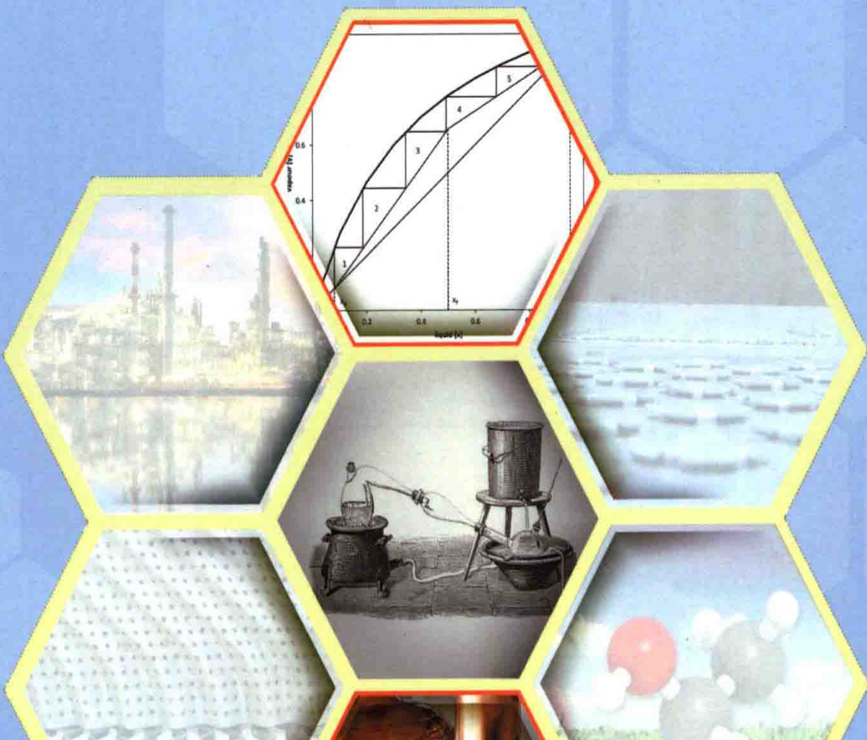
DISTILLATION

FUNDAMENTALS AND PRINCIPLES



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Distillation: Fundamentals and Principles

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Distillation: Fundamentals and Principles

Preface to the Distillation Collection

For more than 5,000 years distillation has been used as a method for separating binary and multicomponent liquid mixtures into pure components. Even today, it belongs to the most commonly applied separation technologies and is used at such a large scale worldwide that it is responsible for up to 50% of both capital and operating costs in industrial processes. It moreover absorbs about 50% of the total process energy used by the chemical and petroleum refining industries every year. Given that the chemical industry consumed 19% of the entire energy in Europe (2009), distillation is *the* big driver of overall energy consumption.

Although distillation is considered the most mature and best-understood separation technology, knowledge on its manifold aspects is distributed unevenly among different textbooks and manuals. Engineers, by contrast, often wish for just one reference book in which the most relevant information is presented in a condensed and accessible form. *Distillation* aims at filling this gap by offering a succinct overview of distillation fundamentals, equipment, and applications. Students, academics, and practitioners will find in *Distillation* a helpful summary of pertinent methods and techniques and will thus be able to quickly resolve any problems in the field of distillation.

This book provides a comprehensive and thorough introduction into all aspects of distillation, covering distillation history, fundamentals of thermodynamics, hydrodynamics, mass transfer, energy considerations, conceptual process design, modeling, optimization and control, different column internals, special cases of distillation, troubleshooting, and the most important applications in various industrial branches, including biotechnological processes.

Distillation forms part of the "Handbook of Separation Sciences" series and is available as a paper book and as an e-book, thus catering to the diverging needs of different readers. It is divided into three volumes: "Fundamentals and Principles" (Editors A. Górak and E. Sorensen), "Equipment and processes" (Editors A. Górak and Ž. Olujić), and "Operation and applications" (Editors A. Górak and H. Schoenmakers). Each volume contains chapters written by individual authors with acclaimed expertise in their fields. In addition to that, readers will find cross-references to other chapters, which allow them to gain an extensive overview of state-of-the-art technologies and various research perspectives. Helpful suggestions for further reading conclude each chapter.

A comprehensive and complex publication such as *Distillation* is impossible to complete without the support of an entire team whose enduring help I wish to acknowledge. In particular, I wish to express my heartfelt gratitude to the 42 leading world experts from the academia and industry who contributed to the chapters of this book. I thank the co-editors of the three volumes of *Distillation*—Dr Eva Sorensen,

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UCL, Dr Žarko Olujić, Delft University of Technology, and Dr Hartmut Schoenmakers, former member of BASF SE, Ludwigshafen—for their knowledgeable input and expertise, unremitting patience, and continuous encouragement. The invaluable editorial assistance of Dipl.-Ing. Johannes Holtbrügge during the entire editorial process is also greatly acknowledged.

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Preface to *Distillation: Fundamentals and Principles*

This is the first book in a three-volume series covering all aspects of *Distillation*. This volume focuses on the fundamental principles of distillation with particular emphasis on practical understanding of design and operation. The chapters are written by different authors and the approach, depth, and extent of subject matter coverage may therefore differ from chapter to chapter, however, together they represent a comprehensive overview of the current state of the art.

The first chapter traces the historical development of distillation from the first applications over 5000 years ago, via the medieval period, and the nineteenth-century industrial developments, to contemporary applications with emphasis on the applications and equipment which led to our current technology. A prerequisite for the design of distillation columns is knowledge of vapor–liquid equilibrium (VLE) and of mass transfer phenomena. Chapter 2 considers thermodynamic models for the prediction of VLEs, and the conditions for the occurrence of azeotropes. In Chapter 3, an account is given of the fundamental principles of mass transfer including diffusion, mass transfer coefficients, and mass transfer of both binary and multicomponent mixtures in both tray and packed columns.

Chapter 4 sets out the fundamental principles of binary distillation including simple calculation and analysis methods. This is followed by an account of batch distillation in Chapter 5, giving an overview of the fundamentals of batch distillation, including different operating modes, alternative column configurations and more complex batch distillation processes. Chapter 6 considers energy-efficient distillation design and operation, including columns operating both above and below ambient temperatures. Various advanced and complex distillation column configurations are also introduced.

Chapters 7 and 8 consider design of distillation processes. Chapter 7 describes the conceptual design of zeotropic multicolumn distillation configurations. A computationally efficient mathematical framework is described that synthesizes configurations that use $n-1$ distillation columns for separating a zeotropic mixture into n product streams. Chapter 8 turns the attention to azeotropic systems and describes a systematic framework for their conceptual design, considering and comparing different approaches. Several shortcut methods are presented, followed by an account of rigorous optimization, and their applicability for design is discussed.

Aspects of design, analysis, and application of hybrid distillation schemes are covered in Chapter 9. These hybrid distillation schemes become necessary when separation tasks such as separation of azeotropic or close-boiling mixtures cannot be achieved in a single conventional distillation column. Chapter 10 presents an overview of modeling methods covering both simplified and rigorous models. Conceptual features are highlighted and basic equations are shown for both equilibrium- and nonequilibrium-based approaches. In addition to classical distillation, modeling of related and more complex processes is also discussed. Finally, Chapter 11 presents an overview of the main advances in optimization of zeotropic systems, ranging from systems using only conventional columns, to fully thermally coupled systems, with main focus on mathematical programming approaches for design.

I would like to thank all the authors for their contributions and assiduous efforts in making this the most comprehensive account of distillation fundamentals available to date.

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List of Symbols and Abbreviations

Latin symbols

Symbol	Explanation	Unit	Chapter
A	Matrix of constant coefficients		11
A_{AB}	Coefficient in van Laar's equation	–	4
A_c	column cross section area	m^2	10
A_e	Effective adsorption factor (Group methods)	–	11
A_{ht}	Heat transfer area	m^2	6
A_i	Coefficient in Antoine's equation for component i	Pa, bar	4
A_z	Azeotropic composition	mol/mol	5
a	Attractive parameter in cubic equations of state	Jm^3/mol^2	2
a'	specific vapor-liquid interfacial area	m^2/m^3	10
a_i	Activity of component i	–	2
B	Bottom stream flow rate	kmol/s, kg/s	4, 11
B	Matrix of coefficients		11
B_i	Coefficient in Antoine's equation for component i	Pa K, bar °C, Pa °C,...	4
BT	Total molar bottom stream flow rate	kmol/s	11
b	Co-volume in cubic equations of state	cm^3/mol, m^3/mol	2
b	*Content dependent* Binary variable Vector of constant coefficients		11
C_A	Price of distillate product	\$, €	5
C_C	Unit costs for cooling in the condenser	\$/kW	11
C_F	Price of feed	\$, €	5
$C_{fix,k}$	Annualized fixed charge cost of column k	\$/a	11
C_H	Unit costs for heating in the reboiler	\$/kW	11
C_i	Coefficient in Antoine's equation for component i	K, °C	4
C_k	Annualized cost of column k	\$/a	11

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Symbol	Explanation	Unit	Chapter
c	Parameter in the VTPR equation of state	m^3/mol	2
c	Constant/vector of constant coefficients		11
c	molar concentration	mol/m^3	10
c_p	Molar heat capacity at constant pressure	J/(mol K)	2
c_{pL}	Liquid heat capacity at constant pressure	J/K	4
c_{pLi}	Liquid heat capacity of component i at constant pressure	J/K	4
c_{pV}	Vapor heat capacity at constant pressure	J/K	4
d	generalized driving force, Eq. (10-30)	1/m	10
D	Distillate flow rate	mol/s, kmol/s, kg/s	4, 5, 8, 10, 11
D_{AB}	binary diffusion coefficient	m^2/s	10
D_{ax}	axial dispersion coefficient	m^2/s	10
D_i	effective diffusion coefficient of component *i*	m^2/s	10
D_{ij}	Driving Force		9
$Đ_{ij}$	Maxwell-Stefan diffusion coefficient	m^2/s	10
DT	Total molar distillate flow rate	kmol/s	11
E	Entrainer flow rate	kmol/s	5, 8
E_{MV}	Murphree vapor efficiency	–	4
E_O	Overall tray/stage efficiency	–	4
E_{OL}	Murphree efficiency for the liquid phase	–	10
E_{OV}	Murphree efficiency for the vapor phase	–	10
Ex	Exergy	W, W/K	6
F	Feed flow rate	mol/s, kmol/s, kg/s	4, 5, 8, 10, 11
FT	Total molar feed flow rate	kmol/s	11
f	Vaporized fraction of the feed	–	4
$f(\cdot)$	Scalar function		11
f_i	Fugacity of component i	Pa	2
$f_{obj}(\cdot)$	Objective function		2, 5
G^E	Total excess Gibbs energy	J	2, 8
G_{ij}	NRTL parameter		2
$g(\cdot)$	Equality constraints Scalar/vector functions		5 11
g^E	Molar excess Gibbs energy	J/mol	2
Δg_{ij}	Interaction parameter between component i and j	K	2

—cont'd

Symbol	Explanation	Unit	Chapter
H	Enthalpy	W, W/K	6
h	partial molar enthalpy	J/mol	10
H_A	Amount of distillate	mole	5
H_F	Amount of feed	mole	5
$H_{i,j}$	Henry constant of component i in j	Pa	2
ΔH_{vap}	Molar heat of vaporization	J/mol	4
h	Specific enthalpy	J/kg, J/mol	4, 8, 11
h(·)	Inequality constraints Scalar/vector functions		5 11
Δhv	Enthalpy of vaporization	J/mol	2
h^E	Molar excess enthalpy	J/mol	2
HETP	height equivalent to a theoretical plate	m	10
HTU	height of a transfer unit	m	10
H_c	column height	m	10
J	diffusion flux	mol/(m^2 s)	10
$\mathbf{J}$	column vector consisting of J_i	mol/(m^2 s)	10
K_i	Chemical equilibrium constant of component i	–	2
K_i	Distribution coefficient/K-factor of component i	–	2, 4, 8, 11
K_k	Relation between feed and heat flow (Andrecovich & Westerberg model)	–	11
k_{ij}	Binary parameter in cubic equations of state	–	2
K^{eq}	vapor-liquid equilibrium constant	–	10
K_{OL}	overal mass transfer coefficient in terms of the liquid phase	mol/(m^2 s)	10
K_{OV}	overal mass transfer coefficient in terms of the vapor phase	mol/(m^2 s)	10
L	Liquid flow rate	kmol/s, kg/s	4, 8, 11
Ld	Reflux flow rate returned to the column	kmol/s	11
L_R	Liquid flow rate in a rectifying column section	kmol/s	11
L_S	Liquid flow rate in a stripping column section	kmol/s	11
l	axial coordinate directed from column top to bottom	m	10
L	liquid molar flow rate	mol/s	10
M	Scalar (Big M parameter)		11
m	slope of the operating line, Eq. (10-A2)	–	10

(continued)

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Symbol	Explanation	Unit	Chapter
N	*Content dependent* Number of trays/stages Number of components	–	4, 6, 8, 11
N_R	Number of trays/stages in the rectifying section	–	4, 8, 11
N_S	Number of trays/stages in the stripping section	–	4, 8, 11
NT	Total number of trays in column section	–	4
NF	Feed tray location	mole	4
n	Number of moles		2
n_C	Number of components	–	8
n	number of mixture components	–	10
N	Content dependent molar flux	mol/(m^2 s)	10
NTU	number of transfer units	–	10
O_i	Offcuts	–	5
P	Hourly profitability	profit/hr	5
P_i	Product cuts	–	5
Poy_i	Poynting factor of component i		2
p	Pressure	Pa (or bar, atm)	2, 4, 8, 11
$p_{0,i}^{LV}$	Vapor pressure of component i	Pa	4
pb_i	Individual flow rate of the bottom product	kmol/s, kg/s	11
p_i	Partial pressure of component i	Pa (or bar, atm)	4
pt_i	Individual flow rate of the top product	kmol/s, kg/s	11
Q_{EX}	Exchanged heat	kJ	11
$\dot{Q}$	Duty	W	4, 5, 6, 8, 11
$\dot{Q}_{flash}$	Energy added or removed in the flash drum	W	4
$\dot{Q}_{ht}$	Heat transfer duty	W	6
$\dot{Q}_{hx}$	Energy added or removed in the heat exchanger	W	4
$\dot{Q}_k$	Heat duty for column k	W	11
Q_B / Q_R	reboiler/boilup heat duty	–	8
q	Energy to convert one mol of feed to saturated vapor at dew point divided by the molar heat of vaporization	–	4
q_{LS}	Liquid fraction of a stream	mol/mol	11
q	liquid molar fraction in the feed stream	–	10
Q	heat flux	W/m^2	10
R	Gas constant	J/mol·K	2

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Symbol	Explanation	Unit	Chapter
R	Boolean variable		11
R_{min}	Reflux ratio	–	4, 5, 6, 8, 11
r	*Content dependent* Binary variable Interest rate Scalar function		11
rec	Component recovery		11
$\Re$	gas constant	8.3144 J/(mol K)	10
R_b	reboil ratio	–	10
R_f	reflux ratio	–	10
S	Stripping factor	–	11
S	Entropy	W, W/K	6
S	Side stream flow rate	kmol/s, kg/s	4
S_e	Effective stripping factor (Group methods)	–	11
S_{ij}	Selectivity	–	2, 8
s	Renewal frequency, parameter of the surface renewal model	1/s	10
T	Absolute temperature	K	2, 4, 6, 8, 11
T_{bp}	Boiling temperature	K, (°C)	4, 5
T_0	Reference temperature	K	6
$T_{min,ea}$	Minimum exchanger approach temperature	K	11
T_{st}	Steam temperature	K	11
ΔT_{lm}	Logarithmic mean temperature difference	K	6
t	Time	s	5,10
t_f	Total operating/final time	s	5
t_e	exposure time, parameter of the penetration model	s	10
T	temperature	K	10
U	Overall heat transfer coefficient	W/m^2K	6
U	Big M Parameter		11
u	Control variables		5
u_L	liquid-phase velocity	m/s	10
U	length-specific molar holdup	mol/m	10
V	Vapor flow rate	kmol/s, kg/s	4, 8, 11
V_R	Vapor flow rate in a rectifying column section	kmol/s	11
Vr	Reboil flow rate returned to the column	kmol/s	11

(continued)

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Symbol	Explanation	Unit	Chapter
V_S	Vapor flow rate in a stripping column section	kmol/s	11
v	Molar volume	cm^3/mol, m^3/mol	2
v	Design variables		5
V	vapor molar flow rate	mol/s	10
W	Still holdup in differential distillation	mole	4, 5
W	Boolean variable		11
W_{ideal}	Ideal compression power demand	W	6
WC	Boolean variable (determine if a condenser exists)		11
WR	Boolean variable (determine if a reboiler exists)		11
w	Binary variable	–	11
X	Parameter in the Gilliland graphical correlation		11
x	Vector of real variables		11
x	liquid mole fraction	mol/mol	10
$\mathbf{x}$	liquid-phase composition vector	mol/mol	10
x_i	Mole fraction of component i in the liquid phase	mol/mol	2, 4, 5, 8, 11
Y	*Content dependent* Parameter in the Gilliland graphical correlation Boolean variable		11
y	Algebraic variable		5, 11
y_i	Mole fraction of component i in the vapor phase	mol/mol	2, 4, 5, 8, 11
y	vapor mole fraction	mol/mol	10
$\mathbf{y}$	vapor-phase composition vector	mol/mol	10
Z	*Content dependent* Boolean variable Objective variable in optimization problems	–	11
z	Boolean variable		11
z	Compressibility factor	–	2
z_i	Mole fraction of component i	mol/mol	2, 4, 8, 11
z	film coordinate; transformed liquid-phase concentration, Eq. (10-A11)	m –	10
$\mathbf{z}$	liquid-phase composition vector consisting of z_i	–	10

Greek Symbols

Symbol	Explanation	Unit	Chapter
α	Relative volatility	–	2, 4, 5, 10, 11
$\boldsymbol{\alpha}$	relative volatility vector consisting of α_i	–	10
α^T	heat transfer coefficient	W/(m^2 K)	10
α_{ij}	Non-randomness parameter in the NRTL equation ($\alpha_{ij} = \alpha_{ji}$)	–	2
β_k	Size factor for column k (Andrecovich & Westerberg model)		11
β, β_{ik}	binary mass transfer coefficient	mol/(m^2 s)	10
$[\beta]$	matrix of mass transfer coefficients	mol/(m^2 s)	10
γ_i	Activity coefficient of component i	–	2, 4
γ	component net interstage flow, Eq. (10-A3)	–	10
$\boldsymbol{\gamma}$	component net interstage flow vector consisting of γ_i	–	10
Γ	Group activity coefficient	–	2
$[\Gamma]$	matrix of thermodynamic correction factors	–	10
δ	film thickness	m	10
ζ	Split fraction	–	11
λ	Eigenvalue	–	8
ρ	Density	kg/m, mol/m^3	2
ν_k	Number of structural groups in the mixture	–	2
$\nu_k^{(i)}$	Number of structural groups in pure solvent	–	2
ϕ	Liquid phase ratio	–	8
ϕ_A	Recovery factor for absorption section	–	11
ϕ_i	Recovery factor for component i	–	11
ϕ_R	Underwood root	–	11
ϕ_S	Recovery factor for stripping section	–	11
ϕ	Fugacity coefficient	–	2
φ_{FB}	Fischer–Burmeister function		11
ϕ	volumetric holdup	m^3/m^3	10
μ	chemical potential	J/mol	10
θ	root of Underwood's equation	–	10
$\boldsymbol{\theta}$	vector of roots of Underwood's equation	–	10
τ	transformed time parameter, Eq. (10-1)	–	10
ψ	Recovery fraction	–	11
ϑ	Temperature	°C	2
τ	Dimensionless time	–	8
τ_{ij}	NRTL parameter	–	2
ξ	Dimensionless time scale	–	2
$\boldsymbol{\Omega}(\cdot)$	Boolean function		11
ω	Acentric factor	–	2

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