut (158 min), and 5.7 during the after-cut (12 min). The B recovery was 95.0 % with a purity of 99.8 mass%, by the addition of 279 cm^3 water, which did not increase the liquid volume in the still. Figure 5.8 shows the evolution of the measured top vapour composition (time zero is the start of water feeding). The $x_{D,B}$ was moderate during the heating-up and started to increase rapidly during the main-cut, while $x_{D,C}$ decreased and $x_{D,G}$ had a maximum. The main-cut was finished when $x_{D,E}$ and $x_{D,F}$ in the distillate began to rise.

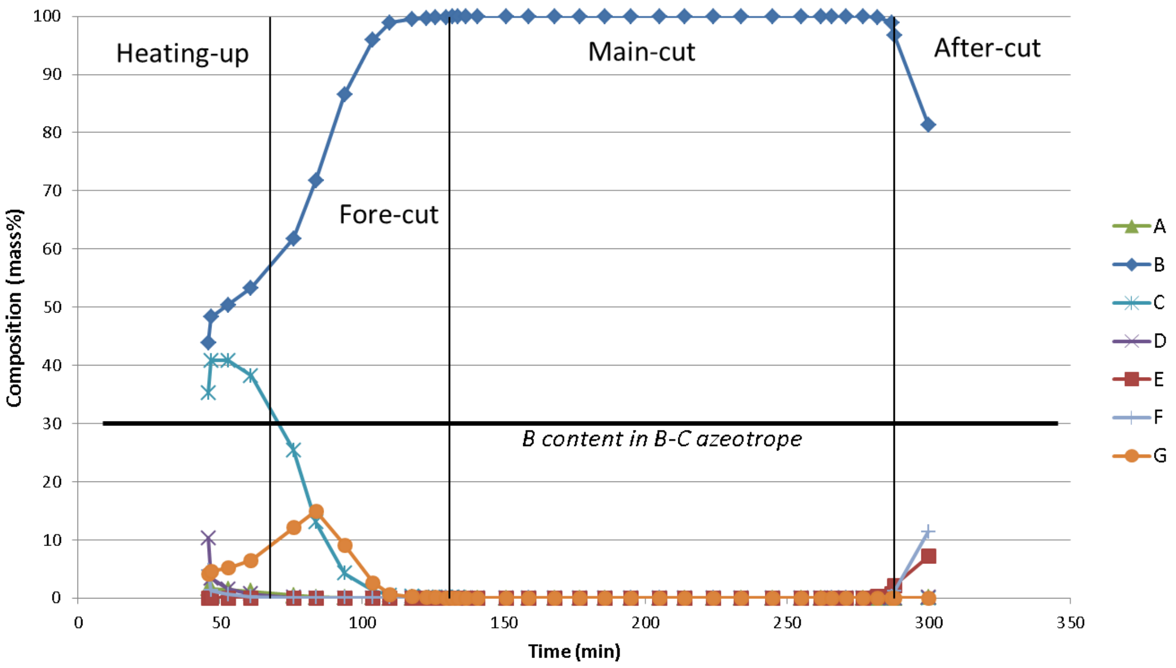


Figure 5.8. The evolution of measured top vapour composition of the BED1 laboratory experiment for the regeneration of methanol from a waste solvent mixture
(A: acetone, B: methanol, C: THF, D: n-hexane, E: ethanol, F: water, G: toluene).

5.2.3.3. BED2 Experiment

The third experiment (BED2) was performed with a mixture of slightly different composition (0.04 % A, 59.2 % B, 1.84 % C, 0.04 % D, 0.07 % E, 37.2 % F, 0.90 % G), whose mass was 1111.4 g. Water feeding was started after 25 min with a flow rate of 286 cm^3/h. After 50 min of water feeding, the taking of fore-cut fractions was started and the flow rate was reduced to 205 cm^3/h. The reflux ratio was 5.5 during the fore-cut (58 min). Between the fore-cut and the main-cut, a 32 min long period of total reflux operation without water feeding was applied. The average reflux ratio was 2.1 during the main-cut. The same value was applied during the after-cut (11 min), as well. The recovery was 83.4 % (with a purity of 99.6 mass%), which is higher than that of the BD experiment, but lower than that of BED1, even though the amount of water fed was higher (436 cm^3). Once again, the water feeding did not increase the still liquid volume.

Both BED experiments highlighted an additional advantage of BED, namely that the heating surface of still was covered by liquid even at the end of operation, unlike BD where it became partially dry.

5.2.4. Rigorous Simulation of Laboratory Experiments

The rigorous dynamic simulation of the laboratory experiments was performed using the ChemCAD professional flow-sheet simulator. The charge data, the reflux ratios, and the duration of the operation steps were set based on the measured values. The heat duty of the different steps was calculated on the basis of the measured average distillate flow rate and the reflux ratio. The theoretical plate number was taken as 14, including the still, the feed location was the fourth plate (counted from the top). For column hold-up, the value of 15 cm^3/plate was used. The hold-up and theoretical plate number were determined by previous experiments.

Figure 5.9 presents the evolution of the calculated top vapour composition for BED1. The results show an acceptable agreement with the measured values. The greatest differences can be observed in the heating-up period. The $x_{D,C}$ shows good agreement, but the calculated $x_{D,B}$ is much lower. This can be explained by higher $x_{D,G}$ and surprisingly high $x_{D,D}$. However, the low $x_{D,D}$ values measured could be explained by the influence of sampling. The first sample, which has a high (10.3 mass%) D content, contains approximately half of the total amount of D in the mixture.

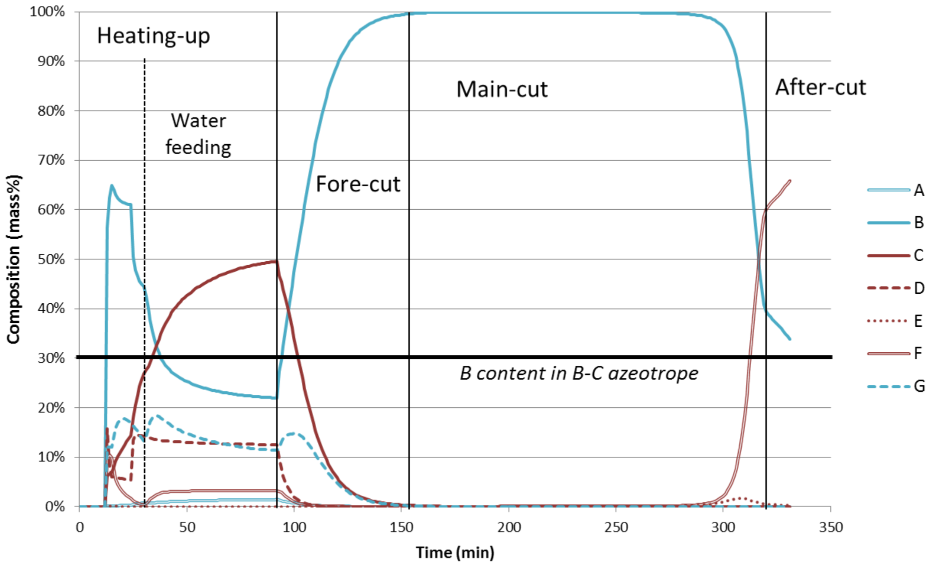


Figure 5.9. The evolution of calculated top vapour compositions (BED1) with simulation based on laboratory experiment values.

The effect of water feeding can be clearly seen on the $x_{D,B}$ curve at the end of the heating-up period (t_1), that is, at the start of production: it is 39.4 % by BD, while only 21.9 % and 27.9 % by BED1 and BED2. To compare the measured and calculated recoveries, the values without correction are used, that is, the original classification of the fractions as fore- or main-cut is respected. The calculated values are close to the measured ones (Table 5.11), although they are lower in all the cases. The order of the separation methods is the same, that is, the greatest recovery can be obtained by BED1, while BD is the least effective.

Method	Measured (%)	Calculated (%)
BD	53.6	52.7
BED1	84.2	75.1
BED2	70.9	69.3

Table 5.11. The calculated and measured recoveries of the laboratory experiments for the regeneration of methanol from a waste solvent mixture.

5.2.5. Industrial-Size Pilot Productions

After the favourable results of the laboratory experiments, two industrial-size pilot productions were performed, the first by traditional batch distillation, and the second by BED1. The main data of the industrial column: number of bubble cap plates: 50, internal diameter: 1.25 m, volume of the reboiler: 25 m^3, surface of the reboiler: 50 m^2, surface of the condenser: 100 m^2. The reboiler was heated with steam of 5 bar. The holdup of the condenser is 0.5 m^3, that of the column: 1.5 m^3. Based on preliminary calculations and the possibilities available, water (1.1 m^3/h, no preheating) was fed into the reflux stream.

The results for the BD production can be seen in Table 5.12. B was produced with a high purity (99.85 mass%) and a recovery of 68.5 %. The $x_{D,B}$ at t_1 (22.87 mass%) was already lower than the B content in the B-C azeotrope, and much lower than it was in the laboratory experiment (52.2 %). This can be explained by the accumulation of the low concentration organic pollutants in the condenser, as a result of the higher relative hold-up of condenser (2 vol% of charge) and higher theoretical plate number of the industrial column. Consequently, the relative loss of B in the fore-cuts was also lower than in the laboratory experiment. The composition of the condensate was also measured after t_3=590 min of fore-cut. At this moment, the methanol concentration is already high. The mass of the final residue, calculated from the material balance, was 15000 kg.

	Duration (min)	R	Mass (kg)	A (mass%)	B	C	F	G
Charge	-	-	23525	0.06	33.32	4.38	61.40	0.83
Heating-up	220	∞	-	-	-	-	-	-
Condensate at t_1	-	-	-	1.78	22.87	71.04	0.06	0.69
Condensate at t_3	-	-	-	0.04	98.78	1.03	0.03	0.13
Fore-cuts	650	7.33	2472	0.00	49.56	42.16	0.14	6.85
Main-cuts	740	2	5379	0.00	99.85	0.00	0.04	0.01
After-cut	105	3	674	0.00	81.74	0.00	17.55	0.07

Table 5.12. Results of the industrial-scale BD experiment
(A: acetone, B: methanol, C: THF, F: water, G: toluene).

By the industrial-scale BED1 experiment (Table 5.13), water feeding was started during the heating-up, after 55 min of operation. B was produced with increased recovery (73.1 %), and in a very high purity (99.93 mass%). $x_{D,B}$ was significantly lower (1.82 %) at the end of the heating-up period (t_1) than by the BD production, due to the water feeding that increased the concentration of C, G and water in the condensate, as well. Consequently, the relative loss of *B* with the fore-cut was reduced from 15.6 % to 12.1 %. Because of the high position of water feeding, $x_{D,F}$ was high during the taking of fore-cut, and thus the water content of the fore-cut was also much higher than by BD.

The composition of the condensate was also measured after t_2=455 min of fore-cut, and at the end of the fore-cuts (t_4), as well. The water concentration was just as low as for the BD production at t_3, which means that after finishing water feeding, the water content of the condensate quickly decreased. At t_4 the A concentration was also very low, although the distillate still contained nearly 1 % of C.

BED had a lower specific energy demand than BD, since its recovery is higher, while the operation times are almost equal. The specific water consumption (the ratio of the mass of the water introduced and that of the main-cut) was 0.43 kg/kg. The mass of the final residue, calculated from the material balance, was 16380 kg, which means a moderate increase (9.6 %) compared to BD.

	Duration (min)	*R*	Mass (kg)	A (mass%)	B	C	F	G
Charge	-	-	23320	0.07	37.14	4.89	56.3	1.56
Heating-up	205	∞	-	-	-	-	-	-
Condensate at t_1	-	-	-	1.44	1.82	78.43	7.4	8.85
Condensate at t_2	-	-	-	0.2	95.28	3.73	0.03	0.67
Condensate at t_4	-	-	-	0.05	98.78	0.95	0.03	0.09
Fore-cuts	575	5.25	2779	0.00	37.88	42.90	3.88	16.37
Main-cuts	840	2	6328	0.01	99.93	0.00	0.04	0.00
After-cut	85	2	583	0.00	83.68	0.00	15.1	0.02

Table 5.13. Results of the industrial-scale BED experiment
(A: acetone, B: methanol, C: THF, F: water, G: toluene).

5.2.6. Rigorous Simulation of Industrial-Size Pilot Productions

The posterior simulation of the pilot productions were performed by the CC-DCOLUMN dynamic simulator of ChemCAD. The temperature of the charge was taken as 15 °C. The durations of the operation step were the same as in the pilot production, and the heat duty of the reboiler was adjusted in each step in order to obtain the measured volume of the cuts. The heating-up period was divided into two parts: in the first one, the charge was warmed up to its boiling point; in the second one, the column operated under total reflux. For the latter part, the same heat duty was used as for the fore-cut (BD), or it was estimated on the basis of the measured condensate flow rate (BED). The calculations underestimated the methanol purity and recovery, probably because of the difficulties in describing the multicomponent equilibria of the system. In order to obtain a product of the purity prescribed, a higher amount of fore-cut, and a lower amount of main-cut had to be taken.

5.2.6.1. BD Production

The heat duties applied are given in Table 5.14, while Table 5.15 contains the mass and composition of different cuts, and the composition of the condensate at different times (t_1 and t_3).

	Heat duty (MJ/h)
Heating-up, 1st part	3100
Heating-up, 2nd part	1750
Fore-cuts	
Main-cuts	1300
After-cut	2000

Table 5.14. The heat duties in the simulation of industrial-size BD experiment.

The calculated concentrations clearly show that the separation task is more difficult in the simulation. At t_1, $x_{D,B}$ is higher; during the fore-cut, at t_3, it is lower than the concentration measured. This means that $x_{D,B}$ – time function is less steep, and this results in an increased B content in the fore-cut, as well. The recovery of B is 60.2 %, which is also lower than the measured one (68.2 %). The specific energy consumption (the ratio of the total heat transmitted in the reboiler and the mass of the main-cut) is 9.95 MJ/kg.

	Mass (kg)	A (mass%)	B	C	F	G
Condensate at t_1	-	0.96	35.95	57.28	0.62	5.20
Condensate at t_3	-	0.11	92.15	5.08	0.00	2.62
Fore-cuts	2758	0.48	56.99	35.84	0.03	6.65
Main-cuts	4741	0.00	99.50	0.31	0.03	0.14
After-cut	652	0.00	87.95	0.00	12.05	0.00

Table 5.15. Results of the posterior simulation of industrial-size BD experiment
(A: acetone, B: methanol, C: THF, F: water, G: toluene).

5.2.6.2. BED Production

The temperature of the water feeding was estimated as 15 °C. The heat duties applied are given in Table 5.16, while Table 5.17 contains the mass and composition of different cuts, and the composition of the condensate at different times (t_1 and t_3).

	Heat duty (MJ/h)
Heating-up, 1st part	3850
Heating-up, 2nd part	1770
Fore-cuts	1505
Main-cuts	1390
After-cut	1630

Table 5.16. The heat duties in the simulation of industrial-size BED experiment.

At the end of the heating-up (t_1), the calculated and the measured condensate concentrations show an acceptable agreement, except for G, whose calculated concentration is well below the measured one. The higher concentration of A and C shows a more significant effect of water feeding. At t_2, however, the calculated $x_{D,G}$ is significantly higher than the measured one. These results suggest that the concentration change of G might be shifted in time, and the calculated $x_{D,G}$ – time function has its maximal value at a later moment of time.

The water concentration shows the same behaviour as in the pilot production, that is, after the end of water feeding, the condensate is quickly depleted in water. Nevertheless, the measured water content of the fore-cut is higher.

The methanol concentrations, both in the condensate and in the cuts, are underestimated. Therefore, the calculated recovery is also lower (66.3 %) than the measured one (73.1 %). The difference between the recoveries of BD and BED is higher by the simulation (6.1 instead of 4.6 percentage point), hinting at a more significant effect of water feeding in the simulation.

The specific energy consumption of BED is 7.81 MJ/kg, which means a considerable decrease (27.4 %) compared to BD. The calculated specific water consumption is 0.48 kg/kg.

	Mass (kg)	A (mass%)	B	C	F	G
Condensate at t_1	-	3.09	0.16	89.69	6.74	0.43
Condensate at t_2	-	0.22	65.36	11.49	0.01	22.92
Condensate at t_4	-	0.14	91.10	5.19	0.00	3.57
Fore-cuts	2874	0.52	48.84	37.74	0.68	12.21
Main-cuts	5767	0.02	99.50	0.42	0.02	0.05
After-cut	573	0.00	83.86	0.00	16.14	0.00

Table 5.17. Results of the posterior simulation of industrial-size BED experiment
(A: acetone, B: methanol, C: THF, F: water, G: toluene).

Despite the differences in the measured and calculated values, the principal findings are also verified by the simulations: the water feeding reduces the methanol concentration in the condensate at the end of the heating-up, which leads to the decrease of methanol loss with the fore-cut, and thus, to increased recovery.

5.3. Conclusions

In this chapter, the application of batch extractive distillation (BED) and that of the hybrid process (HP) were investigated for pharmaceutical waste solvent mixtures, whose separation is made infeasible or limited by azeotropes.

First, the performance of the basic and a modified operational policy of BED and HP for the recovery of THF from a five-component industrial waste solvent mixture (methanol-THF-acetonitrile-water-pyridine) was studied. The components form seven azeotropes, which disturb the production of THF. The effects of water and pyridine as entrainer were investigated, and it was stated that, though both entrainers influence the relative volatility favourably, water is more practical to use. Experiments performed on a laboratory packed column were evaluated with rigorous simulations. The experimental results were described with acceptable agreement. The prescribed separation task was not feasible with batch rectification, but it was possible to produce THF with the desired quality by BED and HP by using water as entrainer. The highest recovery and production rate were achieved with the HP, while the least efficient process was the basic policy of BED. However, the water content of the product was also the highest in the case of HP. The results of the posterior simulations verified that experimental parameters were well chosen. The effect of operational parameters was also investigated. With modified values of the operational parameters, the recovery of the modified policy of BED nearly reached that of HP.

Secondly, the recovery of methanol from a seven-component aqueous waste solvent mixture was studied. The components form several minimum azeotropes, which limit the recovery of methanol by traditional batch distillation (BD), by causing a significant loss of methanol since they must be removed as side-cuts. As the addition of water showed a favourable effect on the VLE conditions, the BED separation of the mixture was studied. A new BED operational policy was suggested, where water feeding as entrainer was applied only during the heating-up of the column (BED1). At the end of the heating-up, the concentration of organic pollutants increased, compared to BD, and the methanol concentration decreased significantly in the top of the column. Water feeding can continue during the fore-cut (this is BED2), but it increases the amount of fore-cut and dilutes further the mixture from which methanol is recovered.

Laboratory experiments were performed in a packed column to compare the BD and the two BED operational policies. The highest recovery was obtained by BED1, the lowest one by BD. The posterior rigorous dynamic simulation of the experiments gave the same order of separation methods with respect to recovery. Industrial-size pilot productions of BD and BED1 were performed in a 50 bubble cap tray column. By BED1 the recovery increased from 68.5 % to 73.1%, which is explained by the significant decrease of methanol concentration in the distillate at the end heating-up period by BED, and thus lower methanol loss with the fore-cut. The pilot productions were also investigated by rigorous simulations. The calculated specific energy consumption of the BED production was 27.4 % lower than that of BD.

The batch extractive processes (BED and HP) were successfully applied for the separation of the multicomponent azeotropic mixtures in laboratory experiments, industrial-size pilot productions and rigorous simulation.

CHAPTER 6

General Model of Batch Heteroazeotropic Distillation

Related publications: Hegely et al. (2012a, 2012b, 2013)

A general model of batch heteroazeotropic distillation is proposed (Hegely et al., 2013). As in the model of Lang and Modla (2006), any fraction of both liquid phases can be refluxed and distillate can be withdrawn from both phases. This is combined with the possibility of varying the liquid hold-up of the entrainer-rich phase in the decanter proposed by Rodriguez-Donis et al. (2002), however, the variation of the hold-up of the entrainer-lean phase is considered as well. By assuming maximal separation, that is, that the composition of the condensate is always equal to that of the heteroazeotrope, the still path (defined as the trajectory of the still composition by Bernot, 1990) is derived. The 16 possible operational policies are systematically identified, including several policies previously not published. The still path directions are determined for all the operational policies. The predicted directions are validated by rigorous simulation for three policies not published yet by using the mixture water – formaldehyde – propyl formate. To demonstrate the advantage of using a non-traditional policy, the separation of the mixture aniline – ethylene glycol – water is investigated, as well.

6.1. Generalised Model for Feasibility Studies

Figure 6.1 shows the scheme of the batch heterogeneous distillation column of the generalised model.

In the feasibility analysis the following simplifying assumptions are applied:

- the composition of the condensate is constant and equals that of the heteroazeotrope,
- the composition in the decanter equals that of the condensate,
- the vapour and liquid hold-ups of the column and of the condenser are negligible,
- constant molar overflow.

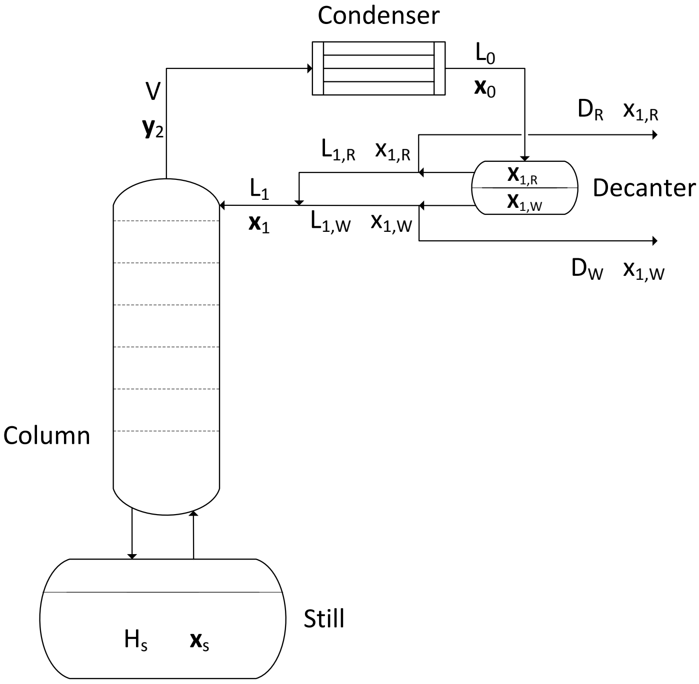


Figure 6.1. Heteroazeotropic batch distillation column model.

The condensate of the top vapour, which has a molar flow rate of V and molar composition of y_2, gives rise to a two-phase liquid stream with a flow rate of L_0, and composition x_0. Considering that x_0 lies in the heterogeneous region, near the unstable node heteroazeotrope, the condensate is a heterogeneous liquid. $L_{0,R}$ and $L_{0,W}$ are the flow rates of the E-rich and E-lean (E-weak) phase in the condensate. The liquid phase split ratio is η_R, which is defined as the ratio of the flow rate of the E-rich phase and the total flow rate of the condensate:

$$\eta_R = \frac{L_{0,R}}{L_0} \tag{6.1}$$

Accordingly, the ratio of the flow rate of the E-lean phase and the total flow rate is:

$$\frac{L_{0,W}}{L_0} = 1 - \eta_R \tag{6.2}$$

The first two simplifying assumptions also mean that the phase ratio (η_R), and the composition of the phases leaving the decanter ($x_{1,R}$ and $x_{1,W}$) are not changing with time, although they may change slightly during a real operation (Pommier, 2008).

Both liquid phases can be refluxed or withdrawn as distillate. Besides, the hold-up of both phases can be increased, decreased or kept constant in the decanter. The change in the hold-up of the E-rich (E-lean) phase is characterised by the accumulation ratio a_R (a_W), which is defined as the ratio of the difference between the E-rich (E-lean) phase flow rate entering and leaving the decanter and the flow rate of this phase entering the decanter:

$$a_R = \frac{L_{0,R} - L_{1,R} + D_R}{L_{0,R}} \tag{6.3}$$

$$a_W = \frac{L_{0,W} - L_{1,W} + D_W}{L_{0,W}} \tag{6.4}$$

where D_R and D_W are the flow rates of E-rich and E-lean phases withdrawn as distillate, $L_{1,R}$ and $L_{1,W}$ are the flow rates refluxed, respectively. If the value of the accumulation ratio is higher than zero, the incoming flow rate of the respective phase is higher than its flow rate leaving the decanter, thus this phase is accumulated in the decanter. If the accumulation ratio is lower than zero, the hold-up of this phase decreases in the decanter.

The reflux splitting ratios rs_R and rs_W characterise how the stream of the E-rich and E-lean phases leaving the decanter are divided into reflux and distillate. They are defined as the ratio of the flow rates refluxed and leaving the decanter:

$$rs_R = \frac{L_{1,R}}{L_{1,R}+D_R} \tag{6.5}$$

$$rs_W = \frac{L_{1,W}}{L_{1,W}+D_W} \tag{6.6}$$

Multiplying rs_R by (1-a_R) (rs_W by (1-a_W)), we obtain r_R (r_W), the ratio of the flow rates refluxed and condensed:

$$r_R = \ 1 - a_R \ rs_R = \frac{L_{1,R}}{L_{0,R}} \tag{6.7}$$

$$r_W = \ 1 - a_W \ rs_W = \frac{L_{1,W}}{L_{0,W}} \tag{6.8}$$

where:

$$1 - a_R = 1 - \frac{L_{0,R} - \ L_{1,R} + D_R}{L_{0,R}} = \frac{L_{0,R} - L_{0,R} + \ L_{1,R} + D_R}{L_{0,R}} \tag{6.9}$$

$$1 - a_R = \frac{L_{1,R} + D_R}{L_{0,R}} \tag{6.10}$$

The reflux ratio of the E-rich (E-lean) phase can be defined as the ratio of the flow rates refluxed and non-refluxed:

$$R_R = \frac{L_{1,R}}{L_{0,R} - L_{1,R}} \tag{6.11}$$

Similarly for the E-lean phase:

$$R_W = \frac{L_{1,W}}{L_{0,W} - L_{1,W}} \tag{6.12}$$

Compared to the traditional definition of the reflux ratio, the distillate flow rate is replaced with the non-refluxed one, in order to take into account the effect of hold-up change. The phase reflux ratio has a negative value, in the case of refluxing the decanter hold-up of the phase to the column. Through a series of transformations, we can obtain the relationship between r_R and R_R (r_W and R_W):

$$r_R = \frac{L_{1,R}}{L_{0,R}} = \frac{\dfrac{L_{1,R}}{L_{0,R} - L_{1,R}}}{\dfrac{L_{0,R}}{L_{0,R} - L_{1,R}}} = \frac{R_R}{\dfrac{L_{1,R}}{L_{0,R} - L_{1,R}} + 1} = \frac{R_R}{R_R + 1} \tag{6.13}$$

$$r_W = \frac{R_W}{R_W + 1} \tag{6.14}$$

r_R is always nonnegative, and for positive, finite R_R, its value is between one and zero. As R_R tends to infinity, r_R approaches unity. In the case of negative R_R, r_R is greater than unity.

The flow rate of the condensate is equal to that of the top vapour V:

$$L_0 = L_{0,R} + L_{0,W} = \eta_R L_0 + (1 - \eta_R) L_0 = V \tag{6.15}$$

The total flow rate of the reflux stream:

$$L_1 = L_{1,R} + L_{1,W} = r_R L_{0,R} + r_W L_{0,W} \tag{6.16}$$

$$L_1 = \left(r_R \eta_R + r_W (1 - \eta_R)\right) V \tag{6.17}$$

The total component flow rates in the reflux:

$$L_1 x_1 = L_{1,R} x_{1,R} + L_{1,W} x_{1,W} \tag{6.18}$$

The evolution of the still composition is described by a differential equation, which can be derived from the differential total and component material balances of the still pot.

The total material balance:

$$\frac{dH_S}{dt} = L_1 - V \tag{6.19}$$

$$\frac{dH_S}{dt} = \left(r_R \eta_R + r_W (1 - \eta_R) - 1\right) V \tag{6.20}$$

$$\frac{dH_S}{dt} = \left((r_R - 1) \eta_R + (r_W - 1)(1 - \eta_R)\right) V \tag{6.21}$$

The component material balance of the still:

$$\frac{d(H_S x_S)}{dt} = L_1 x_1 - V x_0 \tag{6.22}$$

$$\frac{d(H_S x_S)}{dt} = \left((r_R - 1) \eta_R x_{1,R} + (r_W - 1)(1 - \eta_R) x_{1,W}\right) V \tag{6.23}$$

By applying the product rule of differentiation, the equation of the still path:

$$H_S \frac{dx_S}{dt} = \frac{d(H_S x_S)}{dt} - x_S \frac{dH_S}{dt} \tag{6.24}$$

The final form of the equation describing the evolution of the still composition is:

$$\frac{dx_S}{dt} = \frac{V}{H_S}\left((1 - r_R) \eta_R (x_S - x_{1,R}) + (1 - r_W)(1 - \eta_R)(x_S - x_{1,W})\right) \tag{6.25}$$

The Equation 6.25 consists of two terms, which represent the removal of the E-rich and the E-lean phase from the column, respectively, by either withdrawal as distillate, or accumulating in the decanter. When the assumption of constant condensate composition is valid, the two ways of removal have exactly the same effect. If one of the phases is completely refluxed (no distillate is withdrawn and the hold-up of the respective phase in the decanter is constant), the right hand side of Equation 6.25 will only consist of the term related to the other phase, as either r_R (total reflux of E-rich phase) or r_W (total reflux of E-lean phase) equals one.

6.2. Operational Policies

In this section, the possible operational policies are identified based on the operational parameters r_R and r_W, then the still path directions is determined for each policy, and the feasibility of recovering one of the original components in the still at the end of operation is discussed.

6.2.1. Identification of Possible Operational Policies

The model has three independent operational parameters: r_R, r_W and V. While V, which is related to the heat duty of the still, only influences the speed of the distillation, r_R and r_W determine the direction of the still path, as well. By changing the values of these two operational parameters, either by varying the decanter hold-up or the reflux splitting ratios, the direction of the still path can be changed. As the still composition is a very important parameter of batch distillation, it is expedient to distinguish the possible operational policies on the basis of the values of the operational parameters r_R and r_W. The 16 different possible policies are shown in Table 6.1. If r_R (r_W) is zero, the E-rich (E-lean) phase is not refluxed. If r_R (r_W) is one, the E-rich (E-lean) phase is refluxed entirely. If r_R (r_W) is between zero and one, the respective phase is partially refluxed, while the remaining amount of the phase is either withdrawn as distillate or accumulated in the decanter. If r_R (r_W) is greater than unity, the amount of the E-rich (E-lean) phase refluxed is greater than what is removed from the column with the top vapour. To supply this difference in the flow rates, the hold-up of the respective phase must be decreased.

	r_R	r_W	Reflux	Example in the literature
1	0	0	No reflux	
2		<1	E-lean phase (partial)	
3		1	E-lean phase (total)	
4		>1	E-lean phase (reintr.)	
5	<1	0	E-rich phase (partial)	Mode II, Strategy B, Version 1 (Skouras et al., 2005a; Lang and Modla, 2006); Mode II, Strategies 2' and 2" (Gerbaud and Rodriguez-Donis, 2010)
6		<1	E-rich (partial) and E-lean phase (partial)	Mode II, Strategy B, Version 2 (Lang and Modla, 2006)
7		1	E-rich (partial) and E-lean phase (total)	
8		>1	E-rich (partial) and E-lean phase (reintr.)	
9	1	0	E-rich phase (total)	Mode II, Strategy A, Version 1 (Skouras et al., 2005a; Lang and Modla, 2006); Mode II, Strategy 1 (Gerbaud and Rodriguez-Donis, 2010)
10		<1	E-rich (total) and E-lean phase (partial)	Mode II, Strategy A, Version 2 (Lang and Modla, 2006)
11		1	E-rich (total) and E-lean phase (total)	Total reflux operation
12		>1	E-rich (total) and E-lean phase (reintr.)	
13	>1	0	E-rich phase (reintr.)	Mode II, Strategy 3 (Gerbaud and Rodriguez-Donis, 2010)
14		<1	E-rich (reintr.) and E-lean phase (partial)	
15		1	E-rich (reintr.) and E-lean phase (total)	
16		>1	E-rich (reintr.) and E-lean phase (reintr.)	

Table 6.1. The possible operational policies (reintr.: reintroduction - a greater amount of liquid is refluxed than what leaves the column as condensate).

In Equation 6.25, the reflux splitting ratios (rs_R and rs_W) and the accumulation ratios (a_R and a_W) are only present in the form of their products (r_R and r_W). That is, the same effect can be achieved either by accumulating one of the phases, or by its withdrawal as distillate. The practical realization of the withdrawal is of course easier, whereas a hold-up change of the phases in the decanter would require the application of a controller. However, accumulating one of the phases in the decanter may be useful, e.g. in order to maintain longer the existence of two liquid phases and to improve the final product recovery yield as shown by Rodriguez-Donis et al. (2002). The case is different if r_R or r_W is greater than unity, as this is only possible if the decanter hold-up is reduced, that is, a_R or a_W is greater than one.

6.2.2. The Still Path Direction of the Different Operational Policies

As recalled by the general Equation 6.25, the still path can be characterised by the direction of the sum of two other vectors with direction of $(x_S - x_{1,R})$ and $(x_S - x_{1,W})$, respectively, whose magnitude depends on r_R and r_W, respectively. If the value of r_R and r_W is positive, the two vectors, both starting at x_S, point away from $x_{1,R}$ and $x_{1,W}$, respectively. Their direction can be reversed, if r_R or r_W is greater than one. Therefore, the direction of the resultant vector depends on the operation policy through the value of the operational parameters r_R and r_W.

The results are illustrated for a mixture, where A and E form a binary heteroazeotrope, which is the only unstable node in the system. As the derivation of the equation did not exploit the type of the heteroazeotrope, the results are also valid for ternary heteroazeotropes. A and B can be a homoazeotropic (minimum or maximum) or a zeotropic mixture. With a (minimum or maximum) azeotrope A-B, there may exist a distillation boundary, but as already hinted by Rodriguez-Donis et al. (2002), and demonstrated through the distillation regions for heteroazeotropic batch distillation by Lang and Modla (2006) this does not affect the separation feasibility.

The two vectors influencing the still path are presented in Figure 6.2. Both vectors originate from x_S, the actual still composition. The vector corresponding to the E-lean phase points away from $x_{1,W}$ if $r_W<1$, and towards it if $r_W>1$, as the removal of E-lean phase ($r_W<1$: less than total reflux of the phase) drives the still composition away from the E-lean phase composition. The other vector, corresponding to the E-rich phase points away from $x_{1,R}$ if $r_R<1$, and towards it if $r_R>1$. If r_R or r_W equals 1, the respective vector does not exist.

This is the case by the classical operational policy, Mode II, Strategy A, Version 1 (Policy 9 in Table 6.1), where $r_R=1$ and $r_W=0$, thus the single influencing vector points away from the composition of the E-lean phase.

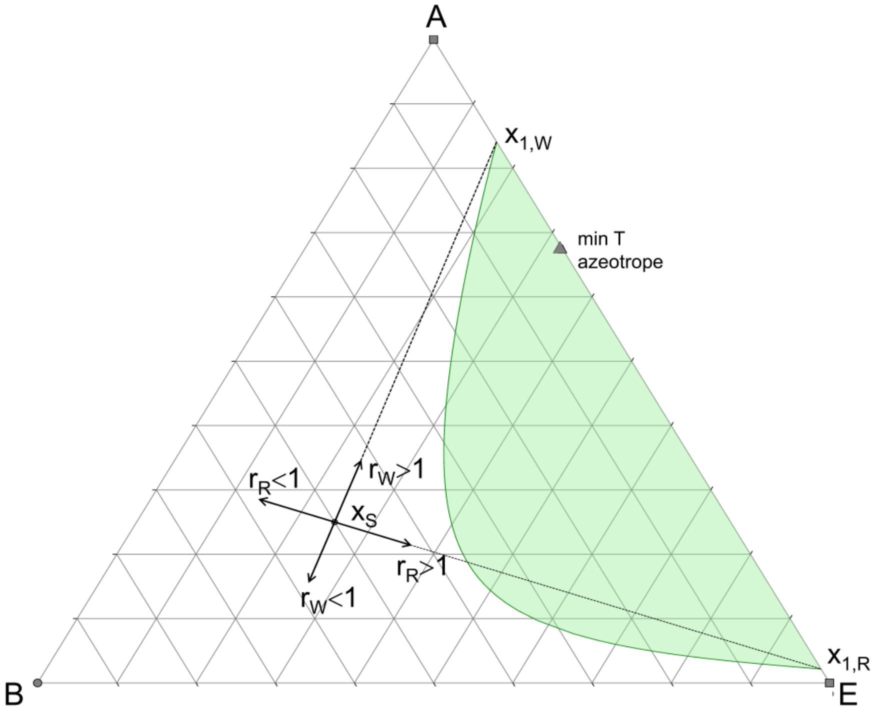
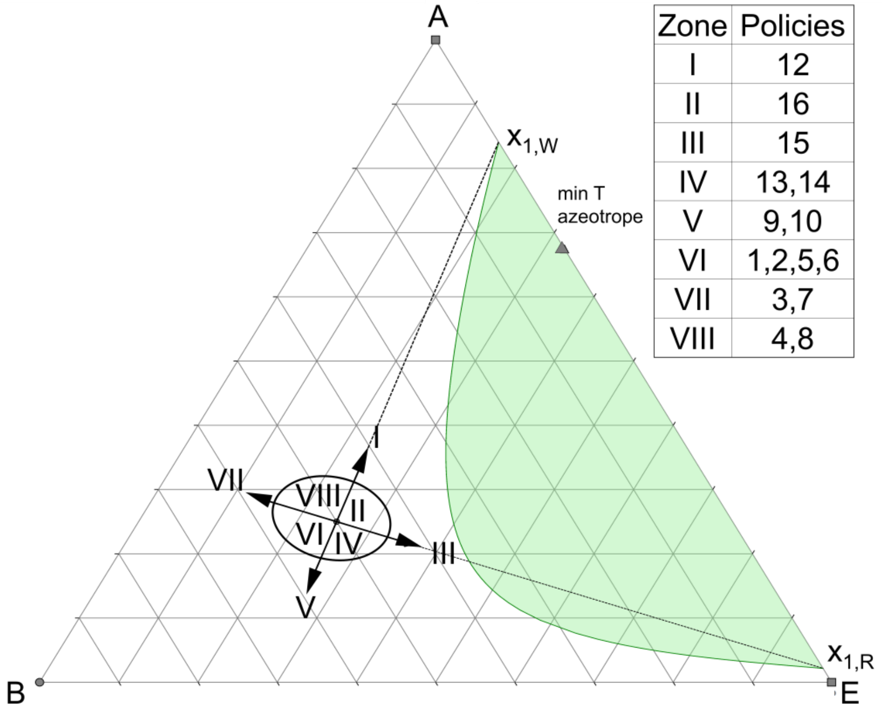


Figure 6.2. The possible directions of the vectors influencing the still path in heteroazeotropic batch distillation.

The possible directions of the derivative vector, that is, the direction of the still path for every possible operational policy can be obtained by adding up the two vectors above for each operational policy. The possible directions of the derivative vector calculated in this way can be classified into eight zones (Figure 6.3). The vector points either towards or away from the composition of one of the phases (Zones I, III, V and VII), or they are situated between these four main directions (Zones II, IV, VI and VIII).

It can be seen that the still composition can be modified in any desired direction. Zones I, II and VIII, where r_W is higher than one, correspond to directions, which were not reported previously. At least one operational policy belongs to every zone, as it is shown in Figure 6.3. Policy 11 (total reflux operation) is an exception not belonging to any zone, as the still composition remains constant.



Zone	Policies
I	12
II	16
III	15
IV	13,14
V	9,10
VI	1,2,5,6
VII	3,7
VIII	4,8

Figure 6.3. The direction of the still path for the different operational policies of heteroazeotropic batch distillation.

6.2.3. Feasibility of Recovering One of the Original Components in the Still

Since the A–B mixture, azeotropic or zeotropic, is the one to be separated, the still path should not in practice end on this edge (except close to B, where the purity requirement is satisfied). By directing the still path appropriately, it can be possible to recover B in the still, thus eliminating the need of a further separation step, the separation of B and E. This requires the adjustment of the operational parameters r_R and r_W, since by using the traditional Policy 9 (refluxing the whole amount of E-rich phase only), the still path will reach either the A-B or B-E edge, depending on the composition of the charge and the heteroazeotrope.

The composition space can further be divided into three regions (Figure 6.4), with different necessary values of r_R and r_W, to enable the recovery of B from the still compositions lying in the region in question. If the still composition lies on the line joining $x_{1,W}$ and B, which coincides with Zone V, Policy 9 or 10, that is, r_R=1 and r_W<1 (total reflux of E-rich phase, partial or no reflux of E-lean phase), has to be applied. In this way, the still composition will stay on this line, and approach B. Similarly, if the still composition lies on the line joining $x_{1,R}$ and B, which coincides with Zone VII, Policy 3 or 7, that is r_R<1 and r_W=1, (partial or no reflux of E-rich phase, total reflux of E-lean phase) has to be applied. Between these two lines, the still path direction has to be in Zone VI, in order to move towards B. This means that both r_R and r_W have to be lower than one, that is, the phases are refluxed partially, or not at all. Outside this region, the still path direction must lie in either Zone IV (if the still composition is close to the A-B edge) or in Zone VIII (if the composition is close to the B-E edge). Thus, one of the parameters must be higher than one, which means the reduction of the hold-up of one of the phases. If the still composition is close to the A-B edge, this phase is the E-rich one (r_R>1); if the composition is close to the B-E edge, it is the E-lean one (r_W>1).

As the decanter hold-up is physically limited, it is usually necessary to combine the different operational policies. It must be noted that in real columns, the influence of the variation of the decanter hold-up is only significant in the case where the column (and condenser) hold-up is relatively small.

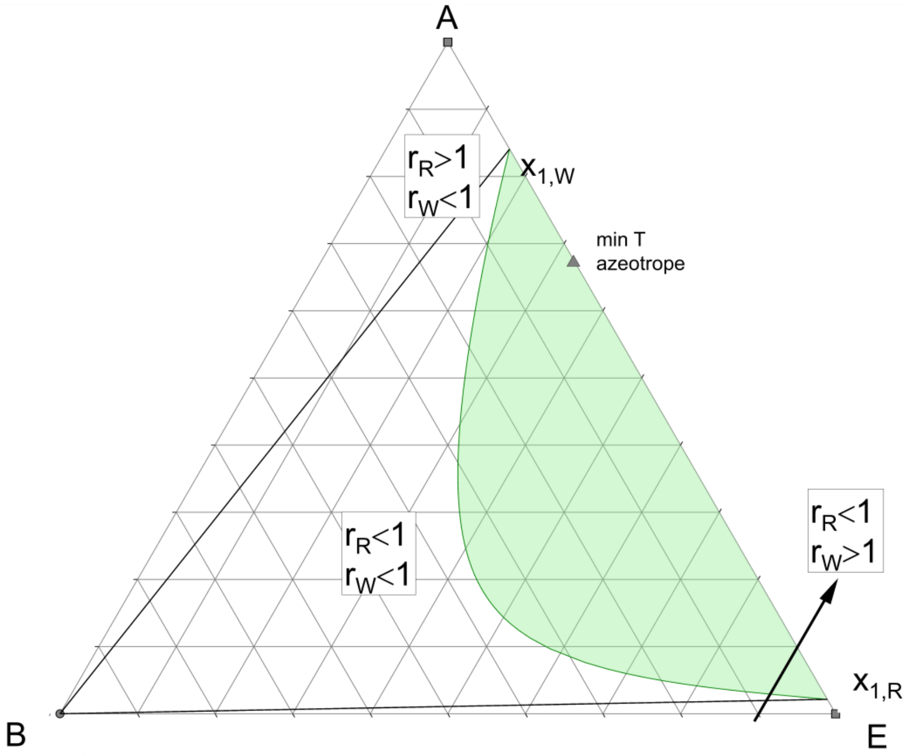


Figure 6.4. Feasibility regions with the parameter values required to recover B in the still for heteroazeotropic batch distillation.

6.3. Rigorous Simulation

In order to validate the results of the feasibility analysis by using less simplifying assumptions, and to illustrate the advantage of using a non-traditional operational policy, rigorous simulation calculations were performed with the dynamic module (CC-DCOLUMN) of the professional flowsheet simulator ChemCAD.

6.3.1. Calculation Method

For rigorous simulation, the following simplifying assumptions are applied:

- theoretical trays,

- constant volumetric liquid hold-up on the trays and in the decanter,
- negligible vapour hold-up.

All the calculations were performed with the same ChemCAD model (Figure 6.5). The column was modelled with a SCDS column with a separate total condenser. The still was a heated DYNAMIC VESSEL. Two other DYNAMIC VESSELs served as product tanks for the E-rich and E-lean phases, respectively, while a third one was used as a decanter with constant E-rich and E-lean liquid levels. The values of the liquid levels were supplied by two RAMP modules, which change the value of an operating parameter (in our case, the liquid levels) with time following a specified piecewise linear function.

The number of theoretical plates was chosen in such a way that the distillate composition approached closely the heteroazeotropic one. The value of decanter hold-up was chosen to be high enough to enable the demonstration of the effect of phase hold-up variation, but low compared to the charge volume.

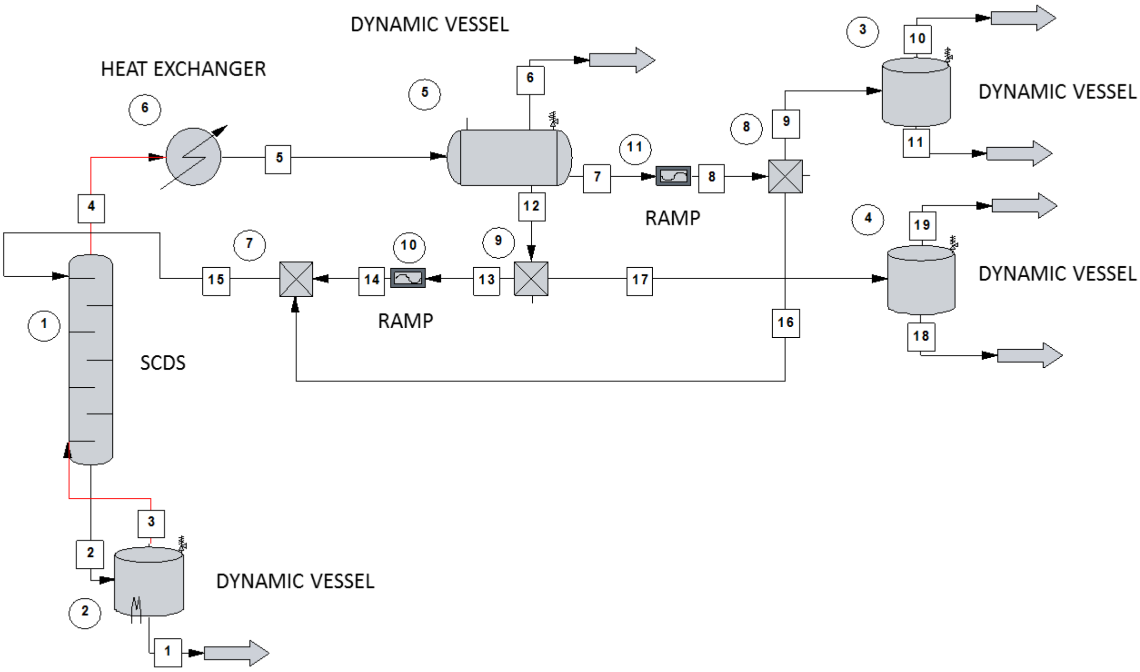


Figure 6.5. The CHEMCAD model of the batch rectifier with variable liquid hold-up in the decanter.

6.3.2. Assessment of the Practical Interest of Operational Policies

Out of the 16 possible operational policies, not all are of practical interest. For those, which were already published earlier, references are given in Table 6.1. The practically useful policies for regular operation are:

- Policy 9 with r_R=1 and r_W=0 is, what Lang and Modla (2006) call Mode II, Strategy A, Version 1, where the E-rich phase is entirely refluxed, and the E-lean phase is withdrawn as distillate. This is the traditional and conceptually most straightforward operational policy (Skouras et al., 2005b).

- Policy 5, where the E-rich phase is only partially refluxed and the E-lean phase is not refluxed (Mode II, Strategy B, Version 1), results in a deviation of the still path in the direction pointing away from the E-rich phase composition (Zone VI), compared to the still path of Policy 9.
- Policy 13 shows a similar deviation compared to Policy 5, but towards the E-rich phase composition (Zone IV).
- If necessary, the reflux ratio can be increased by partially refluxing the E-lean phase, without changing the still path direction, but at the cost of an increased operation time. By applying partial E-lean phase reflux to the three policies presented above, Policies 10, 6 and 14 are obtained, respectively.
- Policies 7 and 8 are useful if the still composition is located between the line joining the E-rich phase composition (x_R) and the original component (B in Figure 6.3) miscible with E, and the B-E edge of the composition triangle.

There are some policies, which do not seem to be of practical interest:

- Policies 3 and 4 provide the same still path as Policies 7 and 8, but without the partial reflux of the E-rich phase. With the resulting increased E-loss, the condensate can become homogeneous after a shorter period of time, therefore Policies 3 and 4 are not recommended.
- Policies 1 and 2 are not recommended either, as the still path has the same direction as by Policies 5 and 6, but the lack of reflux (Policy 1), or that the E-lean phase is only partially refluxed (Policy 2), is likely to cause problems in the practical operation.

There are also a few policies, which can be useful only for special purposes, but not for the regular operation of the column:

- Policies 12 and 15 are similar to each other: one of the phases (12: E-rich, 15: E-lean) is entirely refluxed, while the hold-up of the other phase is reduced through refluxing it to the column. These policies could be used for a short time (as the decanter hold-up is limited) to quickly change the still composition towards the E-lean (Policy 12) or the E-rich (Policy 15) phase composition, respectively.
- Finally, Policy 11 is the total reflux operation, where both r_R and r_W equal one, normally applied during the start-up of the column.

6.3.3. Validation of Some New Operational Policies

The new policies 8, 12 and 16, proposed for the first time here, are applied in order to demonstrate that the still path can be turned into directions previously not reported, that is, towards the E-lean phase. The test mixture studied is water (A) – formic acid (B) – propyl formate (E), where propyl formate is the entrainer. The residue curve map of the mixture along with the binodal curve at

T=25 °C is presented in Figure 6.6. The vapour-liquid-liquid equilibria are described with the NRTL model. The NRTL parameters can be found in Appendix 2. The mixture A – B exhibits a maximum boiling-point homoazeotrope, while A and E form a heteroazeotrope, enabling the separation of the A – B mixture.

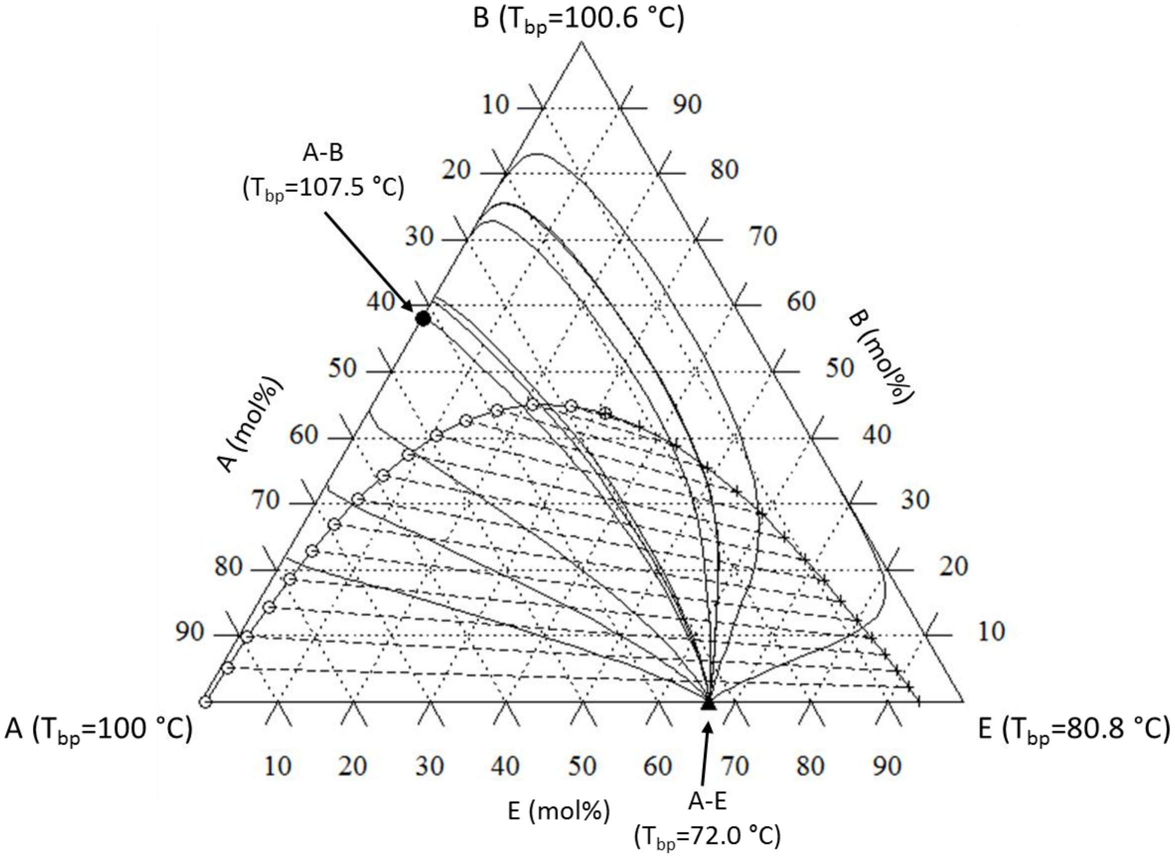


Figure 6.6. The residue curve map of the mixture water (A) – formic acid (B) – propyl formate (E).

The column has 50 theoretical trays; the heat duty applied is 2 kW. The hold-up of the decanter is 0.5 dm^3; that of the column is 0.01 dm^3/plate. The charge has a molar amount of 160 mol (5.08 dm^3) and a composition of 52.5 mol% A, 40.5 mol% B and 7% E. The column is operated for 40 minutes under total reflux, after which one of the policies previously mentioned is applied. The decanter is empty at the start of the operation; at the end of the total reflux period, the volumes of liquid phases inside it are equal (0.25 dm^3). The values of the operational parameters are shown in Table 6.2, while the respective still paths are presented in Figure 6.7. Each path starts from the composition at the end the total reflux period ($x_{S,0}$). For Policy 12, the still composition moves towards that of the E-lean phase, while for Policies 8 and 16, the path deviates from this direction as predicted: towards the edge A-B (Zone VIII, Policy 8) or vertex E (Zone II, Policy 16). That is, the still path directions are in accordance with the results of the feasibility analysis.

Policy	r_R	r_W
8	0.986	1.21
12	1.0	
16	1.014	

Table 6.2. The operational parameters of the policies investigated.

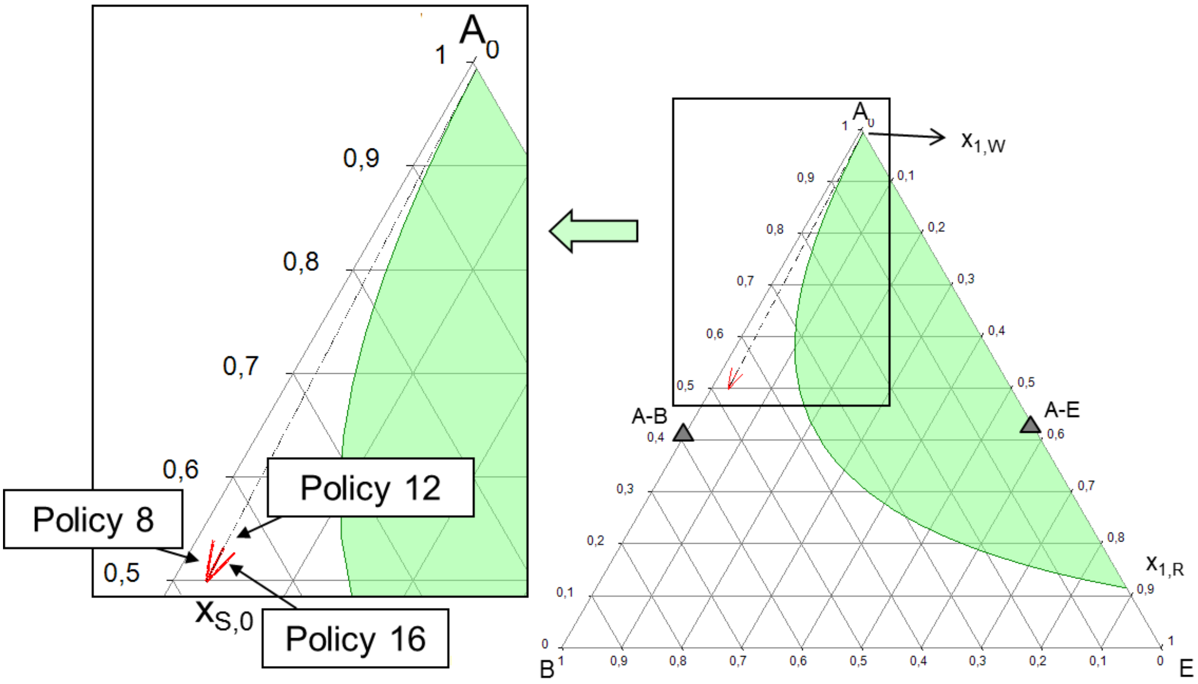


Figure 6.7. The calculated evolution of still composition (Policies 8, 12, 16) for the separation of the water (A) – formic acid (B) – propyl formate (E) mixture.

6.3.4. The Advantage of Using a Non-Traditional Policy

In order to demonstrate the advantage of using a non-traditional policy, two production processes (Productions 1 and 2) are investigated, as well. The calculations are carried out for the mixture aniline (A) – ethylene glycol (B) – water (E). The vapour-liquid-liquid equilibria are described with the NRTL model. The NRTL parameters can be found in Appendix 2. A and B form a minimum boiling-point homoazeotrope, while A and E a heteroazeotrope, thus enabling the separation of the mixture A – B. The column has 50 theoretical plates, and the hold-up is 0.01 dm^3/plate. The volume of the decanter is 0.75 dm^3, the hold-up of both phases at the end of the total reflux period is 0.125 dm^3. The heat duty applied is 2 kW. The charge has a molar amount of 100 mol (6.54 dm^3) and a composition x_F of 47.5 mol% A, 32.5 mol% B and 20% E. The goal of the separation is to obtain ethylene glycol in the still with a minimum purity of 97 mol%, while withdrawing the E-lean phase (aqueous aniline) as distillate.

Production 1 consists of a total reflux period for 30 minutes, required to fill up the decanter, and subsequent operation by the traditional Policy 9, that is, the entire E-rich phase is refluxed (r_R=1,

r_W=0). Figure 6.8 shows the trajectory of the average composition of the still and column hold-ups. The still path equation (Equation 6.25) is derived with the assumption of negligible column hold-up. If this assumption is omitted, and the average hold-up (still+column without the decanter) composition is used instead of the still composition, the equation will have the same form. This means that the results on the still path direction presented in Section 6.2 will be valid for the hold-up path, instead of the still path. During the total reflux period, the decanter hold-up is built up, and the hold-up composition, starting at x_F, moves away from the A-E azeotrope. After this initial period, the E-rich phase is refluxed, the E-lean phase is withdrawn as distillate, so the hold-up composition moves away from the composition of the E-lean phase, which is now the aqueous aniline, as predicted by the feasibility analysis. As the hold-up composition approaches the A-B edge, that is the hold-up is depleted in E, B starts to appear in the two liquid phases in the decanter and finally the liquid phases change place: the E-lean phase, which used to be the lighter phase, became the heavier one. Eventually, this also leads to the disappearance of the liquid-liquid split. The operation is stopped after 427.5 min, immediately before the phase interchange. At this point the final concentration of B in the still is 79.9 mol%, which stayed below the prescribed value.

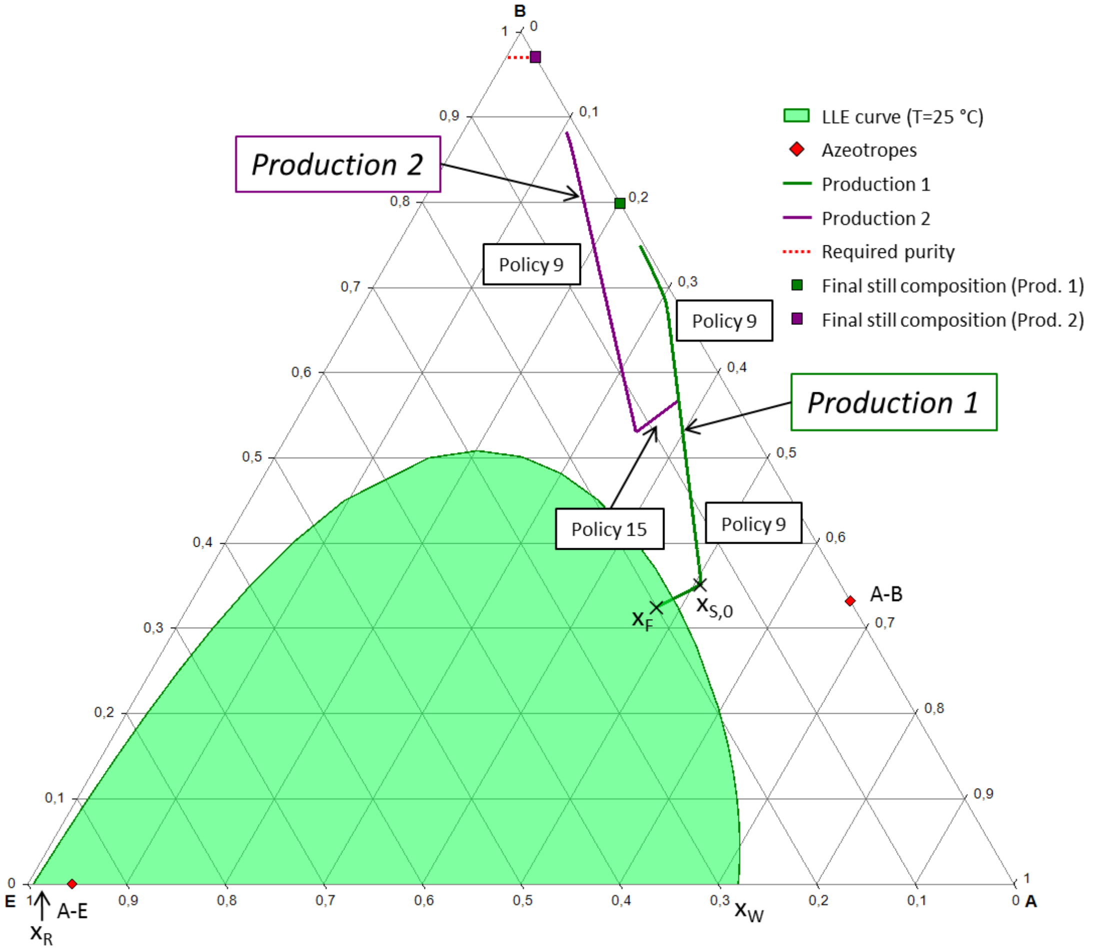


Figure 6.8. The hold-up paths and final still compositions of Productions 1 and 2 for the separation of aniline (A) – ethylene glycol (B) with water (E).

Production 2 is identical to Production 1 during the first period of operation (Δt=396 min). At this point, instead of continuing the operation by Policy 9, Policy 15 is applied for 10 min: the hold-up of the E-rich phase is reduced (r_R>1), and the E-lean phase is entirely refluxed (r_W=1). The E-rich phase hold-up is reduced by 60%, that is, 75 cm^3 of this phase is refluxed to the column, corresponding to r_R≈1.133. The predicted effect of using Policy 15 can be clearly seen in Figure 6.8, as the movement of the average hold-up composition towards the E-rich phase composition. After 10 min, the operation is continued by Policy 9, and the average hold-up path moves away once more from the E-lean phase composition. At the end of the operation, B was obtained in the still residue with an acceptable purity of 97.0% and high recovery (91.6%). The total operation time is 553 min. If the operation was continued, the same phase interchange phenomenon described at Production 1 would be encountered at 560 min. By using a non-traditional operational policy, the liquid-liquid phase split could be maintained longer in the decanter for Production 2 than for Production 1, allowing to reach a higher purity in the still.

The results of the rigorous simulations indicate that the still path directions are in accordance with the results of the feasibility analysis, and that the application of non-traditional operational policies can render such separations feasible, which are infeasible by the traditional policies.

6.4. Conclusions

A general model of batch heteroazeotropic distillation was proposed. Both liquid phases can be refluxed or withdrawn as distillate. Their hold-up in the decanter can be increased, decreased or kept constant, as well. Two operational parameters r_R and r_W were introduced, defining the ratio of the flow rates of the E-rich and E-lean phase refluxed and condensed, respectively. By assuming maximal separation, that is, that the condensate is always the heteroazeotrope, the still path equation was derived. Depending on the values of the parameters r_R and r_W, 16 possible operational policies were distinguished.

The direction of the still path is determined by the sum of two vectors, whose magnitude depends on the value of the operational parameters. The still path direction can lie in eight different zones, which cover all the possible directions. By determining the still path direction for every operational policy, we found that every zone corresponds to at least one policy, that is, still path compositions can be changed in any desired direction by choosing the right values of r_R and r_W. By using appropriate operational policies, it is also possible to recover a pure component in the still, thus eliminating the need for a further separation step. From the 16 operational policies, 11 can be considered as useful in practice. The composition space can be divided into three regions, with different values of r_R and r_W required to recover the least volatile pure component in the still from the still compositions lying in the region in question.

The still path directions for three new operational policies were validated by rigorous simulation for the mixture water – formic acid – propyl formate. The benefit of using a non-traditional operational policy with hold-up reduction in the decanter was demonstrated, as well. The recovery of ethylene glycol in the still from an ethylene glycol – aniline mixture by using water as entrainer was infeasible with the traditional policy of entirely refluxing the entrainer-rich phase. By combining this policy with a short period of a non-traditional one, where the hold-up of the entrainer-rich phase in the decanter was reduced by refluxing it, and the entrainer-lean phase was completely refluxed, the liquid-liquid phase split could be maintained longer, and thus it was possible to obtain ethylene glycol of required purity in the still residue.

CHAPTER 7

The Extension of the General Model of Batch Heteroazeotropic Distillation to Batch Heterogeneous Extractive Distillation

By extending the model for batch heteroazeotropic distillation presented in Chapter 6, a general model is developed for the batch heterogeneous extractive distillation (BHED). An entrainer-rich and an entrainer-lean phase are present in the decanter, where the hold-up of both phases can be reduced, kept constant, or increased. Any fraction of both phases can be refluxed or withdrawn as distillate. The entrainer is fed continuously either onto one of the plates of the column, or mixed to the condensate stream, which is equivalent to feeding it into decanter. The still path equation is derived for both cases. A discussion is given on the literature occurrence and practical applicability of the 16 possible operational policies and the effect of continuous entrainer feeding on the still path direction of all operational policies are determined. The still path directions are validated by rigorous simulation for several operational policies using the mixture water – ethanol – n-butanol.

7.1. The Extended Model for Feasibility Studies

The generalised model of the batch heterogeneous extractive distillation (Figure 7.1) is an extension of the model of batch heteroazeotropic distillation presented in Chapter 6. In this way, both liquid phases can be refluxed or withdrawn as distillate, and the hold-up of both phases can be increased, decreased or kept constant in the decanter.

In the feasibility analysis the following three simplifying assumptions of the batch heteroazeotropic distillation are kept:

- the composition of the condensate is constant and equals to that of the heteroazeotrope,
- the vapour and liquid hold-ups of the column and of the condenser are negligible,
- constant molar overflow.

One of the simplifying assumptions is modified to the following form:

- the overall liquid composition in the decanter equals that of the incoming stream (which might be the condensate, or the condensate mixed with the entrainer stream).

A new simplifying assumption is added, as well:

- the entrainer is boiling point liquid.

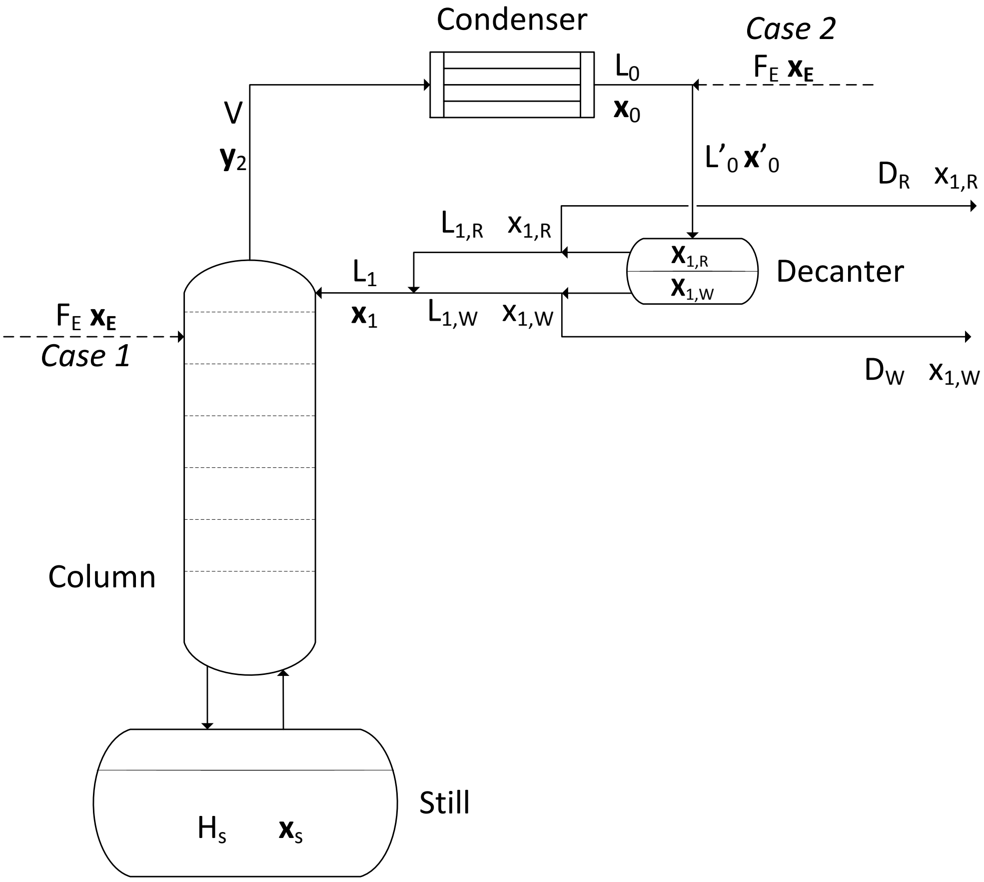


Figure 7.1. Batch heterogeneous extractive distillation column model.

Rodriguez-Donis et al. (2007) presented four different possibilities for entrainer feeding location for continuous heterogeneous extractive distillation. The entrainer could be (1) mixed to the azeotropic feed, (2) fed to the column at a point between the azeotropic feed and the reflux stream, (3) mixed to the refluxed stream, or (4) mixed to condensate stream. In a batch process, the first case is not applicable, as there is no continuous azeotropic feeding. If the entrainer is fed to the column at a lower position than the top, a rectifying section also exists above the feeding location. Feeding the entrainer at the top plate is equivalent to mixing it to the reflux stream. In this case, the column only comprises of an extractive section. During the feasibility analysis, as the column hold-up is neglected, and constant molar overflow is assumed, the two latter configurations are treated together, as Case 1, since the existence of a rectifying section has no influence on our feasibility results. In Case 2, the entrainer stream is mixed to the condensate, or in a practical realization, fed directly to the decanter.

The condensate of the top vapour is usually a two-phase liquid, but in Case 2, a homogeneous condensate can also be feasible. For the following, the notations with an apostrophe will denote the variables related to Case 2. For example in Case 2, after the mixing of the condensate and the entrainer stream, this mixed stream entering the decanter (decanter inlet stream) has a flow rate of L'_0 and a composition of x'_0. x_0 (for Case 1) and x'_0 (for Case 2) lie in the heterogeneous region, that is, the condensate (Case 1) or the decanter inlet stream (Case 2) is a heterogeneous liquid.

The operational parameters r_R (respectively r_W) are now defined as the ratio of the flow rates of the E-rich (resp. E-lean) phase entering the decanter (instead of the flow rate of the condensate as in the previous chapter) and refluxed to the column. In Case 1, the liquid entering the decanter is the condensate, but in Case 2, it is the mixture of the condensate and the entrainer stream, that is the two operating parameters r_R and r_W have the following values:

$$r_R = \frac{L_{1,R}}{L'_{0,R}} \tag{7.1}$$

$$r_W = \frac{L_{1,W}}{L'_{0,W}} \tag{7.2}$$

The still path equation was derived on the basis of the total and component material balances of the still for batch heteroazeotropic distillation. For the BHED process, the entrainer feeding has to be also included into the material balances. The equations have different forms depending on the entrainer feeding location, so Cases 1 and 2 are treated separately.

7.1.1. Case 1

In Case 1, the entrainer is fed to the column either at an intermediate or at the top tray, or, it is mixed to the reflux stream. The flow rate of the entrainer stream is F_E, its composition is x_E. The variables and equations concerning the decanter are unchanged compared to batch heteroazeotropic distillation, as the operation of the decanter is not directly influenced by the entrainer feeding, but the differential material balances (Equations 6.21 and 6.23) of the still must be modified.

The total material balance of the still:

$$\frac{dH_S}{dt} = \quad r_R - 1 \;\; \eta_R + \;\; r_W - 1 \quad 1 - \eta_R \quad V + F_E \tag{7.3}$$

The component material balance:

$$\frac{d\;\; H_S x_S}{dt} = \quad r_R - 1 \;\; \eta_R x_{1,R} + \;\; r_W - 1 \quad 1 - \eta_R \;\; x_{1,W} \;\; V + F_E x_E \tag{7.4}$$

The equation of the still path by applying Equation 6.24:

$$\frac{dx_S}{dt} = \frac{V}{H_S} \quad 1 - r_R \;\; \eta_R \;\; x_S - x_{1,R} \;\; + \;\; 1 - r_W \quad 1 - \eta_R \quad x_S - x_{1,W} \quad - \frac{F_E}{H_S} \;\; x_S - x_E \tag{7.5}$$

In Equation 7.5, besides the first two terms, which represent the removal of the E-rich and the E-lean phase from the column, respectively, a new term appeared compared to Equation 6.25, which describes the effect of the continuous feeding of the entrainer, that is, a change in the still composition towards the entrainer composition. As stated before, the removal of either liquid phase from the column can be realized by either withdrawing it as distillate, or accumulating it in the decanter. In the case of total reflux (no distillate, constant decanter hold-up) of a liquid phase (r_R=1 or r_W=1), the corresponding term disappears from Equation 7.5. Nevertheless, entrainer feeding can be applied during total reflux operation, as well, in which case the still composition is not constant, but approaches the entrainer composition.

7.1.2. Case 2

In Case 2, the entrainer is mixed to the condensate or fed to the decanter. In this way, the operation of the decanter is directly influenced by the entrainer feeding. The flow rate of the stream entering decanter is now:

$$L'_0 = L_0 + F_E = V + F_E \tag{7.6}$$

By mixing the entrainer with the condensate, the global composition (x'_0) of the decanter no longer equals to that of the heteroazeotrope. However, assuming that the entrainer stream is the pure component, x'_0 still lies on the same edge (A-E or B-E) of the composition triangle as the heteroazeotrope. Moreover, unless the entrainer flow rate does not exceed a critical value, the global composition is in the heterogeneous region, and thus the composition of the phases is not changed:

$$x'_{1,R} = x_{1,R} \tag{7.7}$$

$$x'_{1,W} = x_{1,W} \tag{7.8}$$

The liquid phase split ratio of the decanter liquid, however, has a different value:

$$\eta'_R = \frac{L'_{0,R}}{L'_0} \tag{7.9}$$

The phase split ratio of both the decanter liquid and the condensate can be expressed as the function of compositions, and a relation between the two phase split ratios can be derived in the following way. A relation between $L'_{0,R}$ can be calculated from the following equation, describing the decanter inlet flow as the sum of its E-rich and E-lean phases:

$$L'_0 x'_0 = L'_{0,R} x'_{0,R} + L'_{0,W} x'_{0,W} = L'_{0,R} x_{1,R} + L'_{0,W} x_{1,W} \tag{7.10}$$

$$L'_{0,R} x_{1,R} = L'_0 x'_0 - \quad L'_0 - L'_{0,R} \quad x_{1,W} \tag{7.11}$$

$$L'_{0,R} \quad x_{1,R} - x_{1,W} \quad = L'_0 \quad x'_0 - x_{1,W} \tag{7.12}$$

$$L'_{0,R} = L'_0 \frac{x'_0 - x_{1,W}}{x_{1,R} - x_{1,W}} \tag{7.13}$$

This means that the phase split ratio of the decanter liquid can be written as:

$$\eta'_R = \frac{x'_0 - x_{1,W}}{x_{1,R} - x_{1,W}} \tag{7.14}$$

A similar equation can be derived for the phase split ratio of the condensate:

$$\eta_R = \frac{x_0 - x_{1,W}}{x_{1,R} - x_{1,W}} \tag{7.15}$$

By subtracting Equation 7.15 from Equation 7.14, a relation can be obtained between the two phase split ratios:

$$\eta'_R - \eta_R = \frac{x'_0 - x_{1,W} - \quad x_0 - x_{1,W}}{x_{1,R} - x_{1,W}} = \frac{x'_0 - x_0}{x_{1,R} - x_{1,W}} \tag{7.16}$$

From the component material balance of the mixing of the condensate and the entrainer, x'_0 can be expressed:

$$L'_0 x'_0 = L_0 x_0 + F_E x_E \tag{7.17}$$

$$x'_0 = \frac{L_0}{L'_0} x_0 + \frac{F_E}{L'_0} x_E = \frac{L_0}{L_0 + F_E} x_0 + \frac{F_E}{L_0 + F_E} x_E \tag{7.18}$$

By substituting Equation 7.18 into Equation 7.16:

$$\eta'_R - \eta_R = \frac{\frac{L_0}{L_0 + F_E} x_0 + \frac{F_E}{L_0 + F_E} x_E - \frac{L_0 + F_E}{L_0 + F_E} x_0}{x_{1,R} - x_{1,W}} \tag{7.19}$$

By rearranging Equation 7.19, the split ratio of the decanter liquid can be expressed as a function of the phase split ratio of the condensate:

$$\eta'_R = \eta_R + \frac{F_E}{L_0 + F_E} \frac{x_E - x_0}{x_{1,R} - x_{1,W}} \tag{7.20}$$

It can be seen that the phase split ratio of the decanter liquid is always higher than that of the condensate, and increases with the entrainer flow rate. At a critical entrainer flow rate, η'_R reaches one.

The reflux flow rate can be written as:

$$L_1 = r_R L'_{0,R} + r_W L'_{0,W} \tag{7.21}$$

$$L_1 = r_R \eta'_R L'_0 + r_W \ 1 - \eta'_R \ L'_0 \tag{7.22}$$

In this way, the total material balance of the still (Equation 6.19) has the following form:

$$\frac{dH_S}{dt} = \ r_R \eta_R + r_W \ 1 - \eta_R \ \ L'_0 - V \tag{7.23}$$

The component flow rates in the reflux stream are:

$$L_1 x_1 = L_{1,R} x_{1,R} + L_{1,W} x_{1,W} = r_R \eta'_R L'_0 x_{1,R} + r_W \ 1 - \eta'_R \ L'_0 x_{1,W} \tag{7.24}$$

Meanwhile, the component flow rates in the top vapour can be expressed from the component material balances for mixing the condensate and the entrainer (Equation 7.17), by taking into consideration that $V=L_0$:

$$V x_0 = L'_0 x'_0 - F_E x_E \tag{7.25}$$

If we substitute $L'_0 x'_0$ from Equation 7.10:

$$V x_0 = L'_{0,R} x_{1,R} + L'_{0,W} x_{1,W} - F_E x_E \tag{7.26}$$

$$V x_0 = L'_0 \eta'_R x_{1,R} + L'_0 \ 1 - \eta'_R \ x_{1,W} - F_E x_E \tag{7.27}$$

Substituting Equations 7.24 and 7.27 into the component material balance of the still (Equation 6.22):

$$\frac{d\ H_S x_S}{dt} = r_R \eta'_R L'_0 x_{1,R} + r_W \ 1 - \eta'_R \ L'_0 x_{1,W} - L'_0 \eta'_R x_{1,R} - L'_0 \ 1 - \eta'_R \ x_{1,W} + F_E x_E \tag{7.28}$$

$$\frac{d\ H_S x_S}{dt} = \ r_R - 1 \ \eta'_R L'_0 x_{1,R} + \ r_W - 1 \ \ 1 - \eta'_R \ L'_0 x_{1,W} + F_E x_E \tag{7.29}$$

The equation of the still path is by applying Equation 6.24:

$$\begin{aligned} H_S \frac{dx_S}{dt} = \ & r_R - 1 \ \eta'_R L'_0 x_{1,R} + \ r_W - 1 \ \ 1 - \eta'_R \ L'_0 x_{1,W} + F_E x_E - \\ & r_R \eta_R + r_W \ 1 - \eta_R \ \ L'_0 x_S + V x_S \end{aligned} \tag{7.30}$$

Using Equation 7.6 to substitute V, and rearranging the equation:

$$H_S \frac{dx_S}{dt} = \ r_R - 1 \ \eta'_R L'_0 x_{1,R} + \ r_W - 1 \quad 1 - \eta'_R \ \ L'_0 x_{1,W} + F_E x_E -$$

$$r_R - 1 \ \eta_R + \ r_W - 1 \quad 1 - \eta_R \ \ L'_0 x_S - F_E x_S \tag{7.31}$$

The final form of the still path equation for Case 2 is:

$$\frac{dx_S}{dt} = \frac{V+F_E}{H_S} \quad 1 - r_R \ \eta'_R \ \ x_S - x_{1,R} \ \ + \ \ 1 - r_W \quad 1 - \eta'_R \ \ \ x_S - x_{1,W} \quad - \frac{F_E}{H_S} \ x_S - x_E \tag{7.32}$$

The comparison of the still path equation of Case 2 to that of Case 1 (Equation 7.5) reveals that while the term describing the continuous entrainer feeding is the same, two differences occur:

1. The phase split ratio of the condensate is replaced by that of the decanter liquid, which always has a higher value.
2. The influence of the first two terms (removal of either the E-rich or the E-lean phase) is increased, as *V* is replaced by V+F_E.

In the case of total reflux operation, the first two terms disappear, and the still path equation for Case 1 and 2 become identical.

7.2. The Effect of the Continuous Entrainer Feeding

In this section, the effect of continuous entrainer feeding on the possible operational policies and on the still path directions is discussed.

7.2.1. The Effect of Continuous Entrainer Feeding on the Operational Policies

The model has four independent operational parameters: r_R, r_W, V and F_E. While in batch heteroazeotropic distillation r_R and r_W determines the still path direction, and V only influences the speed of distillation, in batch heterogeneous extractive distillation the still path direction is determined also by the relative magnitude of F_E and V. A higher F_E/V ratio obviously diverts the still path in a more prominent way towards the entrainer composition. The continuous entrainer feeding does not change the classification of the operational policies presented in Chapter 6, as the value of the entrainer flow rate can not be divided into separate categories (assuming that it is higher than the minimum value necessary for process feasibility, and not so high as to render the decanter hold-up homogeneous). In Table 7.1 literature examples are shown for the different operational policies. The majority of the literature suggests either Policy 9 or 10. By Policy 9, the E-rich phase is totally refluxed, while the E-lean phase is not refluxed at all. The E-lean phase could be accumulated in the decanter or withdrawn as distillate; the latter one is applied in the literature examples. By Policy 9, the reflux ratio is completely determined by the phase split ratio of the decanter liquid. If this reflux ratio is insufficient for a feasible separation, or if the liquid-liquid split has to be maintained longer than it is possible by Policy 9, Policy 10 can be applied. In this case, beside the total reflux of the E-rich phase, the E-lean phase is partially refluxed, as well. Policy 10 is practically realized in the following way.

One part of the vapour is condensed and refluxed, while the other one is led to the decanter, from which the total amount of the E-rich phase is refluxed at a constant E-rich phase hold-up. The E-lean phase is withdrawn as distillate. Van Kaam et al. (2008) performed a BHED experiment, which was originally intended to be a realization of Policy 10. The top vapour was condensed and partially refluxed. The non-refluxed part of the condensate was led to the decanter. Instead of refluxing the E-rich phase, the continuous entrainer feeding was increased to make up for the loss of entrainer in the decanter. In this way Policy 6 was realized, as both liquid phases were partially refluxed.

Policy	r_R	r_W	Reflux	Example in the literature
1	0	0	No reflux	
2		<1	E-lean phase (partial)	
3		1	E-lean phase (total)	
4		>1	E-lean phase (reintr.)	
5	<1	0	E-rich phase (partial)	
6		<1	E-rich (partial) and E-lean phase (partial)	Van Kaam et al. (2008): BHED experiment
7		1	E-rich (partial) and E-lean phase (total)	
8		>1	E-rich (partial) and E-lean phase (reintr.)	
9	1	0	E-rich phase (total)	Koehler et al. (1995), Rodriguez-Donis et al. (2003): mixture ethyl-acetate-ethanol-water
10		<1	E-rich (total) and E-lean phase (partial)	Modla et al. (2001, 2003), Rodriguez-Donis et al. (2003): mixture acetonitrile-water-butyl-acetate, Van Kaam et al. (2008), Barreto et al. (2011)
11		1	E-rich (total) and E-lean phase (total)	Total reflux operation with entrainer feeding
12		>1	E-rich (total) and E-lean phase (reintr.)	
13	>1	0	E-rich phase (reintr.)	
14		<1	E-rich (reintr.) and E-lean phase (partial)	
15		1	E-rich (reintr.) and E-lean phase (total)	
16		>1	E-rich (reintr.) and E-lean phase (reintr.)	

Table 7.1. The literature examples for the sixteen possible operational policies of BHED (reintr.: reintroduction - a greater amount of liquid is refluxed than what leaves condenser).

7.2.2. The Possible Still Path Directions

The still path direction is determined by the sum of the same three vectors (Figure 7.2) both for Case 1 (Equation 7.5) and 2 (Equation 7.32), which originate from x_S, the actual still composition and have a direction of ($x_S - x_{1,R}$), ($x_S - x_{1,W}$) and ($x_E - x_S$), respectively. The first two vectors, whose magnitude depends on r_R and r_W, were already present in the BHAD. These vectors point away (towards) from the E-rich phase composition $x_{1,R}$ and the E-lean phase composition $x_{1,W}$, if the value of r_R and r_W is less (higher) than one, respectively. However, a new vector appears which points always towards the entrainer composition, and whose direction is proportional to the entrainer flow rate. The direction of the resultant vector of the first two vectors (which are related to the decanter) depends on the operational parameters r_R and r_W, that is, on the operational policy. This direction is modified by the addition of the vector of the entrainer feeding to an extent depending on the relative magnitude of the vectors, that is, on all the four operational parameters (r_R, r_W, V and F_E) and also on the split ratio of the condensate or in the decanter.

The results are illustrated for a ternary fictive mixture, where A and B can be a homoazeotropic (minimum or maximum) or a close boiling mixture, while A and E form a binary heteroazeotrope, which is a saddle point of the system. With an azeotrope A-B, a distillation boundary may exist, but it does not affect the feasibility of the separation (Rodriguez-Donis et al., 2003; van Kaam et al., 2008)..

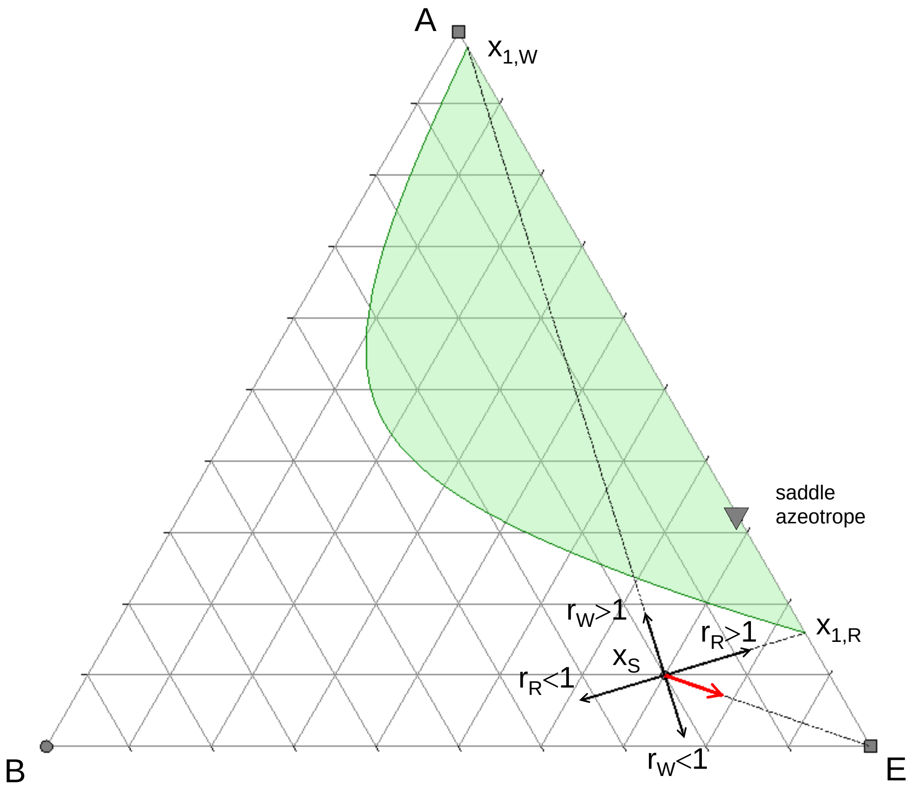
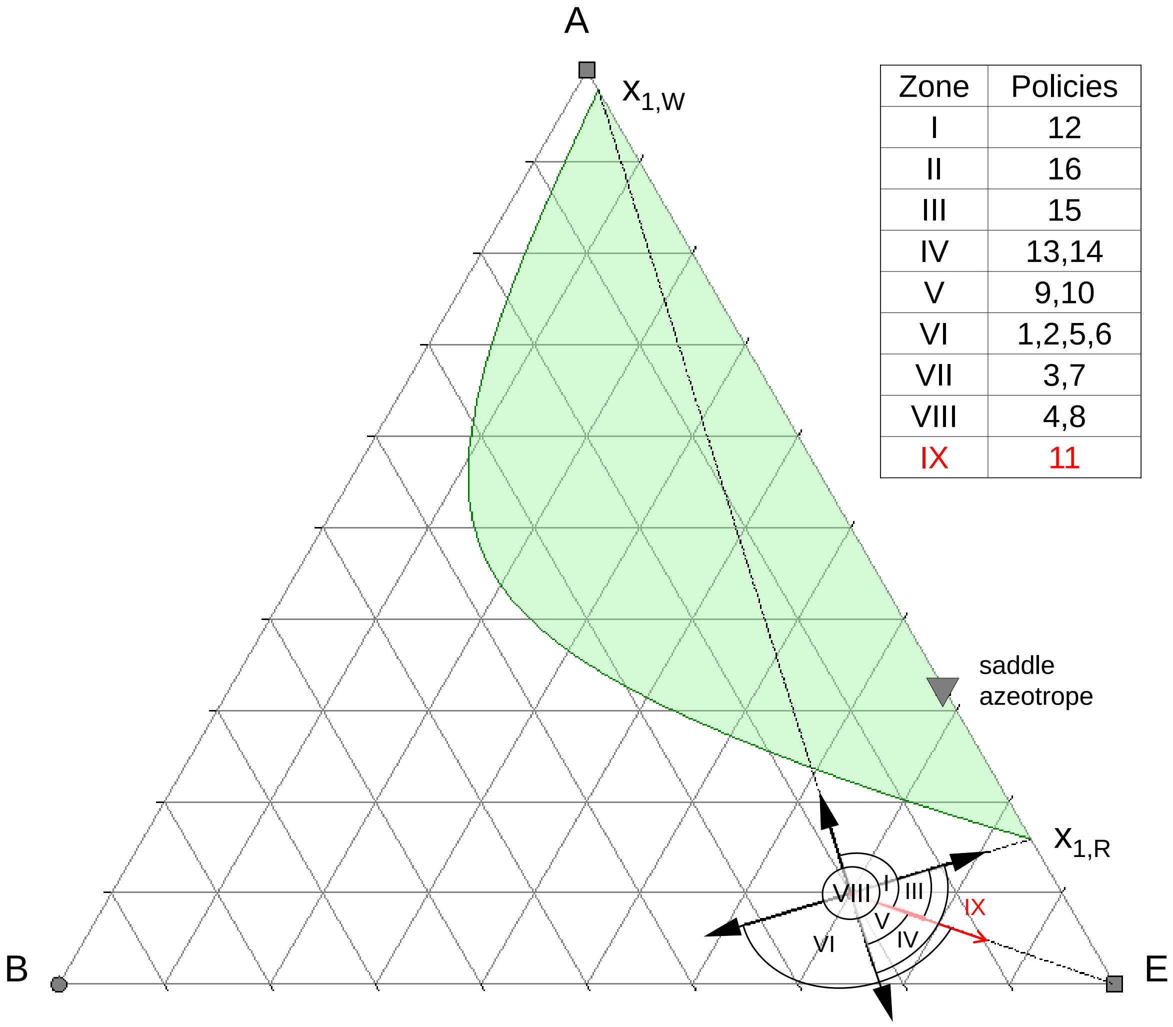


Figure 7.2. The possible directions of the vectors influencing the still path of batch heterogeneous extractive distillation.

The continuous E-feeding has the following effects on the eight still path zones presented for batch heteroazeotropic distillation (Figures 6.3 and 7.3):

- The zones having comprising only of a single direction in the case of BHAD are opening into the direction of the entrainer composition and every zone widens towards the entrainer feeding vector.
- As all the zones contain the direction of the entrainer feeding vector, every one of them is overlapping other zones. For example, the new Zone I partially overlaps with the new Zones III, IV and VIII.
- There are zones which disappear (Zones II and VII), as they have become identical to other zones (Zones I and VI, respectively).
- The operation under total reflux (Policy 11) appears as a new zone (Zone IX), pointing towards the entrainer composition. This is the only new zone, which has a single direction.



Zone	Policies
I	12
II	16
III	15
IV	13,14
V	9,10
VI	1,2,5,6
VII	3,7
VIII	4,8
IX	11

Figure 7.3. The direction of the still path for the different operational policies of batch heterogeneous extractive distillation.

As the new still path zones cover all possible directions, similarly to the batch heteroazeotropic distillation, the still composition can be moved into any desired direction by varying the value of the parameters r_R and r_W.

It can be still mentioned that, in spite of the continuous E-feeding, the still composition can remain constant by Policies 4 and 8 (Zone VIII), if the direction of the resultant of vectors related to the operational parameters r_R and r_W is just opposite to the vector of E-feeding and their lengths are equal.

Similarly to batch heteroazeotropic distillation, it is possible to direct the still path to achieve a desired final still composition by applying an appropriate operational policy or a combination of several policies. Reaching the A – B edge, unless at a location where the purity requirement for the product B is already satisfied, is unwanted as, in this way the original mixture to be separated is obtained once again. By batch heterogeneous extractive distillation, this problem is less likely to be encountered due to the continuous feeding of entrainer. Another objective could be to recover one of the original components (in this case B) in the still, rendering a further separation step unnecessary. However, the concentration of E is increasing in the still compared to batch heteroazeotropic distillation, which can prevent recovering the original component.

7.2.3. The Practical Significance of the Different Operational Policies

Not all the possible operational policies are of practical interest. The most conceptually straightforward one is Policy 9, the total reflux of the E-rich phase. If necessary, the reflux ratio can be increased by using Policy 10, that is, partially refluxing the E-lean phase besides the total reflux of the E-rich one. Policy 11, the total reflux of both phases, is applied in the start-up period, in order to obtain the heteroazeotrope as condensate. A desirable goal could be to reach B-E edge, relatively far from the E vertex, so that B could be easily recovered in a second separation step. In order to reach this goal, the still path should be directed towards the B-E edge, that is, it should lie in one of the following zones (Figure 7.3):

- Zone V (operation by Policies 9 or 10). These are the traditional operational policies. However, if the influence of the vector of E-feeding is large, they may result in a still path moving towards rather the E vertex than straight towards the B-E edge.
- Zone VI (operation by Policies 1, 2, 5 or 6). The two phases are not or only partially refluxed. If neither of the phases is refluxed, and the entrainer is fed into the column (Case 1), the column is operated according to the hybrid process. Policy 6 was already applied experimentally by Van Kaam et al. (2008), even if it was unintended. By these policies, the still path can move directly towards the B-E edge, and can even move away from the E vertex. In order to compensate the influence of the continuous entrainer feeding, the vectors pointing away from the E-rich and E-lean phase composition, respectively, should be as long as possible (r_R and r_W as low as possible). A low r_R value moves the still composition

towards lower E concentrations, while a low r_W value moves it towards the B-E edge. As a certain amount of reflux is usually necessary to the feasibility of the separation, these operational parameters might have minimum values.

- Zone VIII (operation by Policies 4 or 8). In this still path zone, the hold-up of the E-lean phase in the decanter is reduced. This results in a vector pointing towards the E-lean phase composition (away from the B-E edge), therefore, although the still path can still move towards the B-E edge by these policies, these policies are not recommended.
- Zone IV (operation by Policies 13 or 14). Because of the reduction of the E-rich phase hold-up in the decanter, the still path moves even faster towards higher entrainer concentrations. Similarly to Zone VIII, even though the still path can theoretically move in the right direction, these policies are not recommended.

The reduction of the E-rich phase hold-up (Policies 13-16) can be replaced with the continuous entrainer feeding, which is more efficient, since this latter one is not limited by the original hold-up of E-rich phase in the decanter. However, the composition of the E-rich phase and that of the entrainer feeding are different to an extent depending on the liquid-liquid equilibrium conditions. The smaller the difference between the composition of the E-rich phase and the entrainer, and the further the still path is located from these points, the more similar are the effects of the continuous entrainer feeding and of the reduction of the E-rich phase hold-up.

As seen above, even though the variation of the hold-up of the phases in the decanter is possible, its effect is smaller than by batch heteroazeotropic distillation due to usually strong influence of the continuous entrainer feeding.

7.3. Rigorous Simulation

The results of the feasibility analysis are validated by rigorous simulation calculations performed with the dynamic module (CC-DCOLUMN) of the professional flowsheet simulator ChemCAD. Our goal is to study the applicability of new BHED operational policies.

For the rigorous simulation, the same simplifying assumptions are used as for the rigorous simulation of BHAD.

The calculations were performed with a ChemCAD model similar to that presented in Section 6.3.1. The only exception is the presence of the two possible entrainer feeding locations, one to the condensate stream, the other one to the column.

7.3.1. Example 1

The mixture studied is water (A) – ethanol (B) + n-butanol (E), which exhibits a minimum boiling point A-B homoazeotrope, while A and E form a saddle heteroazeotrope. The calculated residue curve map of the mixture along with the binodal curve at T=25 °C is presented in Figure 7.4.

The vapour-liquid-liquid equilibria were described by the NRTL model. The NRTL parameters can be found in Appendix 2. The aim is the dehydration of the mixture by removing water from the decanter in the aqueous phase. First, Policy 9 is applied (total reflux of the E-rich phase only) after the start-up. The composition of the charge (x_F) is 50 mol% A and 50 % B. The amount of charge: 100 mol (3.8 dm^3 at 25 °C) in the still pot, and 6.52 mol in the decanter (0.25 dm^3 at 25 °C, which equals the maximum decanter hold-up). The column has 50 theoretical trays; the heat duty applied is 2 kW. The hold-up of the column is 0.01 dm^3/plate. The column is operated for 82 minutes under total reflux, at the end of this period the still composition is $x_{S,0}$. The E-feeding (120 mol/h, 25 °C) is already started at t=8 min into the column (Case 1 of the entrainer feeding). The feeding location is the second plate of the column (from the top), as a rectifying section of minimum one plate is required, if the decanter has been filled up before the start of the operation, in order to reach the two liquid phase region in the decanter. After the start-up under $R=\infty$, the whole amount of aqueous (E-lean) phase is withdrawn as distillate. The hold-ups of the two phases are constant and equal (125 cm^3) in the decanter. Since the assumption of negligible column hold-up is omitted results of the feasibility analysis are valid for the average (still+column) hold-up composition instead of the still composition. The (average) hold-up path calculated is shown in Figure 7.5, along with the influencing vectors at two different times, at the end of the start-up ($x_{S,0}$) and at 182 min ($x_{S,1}$).

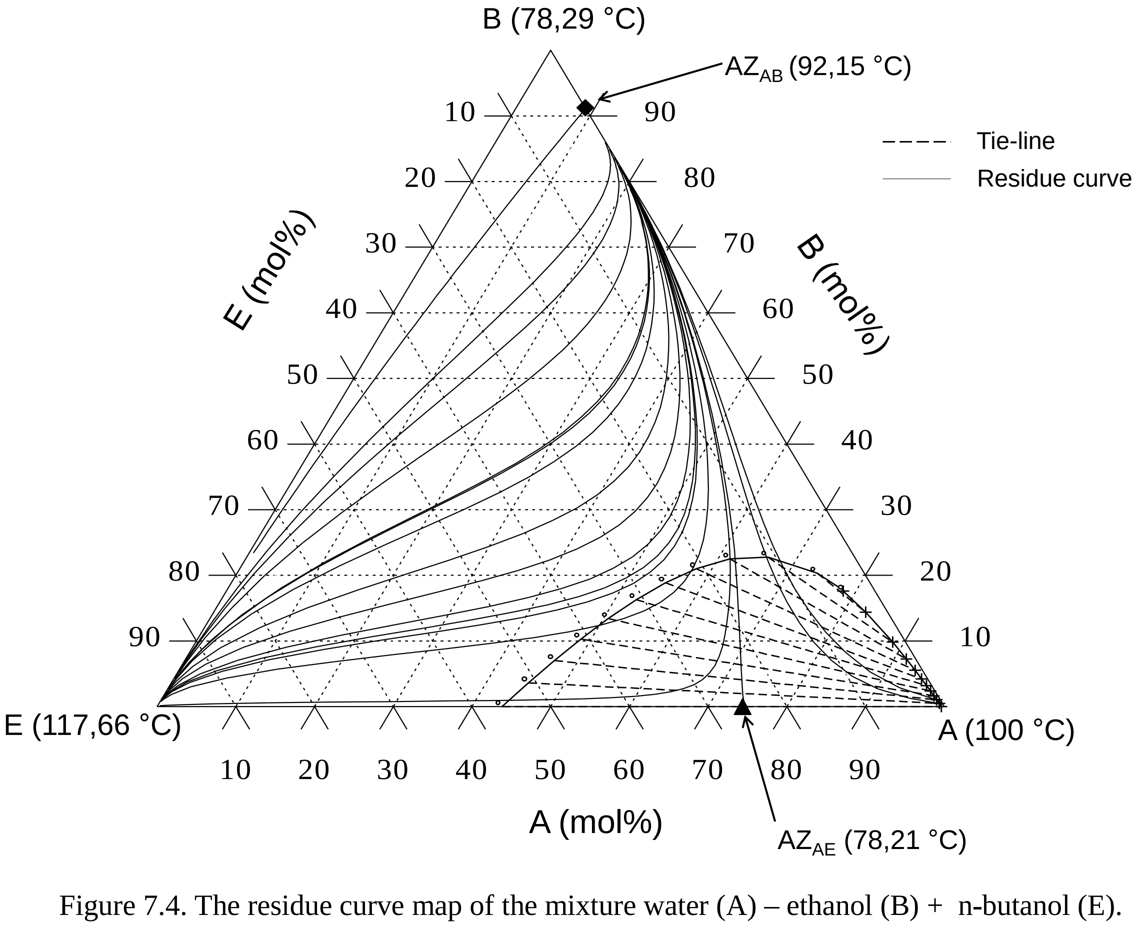


Figure 7.4. The residue curve map of the mixture water (A) – ethanol (B) + n-butanol (E).

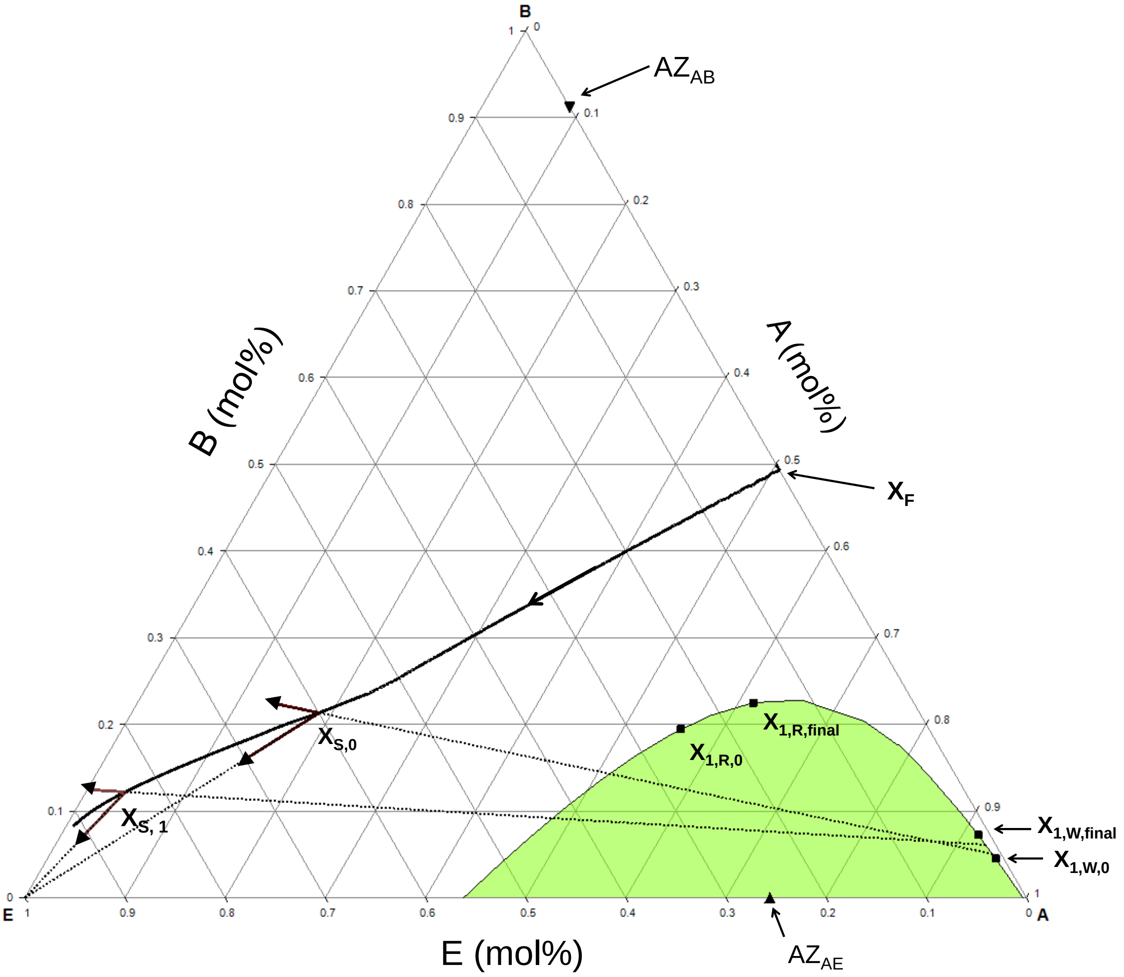


Figure 7.5. The hold-up path calculated for Policy 9 (r_R=1, r_W=0) for the separation of water (A) and ethanol (B) using n-butanol (E) as entrainer.

The still path moves into the direction predicted by the feasibility analysis, that is, between the vector pointing away from the E-lean phase composition ($x_{1,W}$) and that of pointing towards E. It must be noted that the E-lean phase composition is slightly changing during the operation, and always contains some ethanol. At the end of the operation (t=282 min), the still composition hardly contains water (0.53 %). Since a large amount of E is needed for the separation, its concentration is high (91.55 %) in the residue.

7.3.2. Example 2

The only difference between this and the previous example is that Policy 5 (only partial reflux of E-rich phase) is applied after the start-up instead of Policy 9. 10 % of the E-rich phase is withdrawn as distillate.

The hold-up path (Figure 7.6) is influenced not only by the two previous vectors, but by a new vector pointing away from the point of E-rich phase ($x_{1,R}$), whose direction is towards the B-E edge in this case. Figure 7.6 shows all the three vectors influencing the hold-up, at two different times.

Consequently, the still composition approaches better the B-E edge (0.39 mol% water in the residue (at 282 min)).

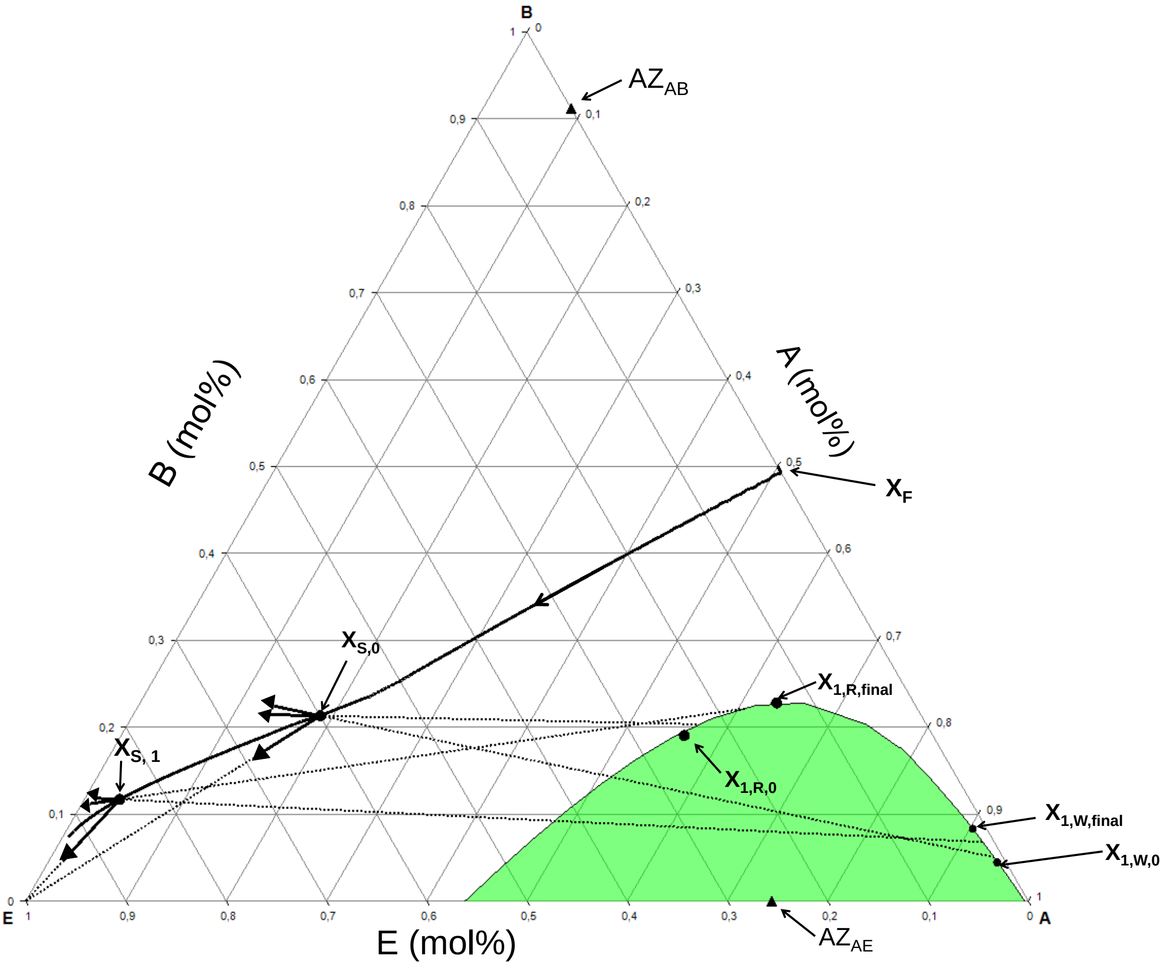


Figure 7.6. The hold-up path calculated for Policy 5 (r_R=0.9, r_W=0) for the separation of water (A) and ethanol (B) using n-butanol (E) as entrainer.

7.3.3. Example 3

The only difference between this and Example 1 is that Policy 6 (partial reflux of both phases) is applied after the start-up: 10 % of the E-rich phase and 60 % of the E-lean phase is withdrawn as distillate.

The still path (Figure 7.7) is influenced by the vector

- of continuous entrainer feeding, which is unchanged,
- of the E-lean phase, which gets shorter than in Example 1, and
- of the E-rich phase (similarly to Example 2).

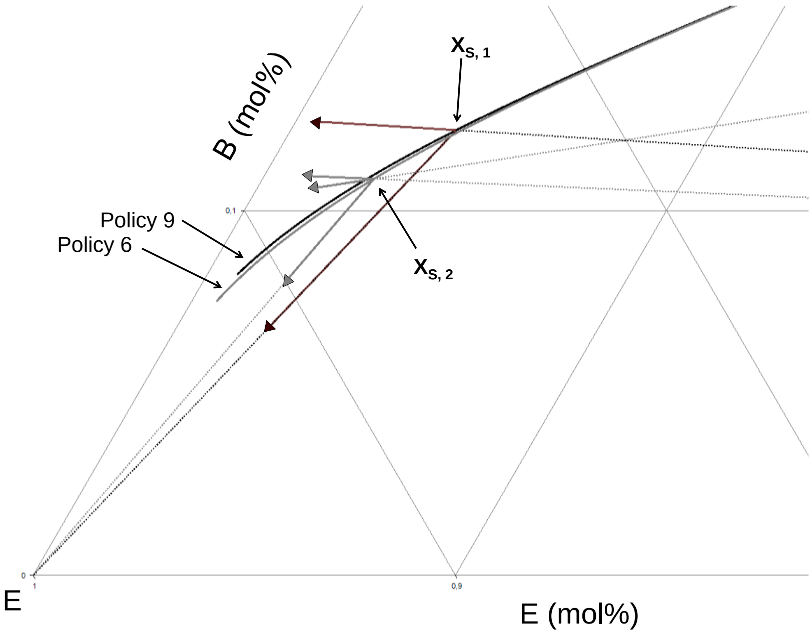


Figure 7.7. The comparison of the hold-up paths calculated for Policy 6 (r_R=0.9, r_W=0.4) and Policy 9 (r_R=1, r_W=0) for the separation of water (A) and ethanol (B) using n-butanol (E) as entrainer.

The resulting vector is located in Zone VI, and points less prominently in the direction of E, but due to the large influence of the continuous entrainer feeding, the difference is not significant. Due to the fact that the vector of the E-rich phase points towards the B-E edge, as well, the final residue contains less water (0.42 %) at the same time than in Example 1.

7.3.4. Example 4

The difference between this and Example 1 is that in this case hold-up reduction is applied by the combination of Policies 9 (total reflux of the E-rich phase) and 8 (partial reflux of E-rich phase, reduction of the hold-up of the E-lean phase). Policy 9 is applied after the start-up until the butanol content of the still exceeds 80 mol% (Figure 7.8), then the operation is continued by Policy 8. By Policy 8 10% of the E-rich phase is withdrawn as distillate, and the E-lean phase hold-up in the decanter is reduced by 75 cm^3 (by 60 %) during a period of 10 min. This corresponds means r_R=0.9 and r_W≈1.5

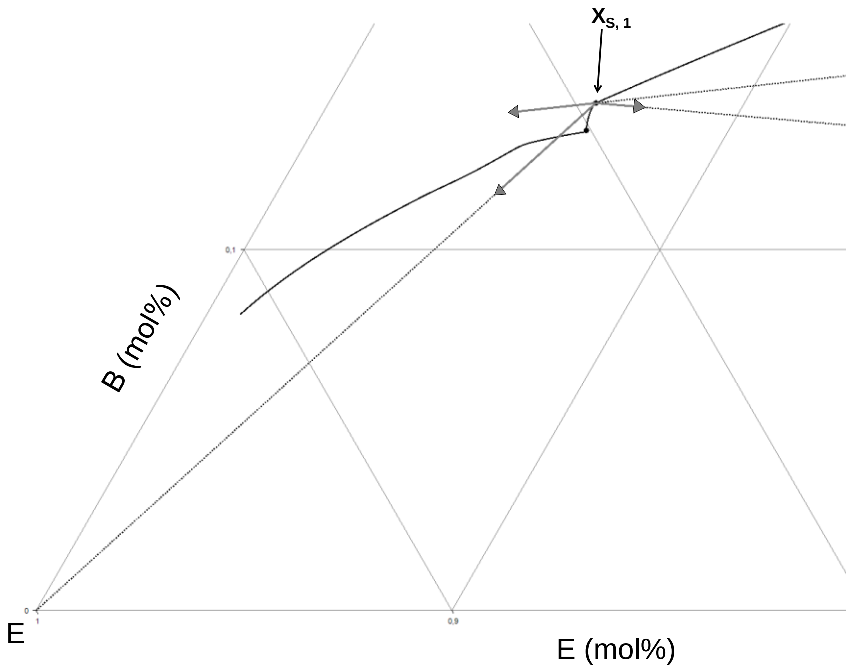


Figure 7.8. The hold-up path calculated for Example 4 (Policy 9 then Policy 8) for the separation of water (A) and ethanol (B) using n-butanol (E) as entrainer.

During the application of Policy 8 (between $x_{S,1}$ and $x_{S,2}$), the direction of the hold-up path is in Zone VIII, and it clearly deviates from trajectory of Policy 9 (Example 1). Due to the large influence of the continuous entrainer feeding, however, it moves rather towards the A-E edge than the B-E one, which is not advantageous. The water content of the residue (at 282 min) is 0.62 mol%, although the E-content (91.49 mol%) is slightly less than in Example 1.

The results of the rigorous simulations indicate that the still path directions are in accordance with the results of the feasibility analysis, and that batch heterogeneous extractive distillation can be performed by new operational policies (e.g. Policy 5), as well.

7.4. Conclusions

The general model for batch heteroazeotropic distillation presented in Chapter 6 was extended to batch heterogeneous extractive distillation by taking into consideration continuous entrainer feeding. The possibility of refluxing or withdrawing both liquid phases as distillate was maintained, as well as the variability of the hold-up of the phases in the decanter. Two different entrainer feeding locations are distinguished: in Case 1 the entrainer is fed into the column, in Case 2 it is added to the decanter. The equation describing the evolution of the still composition was derived for both cases. Compared to batch heteroazeotropic distillation, a new term, related to the continuous entrainer feeding appeared, and by Case 2, the influence of the existing terms, related to the operation of the decanter was increased.

Sixteen operational policies can be distinguished on the basis of the two operational parameters r_R and r_W, which are the ratio of the flow rates of the E-rich and E-lean phase refluxed and condensed, respectively. The occurrence of the operational policies in the literature and potential practical applicability were discussed. The effect of the continuous entrainer feeding on the still path direction, which is now influenced by three vectors with magnitudes depending on the operational policy and the entrainer flow rate, was studied. The eight original still path zones of batch heteroazeotropic distillation are modified: some of them disappear, and the remaining zones overlap each other. Beside the entrainer feeding, the still path zones still cover all possible directions, that is, by using an appropriate operational policy it is possible to direct the still composition into any direction. In practice, however, the influence of the entrainer feeding is large, and it is difficult to move the still path away from the entrainer composition. For the same reason, the variation of the hold-up of the phases in the decanter has only small effect on the still path.

The still path directions were validated by rigorous simulation of the dehydration of the mixture water – ethanol using n-butanol as entrainer. Four examples were presented: operation by Policy 9 (total reflux of entrainer-rich phase only), Policy 5 (partial reflux of E-rich phase only), Policy 6 (partial reflux of both phases) and a combination of Policies 9 and 8 (partial reflux of E-rich phase, reduction of the E-lean phase hold-up in the decanter). The average (still and column) hold-up composition moved in accordance with the directions predicted by the feasibility analysis. By using the new Policy 5, it was possible to slightly reduce the water content of the still residue mainly containing ethanol and butanol.

GENERAL CONCLUSIONS AND PERSPECTIVES

Conclusions

The separation of azeotropic mixtures requires the application of special distillation methods. Minimum and maximum boiling azeotropes are often encountered in the pharmaceutical and fine chemical production industries, where the mixtures to be separated are often of varying amount and composition, and therefore batch distillation is applied. The present work investigates the possibilities to improve the batch distillation separation of azeotropic mixtures.

Chapter 1 is a literature review on the principles of vapour-liquid phase equilibria, including azeotropy, and the special distillation methods applied for the separation of azeotropic and close-boiling mixtures. Emphasis is placed on the batch processes.

In Chapter 2, an algorithm is developed for the determination of product sequences of batch distillation for any number of components based only on the boiling points of pure components and azeotropes, and azeotropic compositions. The former algorithms required the use of a vapour-liquid equilibria (VLE) model for mixtures containing more than three components. The method is suitable for heteroazeotropes and for taking into consideration pressure change, as well. The stability of fixed points is determined with assumption that every ternary submixture occur in practice. On the basis of the stabilities, all feasible product sequences are determined. Finally, the relative amount of cuts are determined for the given charge composition. The results are presented for two mixtures. For Mixture 1, the stabilities and the set of product sequences calculated without using a VLE model agree with the ones obtained by Ahmad et al. (1998). The calculations for Mixture 2 demonstrated that the new algorithm is able to handle heteroazeotropes as well. These results verify that the new algorithm is suitable for the determination of the sequence of the cuts without using a VLE model.

In Chapter 3, the open and six different closed operation modes (which differ from each other in the operation of the vessels) of batch rectifier and middle-vessel column were studied by rigorous dynamic simulation with the professional flowsheet simulator ChemCAD. Four closed modes of the multivessel column were also investigated. The recoveries were compared under constant product quality and energy consumption. For the batch rectifier closed operation provided better recoveries in case of negligible liquid hold-up. Level control with initially filled up top vessel and temperature control with initially empty top vessel proved to be the best closed modes. For a ternary mixture, the open operation mode of middle-vessel column provided greater recoveries for two products, but smaller for a third one, than the open mode of batch rectifier. The average recovery was higher for the non-conventional configuration. For the middle-vessel column the open operation mode proved to be better than the closed ones in every case. It was not possible to choose the best closed mode, as the order of the closed modes (with respect to the recoveries) depends on the product and the hold-up. For low liquid hold-up, temperature control, for higher hold-ups level control with initially empty top and bottom vessels can be recommended. For the multivessel column the energy consumption of level control with initially empty vessels was the lowest. The division of the charge between the vessels (instead of filling the charge into the bottom vessel only) had adverse effect on energy consumption.

In Chapter 4, the influence of recycling off-cuts for the batch distillation (BD) and batch extractive distillation (BED) regeneration of a four component (methanol - THF - water - toluene) waste solvent mixture of a pharmaceutical plant was studied by rigorous dynamic simulation. A batch rectification process of 6 consecutive productions, where the first fore-cut was incinerated, whilst the second fore-cut, the after-cut and the column hold-up were recycled, was investigated. In the BED process, water as entrainer was fed into the top of the column during the heating-up period. The volume of the first fore-cut had an optimal value, which was slightly lower for BED. A minimum volume (which is higher for BED) of first fore-cut must be taken to avoid the accumulation of THF and toluene in the charge, which would render the 6-batch process infeasible, that is, methanol of prescribed purity could not be obtained from all the batches. The optimal case of BED process gave significantly (18 %) higher profit than that of the traditional one.

In Chapter 5, the application of BED and that of the hybrid process (HP) was investigated for two pharmaceutical waste solvent mixtures, whose separation is prevented (Mixture 1: methanol, THF, acetonitrile, water, pyridine) or limited by azeotropes (Mixture 2: acetone, methanol, tetrahydrofuran, n-hexane, ethanol, water and toluene).

The performance of the basic and a modified operational policy of BED and HP for the recovery of THF from Mixture 1 was studied. Both water and pyridine are suitable as entrainers, but water is more practical to use. Experiments performed on a laboratory packed column were evaluated with rigorous simulations. The prescribed separation task was not feasible with BD, but it was possible to produce THF of desired quality by BED and HP. The highest recovery and production rate were achieved with the HP, while the least efficient process was the basic policy of BED. The effect of operational parameters was also investigated.

In the case of Mixture 2 several azeotropes limit the recovery of methanol by BD by causing a significant loss of methanol. A new BED operational policy was suggested, where water (entrainer) feeding was applied only during the heating-up of the column (BED1). At the end of the heating-up, the concentration of organic pollutants increased (compared to BD) and methanol concentration decreased significantly at the top of the column. Water feeding can continue during the fore-cut (BED2), but this increases the amount of fore-cut and dilutes the mixture from which methanol is recovered. Laboratory experiments were performed to compare the BD and the two BED operational policies. The highest recovery was obtained by BED1, the lowest one by BD. Industrial-size pilot productions of BD and BED1 were performed in a 50 bubble cap tray column. By BED1 the recovery increased considerably (from 68.5 % to 73.1%), which is explained by the significant decrease of methanol concentration in the distillate at the end heating-up period by BED, and thus lower methanol loss with the fore-cut.

In Chapter 6, a general model of batch heteroazeotropic distillation was proposed. Both liquid phases can be refluxed or withdrawn as distillate. Their hold-up in the decanter can be increased, decreased or kept constant, as well. Two operational parameters r_R and r_W were introduced, defining the ratio of the flow rates of the E-rich and E-lean phase refluxed and condensed, respectively. By assuming maximal separation, the still path equation was derived. Depending on the values of r_R and r_W, 16 possible operational policies were distinguished.

The still path direction depending on the value of the operational parameters can be located in eight different zones, which cover all the possible directions, that is, still path can be changed in any desired direction. It is also possible to recover a pure component in the still, thus eliminating the need for a further separation step.

The still path directions for three new operational policies were validated by rigorous simulation for the mixture water – formic acid – propyl formate. The benefit of using a non-traditional operational policy with hold-up reduction in the decanter was demonstrated, as well.

In Chapter 7, the model of batch heteroazeotropic distillation was extended to batch heterogeneous extractive distillation by taking into consideration continuous entrainer feeding. Two different entrainer feeding locations are distinguished: in Case 1 the entrainer was fed into the column, in Case 2, it was added to the decanter. The equation describing the evolution of the still composition was derived for both cases. Compared to batch heteroazeotropic distillation, a new term, related to the continuous entrainer feeding appeared, and by Case 2, the influence of the existing terms, related to the operation of the decanter was increased.

The practical applicability of the possible operational policies was discussed. The effect of the continuous entrainer feeding on the still path direction was also studied. The eight original still path zones of batch heteroazeotropic distillation are modified: some of them disappear, and the remaining zones overlap each other. It is still possible to direct the still composition into any direction, however, the influence of the entrainer feeding is large in practice, and it is difficult to move the still path away from the direction of entrainer composition. For the same reason, the variation of the hold-up of the phases in the decanter only has small effect on the still path.

The still path directions were validated by rigorous simulation of the dehydration of the mixture water – ethanol using n-butanol as entrainer. By using the new Policy 5 (partial reflux of E-rich phase only), it was possible to slightly reduce the water content of the still residue mainly containing ethanol and butanol.

Perspectives

According to my opinion, future works in the area of batch distillation may treat the following topics:

1. The optimization of the BED separation described in Section 5.2 could be performed. This could include the optimization of the reflux ratios of the different steps, the termination criteria of the steps, and the parameters of the entrainer feeding (flow rate, duration, feeding location). It can be suspected that optimal entrainer feeding duration is somewhere between that of policies BED1 (during the heating-up only) and BED2 (during the heating-up and the first fore-cut). It would be also interesting to perform the optimization with taking off-cut recycle into account, as well, as it could significantly alter the optimal policy obtained.
2. The investigation of the different closed operation modes of batch distillation could be extended for non-ideal, even azeotropic mixtures. The advantage of closed modes over the open is expected to increase with the decrease of relative volatility.
3. The theory of optimal control could be applied to find optimal combinations of the possible operational policies of both batch heteroazeotropic and batch heterogeneous extractive distillation to obtain the desired products in minimum amount of time.

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Appendix 1: Supplementary Calculation Results for Chapter 3

Supplementary calculation results for the open and different closed modes of batch rectifier (Section 3.2.1) can be found in Table A1.1.

N	8	10					12
R_{open}	9	7	9			11	9
Hold-up (cm^3/p.)	0	0	0	50	100	0	0
Open	92.2	90.6	93.3	95.2	94.4	94.7	93.6
Mode 1	88.7	89.5	92.0	91.7	89.8	93.3	92.5
Mode 2a	93.0	94.1	97.1	92.8	88.4	97.1	97.9
Mode 2b	93.9	96.3	97.7	93.3	88.9	97.9	98.5
Mode 3	93.3	94.4	97.1	92.8	88.4	97.3	98.0
Mode 4a	94.1	96.9	97.4	93.2	88.8	97.5	98.0
Δt_{total} (min)	364.5	294	368	379.5	380.5	441.5	369

Table A1.1. Recoveries (%) of A for the open and different closed modes of batch rectifier for different values of operational parameters (N: number of theoretical plates, R_{open}: reflux ratio of open mode, Δt_{total}: operation time).

Appendix 2: Binary Interaction Parameters

This Appendix contains the binary interaction parameters used in this work. The UNIQUAC parameters used in Chapter 4 can be found in Table A.1. These parameters are taken from the database of ChemCAD, except the ones for the THF (B) – toluene (D) pair, which were found in the DECHEMA Vapor-Liquid Equilibrium Data Collection (Gmehling et al., 1977).

i	j	U_{ij}-U_{jj} [cal/mol]	U_{ji}-U_{jj} [cal/mol]
A	B	-175.228	695.882
A	C	95.259	-10.377
A	D	-59.2844	1171.91
B	C	770.86	84.566
B	D	40.91421	-36.55233
C	D	572.67	32865

Table A.1. UNIQUAC parameters for methanol (A) – THF (B) – water (C) – toluene (D) mixture.

The UNIQUAC parameters used in Chapter 5 are given in Table A.2 (Section 5.1) and A.3 (Section 5.2). The parameters are taken from the database of ChemCAD, except for the following component pairs, in Table A.2: THF (B) – acetonitrile (C), THF (B) – pyridine (E), acetonitrile (C) – pyridine (E); in Table A.3: acetone (A) – THF (C), THF (C) – n-hexane (D), THF (C) – toluene (G). The VLE parameters missing from the ChemCAD database were found in the DECHEMA Vapor-Liquid Equilibrium Data Collection (Gmehling et al., 1977).

i	*j*	U_{ij}-U_{jj} [cal/mol]	U_{ji}-U_{jj} [cal/mol]
A	B	-175.228	695.882
A	C	-21.0988	491.712
A	D	95.259	-10.377
A	E	238.372	-349.4
B	C	122.4142	96.83603
B	D	770.86	84.566
B	E	271.7731	-249.9466
C	D	766.74	-17.727
C	E	279.1163	-345.4131
D	E	1412.17	-752.987

Table A.2. UNIQUAC parameters for methanol (A) – THF (B) – acetonitrile (C) – water (D) – pyridine (E) mixture.

i	j	U_{ij}-U_{jj} [cal/mol]	U_{ji}-U_{jj} [cal/mol]	A_{ij} [-]	A_{ji} [-]	C_{ij} [-]	C_{ji} [-l]
A	B	434.944	-101.228	0	0	0	0
A	C	-151.2608	262.5485	0	0	0	0
A	D	-43.308	491.96	0	0	0	0
A	E	131.164	69.3872	0	0	0	0
A	F	601.61	-52.302	0	0	0	0
A	G	-315.28	555.74	0	0	0	0
B	C	-175.228	695.882	0	0	0	0
B	D	26.0288	1538.35	0	0	0	0
B	E	-181.286	247.378	0	0	0	0
B	F	95.259	-10.377	0	0	0	0
B	G	-59.2844	1171.91	0	0	0	0
C	D	-3.8016	127.8955	0	0	0	0
C	E	514.441	-254.883	0	0	0	0
C	F	770.86	84.566	0	0	0	0
C	G	40.91421	-36.55233	0	0	0	0
D	E	830.2	-49.213	0	0	0	0
D	F	-6440.65	-8329.79	-150.059	-95.1219	23.6647	13.8908
D	G	62.6301	-19.2546	0	0	0	0
E	F	50.88	232.01	0	0	0	0
E	G	-174.305	961.671	0	0	0	0
F	G	572.67	32865	0	0	0	0

Table A.3. UNIQUAC parameters for acetone (A) – methanol (B) – tetrahydrofuran (C) – n-hexane (D) – ethanol (E) – water (F) – toluene (G) mixture.

The NRTL parameters used for the calculations presented in Chapter 6, for the mixtures water – formic acid – propyl formate and aniline – ethylene glycol – water, respectively, are given in Tables A.4 and A.5. All the parameters were taken from the database of ChemCAD.

i	*j*	B_{ij} [K]	B_{ji} [K]	α [-]	A_{ij} [-]	A_{ji} [-]	C_{ij} [-]	C_{ji} [-]
E	A	-327.315	-6253.91	0.2	33.8478	124.491	-5.51839	-17.4194
E	B	78.3303	127.613	0.3013	0	0	0	0
A	B	-362.885	342.424	0.2921	0	0	0	0

Table A.4. NRTL parameters for water (A) – formic acid (B) – propyl formate (E) mixture

i	*j*	B_{ij} [K]	B_{ji} [K]	α [-]
A	B	256.926	343.831	0.29
A	E	-245.828	1790.56	0.1617
B	E	-338.073	405.263	0.2977

Table A.5. NRTL parameters for aniline (A) – ethylene glycol (B) – water (E) mixture

The NRTL parameters for the mixture ethanol – water – n-butanol (Chapter 7) are given in Table A.6. The parameters were taken from the database of ChemCAD.

i	*j*	B_{ij} [K]	B_{ji} [K]	α [-]
A	B	670.441	-55.1681	0.3031
A	E	1468.34	215.427	0.3634
B	E	19.1588	-16.5768	0.3038

Table A.6. NRTL parameters for water (A) – ethanol (B) – n-butanol (E) mixture

Appendix 3: The Effect of Operational Parameters for the Regeneration of THF Using Batch Extractive Distillation and Hybrid Process

The effect of the operational parameters on the recovery of THF, the specific energy consumption (SEC) and specific water consumption (SWC) was investigated by rigorous simulation for the regeneration of THF from a five-component waste solvent mixture (Section 5.1.4.3). This investigation was performed for the modified operational policy of BED (BEDM) and for the hybrid process (HP). The detailed numerical results are presents in the following tables:

- the effect of the location of feed plate (*f*), BEDM: Table A3.1,
- the effect of the reflux ratio (*R*), BEDM: Table A3.2,
- the effect of water flow rate during heating-up (W_1), BEDM: Table A3.3,
- the effect of water flow rate during production (W_2), BEDM: Table A3.4,
- the effect of water flow rate during heating-up (W_1), HP: Table A3.5,
- the effect of water flow rate during production (W_2), HP: Table A3.6.

The basic values of the parameters, set in bold, were the experimental ones.

f	Recovery (%)	*SEC* (MJ/kg)	*SWC* (kg/kg)
1	90.9	4.24	2.13
3	83.9	4.56	2.33
5	77.3	4.88	2.54
7	**72.8**	**5.15**	**2.69**
9	67.9	5.48	2.89

Table A3.1. The effect of the location of feed plate (*f*) for the BED process of a five-component THF rich waste solvent mixture.

R	Recovery (%)	*SEC* (MJ/kg)	*SWC* (kg/kg)
3	68.1	4.03	2.87
4	73.3	4.50	2.67
5	**72.8**	**5.15**	**2.69**
7	63.6	6.65	3.08

Table A3.2. The effect of the reflux ratio (*R*) for the BED process of a five-component THF rich waste solvent mixture.

W_1 (dm^3/h)	Recovery (%)	*SEC* (MJ/kg)	*SWC* (kg/kg)
0.4	72.4	5.18	2.68
0.436	**72.8**	**5.15**	**2.69**
0.55	73.2	5.13	2.72
0.6	73.9	5.07	2.74
0.8	74.9	5.03	2.84
1	74.9	5.05	2.97

Table A3.3. The effect of water flow rate during heating-up (W_1), for the BED process of a five-component THF rich waste solvent mixture.

W_2 (dm^3/h)	Recovery (%)	*SEC* (MJ/kg)	*SWC* (kg/kg)
0.3	67.4	5.41	2.21
0.393	**72.8**	**5.15**	**2.69**
0.5	74.9	5.11	3.31
0.7	75.6	5.20	4.62

Table A3.4. The effect of water flow rate during production (W_2), for the BED process of a five-component THF rich waste solvent mixture.

W_1 (dm^3/h)	Recovery (%)	*SEC* (MJ/kg)	*SWC* (kg/kg)
0.15	98.0	2.74	2.56
0.25	98.1	1.99	2.65
0.35	98.1	2.02	2.75
0.417	**98.1**	**2.04**	**2.82**
0.5	98.1	2.06	2.90
0.8	97.8	2.15	3.71

Table A3.3. The effect of water flow rate during heating-up (W_1), for the HP process of a five-component THF rich waste solvent mixture.

W_2 (dm^3/h)	Recovery (%)	*SEC* (MJ/kg)	*SWC* (kg/kg)
0.8	97.1	1.78	2.04
0.926	**98.1**	**2.04**	**2.82**
1.05	98.5	2.44	3.71
1.2	98.7	3.38	6.75

Table A3.4. The effect of water flow rate during production (W_2), for the HP process of a five-component THF rich waste solvent mixture.

Glossary

Adjacency matrix (A): the set of binary elements A_{ij} describing the existence of residue curves between two stationary points. If A_{ij} equals 1, it means that a residue curve connects the stationary point i with the point j. An equivalent definition is that the stationary point j is in the unstable boundary limit set of the point i.

***Azeotropic composition (azeotropic point)*:** a composition of a mixture, where the equilibrium composition of the liquid and vapour phases are identical.

***Azeotropic mixture*:** a mixture that forms at least one azeotrope. It can be a homoazeotrope, where one liquid phase is in equilibrium with the vapour phase in the azeotropic point, or a heteroazeotrope, where two liquid phases are in equilibrium with the vapour phase.

***Batch distillation region*:** the set of liquid composition, from which the same cuts can be obtained by using batch distillation (rectification), assuming of maximal separation.

Close boiling mixture: a zeotropic mixture with relative volatility very close to unity.

Closed operation: the operation of a batch column configuration without continuous product withdrawal.

Common unstable boundary limit set: The common unstable boundary limit set of two unstable nodes is the intersection of their unstable boundary limit sets, that is, the set of stationary points connected to both unstable nodes by residue curves. These stationary points are the ones located on the stable dividing boundary separating the two unstable nodes.

Constant molar overflow: the assumption that for every mole of vapour condensed, one mole of liquid is vaporised.

Continuous distillation region: a region with only one unstable and stable node, which has the same feasible products for any initial composition within this region.

Distillation: the most frequently method for the separation of liquid mixtures. The separation is based on the difference in the volatility of the components.

Distillation boundary: a set of composition separating the composition space into distillation regions. A residue curve boundary separates residue curve regions, a batch distillation boundary separates batch distillation regions.

Distillation boundary map: a simplified residue curve map that shows the basic pattern of the residue curve map temperature directions and the distillation boundaries when they exist.

Entrainer: a mass separating agent added to the original mixture to be separated, in order to favourably influence the vapour-liquid equilibrium conditions, and thus the separability of the mixture. It can be liquid or solid, pure component or a mixture, as well.

Extractive section: the section of the column between the entrainer feeding and the feed (continuous distillation), or below the entrainer feeding (batch distillation).

***Global indeterminacy*:** the stability of stationary points does not unambiguously determine the Serafimov class of the mixture.

Heteroazeotropic composition (point): a composition of a mixture, where two liquid phases are in equilibrium with the vapour phase and the overall equilibrium composition of the liquid and vapour phases are identical.

Hold-up path: the trajectory of the average (still+column) hold-up composition in batch distillation.

Homoazeotropic composition (point): a composition of a mixture, where only one liquid phases are in equilibrium with the vapour phase and the equilibrium composition of the liquid and vapour phases are identical

Ideal mixture: a mixture, whose vapour-liquid equilibrium conditions can be described by the Raoult-Dalton's Law.

Local indeterminacy**:** the same set of boiling points may occur for two different types of residue curve maps (two Serafimov-classes), but the stability of stationary points unambiguously determined the Serafimov class of the mixture.

Maximal separation: the assumption of infinite number of theoretical plates and very high reflux ratio.

Node (stationary point of residue curve maps):

- stable node (SN): the end point of residue curves (except unstable separatrices). Stable nodes are obtained as final residues in batch distillation,
- unstable node (UN): the starting point of residue curves (except stable separatrices). An unstable node is obtained as first cut in batch distillation.

Relative volatility**:** the ratios of the vapour-liquid distribution ratios of two components. A relative volatility close to one indicates a difficult separation.

Rectifying section**:** the section of the column above the feed, or the entrainer feeding if present.

Residue curve: the trajectory of the still composition during the open evaporation of a mixture. The boiling point increases along residue curves.

Residue curve map: the set of all the residue curves of a mixture.

Residue curve region (basic distillation region): a set of residue curves, which have common initial and end points (unstable and stable nodes, respectively).

Saddle (S) (stationary point of residue curve maps): residue curves approach saddles, and then move away from them. Only separatrices reach or start from saddles. The boiling point increase along the stable separatrices and decreases along the unstable ones.

Separatrix (on residue curve maps):

- stable separatrix: a residue curve running from a saddle to a stable node,
- unstable separatrix: a residue curve running from an unstable node to a saddle.

Separatices are the boundaries of residue curve regions.

Serafimov classification: a classification of ternary mixtures based on the number and stability of the stationary points of the residue curve map.

Stable boundary limit set: The stable boundary limit set of the stationary point *i* is the set of all the stationary points which can be reached from *i* by following residue curves in the direction of decreasing temperature. A stable node is not an element of the stable boundary limit set of any stationary point. The stable boundary limit set of an unstable node is empty.

Stable dividing boundary or maximum residue surface (MaxRS): a boundary surface separating the unstable nodes. It is the set of stationary points reachable from two unstable nodes, that is, those that form a boundary between the unstable nodes.

Stability (residue curve maps): the type of a stationary point (unstable node, saddle or stable node).

State-task network (STN)*:* a graph representation of batch processes that has two types of nodes: state nodes that correspond to feeds, intermediates, and final products; and task nodes that represent processing steps.

Stationary point: a point, where the first derivatives of a function equal zero. The stationary points of residue curve maps are the pure components and the azeotropes.

Still path: the trajectory of still composition in batch distillation.

Stripping section: the section of the column below the feed.

Unidistribution line**:** a set of composition where the vapour-liquid distribution ratio of a component equals unity.

Univolatility line**:** a set of composition where the relative volatility of a component pair equals unity.

Unstable boundary limit set: The unstable boundary limit set of the stationary point *i* is the set of all the stationary points which can be reached from *i* by following residue curves in the direction of increasing temperature. An unstable node is not an element of the unstable boundary limit set of any stationary point. The unstable boundary limit set of a stable node is empty.

Unstable dividing boundary or minimum residue surface (MinRS): a boundary surface separating the stable nodes. It is the set of stationary points reachable from two stable nodes, that is, those that form a boundary between the stable nodes.

Vapour-liquid distribution ratio: the ratio of the vapour phase and liquid phase mole fractions of a component.

Zeotropic mixture: a mixture, whose components do not form any azeotrope.