UNDERSTANDING MEMBRANE DISTILLATION AND OSMOTIC DISTILLATION

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This edition first published 2017

Registered Offices
John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA

Editorial Office
111 River Street, Hoboken, NJ 07030, USA

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Library of Congress Cataloguing-in-Publication Data

Names: Johnson, Robert A. | Nguyen, Minh H.
Title: Understanding membrane distillation and osmotic distillation / Robert A. Johnson, Minh H. Nguyen.
Description: Hoboken, NJ : John Wiley & Sons, Inc., 2017. | Includes bibliographical references and index.
Identifiers: LCCN 2016052029 (print) | LCCN 2016053443 (ebook) | ISBN 9780470122167 (cloth) | ISBN 9781118880326 (pdf) | ISBN 9781118880395 (epub)
Subjects: LCSH: Membrane distillation. | Membranes (Technology) | Osmosis.
Classification: LCC TP156.D5 J64 2017 (print) | LCC TP156.D5 (ebook) | DDC 660/.28424–dc23
LC record available at https://lccn.loc.gov/2016052029

Cover image: Valery_Plotnikov/Gettyimages
Cover design by Wiley

Set in 11/13pt, WarnockPro by SPi Global, Chennai, India.

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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Preface

Distillation processes are at the center of numerous manufacturing facilities spanning a wide range of industries. Common applications include desalination, the manufacture of alcoholic beverages, fractionation of organic liquids, water removal in preparation for crystallization or spray drying, and the production of fruit juice concentrates. Several different types of industrial distillation processes are in use, the choice depending on process requirements. Membrane distillation (MD) and osmotic distillation (OD) are important additions to this range of processes as they represent the mergence of conventional distillation processing and modern membrane separation science. The advantages offered by these emerging processes include unprecedented product quality and substantial energy savings.

Accordingly, this book is intended to provide the reader with an understanding of the theoretical and practical aspects of MD and OD. While these processes have overlapping areas of application, their individual development paths have largely been driven by their different operational requirements. Historically, the main interest in MD has arisen from growing desalination demands from a world in which 1 billion people are without safe drinking water. The main interest in OD on the other hand has come from the food industry in response to a growing consumer preference for high-quality liquid concentrates. Fruit and vegetable juices with their delicate aromas and prevalence of heat-sensitive vitamins and antioxidants have been at the forefront of this interest. These factors have been reflected by a rapid increase in the number of journal articles and conference presentations on MD and OD in recent years. Indeed, MD and OD have been transformed from laboratory novelties into processes that are now in the initial stages of industrial implementation in applications long accepted as

being the exclusive domain of multiple-stage flash (MSF) distillation, multiple-effect distillation (MED), vapor compression distillation (VCD), freeze concentration (FC), and reverse osmosis (RO).

A major impetus for writing this book was a need to address the fact that most of this recently disseminated information has been individualistic in nature. That is, the experimental results and conclusions presented have been highly specific with respect to membrane type, module (membrane housing) type, operating conditions, nature of the feed material, and process objectives. The authors believe that a general text incorporating basic physical chemistry and chemical engineering theory presented in an uncomplicated format will assist researchers to unravel this web of information and provide the tools for further technological advancements. It is also intended that this book will find use as a general reference for those involved in the manufacture of industrial MD and OD plants.

The general introduction to this book includes a historical perspective of this current surge of interest in MD and OD. It also examines the operation of established desalination and concentrate production processes and attempts to provide the reader with an understanding of where MD and OD may potentially take their places among these processes. The theoretical aspects of MD and OD are then considered using a general approach that is readily adaptable to specific systems. Attention is then turned to more practical aspects and in particular the properties of the various types of membranes that are central to each process. This section includes a discussion of problems relating to membrane module design that have yet to be overcome. Specific examples of MD and OD applications are then discussed in sufficient detail to equip the reader with the knowledge to devise appropriate stand-alone or integrated membrane systems for any given application. Finally, some future prospects of both processes are proposed to stimulate the imagination of the reader.

Robert A. Johnson
Brisbane, Australia
2016

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Sydney, Australia
2016

Acknowledgments

Robert A. Johnson

I wish to thank the Queensland University of Technology (QUT) for the assistance provided during the preparation of this book. I also wish to thank my former postgraduate students who have made major contributions to the development of osmotic distillation and associated technologies over many years. Finally, I extend my deep appreciation to my wife Frances for her love, support, and patience during the several years spent writing this book.

Minh H. Nguyen

I thank all my friends and colleagues, including my graduate students who have worked with me over the years, from the industry and research laboratories in the areas of membrane and osmotic distillation.

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Nomenclature

a	activity
b	air gap thickness (m)
c	concentration (kg m^{-3}, wt%, °Brix)
C_p	heat capacity (kJ kg^{-1} K^{-1})
D	diffusion coefficient (m^2 s^{-1})
d_h	hydraulic diameter (m)
d_p	pore diameter (m)
ΔH_v	latent heat of vaporization (kJ kg^{-1})
h	individual heat transfer coefficient (J m^{-2} s^{-1} K^{-1})
J	mass flux (kg m^{-2} s^{-1})
K	overall mass transfer coefficient (kg m^{-2} s^{-1} Pa^{-1})
k	individual mass transfer coefficient (kg m^{-2} s^{-1} Pa^{-1})
k	thermal conductivity (W m^{-1} K^{-1})
k_B	Boltzmann constant (1.380×10^{-23} J K^{-1})
Kn	Knudsen number
M	molecular weight (kg kmol^{-1} or kDa)
Nu	Nusselt number
P	hydraulic pressure (Pa)
ΔP	hydraulic pressure gradient (Pa)
p	vapor pressure (Pa)
Δp	vapor pressure gradient (Pa)
ΔP_{LEP}	liquid entry pressure (Pa)
Pr	Prandtl number
Q	total heat flux (J m^{-2} s^{-1})
R	universal gas constant (8.314 J mol^{-1} K^{-1})
r	pore radius (m)
Re	Reynolds number
Sc	Schmidt number

Sh	Sherwood number
T	temperature (K)
U	overall heat transfer coefficient ($J\,m^{-2}\,s^{-1}\,K^{-1}$)
x	mole fraction
w	humidity ratio

Greek Letters

γ	surface tension ($N\,m^{-1}$)
δ	membrane thickness (m)
ϵ	membrane porosity
η	viscosity (Pa s)
θ	contact angle (°)
θ_c	concentration polarization coefficient
θ_t	temperature polarization coefficient
θ_v	vapor pressure polarization coefficient
λ	mean free path (m)
ζ_w	water activity coefficient
σ	collision diameter (m)
Π	osmotic pressure (Pa)
ρ	density ($kg\,m^{-3}$)
φ	relative humidity
χ	tortuosity

Frequently Used Subscripts

f	feed side
s	strip side
m	membrane
b	bulk stream
fb	bulk feed stream
sb	bulk strip stream
fm	feed–membrane interface
sm	strip–membrane interface
v	vapor

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General Introduction

1.1 Overview of Distillation Processes

The term "distillation" refers to any process that facilitates the separation of solution components using their different volatilities. Distillation processes are categorized according to the number and nature of the components being separated as shown in Figure 1.1. At a primary level, distillation processes can be categorized as simple distillation or fractional distillation. Simple distillation utilizes a still to effect the separation of two miscible liquids or a single liquid and its nonvolatile solutes in a single vaporization–condensation process. Fractional distillation refers to the separation of two or more liquids using repeated vaporization–condensation steps in a single column.

Simple distillation of a mixture of two liquids facilitates enrichment of the distillate (vaporized fraction) with the most volatile component with a corresponding enrichment of the residue with the second component. The distillate is the desired component in typical industrial applications. The degree of enrichment depends on the relative volatilities of the liquids. In some applications, the distillate is subjected to a second simple distillation step in a separate still to obtain the required separation. In simple distillation involving a liquid and its nonvolatile solutes, a high degree of separation can be achieved by prolonged boiling of the liquid. Here, the distillate is free of solutes other than trace amounts transferred by the entrainment of liquid droplets in the vapor. In many cases, distillation is carried out progressively through a series of simple distillation steps in a continuous process. Removal of the liquid from its nonvolatile solutes defines this process as a stripping operation. Furthermore, the still or series of stills in which stripping occurs is referred to as an evaporator. Fractional distillation results in a high degree of

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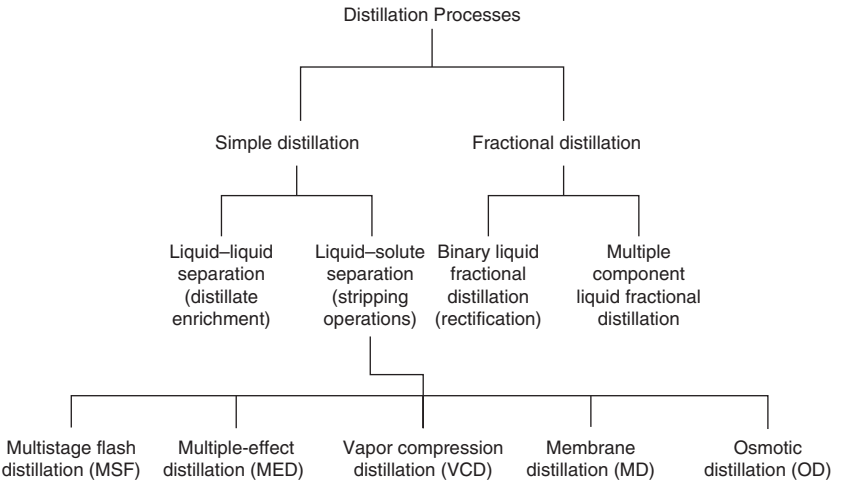

Figure 1.1 Overview of distillation processes.

liquid–liquid separation due to repetitive distillation steps. This process is referred to as rectification when used for the separation of just two liquids. Examples highlighting the importance and widespread use of simple distillation and fractional distillation processes in society are discussed below.

The production of whisky and brandy are examples of simple distillation involving two liquids, water with a boiling point of 100 °C and ethanol with a boiling point of 78 °C. Whisky is distilled from grain mash that has been fermented to an ethanol concentration of 5–7% v/v, while brandy is distilled from wine having an ethanol concentration of 8–12% v/v. These low-alcohol solutions are boiled in a pot still to produce a distillate with an ethanol concentration of 20–35% v/v. The distillate is then subjected to simple distillation in a second pot still to produce a spirit with an ethanol concentration of about 70% v/v. The volatile organic aroma components of the base material are transferred and condensed with the vapor in both steps of the process. Finally, the spirit is subjected to maturation in accordance with product identification requirements.

Simple distillation involving a single liquid and its nonvolatile solutes is a widely used form of industrial distillation. An important example in which the distillate is the desired product is the desalination of seawater or brackish water. Water is evaporated from the salty solution for subsequent condensation and consumption. This stripping process is generally carried out using multistage flash distillation (MSF),

multiple-effect distillation (MED), or vapor compression distillation (VCD). These simple distillation processes owe their success to internal energy recovery mechanisms as discussed in Section 1.5. With an estimated one billion people currently without access to safe drinking water [Blanco et al. (2009)] and a rapidly expanding global population, the role of desalination processes will continue to expand.

There are numerous examples of stripping operations in the food industry where the residue is the desired product. Water is stripped from materials such as fruit juices and dairy products to produce concentrates for cost-effective transport, storage, preservation, or spray drying. MED and VCD are typically used for such purposes with MSF confined to desalination applications. In other food industry applications, water stripping is undertaken to effect solute crystallization. Indeed, one of the largest operations of this type is the concentration of sugarcane juice for subsequent sugar recovery. In this case, MED is used to concentrate the juice to near saturation before entering a separate (pan) stage where crystallization is induced. An example of rectification is the production of industrial alcohol with an ethanol concentration in excess of 90% v/v for use in formulations such as biofuels, antiseptics, and solvents. Sugars from several different sources may be fermented to produce dilute aqueous ethanol solutions for this purpose. An upper limit of 96% v/v ethanol is dictated by the formation of an ethanol–water azeotrope from which no further separation can be achieved using conventional distillation processes. Rum and vodka are also produced by rectification using feedstocks produced by the fermentation of molasses and potatoes, respectively.

A basic requirement for rectification is a column filled with high-surface area packing material. A dilute aqueous ethanol solution for example is boiled at the base of the column to produce a vapor enriched in ethanol. The vapor cools as it rises to the point where condensation occurs on the surface of the packing material. The condensate then trickles toward the base of the column. Rising hot vapor from the increasingly higher boiling residue boils some of the returning liquid to produce a vapor that is further enriched in ethanol. The new vapor rises further up the column due to its higher volatility. This process is repeated many times as vapor ascends the column to produce the required ethanol concentration for external condensation. The vapor is removed from the top of the column while the water-enriched residue remains at the base. This process may be carried out in batch or continuous steady-state mode.

A modified fractional distillation column is used when several liquid fractions require separation. A well-known example of this is the refining of crude oil using a column containing horizontal condensation plates at different heights. The feedstock is boiled at the base of the column at a temperature at which all but the heaviest components vaporize. Controlled temperature reduction with increasing column height facilitates the condensation of different boiling point fractions on plates at different heights. In this way, the crude oil is separated into fuel oil, lubricating oil, diesel, kerosene, naptha, and gasoline in ascending order for removal through ports at the side of the column. Heavy residuals such as tar, asphalt, and waxes are collected from the base of the column while light hydrocarbon gases (C_1–C_4) are collected from the top of the column for external condensation. This process is operated as a continuous process.

Membrane distillation (MD) and osmotic distillation (OD) separate water from its nonvolatile solutes through vaporization and condensation and can therefore be classified as stripping distillation processes. Accordingly, desalination applications involve recovery of the distillate whereas concentrate production applications involve recovery of the residue.

In accordance with normal practice, the terminology applicable to conventional distillation processes has been changed in favor of membrane process terminology when discussing MD and OD. That is, the residue is referred to as retentate, while the distillate is referred to as permeate. In concentrate production applications, the fully concentrated retentate is referred to as concentrate.

MD and OD differ from MSF, MED, and VCD by effecting distillation through a porous, air-filled (usually) hydrophobic membrane using opposing membrane faces as evaporation and condensation surfaces. Membrane hydrophobicity excludes liquid water and its nonvolatile solutes from entering the porous structure and mixing with the permeating vapor. Furthermore, the small vapor gap afforded by the membrane reduces the resistance to vapor transfer to the point of condensation. Despite the success of MSF, MED, VCD, and other nondistillation stripping processes including freeze concentration (FC), reverse osmosis (RO), and electrodialysis (ED), MD and OD have attracted considerable attention as potential alternatives to these processes in some applications. This has been due to their special characteristics with respect to product quality, simplicity of operation, and potential energy savings.

This chapter traces the development of MD and OD from laboratory novelties to their present status as advanced stripping processes entering commercialization. Qualitative descriptions of the fundamental principles and characteristics of each process are provided and compared with those of established processes. Here, a heavy emphasis is placed on the factors that affect product quality. Before proceeding, however, it is beneficial to consider the meaning of the term "°Brix" frequently encountered in this and subsequent chapters. Strictly, the term refers to the percent by weight of pure sucrose in water at 20 °C. More generally, it has been used as a measure of the approximate sugars concentration in multisolute solutions in several industries. Indeed, °Brix has been adopted as the standard unit of concentration in the fruit juice [Bates et al. (2001)] and sugar industries [ICUMSA (2015)]. Simple and rapid measurement as refractometer or hydrometer Brix is convenient for use in process control.

1.2 Membrane Distillation (MD)

1.2.1 Historical Perspective

While MD is currently regarded as an emerging process, it is not new. The concept of MD was introduced during the 1960s and 1970s when several patents on MD equipment appeared [Hassler (1964), Weyl (1967), Miller (1968), Bodell (1968), Rogers (1968, 1969, 1970, 1971, 1972a,b, 1975)]. These included one general process patent [Rogers (1971)], while the others focused on desalination. The first journal articles on MD, which also focused on desalination, were published during that same period [Findley (1967), Findley et al. (1969), Henderyckx (1967), Van Haute and Henderyckx (1967)]. However, a major obstacle faced by workers in the field at that time was the unavailability of membranes with sufficient water vapor permeability and natural hydrophobicity for use in MD. Rather, primitive membranes fabricated from materials such as silicone rubber, paper, glass fibers, cellophane, nylon, and diatomaceous earth were used. Most of these required treatment with water-repelling materials to provide some degree of hydrophobicity.

Without suitable membranes, interest in MD waned in favor of RO, which was itself a relatively new process at that time. The timely fabrication of the first high-flux RO membranes [Loeb and Sourirjan (1963)]

assured the future of this process in desalination applications. Indeed, the rate of production of potable water using RO was several-fold greater than that of MD at that time. In addition, the cost of energy required to generate the high feed pressures required by RO (30–80 bar) was less significant than in the years that followed. As an indicator, the world price of crude oil in the 1960s and early 1970s adjusted for inflation to 2015 prices was about US $20 per barrel compared with US $90–100 in 2015. The interest in desalination applications alone and the lack of concern over energy costs meant that the advantages of MD with respect to product quality and energy savings went largely unrecognized.

However, there was a resurgence of interest in MD in the early 1980s when new types of microfiltration (MF) membranes were found to be suitable for use as MD membranes based on their permeability and hydrophobicity. The best performing membranes were found to be those fabricated from polypropylene (PP), polytetafluoroethylene (PTFE), and polyvinylidinefluoride (PVDF) with nominal pore diameters in the 0.1–0.45 μm range. These membranes remain in common use in MD systems today. Membranes with pores in this size range have variously been referred to as microporous or macroporous membranes by different workers in the field. The International Union of Pure and Applied Chemistry (IUPAC) convention defines materials with pore diameters of greater than 0.05 μm as being macroporous [Rouquerol et al. (1994)] and hence this terminology has been adopted here.

The renewed interest in MD fostered the first attempts to produce modules to house and support these membranes. These included the Gore-Tex MD spiral wound PTFE membrane module in 1982 [Gore (1982)], the Swedish Development Co. plate-and-frame PTFE membrane module in 1983 [Carlsson (1983), Andersson et al. (1985)] and the Enka AG Trans MD tubular PP membrane module in 1984 [Enka AG catalogue (1984)], all of which were intended for desalination applications. The Goretex and Sweedish Development Co. modules were designed for air gap membrane distillation (AGMD), while the ENKA module was designed for direct contact membrane distillation (DCMD), the simplest and most commonly used form of the process. The different forms of MD are discussed below. Problems associated with these modules highlighted the need for future research and development in module construction. Major research programs operated by groups at the University of Calabria (Italy) and the University of New South Wales (Australia) were initiated during that same period

and remain in place today. Similar programs are now commonplace worldwide as reflected by the increasing number of journal articles and conference papers on this topic. The major application studies reported to date are discussed in Chapter 5.

1.2.2 MD Process

The DCMD process is shown in Figure 1.2. Central to the operation of this process is a hydrophobic macroporous membrane that allows water vapor to enter the porous structure while excluding aqueous liquids and their nonvolatile solutes. The aqueous solution from which water is being extracted (feed stream) is passed over one face of the membrane (upstream side), while pure water (strip stream) is passed over the opposite face (downstream side), usually in counter-current flow. Both streams are in direct contact with the membrane. The driving force for mass transfer from the feed to the strip side is a water vapor pressure gradient generated by maintaining the bulk feed stream at a higher temperature than that of the bulk strip stream. Water evaporates at the feed–membrane interface, diffuses through the air-filled (usually)

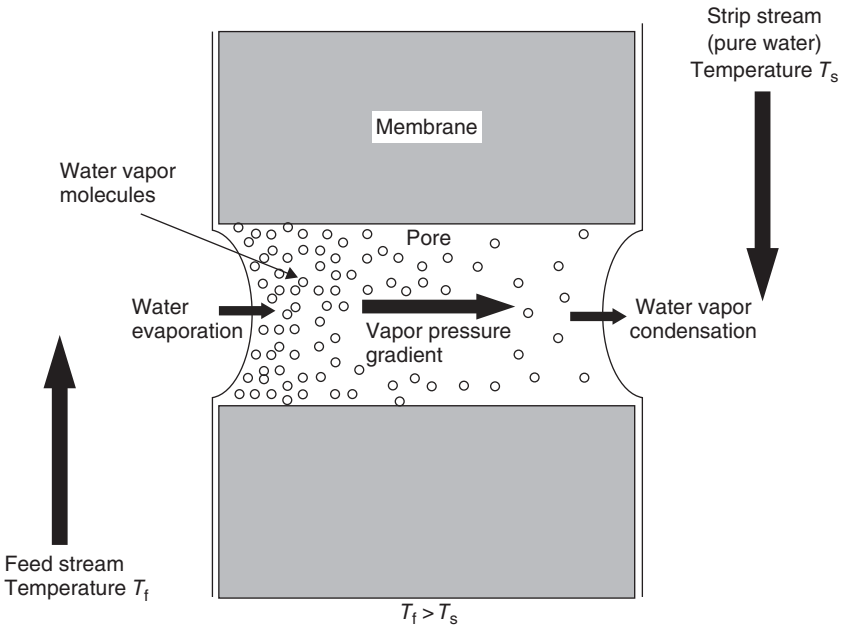

Figure 1.2 Direct contact membrane distillation (DCMD) process.

membrane pores, and condenses at the membrane–strip interface. Depending on the heat sensitivity of the feed material, feed temperatures in the 35–90 °C range are generally used [Bui and Nguyen (2006)]. The strip stream is typically maintained at ambient temperature.

There are three lesser used forms of MD distinguishable from DCMD and each other by the way permeate recovery is achieved. These are AGMD, sweeping gas membrane distillation (SGMD), and vacuum membrane distillation (VMD). The feed and strip flow arrangement for each of the four forms of MD is shown in Figure 1.3. AGMD utilizes a stagnant air gap between the downstream side of the membrane and a cold plate located a few millimeters away inside the membrane module. Permeate diffuses through the air gap to the cold plate where it is condensed and drained from the module. The temperature of the plate is maintained by a stream of cooling water in contact with the opposite surface of the plate. In this case, the driving force is maintained by the applied temperature difference between the bulk feed stream and cooling water stream. This form of the process was designed to minimize conductive heat loss through the membrane. As their names suggest, SGMD and VMD use an inert sweeping gas (air) and a partial vacuum, respectively, to remove water vapor permeate from the downstream side of the membrane. In both cases, permeate condensation takes place externally to the module. Here, the driving force is generated by a combination of an elevated bulk feed temperature (usually) and permeate removal.

DCMD is the form of MD that has attracted most attention from researchers with about 60% of all MD publications focusing on this configuration [El-Bourawi et al. (2006)]. This is despite ranking third behind VMD and then SGMD in achievable water fluxes. A major reason for this has been the simplicity and ease of use of the process. Product can be drawn directly from the strip tank at the rate of permeate production. A schematic layout of a basic DCMD plant is shown in Figure 1.4. The preference for DCMD can also be attributed to some unattractive operational features of the other forms of the process. AGMD, for example, has a relatively low flux due to the high mass transfer resistance provided by the air gap. This is despite a marked reduction in conductive heat loss through the membrane with better maintenance of the driving force. On the other hand, industrial-scale membrane modules developed for desalination in recent years have

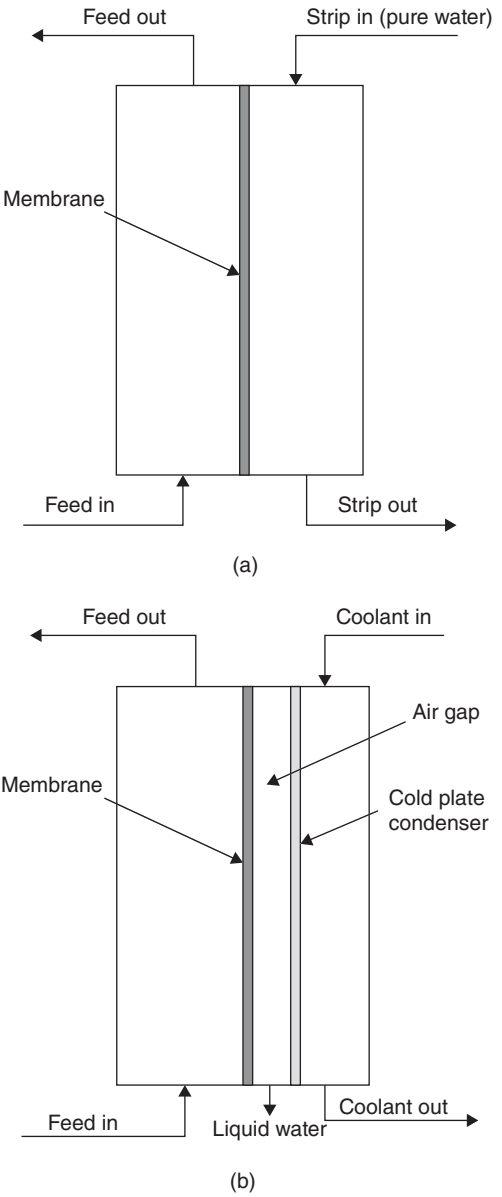

Figure 1.3 The four different forms of membrane distillation. (a) Direct contact membrane distillation (DCMD). (b) Air gap membrane distillation (AGMD). (c) Sweeping gas membrane distillation (SGMD). (d) Vacuum membrane distillation (VMD).