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Abstract: The use of membrane contactor technology is well-known in the process industry and can be employed in many important fields; such as separation and absorption processes, membrane distillation, pervaporation, biotechnology, food industries etc. In recent years, research has been carried out regarding the use of membrane contactors in the components of absorption refrigeration systems. The use of membrane contactors makes it realizable to design compact components with improved heat and mass transfer. Heat and mass transfer performance of the components is significantly enhanced due to the higher area to volume ratio available. Membrane based absorber and desorber allows the reduction in size of the absorption refrigeration systems to a great extent and thus absorption refrigeration technology can be used in transport and small scale applications. In this paper, the applications of membrane contactors in absorption refrigeration systems are reviewed. The application of membrane contactors in the components of absorption refrigeration systems, the configurations of refrigeration cycles that employ membrane contactors and the characteristics of the membrane contactors used in absorption refrigeration systems are all reviewed in detail. Information is collected on the choice of working fluid mixture to be used in absorption refrigeration systems that use membrane based components and the compatibility of working fluid mixtures with the membrane contactor material is discussed. The significance and limitations of using membrane contactors in absorption refrigeration systems is included in this paper.

Response to Reviewers: Please see the attached file.

A Review of Membrane Contactors Applied in Absorption Refrigeration Systems

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Keywords: Membrane Contactors, Absorption Refrigeration, Hydrophobic
Microporous membrane, Hollow Fiber Membrane Module, Plate-and-Frame Membrane
Module

Abstract

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15 and mass transfer performance of the components is significantly enhanced due to the
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29 cycles that employ membrane contactors and the characteristics of the membrane
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37 working fluid mixtures with the membrane contactor material is discussed. The
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39 significance and limitations of using membrane contactors in absorption refrigeration
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Contents

ABSTRACT	2
1. INTRODUCTION	6
2. MEMBRANE CONTACTOR MATERIALS AND CHARACTERISTICS	9
2.1 Membrane Porosity	13
2.2 Mean Pore Size	14
2.3 Membrane Thickness	15
2.4 Membrane Tortuosity	16
2.5 Wettability and Liquid Entry Pressure	17
2.6 Thermal Conductivity	18
2.7 Hydraulic Permeability	19
2.8 Capillary Condensation	20
2.9 Fouling of Membrane Contactors	21
3. WORKING FLUID MIXTURES	23
4. MEMBRANE MODULES	28
4.1 Plate-and-Frame Membrane Module	28
4.2 Hollow Fiber Membrane Module	31
5. MEMBRANE CONTACTORS IN COMPONENTS OF ABSORPTION REFRIGERATION SYSTEMS	33
5.1 Absorber	34
5.2 Desorber	39
5.3 Solution Heat Exchanger	46
6. INFLUENCE OF MEMBRANE CONTACTORS ON THE CYCLE CONFIGURATION	47
7. CONCLUSION	53
ACKNOWLEDGEMENTS	55
REFERENCES	56

Nomenclature

A	Area (m ²)
B	Pore Geometric Factor (—)
d	Diameter (m, μm)
k	Thermal Conductivity (W/m-K)
p	Vapour Pressure (mbar, Pa)
P	Pressure (Pa)
R	General Gas Constant (J/mol-K)
T	Temperature (°C, K)
V	Molar Volume (cm ³ /mol)

Greek letters

ε	Membrane Porosity (—)
θ	Contact Angle (Degree)
ρ	Density (kg/m ³)
σ	Liquid Surface Tension (N/m)
τ	Membrane Tortuosity (—)

Superscripts

0	Equilibrium State
c	Critical

Subscripts

g	Gas
i	Component Index
max	Maximum
mem	Membrane
P	Permeate
p	Pore
pol	Polymer
s	Solid

Abbreviations

COP	Coefficient of Performance
CFI	Cold Fluid Inlet
HFI	Hot Fluid Inlet
LEP	Liquid Entry Pressure
NA	Not Available
PE	Polyethylene
PP	Polypropylene
PTFE	Polytetrafluoroethylene / Teflon
PVDF	Polyvinylidene Fluoride
sqm	Square meter
SS	Strong Solution
UV	Ultraviolet
WS	Weak Solution

Chemical Formulas

1		
2	H ₂ O	Water
3	LiBr	Lithium Bromide
4	LiCl	Lithium Chloride
5	LiI	Lithium Iodide
6	LiNO ₃	Lithium Nitrate
7	NH ₃	Ammonia
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1. Introduction

The application of membranes in the process industry is growing. This is due to the relative simplicity, reliability, high parameters of separation, large interfacial area and lower energy consumption with improved heat and mass transfer. The cost of the membrane based components is also lower under short time of capital recurring and suffers negligible corrosion. Membrane contactors can be utilized in many important fields. These include separation and absorption processes, membrane distillation, pervaporation, biotechnology and food industries among others. Hydrophobic porous membranes are extensively utilized in the field of distillation technology and in air-conditioning systems to remove excess moisture, carbon dioxide and organics. Air moisture content and carbon dioxide concentration can be independently and simultaneously controlled efficiently with the help of membrane contactors. One of the emerging applications of membrane contactors lies in the field of absorption refrigeration systems.

Absorption refrigeration technology, which has the ability to utilize heat directly for cooling purposes, has been one of the most widely used technologies for refrigeration and cooling applications since the early stages of refrigeration technology. Vapour compression systems can achieve high values of the **coefficient of performance (COP)** but at a cost of very high mechanical energy input. However, absorption refrigeration systems can efficiently utilize the renewable energy sources, such as solar energy and low grade thermal energy (i.e. waste heat energy) as a source of energy input instead of using costly mechanical energy. Moreover, the refrigerants used in conventional vapour compression refrigeration systems are not environmental friendly and can contribute to ozone depletion and greenhouse effects, whereas in the absorption refrigeration systems the working fluid mixtures are environmental friendly. Currently, the world is facing an

1 energy shortage problem and it is predicted that the interest in absorption refrigeration
2 systems will increase in the future due to the fact that they can use renewable energy
3 sources and refrigerants that are environmental friendly and do not contribute to Ozone
4 depletion. Absorption refrigeration systems have a high capital cost when compared to
5 vapour compression systems, but for large scale applications the lifecycle cost is very
6 low. However, the absorption refrigeration technology is still relatively little used for
7 cooling applications. In particular, in the sector of mobile refrigeration/air-conditioning,
8 absorption refrigeration has not yet gained much interest. The main drawback of
9 absorption refrigeration systems is the large volume per unit of cooling capacity which
10 has limited their use in mobile applications and small commercial and residential
11 buildings. There is a growing need to design an absorption refrigeration system which
12 has a smaller space requirement for small scale applications. Drost et al. [1] reported
13 that the development of compact absorbers could permit the use of absorption
14 refrigeration systems in small scale heating and cooling applications, heat-actuated
15 automotive air conditioning, and portable cooling. Thus, the success of absorption
16 technology mainly depends on reducing the cost of investment and the size of the
17 components.

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42 Depending on the working fluid mixture used, absorption refrigeration systems are
43 broadly classified into ammonia/water ($\text{NH}_3/\text{H}_2\text{O}$) and water-lithium bromide
44 ($\text{H}_2\text{O}/\text{LiBr}$) systems. The basic components of both types of refrigeration systems are
45 the absorber, desorber, condenser, evaporator and solution heat exchanger. However, in
46 the case of $\text{NH}_3/\text{H}_2\text{O}$ absorption refrigeration systems, a rectifier is also used at the exit
47 of the desorber to purify the ammonia vapour by condensing the water vapour from the
48 refrigerant vapour. As ammonia and water are both volatile, the refrigerant vapour may
49 contain significant amount of water vapour that has a negative effect on the system

1 performance. Therefore, a rectification process is required for the NH₃/H₂O absorption
2 refrigeration systems. NH₃/H₂O absorption refrigeration systems operate at higher
3
4 pressures and are commonly used for low temperature (-40 °C to +5 °C) cooling
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6 applications. H₂O/LiBr absorption refrigeration systems operate under vacuum
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8 conditions and are used in air-conditioning applications where the cooling temperature
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10 requirement is above 7 °C. The basic **single-stage** cycle configurations of both
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12 H₂O/LiBr and NH₃/H₂O absorption refrigeration systems are shown in Figure 1.
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18 The performance of absorption refrigeration systems is primarily dependent on the
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20 absorber and desorber which are the major components of this kind of refrigeration
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22 system. The design of these components is crucial for efficient performance of the
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24 absorption refrigeration system. Both the absorber and desorber used in absorption
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26 technology are relatively expensive and are large in size. In the case of H₂O/LiBr
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28 absorption refrigeration systems the absorber operates under static vacuum pressure
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30 accompanied by a high specific volume of water vapour. It therefore has a direct effect
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32 on the size, weight and space requirement of **absorption** refrigeration systems. Research
33
34 is currently being carried out to design compact absorbers and desorbers for absorption
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36 refrigeration systems. Recently, research has shown that membrane contactor
37
38 technology can be utilized in absorption refrigeration systems, especially in the case of
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40 the absorber and desorber, so as to reduce the size, weight and cost of the system and
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42 also significantly enhance the heat and mass transport processes taking place in the
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44 systems. The use of polymeric hydrophobic microporous membrane contactors in both
45
46 the absorber and desorber could mean a reduction in manufacturing costs. To be
47
48 attractive for usage in small scale applications, the absorption chiller size must be
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50 compact, lightweight and resistant to mechanical shocks. Thus, utilizing polymeric
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52 hydrophobic microporous membrane contactors in the absorber and desorber of an
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1 absorption refrigeration system could reduce both the size and weight of the
2 components and open the use of the system to the sector of transport refrigeration and
3
4 air-conditioning. The driving force for the refrigerant mass transfer in the case of
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6 ammonia/water and water/LiBr solutions is considered to be the difference in
7
8 concentration and water vapour partial pressure, respectively. A membrane based
9
10 desorber could operate at a lower temperature than a conventional desorber and would
11
12 not require heating the solution to its boiling point to achieve the separation of the
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14 refrigerant from the solution. Therefore, low grade heat sources could be efficient if
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16 membrane module desorbers were used in absorption refrigeration systems.
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22 In this paper the applications and significance of membrane contactors in absorption
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24 refrigeration systems are reviewed in detail and different types of membrane modules
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26 used in components of absorption refrigeration systems are illustrated. Characteristics of
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28 membrane contactors employed in the components of absorption refrigeration systems
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30 are overviewed. Working fluid mixtures employed in membrane based absorption
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32 refrigeration systems are analysed and the compatibility of working fluid mixtures with
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34 membrane contactor characteristics and materials are discussed. The principle of the
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36 operation of membrane contactor modules and its effect on the absorption refrigeration
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38 cycle configuration is described. Different configurations of absorption refrigeration
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40 systems utilizing membrane modules in the components are reviewed.
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47 **2. Membrane Contactor Materials and Characteristics**

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50 Membrane acts as a semi-permeable barrier to separate components of the feed solution
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52 into a retentate and a permeate, by controlling the movement of molecules across the
53
54 membrane. In addition, membrane can be used as a contactor between two components
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56 to enhance the absorption of a gas or vapour molecules in the absorbent. In the open
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58 literature, membrane materials are broadly classified into two categories based on the
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1 membrane structure. These include microporous membranes and dense membranes.
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3 Microporous membranes have interconnected pores which allow one of the components
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5 of the solution mixture to pass through it while restrict the other components depending
6
7 on the pore size. If the relative pore size of the microporous membrane is big then the
8
9 selectivity of the membrane contactor decreases, however, the mass transfer flux
10
11 increases with bigger pore size. Dense membranes are nonporous solid membranes
12
13 which are used for separation of small molecules from the mixture. The mechanism of
14
15 the separation process involves diffusion of the molecules to the surface of the
16
17 membrane, dissolving into the membrane material, diffusing through the solid and
18
19 desorbing at the downstream interface. Though dense membranes have very high
20
21 selectivity but due to their low permeability they have limited applications in the
22
23 industry. The compatibility of the dense membrane with the working fluid mixture is
24
25 very important as the separation process depends on both the solubility and the
26
27 diffusivity of the permeate.
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35 On the basis of material, membranes are generally categorized into organic and
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37 inorganic membranes. Inorganic membranes are made of materials such as ceramic,
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39 carbon, silica, etc. and metals such as palladium, silver and their alloys. Organic
40
41 membranes are made of polymeric microporous materials. Currently, the microporous
42
43 polymeric membranes are widely used in the industrial application because of
44
45 competitive performance and low cost. Inorganic membranes are generally more
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47 expensive than organic polymeric membranes. However they have the advantage to
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49 withstand high temperature and pressure as well as possess high stability. In absorption
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51 refrigeration systems, polymeric microporous membranes are mostly used for the
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53 separation of refrigerant from the solution and also as a contactor between the
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55 refrigerant and absorbent to enhance the absorption performance.
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1 The literature survey regarding the use of membrane contactors in absorption
2 refrigeration systems reveals that various types of membranes with different
3 characteristics and properties were experimentally investigated. Yu et al. [2] used a
4 cellulose triacetate membrane, Riffat et al. [3] used dense membrane and silicon porous
5 membrane, Schaal et al. [4], Thorud et al. [5], Wang et al. [6], Ali and Schwerdt [7]
6 used hydrophobic porous membrane, Isfahani et al. [8, 9], Isfahani and Moghaddam
7 [10] and Bigham et al. [11, 12] used superhydrophobic nanofibrous membrane, Drost et
8 al. [1] used a woven membrane and a laser-machined membrane. The laser-machined
9 membranes have higher water vapour permeability as compared to commercially
10 available hydrophobic porous membranes, albeit with a high cost. Deerberg and Gehrke
11 [13] reported that the specific price of 1 sqm of laser machined membrane with an
12 average pore diameter of 1 to 10 μm is about 1000 € and the price could be more than
13 triple if the pore diameter is less than 1 μm . The common commercially microporous
14 hydrophobic membranes are available in capillary or flat sheet shape and are made of
15 polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF) and
16 polytetrafluoroethylene (PTFE, Teflon), with a high porosity (70–80%), a membrane
17 thickness of 10–300 μm and provide microfiltration properties with pore sizes from 0.1
18 to 1.0 μm .

19 It is essential to know the transport phenomena across the membrane contactor in order
20 to use a suitable membrane contactor. Selection of membrane material and
21 characteristics also depend on the process and properties of the working fluid pair. Care
22 must be taken while selecting a microporous membrane for use in membrane contactors.
23 Schaal et al. [4] suggested the use of porous non-selective membrane because of the low
24 transport resistance. They mentioned that although all components can pass through a
25 non-selective membrane, this issue can be overcome by appropriately selecting the

1 surface properties of the membranes and the difference in vapour pressure between the
2 two phases. In absorption refrigeration systems, the literature review considers that the
3 surface of the membrane contactors used in the cases of ammonia/water and water/LiBr
4 working mixtures should be hydrophobic in nature to allow only the vapours to enter
5 and pass through the membrane pores. This is because due to the hydrophobic nature of
6 the membrane material, the aqueous solution does not penetrate into the membrane
7 pores.
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18 Mass transfer is the most important phenomenon of concern taking place across the
19 membrane contactor. The driving force could be the vapour pressure difference or the
20 concentration difference. The mass transfer across the membrane should be such that
21 only refrigerant is allowed to pass through the membrane. The overall mass transfer
22 across the membrane is significantly affected by the membrane properties. The selection
23 of a suitable membrane for the desired process is of critical importance for optimal
24 performance, as the membrane contactor adds resistance to mass transfer when
25 compared with direct contactors. The characteristics of a membrane contactor have a
26 huge impact on the performance and both the capital and operating costs. Microporous
27 membranes are commonly characterised by measuring the hydraulic permeability,
28 porosity, tortuosity, mean pore size, thickness, thermal conductivity, and liquid entry
29 pressure. Ali and Schwerdt [7] analysed the characteristics of commercially available
30 microporous hydrophobic membranes for use in a compact absorber for water-LiBr
31 based absorption refrigeration systems. They investigated experimentally and
32 analytically the properties that influence the water vapour mass transfer flux into a thin
33 film of water-LiBr solution and defined the criteria for utilizing membranes in the
34 design of a compact absorber for absorption refrigeration systems. Iversen et al. [14]
35 have characterized a wide variety of potential microporous membranes and reported that
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1 the performance of microporous membranes in membrane contactors depends on the
2 porosity, thickness, average pore radius and geometry and the manufacturing method.
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5 The characteristics of the membrane contactors reported in the investigations reviewed
6 in this work are summarized in Table 1. It can be seen from Table 1 that hydrophobic
7 membranes are being used by the researchers as they play a critical role in limiting the
8 mass transfer of the absorbent solution across the membrane due to their surface
9 properties. Similarly most of the researchers have chosen highly porous membranes (0.7
10 – 0.85) because membrane with higher value of porosity can significantly increase the
11 mass transfer process. However, an optimized value of porosity should be selected to
12 avoid the adverse effect of porosity on the mechanical strength of the membrane
13 contactor. It can be noticed that the nominal thickness of membrane contactors used in
14 the components of absorption refrigeration systems lies in the range of micrometers.
15 Although mass transfer resistance increases with increase in thickness however for high
16 mechanical strength a nominal thickness of membrane contactor should be selected. It
17 can be seen from the literature data that the mean pore size of the membrane selected in
18 case of ammonia/water is smaller (0.03 – 0.04 μm) when compared to water-LiBr (0.16
19 – 6 μm). This could be because of the difference in relative size of the absorbent and
20 refrigerant molecules in both cases.
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45 The description of the characteristics of membrane contactors and the corresponding
46 mathematical equations are presented in the following sections.
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51 **2.1 Membrane Porosity**

52 Porosity is the measure of void spaces in the membrane material. It is the fraction of
53 volume of voids in the total volume of the membrane contactor. Mass transfer flux
54 across the membrane contactor is directly related to the porosity of the membrane.
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1 Highly porous membranes exhibit less resistance to the mass transfer flux; however the
2 mechanical strength of the membrane decreases with an increase in porosity. A
3
4 membrane should have enough mechanical strength to withstand the **absorption**
5 **refrigeration system** operating conditions. Ali and Schwerdt [7, 15] recommended
6
7 membrane porosity in the range of 0.7 – 0.8 for the membrane contactors employed in
8
9 the absorber of an absorption refrigeration system. Their results show that the
10
11 membrane mass transfer flux increases with an increase in porosity, regardless of the
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13 membrane pore diameter. However, the results reported by Yu et al. [16] illustrate that
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15 the effect of membrane porosity on the mass transfer flux is less prominent in
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17 membranes with bigger pore sizes, while the mass transfer flux increases with an
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19 increase in porosity of membranes with small pore sizes. It is concluded that membrane
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21 mass transfer resistance is more dominant in membranes with small pore sizes while
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23 membrane mass transfer resistance decreases and diffusion resistance into the solution
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25 becomes a dominant factor in membranes with larger pore sizes. Smolder–Franken
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27 equation [17] can be used to calculate the porosity of a membrane contactor.
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$$\varepsilon = 1 - \left(\frac{\rho_{mem}}{\rho_{pol}} \right) \quad (1)$$

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39 where ε is the porosity, ρ_{mem} is the density of the membrane in kg/m^3 and ρ_{pol} is the
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41 density of the polymer material in kg/m^3 .
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49 **2.2 Mean Pore Size**

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51 Mean pore size refers to the average diameter of the pores in the membrane contactor
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53 and is usually in the range of μm . Pore size can vary in the membrane contactor and
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55 sometimes the pore size distribution can also be used in characterizing a membrane
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57 contactor. Ali and Schwerdt [7] recommended a pore size of 0.45 – 1.0 μm to obtain a
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1 high mass transfer flux across the membrane. Ali and Schwerdt [15] reported that the
2 membrane mass transfer flux increases linearly with an increase in the membrane mean
3 pore size from 0.2 to 1 μm . In addition, their results show that the increase in membrane
4 mass transfer flux with increase in pore size is more prominent for high porous
5 membrane. Yu et al. [16] obtained an exponential increase in the membrane mass
6 transfer flux with increase in the membrane mean pore size from 0.5 to 6 μm . They
7 reported that the membrane mass transfer flux initially increases significantly with an
8 increase in the membrane pore size from 0.5 to 4 μm because the effect of membrane
9 mass transfer resistance is more dominant in membranes with small pore size and the
10 mass transfer resistance decreases with an increase in the membrane mean pore size.
11 However, further increase in the mean pore size has almost no effect on the mass
12 transfer flux because in membranes with larger pore size the diffusion resistance into
13 the solution is a more dominant factor instead of the membrane mass transfer resistance.
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31 **2.3 Membrane Thickness**

32 Membrane contactor thickness is an important characteristic which is inversely related
33 to the mass transfer flux and it has a significant effect on both heat and mass transfer
34 processes. Mass transfer resistance increases with an increase in thickness of the
35 membrane contactor which reduces the mass transfer across the membrane. However,
36 the mechanical strength of the membrane contactor increases with an increase in
37 thickness of the membrane. Yu et al. [16] performed an analysis to investigate the effect
38 of membrane thickness on mass transfer flux. Their results show that the mass transfer
39 flux decreases almost linearly with an increase in the membrane contactor thickness.
40 However, results reported by Ali and Schwerdt [7, 15] reveal that the membrane mass
41 transfer resistance increases exponentially with an increase in the membrane thickness.
42 Mass transfer flux decreases more rapidly initially with an increase in membrane
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1 thickness while at higher values of thickness the change in mass transfer flux is less
2 prominent. Ali and Schwerdt [7, 15] suggested that the active membrane layer thickness
3 should be up to 60 μm so that optimum mechanical stability and low resistance to water
4 vapour flux is achieved. They also reported that an additional highly porous support
5 layer on the vapour side of the membrane can significantly increase mechanical stability
6 without degrading the vapour flux since the mass flux is not disturbed if the supporting
7 layer is placed on the vapour side.
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10 **2.4 Membrane Tortuosity**

11 Tortuosity represents the average length of the pore as compared with membrane
12 thickness. Membranes with pores which are perpendicular to the membrane surface are
13 more favourable, as in such cases the tortuosity of the membrane pore is considered
14 equal to one. Martinez and Rodriguez-Maroto [18] reported that generally the tortuosity
15 is in the range of 1.5 – 2.5 as typically membranes have a more meandering pore
16 pathway. The tortuosity of a membrane is inversely related to its porosity. Different
17 empirical correlations have been reported to calculate the tortuosity value from the
18 membrane porosity. Iversen et al. [14] compared the empirical correlations and the
19 experimental values of tortuosity. They concluded that the empirical correlation
20 developed by Mackie and Mearns [19] best describes the tortuosity of a membrane that
21 is spongier, similar to the interstices between closed packed spheres, and is given as:
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$$48 \tau = \frac{(2 - \varepsilon)^2}{\varepsilon} \quad (2)$$

49 where τ is the tortuosity and ε the porosity of the membrane.
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Iversen et al. [14] reported that the fractal theories of random walks can be used to predict the tortuosity of membrane material with random clusters, similar to loose packed spheres, and is given as:

$$\tau = \frac{1}{\varepsilon} \quad (3)$$

2.5 Wettability and Liquid Entry Pressure

The non-wetting characteristic of membrane contactors is also important as the aqueous solution can enter the larger pores of the membrane by breaking the surface tension at the interface between the aqueous solution and the water vapour at the entrance to the membrane pores, thus affecting the mass transfer. Alkudhiri et al. [20] reported that the maximum pore size which would prevent wetting should be in the range 0.1 – 0.6 μm . LEP (Liquid entry pressure) is the minimum hydrostatic pressure that must be applied around the membrane so that the aqueous solution does not overcome the hydrophobic forces and penetrate into the membrane pores. Alkudhiri et al. [20] reported that the increase in feed concentration and the presence of organic solutes can reduce the LEP. They reported that LEP mainly depends on the maximum pore size and the hydrophobicity of the membrane. Gabino et al. [21] reported the Laplace (Cantor) equation for relating the maximum pore size and the liquid entry pressure which is given as,

$$\Delta P = \frac{4 \cdot B \cdot \sigma \cdot \cos \theta}{d_{p,(\max)}} \quad (4)$$

where B is the pore geometric factor which is 1 for cylindrical pores, σ is the solution surface tension in N/m, θ is the contact angle and $d_{p,(\max)}$ is the maximum pore diameter in meters. Thus for a high value of LEP, a membrane should have a high

1 contact angle, small pore size and a higher value of surface tension for the solution. Ali
2 and Schwerdt [7] mentioned the importance of liquid entry pressure and suggested that
3
4 a membrane should have high LEP and the pore size should be in a range of 0.45 – 1.0
5
6 μm to avoid wettability of the membrane pores by the aqueous solution. Zidu [22]
7
8 reported that the polymeric membrane material that is used in the membrane based
9
10 components should have a surface energy of at least 10 dyne/cm less than the lowest
11
12 among the weak absorbent solution surface tension or the refrigerant surface tension.
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17 **2.6 Thermal Conductivity**

18 Thermal conductivity is the ability of the membrane material to transfer heat energy.
19
20 The thermal conductivity of membrane contactors made of polymeric material is usually
21
22 low as compared to metals; however, the large specific heat transfer area provided by
23
24 membrane contactors can overcome the heat transfer resistance of the membrane
25
26 material. The thermal conductivity measurement of a membrane contactor depends on
27
28 both the thermal conductivity of the membrane material and the gas inside the voids of
29
30 the membrane contactor. The thermal conductivity of PTFE can be estimated using the
31
32 correlation given by Sperati et al. [23].
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$$41 \quad k_s = (4.86 \times 10^{-4} \times T) + 0.253 \quad (5)$$

42 where T is the temperature in $^{\circ}\text{C}$ and k_s is the thermal conductivity in W/m-K .
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47 If the gas inside the membrane voids is air or water vapour then the thermal
48
49 conductivity of gas can be estimated by the correlation of Jonsson et al. [24].
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$$53 \quad k_g = (1.5 \times 10^{-3}) \times \sqrt{T} \quad (6)$$

54 where T is the absolute temperature in Kelvin and k_g is the thermal conductivity in
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56 W/m-K .
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1 The correlation can be used either for air or water vapours as both have a thermal
2 conductivity of the same order at a temperature of around 40 °C.
3

4
5 The thermal conductivity of the membrane is estimated as a volume average of both the
6 conductivities k_s and k_g , as given by Martinez and Rodriguez-Maroto [18].
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$$k_{mem} = \varepsilon \cdot k_g + (1 - \varepsilon) \cdot k_s \quad (7)$$

10 11 12 13 14 15 16 **2.7 Hydraulic Permeability**

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18 Hydraulic permeability is the ability of a membrane to transfer a fluid across the
19 membrane. It is the inverse of resistance to flow across the membrane. Ideally, the
20 membrane should have minimum resistance to the refrigerant mass transfer which
21 depends on the size and tortuosity of the membrane pores and on the porosity and
22 thickness of the membrane. Martinez et al. [25] modelled and evaluated the water
23 vapour permeability in hydrophobic membranes. They used three commercial
24 hydrophobic membranes TF1000, TF450 and TF200 with pore sizes of 1.00, 0.45 and
25 0.20 μm , respectively and a porosity of 0.8. The authors concluded that for applications
26 in which no viscous flux is present, the Knudsen and molecular diffusion resistances are
27 important to be analyzed, while in applications including diffusive and viscous transport
28 mechanisms, the contribution of both mechanisms is important enough to be analyzed.
29
30 However, at low water vapour pressures the viscous contribution is low for the
31 membranes with smaller pores. They also concluded from their study that the
32 membranes have narrow pore size distributions and the values of the average pore sizes
33 are slightly different from those given by the manufacturer. They mentioned that the
34 capillary diameter of the membrane provided by the manufacturer is not sufficient to
35 perform the transport model calculation. Albrecht et al. [26] determined the water
36 vapour permeability of different structured hollow fiber membranes with ultrafiltration
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1 separation profiles. They concluded that membranes with ultrafiltration separation
2 profiles are beneficial alternatives for the preparation of coated membranes and are
3 suitable for the preparation of effective **membrane contactors**. Ali and Schwerdt [7]
4 reported that to obtain a higher water vapour flux, the membrane pore sizes should
5 range from 0.45 to 1.0 μm , and have a porosity of up to 0.8 for high permeability to
6 water vapour.
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15 **2.8 Capillary Condensation**

17 One of the desired characteristics of the membrane contactor is for it to prevent
18 capillary condensation of refrigerant vapour inside the membrane pores which can result
19 in blockage of the pore. Rautenbach and Albrecht [27] reported that as well as the
20 membrane active layer surface, the inner surface of the capillary is also involved in the
21 desorption/evaporation process. They pointed out the significance of the capillary
22 condensation and reported that the membrane effectiveness can decrease if vapours
23 condense inside the membrane pores. By using the Kelvin equation, they proposed an
24 equation which can be used to calculate the critical water vapour pressure at which
25 condensation can occur in large pores, and it is given as:
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$$41 \quad p_i^c = p_i^0 \cdot \exp\left(-\frac{4 \cdot \sigma_p \cdot V_i}{d_p \cdot R \cdot T}\right) \quad (8)$$

42 where p_i^c is the critical water vapour pressure in mbar, p_i^0 is the equilibrium state
43 pressure in mbar, σ_p is the surface tension of the permeate in N/m, V_i is the molar
44 volume in cm^3/mol , d_p is the pore size (diameter) in m, R is the universal gas constant
45 which is 8.314 J/mol-K and T is the temperature in Kelvin.
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1 Ali and Schwerdt [7] recommended that the membrane pore size should be as small as
2 possible to avoid capillary condensation of water vapours. They recommended a pore
3 size of 0.45 μm to limit the capillary condensation in the membrane based absorber of
4 an absorption refrigeration system.
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10 **2.9 Fouling of Membrane Contactors**

11 Membrane materials are non-corrosive and are compatible with most of the materials
12 and working fluids. Fouling of the membrane contactor material is less prominent
13 compared with that of metallic contactors. However, membrane contactors are prone to
14 pore clogging with inorganic salt and biological fouling. Biological fouling is mainly
15 caused by bacteria and algae. Lawson and Lloyd [28] reported that biological fouling
16 can be avoided by adding certain appropriate chemicals to the solution or by UV
17 treatment. They also pointed out that fouling is less significant in membranes with
18 relatively larger pore sizes such as the membranes used in distillation processes.
19 Membrane mass transfer resistance increases due to the fouling phenomenon. In
20 membrane contactors, the mass transfer flux may decrease if the accumulation of
21 crystallized inorganic salt or deposition of any other particulate material occurs at the
22 membrane surface and in the pores of the membranes. However, membrane contactors
23 have the advantage that they can be cleaned easily and thus the reduction of mass
24 transfer flux across the membrane due to membrane fouling can be recovered. The
25 decrease in mass transfer flux across the membrane with time, usually termed as flux
26 decay and which occurs due to membrane fouling, can be classified into reversible and
27 irreversible fouling. Flux decay due to reversible fouling in porous membranes can be
28 recovered by backflushing the membrane contactors, while in the case of irreversible
29 fouling, the membrane contactor either has to be replaced or cleaned with chemical
30 reagents. Riffat et al. [3] investigated two membrane modules, sheet polymer
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1 membranes and tubular silicon membranes for use in the pervaporation absorption
2 refrigerator. They observed that the permeate flux of the silicon membrane module
3
4 decreased with time due to pores being blocked by the salt. However, they were able to
5
6 restore the original permeate flux by cleaning the membrane module with fresh water.
7
8 Pre-treatment of the membrane can also be done to control the fouling. Alklaibi and
9
10 Lior [29] pointed out the importance of pre-treatment and concluded from their
11
12 investigations that the permeate flux can be increased by 25% with the pre-treatment
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14 process. S. Shirazi et al. [30] reported that membrane fouling is mainly dependent on
15
16 the module configuration, solution characteristics and hydrodynamic conditions. They
17
18 pointed out that the high concentration of inorganic salts in the solution can lead to
19
20 fouling of the membrane contactor. They reported that the scale formation on the
21
22 membrane surface is mainly because of the crystallization of the solution and the
23
24 particulate fouling, both of which occur due to the decrease of salt solubility or the
25
26 existence of particulates in the solution. In crystallization, precipitation of ions occurs at
27
28 the surface of membrane, while in particulate fouling, particulate matter from the bulk
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30 solution deposits on the membrane surface as a result of convective transportation. For
31
32 porous membranes, if the particulate matters are smaller than the membrane pore size
33
34 then pore plugging can also occur in addition to the formation of cake on the membrane
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36 surface. Gryta [31] reported that partial wetting of the membrane pores can result in
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38 scale formation on the membrane surface, as the adjacent pores are being filled with the
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40 feed solution. The author pointed out that an additional thermal resistance is created by
41
42 the deposits of inorganic salts and particulates on the membrane surface. Controlled
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44 hydrodynamic and thermal conditions can also limit the fouling phenomenon. Gryta
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46 [32] reported that fouling can be minimized by lowering the feed temperature and
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48 increasing the feed flow rate.
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3. Working Fluid Mixtures

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4 Ammonia/water and water/lithium bromide are the most commonly used working fluid
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6 pairs analysed both analytically and experimentally to investigate the performance of
7
8 membrane based components of absorption refrigeration systems. One of the key
9
10 advantages of these working fluid pairs is that the thermophysical properties are well
11
12 known and established. However, other working fluids such as ammonia/(lithium nitrate
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14 + water), water-multicomponent salt mixtures and ionic liquid based absorbent solutions
15
16 can also be effectively utilized in membrane based absorption refrigeration systems. For
17
18 those absorption refrigeration systems utilizing membrane contactors, the properties and
19
20 requirements of the absorbent/refrigerant combination should be compatible with the
21
22 membrane contactor characteristics and materials. For instance, a hydrophobic
23
24 membrane material should be used when the absorbent solution contains water as a
25
26 mixture component so that the liquid solution molecules do not pass through the
27
28 membrane pores in case of non selective membrane contactors. Water can be employed
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30 in the absorbent solution either as a refrigerant or an absorbent and can be used as an
31
32 additional component to enhance the transport properties of a binary working fluid. For
33
34 selective microporous membrane contactors, the working fluid pair should be carefully
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36 selected in accordance with the membrane properties so that refrigerant molecules
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38 observe less transport resistance than the absorbent molecules and hence only the
39
40 refrigerant molecules pass through the pore. Griesheim and Rodenbach [33] reported
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42 that for a dissolution diffusion membrane, the refrigerant should have the characteristic
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44 properties of dissolving in the membrane material and diffusing through the membrane,
45
46 whereas the absorbent should be insoluble in the membrane material. However, for a
47
48 microporous membrane, a working fluid pair should be selected such that it does not
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50 cause wetting of the microporous membrane. If the driving force across the membrane
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1 contactor is the difference in vapour pressure, then the working fluid pair should be
2 selected such that the vapour pressure of the absorbent is much lower than the vapour
3 pressure of the refrigerant. Griesheim and Rodenbach [33] reported that in an absorption
4 refrigeration machine utilizing semi-permeable membrane, the vapour pressure of the
5 sorption medium should be a factor of more than 10,000 lower than the refrigerant
6 vapour pressure. They suggested that ionic liquids could be used as an absorbent as they
7 have a vapour pressure of almost 0.

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18 Ammonia/water working fluid pair is used in the industrial and commercial applications
19 where the cooling temperature requirement is in the range of -40 °C to +5 °C. NH₃/H₂O
20 based absorption refrigeration systems do not have crystallization problems and the
21 system normally operates at a higher pressure (above atmospheric pressure), hence no
22 vacuum is required. As the working fluid pair contains water as an absorbent, therefore
23 a non-selective membrane contactor with hydrophobic surface can be used in the
24 membrane based components. Despite the high thermal stability of the NH₃/H₂O
25 working pair, the high latent heat of vaporization of NH₃ and the feasibility of using
26 NH₃ as refrigerant for low temperature cooling applications there is still a drawback in
27 that both NH₃ and water are volatile, and thus a rectifier is required to strip away water
28 that normally evaporates with NH₃. The rectification process has a negative effect on
29 the cycle performance and also increases the cost of the absorption refrigeration system.
30 Other disadvantages include the toxicity and corrosive action to copper and copper
31 alloy. To overcome these problems, Oronel et al. [34] investigated absorption
32 refrigeration systems that use NH₃/LiNO₃ and NH₃/(LiNO₃+H₂O) as working fluid
33 mixtures. They suggested that NH₃/LiNO₃ would be a good alternative to the ammonia
34 based conventional working fluid pair. NH₃/LiNO₃ working fluid pair has an advantage
35 that a rectification process is not needed and it can be used at a lower temperature in the
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1 desorber. However, the viscosity of $\text{NH}_3/\text{LiNO}_3$ is very high and can significantly
2 reduce the absorber performance and consequently the performance of the whole
3 absorption refrigeration system. For membrane contactor based components, the
4 compatibility of $\text{NH}_3/\text{LiNO}_3$ with the membrane contactor has to be investigated. As
5 $\text{NH}_3/\text{LiNO}_3$ working fluid pair does not contain water either as a refrigerant or as an
6 absorbent, the hydrophobic surface of the membrane may not be useful in restricting the
7 mass transfer of the solution across the membrane. The high viscosity of the binary
8 working fluid can be overcome by adding water to the binary mixture as reported by
9 Ornel et al. [34]. Thus, the addition of water to the $\text{NH}_3/\text{LiNO}_3$ solution can not only
10 lower the viscosity of the mixture but also make it possible to utilize microporous non-
11 selective hydrophobic membranes.

12 **Water/lithium bromide** working fluid pair is used in those absorption refrigeration
13 applications where the cooling temperature requirement is above 7 °C. $\text{H}_2\text{O}/\text{LiBr}$ based
14 absorption refrigeration systems operate under vacuum conditions. The use of $\text{H}_2\text{O}/\text{LiBr}$
15 for absorption refrigeration systems offers outstanding features such as the non-
16 volatility of LiBr absorbent (the need for a rectifier is eliminated) and high heat of
17 vaporization of water (refrigerant). However, using water as a refrigerant eliminates the
18 applications for which low cooling temperature is required and the system must be
19 operated under vacuum conditions. **$\text{H}_2\text{O}/\text{LiBr}$ based absorption refrigeration systems**
20 **also suffer** from corrosion problems. At high cooling-water temperatures and high
21 concentrations the solution is prone to crystallization. The addition of other salts to the
22 conventional working fluid pair can improve the solubility of the solution. Bourouis et
23 al. [35, 36] investigated the use of a multi-component salt solution ($\text{LiBr} + \text{LiI} + \text{LiNO}_3$
24 + LiCl) as an absorbent with water as a refrigerant. **They reported that the multi-**
25 **component salt solution has higher solubility and is less corrosive.** The safety margin

1 for crystallization of the strong solution leaving the solution heat exchanger is much
2 higher. Mesones [37] performed experimental and theoretical study on the solubility of
3 new absorbents in natural refrigerants. He reported that the solubility of the multi-
4 component salt can be further improved if the mixture of only three components (LiBr +
5 LiI + LiNO₃) is used as an absorbent with water as a refrigerant. As water is used as
6 refrigerant, microporous non-selective hydrophobic membranes can be employed in the
7 membrane based components to achieve efficient performance.
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18 In recent years, intensive research work has been carried out regarding the use of ionic
19 liquids as an absorbent in absorption refrigeration cycles. Advantages of ionic liquids as
20 an absorbent are the low volatility, low melting point, metal-compatibility, high thermal
21 stability and that they are environment friendly and not prone to crystallization problem
22 [38–40]. Ionic liquids have an almost zero vapour pressure, so can be considered a
23 better choice for membrane based absorbers and desorbers. The issue of the high
24 viscosity of ionic liquids can be overcome by adding a small fraction of a ternary
25 component such as water to the ionic liquid based mixtures. A number of refrigerants in
26 combination with ionic liquids have been recommended for the use in absorption
27 refrigeration systems. Among these, carbon dioxide, water and ammonia are the most
28 prominent refrigerants. Water as a refrigerant can be a better choice for absorption
29 refrigeration systems employing hydrophobic microporous membrane contactors in the
30 membrane based components. Yokozeki and Shiflett [41–43] analytically investigated a
31 number of ionic liquids as absorbents with ammonia and water as refrigerants in
32 absorption refrigeration systems. They achieved favourable results with
33 NH₃/[DMEA][Ac] (ammonia/N,N-dimethylethanolammonium acetate) and
34 H₂O/[emim][(CH₃)₂PO₄] (water/1-ethyl-3-methylimidazolium dimethylphosphate) as
35 working fluid pairs in a single-stage absorption refrigeration system. Martin and
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1 Bermejo [44] performed thermodynamic analysis of absorption refrigeration cycles to
2 investigate the application of ionic liquids as absorbents with supercritical carbon
3 dioxide as a refrigerant. They recommended CO₂/[bmpyrr][Tf₂N] (carbon dioxide/1-
4 butyl- 1-methyl-pyrrolidinium) as a favourable working fluid mixture for absorption
5 refrigeration systems. Kim et al. [45] numerically investigated the feasibility of several
6 refrigerant/ionic liquid mixtures and recommended H₂O/[emim][BF₄] (water/1-ethyl-3-
7 methylimidazolium tetrafluoroborate) as a promising working fluid mixture in
8 absorption refrigeration systems for electronic cooling. Absorption refrigeration systems
9 employing ionic liquid as an absorbent and water as a refrigerant could be a better
10 option for membrane based components employing hydrophobic membranes. NH₃ or
11 CO₂ can also be used as a refrigerant with an ionic liquid as an absorbent, however, it is
12 important to select an appropriate membrane contactor with suitable surface properties
13 to limit the solution from crossing the membrane pores. The literature reviewed in this
14 study regarding the use of ionic liquids as an absorbent shows that ionic liquids based
15 absorption refrigeration systems have high solution circulation ratio and thus further
16 investigations are needed for the feasibility of such systems.

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39 Operating conditions and the crystallization behavior of working fluid mixtures
40 discussed in this section are summarized in Table 2. It can be seen that inorganic salt
41 based absorbent solutions exhibit crystallization behavior however ionic liquid based
42 absorbent solutions are not prone to crystallization phenomenon in the working range of
43 absorption refrigeration cycles, as many of the ionic liquids have melting points below
44 the lowest solution temperature in the absorption systems [38–40]. Also it can be seen
45 that absorption refrigeration cycles using ammonia as a refrigerant operate at above
46 atmospheric pressure whereas absorption refrigeration cycles employing water as a
47 refrigerant operate under vacuum pressure.

4. Membrane Modules

Different kinds of membrane modules are being used in the process industry for separation processes and distillation applications. Among these membrane modules, the hollow fiber membrane module, spiral membrane module, plate-and-frame/flat sheet membrane module, tubular membrane module and capillary membrane module are the most widely used. However, hollow fiber membrane module and plate-and-frame/flat sheet membrane modules are the types most widely investigated in absorption refrigeration systems. Intensive research work is being carried out on the utilization of membrane contactors in the form of hollow fibre membrane modules and plate-and-frame membrane modules in the components of absorption refrigeration systems. In the open literature, the plate-and-frame module is generally selected when the aqueous solution of $H_2O/LiBr$ is used as a working fluid mixture in absorption refrigeration systems whereas hollow fibre module is usually selected for the ammonia/water based absorption refrigeration systems. Due to the parallel plates/flat sheets in the plate-and-frame membrane module the pressure drop is small, it is therefore considered as a better option for the water/lithium bromide based absorption refrigeration systems. Nevertheless, the hollow fibre module allows more efficient mass transfer due to external transverse flow and is considered an appropriate choice for the ammonia/water based absorption refrigeration systems. It is also important to select a membrane with adequate properties which uses the mass transfer potential more efficiently for such modules. A brief illustration of these membrane modules is described and discussed in the following sub-sections.

4.1 Plate-and-Frame Membrane Module

The plate-and-frame membrane module is currently being widely investigated as a heat and mass transfer device for use in the absorption refrigeration systems. Thorud et al.

1 [5], Isfahani et al. [8, 9] and Bigham et al. [12] used the concept of the plate-and-frame
2 heat exchanger and manufactured a laboratory scale desorber to investigate the
3 performance of a plate-and-frame membrane module. Ali [49, 50], Ali and Schwerdt [7,
4 15], Yu et al. [16], Isfahani et al. [8], Isfahani and Moghaddam [10] and Bigham et al.
5 [11] used the plate-and-frame membrane module for investigating the application of
6 membrane contactors in the absorber. They built a laboratory scale experimental setup
7 to investigate the heat and mass transfer phenomena in such a module. Due to the ease
8 of use and availability of membrane in flat sheets, the plate-and-frame membrane
9 module is widely used in laboratories to perform experimental analyses. These modules
10 are easy to clean and replace. However, the flat sheets of membrane in the plate-and-
11 frame membrane module have poor mechanical strength and thus a support is required.

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27 The driving force for the vapour transfer into the aqueous solution in a H₂O/LiBr
28 absorber is the difference in water vapour partial pressure. In the conventional falling
29 film absorber, the water vapour pressure difference is usually small. To get a higher
30 mass transfer rate across the membrane contactor there should be minimum pressure
31 drop in the membrane configuration. Baker [51] reported that the plate-and-frame
32 membrane module offers minimum pressure drop among the different membrane
33 configurations. Therefore, to design an efficient and compact absorber with H₂O/LiBr
34 as a working fluid mixture, the plate-and-frame absorber with a non-selective
35 hydrophobic microporous membrane at aqueous solution–water vapour interface is a
36 better alternative. The plate-and-frame membrane module has the potential to enhance
37 the mass transfer flux as a result of narrow confined flow channels formed by the
38 membrane contactor.

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1 frame membrane module is set so that the lattice cell consists of a metallic plate for heat
2 transfer and membrane sheets for both the heat and mass transfer. The membrane
3 contactors are placed at the aqueous solution and water vapour interface in the form of
4 parallel sheets, while the metallic plates are placed along the solution and coolant
5 interface. The membrane sheets and the metallic plates are arranged in such a manner as
6
7 to create individual flow channels for solution, coolant and refrigerant. Each refrigerant
8 channel serves two absorbent solution channels at each side as shown in Figure 2 (b).
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10 Similarly the coolant channels also serve two aqueous solution channels. The first and
11
12 last units of the module have half width coolant channels. The coolant flows along the
13
14 metallic plate to dissipate the heat of absorption from the solution. The refrigerant and
15
16 the absorbent solution are brought into contact with each other using the microporous
17
18 membrane contactor. The refrigerant enters the membrane pores and is absorbed into
19
20 the solution on the other side of the membrane sheet. If water is present in the working
21
22 fluid mixture either as a refrigerant, an absorbent or as a third component, then a
23
24 hydrophobic membrane contactor can be utilized so that the aqueous solution does not
25
26 penetrate the membrane pores as a result of the hydrophobic nature of the membrane
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28 material and that only refrigerant passes through the membrane. The thin channel of
29
30 refrigerant has no exit so all the refrigerant has to be absorbed by the aqueous solution
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32 through the membrane contactor. As the refrigerant vapour pressure is higher than the
33
34 partial pressure of the refrigerant vapour inside the solution, the refrigerant is absorbed
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36 at the liquid-vapour interface and diffuses into the solution film. The parallel assembly
37
38 of the plates and membrane sheets minimizes the pressure drop in the absorber. The
39
40 flow configuration in this module can be concurrent flow or counter current flow.
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42 However, counter current flow direction of the coolant and absorbent is more
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advantageous, while the absorbent solution and refrigerant flow can be either counter current or co-current.

Geometric dimensions and parameters of the plate-and-frame membrane modules reviewed in this work are listed in Table 3.

4.2 Hollow Fiber Membrane Module

Hollow fiber membrane module has been widely investigated for heat and mass transfer enhancement. The vast interfacial area provided by the polymeric hollow fiber membrane significantly improves heat and mass transfer processes. However, the mechanical strength of the polymeric membrane limits the application of polymeric hollow fiber membranes at elevated temperatures and high pressure. Zarkadas and Sirkar [52] proposed a polymeric hollow-fiber membrane heat exchanger for low temperature (up to 150 – 200 °C) applications. Their investigation showed that the large specific interfacial area makes polymeric hollow fiber heat exchangers more efficient than metal heat exchangers for lower heat source temperature applications. Hollow fiber membrane contactors made of non-selective, microporous membranes have been widely accepted as effective gas-liquid or liquid-liquid devices because of the independent gas and liquid velocities which prevent flooding, loading and turn down ratio problems from two-phase flows. Experimental and analytical analyses were performed by Schaal et al. [4] and Chen et al. [53] in order to investigate the performance of a hollow fiber module as an absorber unit in the absorption refrigeration system. Wang et al. [6, 54] used the concept of vacuum distillation to separate the refrigerant from feed solution and investigated the use of the hollow fiber module as a desorber in the absorption refrigeration system. Wang et al. [55, 56] and Wang et al. [57] investigated and proposed the hollow fiber module as an alternative to the solution heat exchanger of the H₂O/LiBr absorption refrigeration system. Hollow fiber membrane modules used in the

1 absorption refrigeration systems can be classified into two types; an ordinary hollow
2 fiber membrane module which is usually utilized as a desorber and a hybrid hollow
3 fiber membrane module which is utilized as an absorber.
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8 The ordinary hollow fiber membrane module consists of hundreds of microporous
9 hydrophobic membrane fibers/tubes, assembled and made into a shell-and-tube module
10 as shown in Figure 3. The microporous hydrophobic membrane fibers in the module
11 allow both heat and mass transfer between the absorbent solution and the refrigerant
12 vapours. **Hollow fiber membrane module** can be specifically used as a desorber or as a
13 solution heat exchanger in the absorption refrigeration systems. The feed solution,
14 which is preheated before entering the module, flows inside the microporous hollow
15 fibers of the module. In the case of vacuum membrane separation processes, vacuum
16 pressure is kept inside the shell for efficient performance of the module. The refrigerant
17 in the feed solution vaporizes and passes through the pores of the membrane and is
18 collected inside the shell and then condensed in the condenser under vacuum conditions.
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36 The hybrid hollow fiber membrane module consists of hundreds of both microporous
37 hydrophobic membranes fibers and non-porous membrane fibers, assembled and made
38 into a shell-and-tube module. The hybrid hollow fiber membrane module is used as an
39 absorber in the absorption refrigeration systems. The refrigerant-absorbent solution
40 flows into the shell side of the hollow fiber module. The refrigerant vapours to be
41 absorbed flow into the microporous hollow fibers while the cooling fluid flows into the
42 non-porous hollow fibers of the module. The non-porous membrane fibers for the
43 cooling fluid are arranged in concentric order at the outer periphery of the shell, while
44 the porous membrane fibers are arranged concentrically in the central portion of the
45 shell. **The configuration of a hybrid hollow fiber membrane module is shown in Fig. 4.**
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60 The hollow fiber membrane module contains a central baffle that deflects the solution
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1 flow on the shell side in the module but not the flows on the lumen side of the fibers.
2 The absorbent solution enters in the shell through the center tube in the upstream half of
3 the module, flows through the gap between the baffle and the module housing and then
4 exits from the shell through the center tube in the downstream half of the module. The
5 solution hence forms cross-flow to the fibers in both upstream half and downstream half
6 of the module. It is reported that the heat transfer process can be enhanced if the cooling
7 fluid and the absorbent solution flow in the counter-current direction, however, the
8 vapour and the absorbent solution flow direction has no prominent effect on the heat
9 and mass transfer and so can be co-current or counter-current.
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22 Geometric dimensions and parameters of the hollow fiber membrane module reviewed
23 in this work are listed in Table 4.
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28 **5. Membrane Contactors in Components of Absorption**

29 **Refrigeration Systems**

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34 Analytical and experimental investigations are being carried out on the use of
35 membrane contactors in the absorber, desorber and solution heat exchanger of
36 absorption refrigeration systems. The utilization of microporous membrane contactors
37 in these components can provide a high specific surface area and therefore higher
38 volumetric mass transfer rates can be achieved compared to conventional absorbers and
39 desorbers. Schaal et al. [4] reported that membrane contactors can provide up to 30,000
40 m^2/m^3 specific area. Due to the high specific interfacial area provided by the membrane
41 contactor, it is possible to manufacture compact components for use in small cooling
42 capacity absorption chillers. In this section, the use of membrane contactors in the
43 absorption refrigeration components is reviewed.
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5.1 Absorber

The absorber is one of the major components in absorption chillers and has a direct effect on the size of the absorption refrigeration system. Introducing polymeric hydrophobic microporous membranes into the absorber design could provide one of the alternatives for achieving highly compact absorbers since microporous membrane contactors can provide a high specific surface area. The absorption rate of the conventional absorbers normally depends upon the working fluid mixture, the corrugated or smooth surface, absorber configuration, operating conditions etc. Different absorber configurations were investigated and adopted to enhance the absorption rate in the literature. In this section, the membrane based absorbers investigated in the literature are discussed and evaluated. As discussed earlier, the membrane based absorbers investigated in the literature are broadly divided into two categories, namely plate-and-frame membrane absorber and hollow fiber membrane absorber.

Chen et al. [53] performed numerical simulations to study and evaluate the performance of an innovative hybrid hollow fiber membrane absorber. The proposed hybrid hollow fiber membrane absorber was designed for an ammonia/water absorption cycle and was made up of both microporous and nonporous fibers for refrigerant and coolant flows, respectively. They reported that, for the same absorption rate, the volume of hollow fiber membrane absorber was only 31% of that of a plate heat exchanger falling film absorber, while the mass transfer interfacial area was 4.3 times of that of plate heat exchanger falling film absorber. From their results it was observed that the COP of a typical ammonia/water absorption system utilizing hollow fiber membrane absorber could be increased by 14.8% and a 26.7% reduction of the overall system exergy loss could be achieved. The solution flow rate reduction obtained in the analysis was 43%

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for the same cooling effect. They reported that the solution side mass transfer coefficient is the most dominating factor affecting the absorption process in the hollow fiber membrane absorber.

Schaal et al. [4] investigated experimentally and performed simulation of an absorption refrigeration cycle with a single hollow fiber microporous membrane module absorber in which ammonia/water was used as a working fluid mixture with integrated cooling. Their results showed a higher mass transfer rate for the membrane absorber compared with the plate absorber. A linear increase in the absorption rate was observed with an increase in the driving force, which is the difference of the ammonia mole fraction at the saturation state and the actual ammonia fraction at the inlet of the membrane module. In addition, increase in the mass transfer flux with an increased driving force was more significant for the membrane absorber than for the plate absorber. Their results also showed that the ammonia mass transfer rate increases with the increase in gas pressure. However, a decrease in the ammonia mass transfer flux was observed with higher ammonia mole fractions in the solution. From the experimental and simulation results, they concluded that the size of the absorber can be reduced up to 10 times as compared to plate absorbers by utilizing the micro-porous hollow fiber membrane module.

Ali [49] performed an analytical analysis to design a compact plate-and-frame absorber possessing a hydrophobic microporous membrane contactor at the aqueous solution–water vapour interface. The author pointed out that the most important factor affecting the absorption rate was the solution film thickness. His results showed that the aqueous solution channel thickness greatly influences the absorber size compactness. Increasing the solution channel thickness from 1.0 to 2.5 mm while keeping the other parameters constant resulted in an increase in the required net membrane contactor area from 5.2 to 6.53 m². In addition a decrease from 238.54 to 139.2 m²/m³ is obtained in the ratio of

1 mass transfer area to net volume. In the experimental study performed by Ali and
2 Schwerdt [7], a solution film thickness of 4 mm was used and a differential pressure of
3 nearly three times the available pressure in a typical absorber was applied. However, the
4 absorption rate was approximately half that of the conventional absorbers. In a
5 conventional absorber, the solution thickness flowing over a tube bundle varies from 0.1
6 to 1.0 mm. Ali [49] observed that reducing the solution film thickness from 2.5 to 1.0
7 mm can result in a higher absorption rate of about 20%. Thus, the low absorption rate
8 obtained in the Ali and Schwerdt [7] analysis could be due to the higher values of the
9 solution film thickness. Also they did not observe a change in the absorption rate when
10 the vapour pressure potential was increased. They ascribed this behavior to the
11 dominant mass transfer resistance of their membrane. However, recent studies [8, 10]
12 suggest that vapour pressure potential has a direct effect on the vapour mass transfer
13 flux across the membrane and that the mass transfer through the solution is the
14 dominant resistance as compared to the membrane mass transfer resistance. Ali and
15 Schwerdt [15] experimentally and analytically analysed the factors that affect the water
16 vapour transfer flux when using a membrane contactor at water/LiBr solution and water
17 vapour interface. They reported that at high solution flow rates, the mass transfer
18 coefficient between the interface boundary layer and the bulk solution is high, as a
19 result of low hydrodynamic boundary layer resistance. They concluded from their
20 experimental results that the water vapour transfer flux through the membrane contactor
21 is improved at higher aqueous lithium bromide solution flow Reynolds numbers for
22 larger pore diameters. Ali [50] analytically performed heat and mass transfer analysis of
23 a plate-and-frame membrane based absorber as a component of a 5 kW single-effect
24 water/lithium bromide absorption refrigeration system. He reported that for the same
25 cooling capacity the required absorber size increased with the increase in the driving hot
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1 water temperature. However, a slight decrease in the required absorber area was
2 observed with a decrease in the cooling water inlet temperature. The author suggested
3 the use of plate-and-frame membrane absorbers in places where lower cooling inlet
4 temperature is available.
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10 Yu et al. [16] performed numerical simulation to analyze the influence of different
11 operational and geometric parameters of a membrane based absorber. They reported that
12 the solution film thickness and solution velocity significantly affect the absorption rate.
13 However, in contrast to conventional absorbers, the solution film thickness and velocity
14 can be independently controlled and adjusted to achieve an optimal performance in
15 plate-and-frame membrane absorber. They obtained a 3-fold increase in the absorption
16 rate when the solution film thickness was reduced from 150 μm to 50 μm . In addition,
17 they observed a 50% increase in the average absorption rate when the solution velocity
18 was increased from 0.009 m/s to 0.036 m/s. Also, they investigated the effect of
19 membrane surface roughness on the absorption rate and obtained a 15% increase in the
20 absorption rate when compared to the smooth surface. The authors concluded that the
21 absorption rate in case of a rough membrane surface increases as a result of convective
22 effects induced by the rough surface.
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43 Isfahani et al. [8] experimentally investigated a membrane based absorber for the
44 absorption of water vapour in the aqueous solution of LiBr. Their results showed that
45 the mass transfer flux can be significantly enhanced if the solution flow velocity is
46 increased and the solution film thickness is reduced to an order of 100 μm . They
47 reported that decreasing the solution film thickness resulted in better cooling of the
48 solution-vapour interface so the water vapour pressure in the solution was lowered and a
49 high absorption rate was achieved. Similarly if the solution temperature was increased
50 then the water vapour pressure in the solution also increased which in turn decreased the
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1 absorption rate. They observed a linear increase in the absorption rate with an increase
2 in the vapour pressure. They reported that the absorption rate was 2.5 times higher than
3 that in falling film absorbers.
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8 Isfahani and Moghaddam [10] experimentally analyzed absorption characteristics of
9 water vapour into a thin LiBr solution constrained by superhydrophobic nanofibrous
10 membrane structures. They reported that the use of a superhydrophobic nanofibrous
11 membrane at the H₂O/LiBr solution and water vapour interface could constrain the
12 solution film thickness and that in this type of configuration the velocity and solution
13 thickness could be independently controlled to achieve higher absorption rates. They
14 studied the effect of water vapour pressure, cooling temperature, solution film thickness
15 and solution mass flow rate on the absorption rate in a membrane based absorber. They
16 achieved an absorption rate of 0.006 kg/m²s with a solution film thickness of 100 μm
17 and a velocity of 0.005 m/s. In contrast to Ali and Schwerdt [7], they obtained a linear
18 increase in the absorption rate with increase in the water vapour driving potential across
19 the membrane.
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38 Bigham et al. [11] experimentally and numerically investigated the implementation of
39 micro-scale features on the flow channel surface to induce vortices within the solution
40 film. They observed that the laminar streamlines within the solution film are stretched
41 and folded as a result of the vortices. They reported that the mass transport mode in
42 such configuration could be changed from diffusive to advective mode. In their analysis
43 they used a 500 μm solution film thickness and obtained an increase in the absorption
44 rate by a factor of 2.5 from 0.0016 kg/m²s to 0.004 kg/m²s.
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56 It is evaluated from the literature review that utilizing the microporous hydrophobic
57 membrane in the absorber can not only reduce the size of the component but also
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1 enhance the mass transfer rate significantly. Both the plate-and-frame membrane
2 absorber and hollow fiber membrane absorber are promising alternatives to the
3 conventional absorbers and can be used with water and ammonia based refrigerants,
4 respectively, in absorption refrigeration systems. Hybrid hollow fiber membrane
5 module can be an interesting replacement of the conventional absorbers as compared to
6 ordinary hollow fiber membrane module as in this type of module non-porous
7 membrane fibers are incorporated within the module for coolant flow to dissipate the
8 heat of absorption from the solution and therefore can enhance the absorption
9 performance of the absorber. In case of the plate-and-frame membrane absorber, it is
10 worth to note that a higher absorption rate can be achieved if the solution film thickness
11 is around 100 μm , therefore, the use of porous membranes to constrain the solution film
12 in narrow micro-channels can significantly enhance the heat and mass transfer
13 performance of the absorber. In addition, constraining the solution film by a
14 hydrophobic membrane contactor can allow design of a compact membrane based
15 absorber utilizing water as a refrigerant under vacuum conditions. Also the use of
16 micro-scale features on the flow channels surface can significantly improve the
17 absorption rate by producing vortices within the solution which continuously bring the
18 concentrated solution to the solution vapour interface. However, the ease and
19 economical viability to manufacture a surface with micro-scale features for membrane
20 based absorbers need to be investigated for the commercial use of such plate-and-frame
21 membrane absorber.

52 **5.2 Desorber**

53 Desorber is also one of the major components in absorption refrigeration systems and is
54 used to separate the refrigerant from the absorbent solution. The performance of the
55 desorber has a direct effect on the coefficient of performance (COP) of the system. The
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1 conventional desorber is usually heavier and bigger in size and thus limits the use of
2 vapour absorption systems in small scale applications. The temperature of the driving
3 heater in the conventional desorber is usually higher than low grade energy resources
4 such as regenerative energy or waste heat energy. These issues can be resolved by
5 replacing the conventional desorption process with a membrane separation process.
6
7 Membrane modules are smaller in size and weight than the conventional desorbers
8 because polymeric fibers/membrane sheets replace the heavy metallic tubes/plates. In
9 the membrane distillation process, vapour extraction from aqueous solution is possible
10 at a lower operating temperature than the boiling point of the solution. Due to the
11 temperature difference across the membrane, a pressure difference arises and acts as the
12 driving force for the mass transfer across the membrane pores. At the liquid–vapour
13 interface of the membrane pores refrigerant molecules evaporate at the hot interface,
14 cross through the membrane pores in vapour phase and condense on the cold side.
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17 Mengual et al. [58] reported that the vapour permeation flux mainly relies on the vapour
18 pressure difference between the two sides of the membrane. Qtaishat et al. [59] reported
19 that adequate permeation flux is possible across the membrane without the need for the
20 hot feed to reach boiling point. Heating of the aqueous solution to the boiling point is
21 not needed as long as the temperature difference exists between the two sides of the
22 membrane pores. Consequently, the membrane based desorber can operate at a lower
23 temperature than conventional desorbers where the solution must be heated to boiling
24 point to achieve the separation of the refrigerant from the solution. This means that low
25 grade heat sources can be efficient if membrane module desorbers are used in
26 absorption refrigeration systems.
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29 Research is currently being carried out on the use of microporous membranes in the
30 desorber for the separation of the refrigerant from the refrigerant-absorbent solution.
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1 Different membrane separation processes are employed for refrigerant separation in the
2 desorber. Riffat and Su [60, 61] proposed a reverse osmosis mechanism to separate the
3 refrigerant from the mixture in the desorber. They replaced the conventional desorber
4 by a centrifuge desorber in which a reverse osmosis membrane was utilized. The
5 centrifuge desorber is a rotary hollow cylinder with a membrane placed around the
6 outside periphery of the cylinder. The centrifuge desorber is rotated at a high angular
7 velocity and as soon as the pressure difference between the two sides of the membrane
8 exceeds the osmotic pressure of the solution, the refrigerant permeates the reverse
9 osmosis membrane. They developed a thermodynamic model to study the osmotic
10 pressure of the absorption solution using its density and vapour pressure. From their
11 analysis they observed that the osmotic pressure increased with an increase in the
12 specific latent heat of evaporation. They pointed out that a high angular speed is
13 required to achieve a high pressure difference in order to separate the refrigerant from
14 the solution using reverse osmosis mechanism. Furthermore, they mentioned that the
15 high rotation speed requirement could give rise to issues related to the mechanical
16 strength of materials and the balance of structures. However, they reported that the
17 angular speed of the centrifuge desorber could be reduced if refrigerants with a lower
18 latent heat of evaporation were used. They concluded that the feasibility of pressure
19 driven absorption systems would also be dependent on the availability of suitable
20 membranes due to the high osmotic pressure involved. Riffat et al. [3] experimentally
21 investigated an absorption refrigeration system in which the pervaporation process
22 replaced the conventional desorption process for vapour extraction. They used aqueous
23 potassium formate solution and two membranes. One was a dense membrane, and the
24 other was a silicon porous membrane. They suggested that the pervaporation membrane
25 material should be compatible with the working fluid mixture. They achieved a

1 permeate flux of above $0.58 \text{ kg/m}^2\text{-h}$ when they used a mixture of potassium formate
2 and caesium formate and was five times that of the potassium only solution. They
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4 observed that the permeate flux decreased with the solution temperature but increased
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6 with decreasing concentration. Similarly, a decrease in the permeate flux was obtained
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8 when the permeate pressure was increased. However, the decrease in the permeate flux
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10 was smaller at high solution temperature because of the high chemical potential of feed
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12 side. They achieved higher permeate flux with silicon membrane module when
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14 compared to the dense membrane due to the porous structure of the silicon membrane
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16 module.
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22 Thorud et al. [5] experimentally tested a constrained thin film desorption scheme to
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24 determine the desorption rates of water from an aqueous solution of LiBr through a
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26 confining hydrophobic porous membrane made up of Teflon material. The assembly of
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28 the module resembled that of a plate-and-frame module in which desorption takes place
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30 in a channel created between two parallel plates with one of the walls being both heated
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32 and porous. Their experimental investigation focused on the performance of vapour
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34 extraction as a function of confined thin film thickness, pressure difference across the
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36 membrane and inlet concentration of LiBr solution. In their experiments, a constant
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38 inlet mass flow rate of 3.2 g/min was kept up at a pressure of 33.5 kPa and a membrane
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40 with surface area of 16.8 cm^2 was used for all cases. The inlet concentration of LiBr
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42 solution was varied from 31.6 wt\% to 50.2 wt\% , and the pressure difference across the
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44 membrane was varied from 5.83 kPa to 11.5 kPa along with two channel heights of 170
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46 μm and $745 \mu\text{m}$. They achieved a maximum desorption rate of 0.51 g/min at the
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48 following conditions: LiBr solution concentration of 32 wt\% , differential pressure of
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50 12.0 kPa , and channel height of $170 \mu\text{m}$. Evaluation of the results showed that vapour
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52 extraction increases with an increase in pressure difference across the membrane,
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decrease in channel height and lower inlet LiBr solution concentration. The heat transfer coefficient was also studied as a function of the wall superheat temperature. Increase in the channel height required larger superheat values for a fixed desorption rate and thus had a negative influence on the heat transfer coefficient.

Kim et al. [62] analysed an absorption based miniature heat pump system and demonstrated with analytical results the feasibility of such a system for electronic cooling applications. To miniaturize the system, they integrated the desorber and condenser as a single unit separated by a hydrophobic membrane which acted as a common interface to separate the refrigerant vapour from the absorbent solution. Their design facilitates to reduce the size of the entire heat pump system to a 150mm x 150mm x 100mm envelope. The analytical results showed that a chip temperature of about 30 °C is achievable with heat removal capability of 100W from the electronic components.

Zidu [22] proposed an absorption refrigeration cycle in which the conventional desorber was replaced with hollow fiber membrane module. The tubes of the membrane module were made up of a microporous hydrophobic membrane material with a pore size in the range of 0.1 to 0.6 μm and a porosity greater than 0.5. The author reported that a higher COP could be achieved with an improved mass transfer rate at a low desorber temperature utilizing a hollow fiber membrane desorber.

Wang et al. [6, 54] demonstrated the application of vacuum membrane distillation processes in absorption refrigeration systems. They experimentally investigated the desorption rate of water vapours from an aqueous solution of lithium bromide with vacuum membrane distillation process which used a hollow fiber membrane module. In such configuration a hot feed of the absorbent solution flows in the tube side, while the

1 shell side is kept under vacuum pressure either by cooling water or by vacuum pump.
2 They concluded from the test results that the permeation flux of water vapour **increases**
3 when the feed flux of solution **is** increased and at high feed temperature in tube side
4 while decreases with an increase in pressure **in** the shell side. Therefore, an increase in
5 the permeation flux is achievable by decreasing the pressure on the shell side. Also,
6 they concluded that the feed temperature had the maximum influence on the desorption
7 rate, followed by the vacuum pressure on the shell side while the feed flux of solution
8 had the lowest influence on the desorption rate.
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10 Isfahani et al. [8] experimentally investigated a membrane based desorber used for the
11 extraction of water vapour from aqueous solution of LiBr. They achieved a desorption
12 rate of about $0.01 \text{ kg/m}^2\text{s}$ which is higher than the reported work of Thorud et al. [5].
13 They observed that the desorption of water vapour from the aqueous solution of LiBr
14 starts at a temperature of approximately $60 \text{ }^\circ\text{C}$ and increases slightly with an increase in
15 temperature, however, the increase in the desorption rate is more pronounced at
16 temperatures over $90 \text{ }^\circ\text{C}$. This is because at higher solution temperatures, the partial
17 pressure of water vapour in the solution increases and **therefore** the pressure difference
18 across the membrane increases **which** improves the desorption rate. In addition, they
19 reported that the effect of vapour pressure on the desorption rate subsides as the solution
20 superheat temperature increases and no significant change for a superheat temperature
21 of about $25 \text{ }^\circ\text{C}$ was **obtained**. They observed that at the same operating conditions, the
22 solution pressure had an insignificant effect on the desorption rate through direct
23 diffusion, as the driving force for mass transfer is the vapour pressure difference.
24 However, the solution pressure significantly affects the desorption rate with the boiling
25 process. They also observed that the solution flow rate **does not influence** the desorption
26 rate **in** the direct diffusion desorption mode. However, they noticed an increase of about
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50% in the desorption rate in boiling mode when the solution flow rate was increased from 0.75 kg/hr to 3.25 kg/hr.

Isfahani et al. [9] experimentally investigated the influence of wall temperature, solution and vapour pressures and solution mass flow rate on the desorption rate of a membrane-based desorber in which the solution was constrained by a thin microporous membrane. They analyzed two mechanism of desorption based on the diffusion of refrigerant molecules across the membrane. In the first case they analyzed direct diffusion of molecules out of the solution and their subsequent flow through the membrane whereas in the second case they investigated the formation of water vapour bubbles within the solution and their venting through the membrane. They reported that the direct diffusion was the dominant desorption mode at low surface temperature in which the desorption rate was directly related to vapour pressure, solution concentration and surface temperature whereas in case of boiling desorption mechanism the solution flow pressure control the desorption mechanism. In addition, they reported that in the boiling desorption mode, at certain solution mass flow rate, some water vapour bubbles are carried out of the desorber through the solution micro-channels rather than passing through the membrane.

Bigham et al. [12] experimentally and numerically investigated the implementation of micro-scale features on the flow channel surface to induce vortices within the solution film to enhance the desorption rate. They observed that the laminar streamlines within the solution film were stretched and folded as a result of the vortices and therefore it was possible to limit the concentration boundary layer growth which in turn had a desirable effect on the desorption mechanism. They achieved an average desorption rate of $0.0068 \text{ kg/m}^2\text{s}$ which was 1.7 times more than the base case without surface features at the same surface temperature.

1 From the literature review on membrane based desorbers it is evident that the desorption
2 rate can be enhanced by direct diffusion at low desorber temperatures. Thus, the
3 absorption refrigeration systems utilizing membrane contactors can operate at lower
4 desorber temperatures. In addition, the desorber size can also be reduced using the vast
5 interfacial area provided by the membrane contactors. It is evaluated from this literature
6 review that both plate-and-frame membrane desorber and hollow fiber membrane
7 desorber are promising alternatives to the conventional desorbers and can be used with
8 water and ammonia based refrigerants respectively in absorption refrigeration systems.
9 Solution flow rate, temperature and solution film thickness are crucial parameters for
10 the plat-and-frame desorber and a nominal value should be selected to achieve high
11 desorption rate. Centrifuge desorber in which reverse osmosis mechanism is used to
12 separate the refrigerant from the absorbent does not seem practically feasible as a higher
13 rotation speed is required which need components with higher mechanical strength. It
14 can be concluded that a lower desorption rate is obtained when a pervaporation
15 membrane is used for the desorption process because of the high selectivity of the
16 pervaporation membranes however it is suggested to select a suitable membrane with an
17 appropriate working fluid mixture in order to effectively utilize the pervaporation
18 process for the refrigerant separation from the solution.

44 **5.3 Solution Heat Exchanger**

45 Solution heat exchangers were investigated by researchers with the aim of improving
46 the performance of the system. Shell and tube configurations are usually adopted for the
47 solution heat exchanger in conventional absorption refrigeration systems. Wang et al.
48 [55, 56] and Wang et al. [57] proposed and analysed a hollow fiber membrane heat
49 exchanger for water/LiBr absorption refrigeration systems. The shell side of the module
50 contains hundreds of membrane tubes through which the hot feed solution from the

1 desorber flows, while the cold feed solution from the absorber is passed to the desorber
2 **through** the shell side. Wang et al. [57] reported that the use of hollow fiber membrane
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4 modules instead of conventional solution heat exchanger could not only enhance heat
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6 transfer as a result of the large heat transfer interfacial area provided by the small
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8 membrane tubes but that the mass transfer of the refrigerant vapour could also
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10 contribute **about** one third of the total heat duty. The water vapour mass transfer in the
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12 membrane based solution heat exchanger also simultaneously increases the
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14 concentration of refrigerant in the solution rich in refrigerant and further decreases the
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16 concentration of refrigerant in the solution weak in refrigerant. This helps to minimize
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18 the circulation ratio. They reported that the flow resistance increases in the membrane
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20 heat exchanger which may cause the solution pump to work harder than in a
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22 conventional heat exchanger, although this could be compensated by reducing the
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24 thermal load in the desorber and absorber.
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32 **Table 5** summarises the operating parameters of the components employing membrane
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34 contactors in the absorption refrigeration cycles that were reported in the investigations
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36 reviewed in this work.
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41 **6. Influence of Membrane Contactors on the Cycle** 42 43 **Configuration** 44 45

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47 Membrane contactors can be used in different components of absorption refrigeration
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49 systems such as the absorber, desorber, solution heat exchanger etc. In this section,
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51 absorption refrigeration cycle configurations of the investigations reviewed in the
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53 present work are discussed. The principle of operation and the use of membrane
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55 contactors in the desorber of absorption refrigeration systems can alter the configuration
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57 of the cycle. However, the use of membrane contactors in the absorber **and solution heat**
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exchanger has no significant effect on the configuration of the cycle. Ali [49, 50] used the plate-and-frame membrane module absorber with the same configuration as the conventional single-effect water/LiBr absorption refrigeration cycle as shown in Figure 1 (a). Schaal et al. [4] and Chen et al. [53] used the conventional configuration of the single-effect ammonia/water absorption cycle with a hollow fiber membrane module absorber. The unconventional cycle configurations used in the investigations reviewed in this work are herein discussed.

Zerweck [63] proposed an absorption refrigeration cycle utilizing the osmotic membrane as shown in Figure 5. The major components of the cycle are a condenser, an evaporator and an absorber-desorber unit. In this configuration the rich-refrigerant solution in the absorber and weak-refrigerant solution in the desorber are separated from each other by an osmotic membrane. Only the refrigerant is allowed to pass through the osmotic membrane. A solution pump is not utilised in the system as the refrigerant from the absorber is transferred to the desorber by osmotic diffusion through the membrane without the use of a mechanical pump. The pressure difference between the desorber and the absorber is dependent on the type of the membrane used. As there is usually a possibility that the absorbent from the absorber may be diffused together with the refrigerant to the desorber, a bleed valve is also used to re-strengthen the solution in the absorber.

Riffat and Su [60] proposed and investigated a centrifugal absorption refrigeration system using reverse osmosis principle as shown in Figure 6. The major components of the cycle were an evaporator, an absorber and a membrane-integrated centrifuge. In this configuration the weak solution from the absorber is pumped to the centrifuge desorber up to the saturated pressure of the refrigerant at the given solution temperature. The centrifuge desorber is rotated at a certain angular velocity so as to achieve the required

1 osmotic pressure of the solution. In the centrifuge desorber, the weak solution is
2 separated into a strong solution and a pure refrigerant using a reverse osmosis
3 membrane. At the osmotic pressure the solution components are separated such that the
4 refrigerant passes out through the reverse osmosis membrane and is collected. As in the
5 reverse osmosis mechanism, the refrigerant is separated from the solution in a liquid
6 state so a condenser is not needed in the cycle. The strong solution returns to the
7 absorber through a throttle valve while the refrigerant is supplied to the evaporator after
8 passing through the refrigerant expansion valve. The vapour at the evaporator exit is
9 absorbed in the absorber and the cycle repeats. Absorption refrigeration cycles using the
10 reverse osmosis mechanism for refrigerant separation have a comparable COP to those
11 of conventional vapour compression cycles depending on the angular speed of
12 centrifuge. However, very high pressure energy is required to separate the refrigerant
13 from the solution using reverse osmosis mechanism.

14 Riffat et al. [3] investigated an absorption refrigeration cycle utilizing a pervaporation
15 membrane to separate the refrigerant from the solution. In this configuration a
16 pervaporation membrane replaces the conventional desorber for concentrating the
17 working fluid. A pervaporation membrane is used for the separation process which
18 involves the partial vaporization of a liquid mixture through a dense membrane while
19 the downstream side of the membrane is kept under vacuum. Components which are
20 separated can undergo dissolution, diffusion and evaporation in the pervaporation
21 process. In the pervaporation process the component is diffused in a liquid phase in
22 contrast to that of the distillation process where the components pass through the
23 membrane in a vapour phase. The basic components and the working principle of the
24 cycle are the same as those of the conventional absorption refrigeration cycle. However,
25 the desorber is replaced by a heater and a pervaporation membrane. The weak solution

1 from the absorber is passed through the solution heat exchanger and is then heated in
2 the heater. The heated solution in the liquid phase is transferred from the heater and
3 enters into the pervaporation membrane unit where a membrane is used to separate the
4 refrigerant from the solution. Only the refrigerant passes through the pervaporation
5 membrane and is collected on the other side. A vacuum is created on the downstream
6 side of the membrane. The refrigerant is condensed and throttled to the evaporator to
7 produce cooling and then is absorbed in the absorber and the cycle repeats. The
8 schematic diagram of this cycle is shown in Figure 7. The COP of the cycle utilizing the
9 pervaporation membrane process for vapour desorption is low compared with
10 conventional absorption systems, as the pervaporation process requires a very high
11 solution feed flow rate. The authors obtained a COP of 0.06 for their prototype working
12 with the pervaporation membrane principle. They argued that the low COP was due to
13 the high circulation ratio as a high feed flow rate is required to operate such pilot
14 membrane modules.

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35 Kim et al. [62] proposed an absorption refrigeration system which could be fitted into a
36 small scale envelope for electronic cooling. Conventional absorption refrigeration is too
37 bulky for the electronic system cooling therefore the concept of a combined micro-
38 channel condenser and desorber was proposed as shown in Figure 8. In this
39 configuration a hydrophobic membrane is placed between the desorber and the
40 condenser while micro-channel heat exchangers are attached at the other ends. The
41 condenser is air-cooled and for heat transfer enhancement, offset strip fins are installed.
42 The overall cycle operating principle is similar to that of the conventional absorption
43 cycle. The refrigerant inside the desorber is vaporized using a waste heat source. Only
44 the refrigerant is allowed to pass through the hydrophobic membrane from the desorber
45 to the condenser. The surface tension and capillary actions, upon interaction with the
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1 hydrophobic membrane, prevent the liquid solution from flowing through the membrane
2 pores. The refrigerant vapour collected in the micro-channel condenser is cooled by
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4 dissipating the heat to the ambient with the aid of an offset strip fin array. The
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6 refrigerant is throttled through an expansion valve and is passed to the evaporator to
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8 produce cold. The refrigerant from the evaporator is absorbed in the absorber and the
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10 cycle continues. The authors reported that a COP in the range of 0.74 to 0.87 of the
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12 proposed cooling system is achievable with a cooling capacity of 100 W.
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18 Zidu [22] proposed an absorption refrigeration cycle in which a hollow fiber membrane
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20 module was used instead of the conventional desorber to separate the refrigerant from
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22 the solution. The cycle consists of the basic absorption refrigeration system components
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24 such as the absorber, evaporator, weak solution heater, cooler, solution circulating
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26 pump, solution recuperator and a membrane distiller as shown in Figure 9. The
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28 refrigerant in the liquid phase is circulated by a refrigerant pump and part of the
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30 refrigerant is supplied to the membrane module while the rest is supplied to the
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32 evaporator, where it is sprayed on the evaporator tubes. The refrigerant vaporizes and is
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34 collected in the absorber because of the vapour pressure difference. In the absorber, the
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36 absorbent solution with lower vapour pressure than the water vapour pressure absorbs
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38 the refrigerant vapours. The absorbent solution is sprayed from a spray tree on the
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40 outside of the cooling tubes in which a cooling medium is used to dissipate the heat of
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42 absorption. The rich solution in LiBr coming from the membrane module is passed
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44 through the recuperator to preheat the weak solution in LiBr before entering the solution
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46 heater. The solution is heated in the heater to a predefined temperature before entering
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48 the hollow fiber membrane module. The feed solution is passed through the shell side
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50 while the liquid refrigerant passes in the tubes made up of microporous hydrophobic
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52 membrane. The volatile refrigerant in the pre-heated feed solution vaporizes at the
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1 membrane interface, passes through the membrane pores in the vapour phase and is
2 condensed on the other side. The pre-heating of the feed absorbent solution to a
3 specified temperature generates a vapour pressure that is higher than that of the liquid
4 refrigerant on the tube side, thus a differential vapour pressure is achieved which acts as
5 a driving force. The strong solution in LiBr is resupplied to the absorber through the
6 recuperator while the refrigerant is transferred to the cooler from where it is pumped
7 back to the evaporator and the membrane module, and the cycle then repeats. In this
8 configuration of the absorption refrigeration cycle, a condenser is not used as the
9 refrigerant is separated and collected in liquid state. The author reported that the cycle
10 could achieve a COP of a conventional single effect absorption refrigeration cycle and
11 could be operated at a lower desorber temperature than that of the conventional cycle.

12 Wang et al. [6] proposed an absorption refrigeration cycle utilizing the vacuum
13 membrane distillation process. The working principle of the cycle is similar to that of
14 the conventional absorption refrigeration systems but the desorber is replaced by a
15 vacuum distillation unit which comprises of a solution heater unit and a hollow fiber
16 membrane module. In the hollow fiber membrane module, the hot feed solution flows in
17 the membrane fibers whereas in the shell side a vacuum pressure is kept. The vacuum
18 pressure is usually decided by the temperature of cooling water. Figure 10 shows a
19 schematic diagram of this cycle. The hot feed solution from the solution heater unit is
20 transported to the hollow fiber membrane module by a pump. Using the concept of a
21 vacuum distillation process, the refrigerant vapours are collected in the shell side and
22 then cooled in the condenser under vacuum conditions. Strong solution in LiBr from the
23 membrane module is transferred back to the solution heater unit which is divided into
24 two parts for storing the strong solution and heating the weak solution. Part of the
25 strong solution in the storage section flows to the absorber and the rest overflows into

1 the solution heater through the overflow plate. In the solution heater, weak solution
2 from the absorber and strong solution from the strong solution storage pool are blended
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4 and then heated by low grade energy. Finally, the hot solution is pumped into the
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6 membrane module by a pump and the process continues. Functions and operating
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8 principles of the other components such as the condenser, expansion valve, evaporator,
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10 absorber, solution heat exchanger and other auxiliary units are similar to the
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12 conventional absorption refrigeration system. This cycle configuration can improve the
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14 COP of the cycle and allow the refrigeration system to produce cooling at a low
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16 desorber temperature as the solution does not require heating to boiling point in the
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18 membrane distillation process.
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25 Table 6 summarises the operating conditions of the absorption refrigeration cycles with
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27 membrane based components that were used in the investigations reviewed in this work.
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31 **7. Conclusion**

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33 From the literature survey it is concluded that the use of light weight polymeric
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35 hydrophobic microporous membrane contactors can provide a larger interfacial area for
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37 heat and mass transfer processes. Thus, not only the size and weight of the components
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39 can be reduced but also the system performance can be enhanced. Use of membrane
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41 contactors in the desorber can extend the use of low grade heat sources effectively in
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43 absorption refrigeration systems. It is evaluated from the literature review that
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45 membrane based desorbers can alter the configuration of absorption refrigeration cycles
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47 and the cycle components can be reduced in some cases. Despite these advantages, there
48
49 are some limitations associated with membrane contactors such as the mechanical
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51 strength of membrane contactors, which is very low and the fact that they can not
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53 operate at very high temperatures.
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In this review the applications of membrane contactors in the field of absorption refrigeration systems are covered. Membrane contactor modules, components employing membrane contactors, cycle configuration, membrane material characteristics and the working fluid mixtures for the membrane contactor based absorption refrigeration systems are all discussed. This review reveals that the applications of membrane contactors for absorption and desorption is an emerging technique in the field of absorption refrigeration systems, however, a commercial plant has not yet been designed to explore the long term operation of membrane contactor based components in absorption refrigeration systems. Further research is needed to explore the long term operation consequences of membrane contactors in absorption and desorption processes. One of the prominent areas for future investigation is the use of non-conventional working fluid mixtures in membrane contactor components. Potential research could be carried out on the use of ionic liquid as an absorbent in absorption refrigeration systems employing membrane based components. Membrane contactor modules are available in different types hence, membrane modules other than plate-and-frame membrane module and hollow fiber module should also be investigated. Membrane contactor surface properties need to be studied further for more efficient use in absorption refrigeration components. In this regard, further research work is required to improve the hydrophobic character of membrane material, enhance the mechanical strength and to improve the compatibility of the membrane material with the working fluid mixtures. Membrane contactors do not suffer corrosion problems as it occurs in conventional absorption refrigeration components. However, fouling of membrane contactors means that more need for research is necessary with regard to absorption refrigeration components employing membrane contactors, so that durability and life span cost of the absorption refrigeration system can be evaluated more

1
2 precisely. Membrane module desorbers should be tested and analysed at higher
3 operating temperatures to investigate the effect of high temperatures on membrane
4 materials and performance.
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List of Figures

Figure 1: Basic absorption refrigeration cycle configuration

Figure 2: Plate-and-Frame membrane module

Figure 3: Hollow fiber membrane module [6]

Figure 4: Hybrid hollow fiber membrane module [53]

Figure 5: Absorption refrigeration cycle proposed by Zerweck [63]

Figure 6: Absorption refrigeration cycle proposed by Riffat and Su [60]

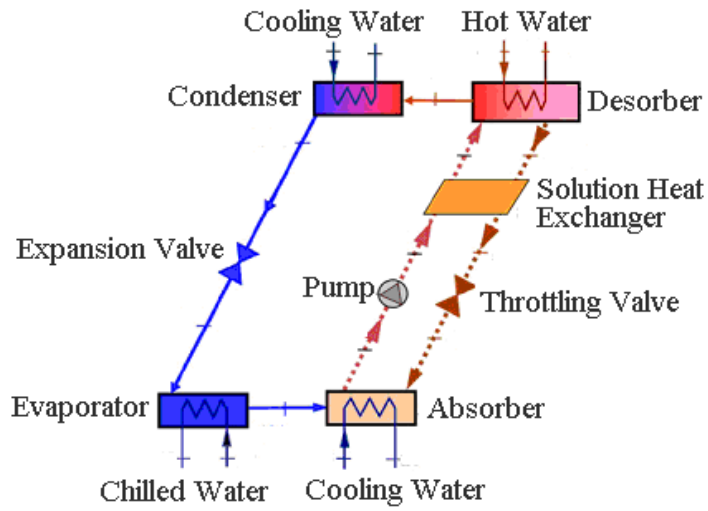
Figure 7: Absorption refrigeration cycle proposed by Riffat et al. [3]

Figure 8: Absorption refrigeration cycle proposed by Kim et al. [62]

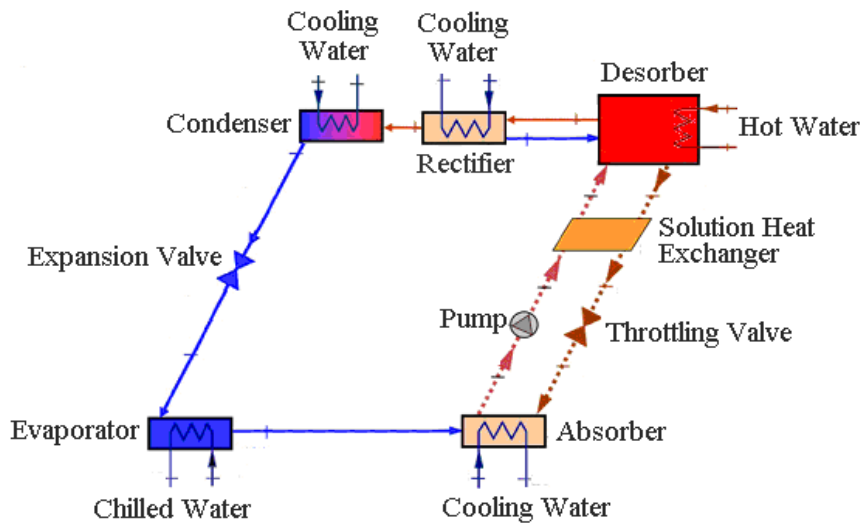
Figure 9: Absorption refrigeration cycle proposed by Zidu [22]

Figure 10: Absorption refrigeration cycle proposed by Wang et al. [6]

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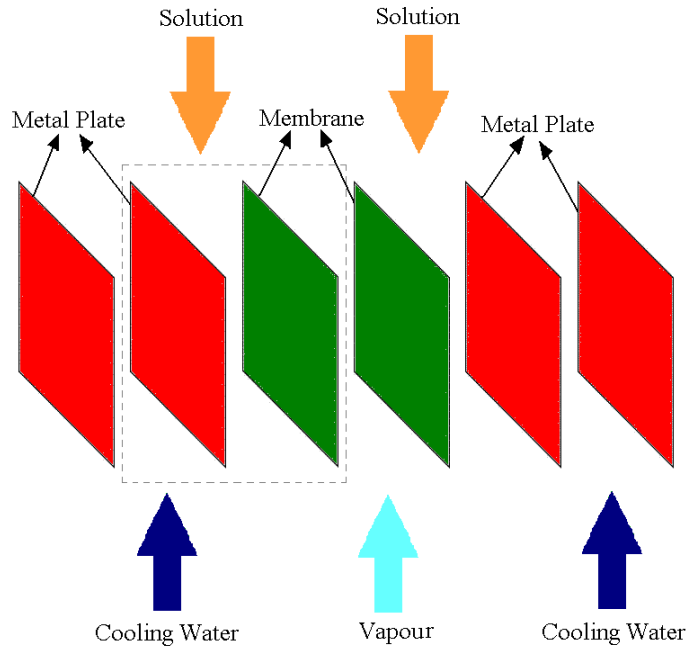
(a) H₂O/LiBr



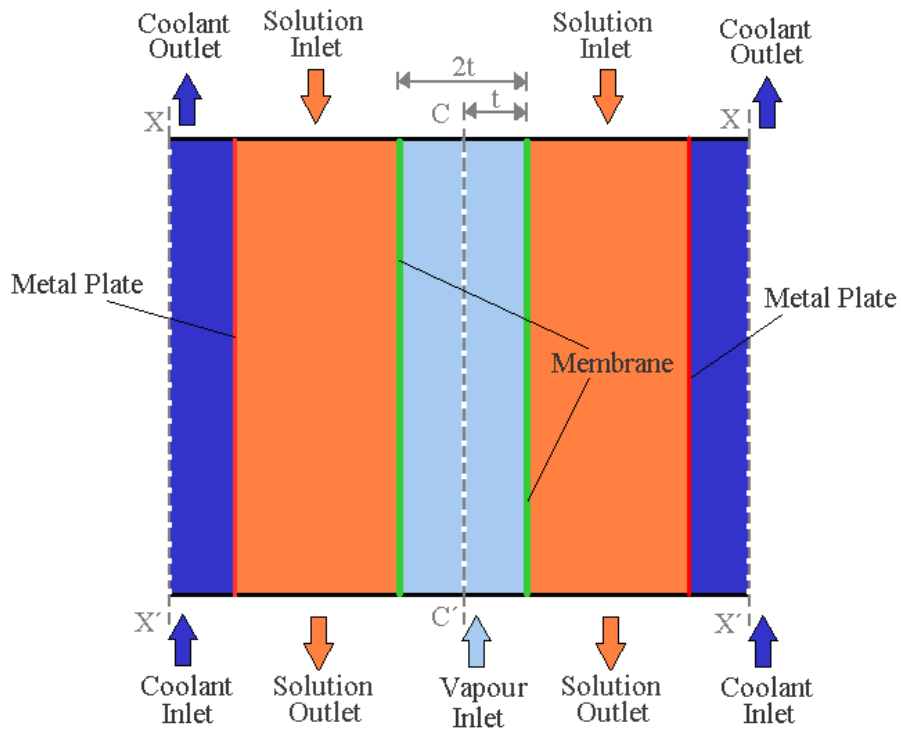
(b) NH₃/H₂O

Figure 1: Basic absorption refrigeration cycle configuration

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(a)



(b)

Figure 2: Plate-and-Frame membrane module

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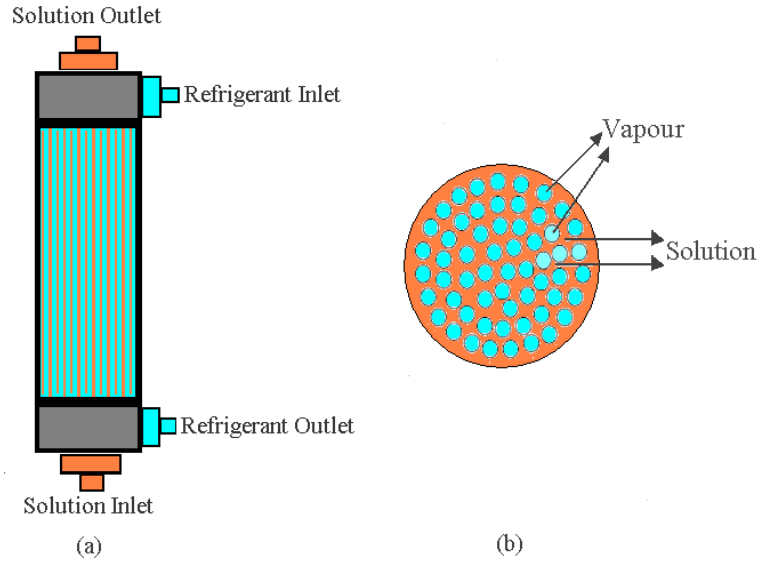


Figure 3: Hollow fiber membrane module [6]

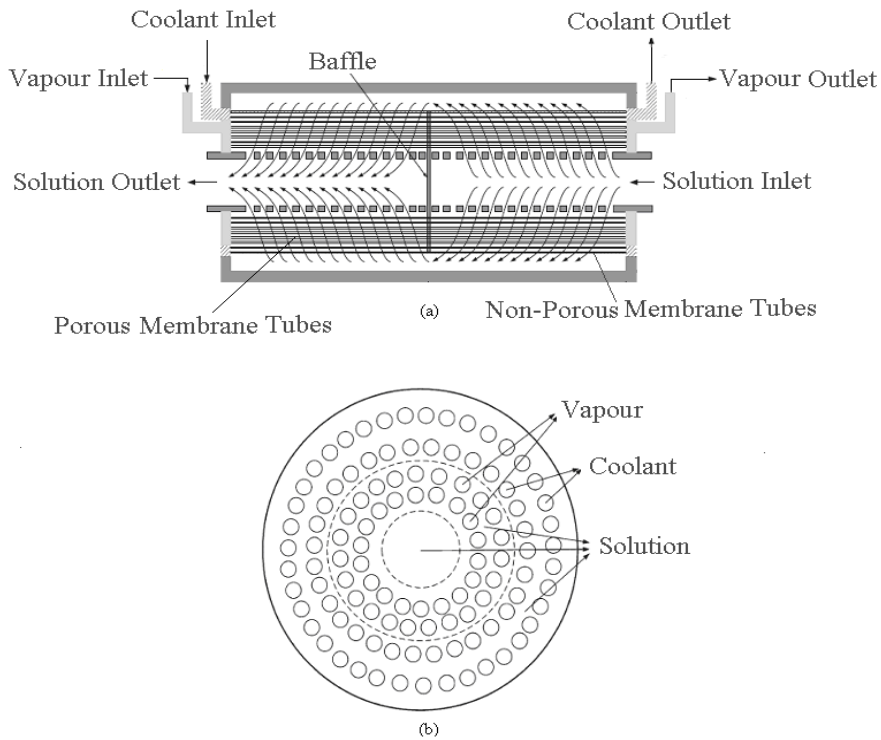


Figure 4: Hybrid hollow fiber membrane module [53]

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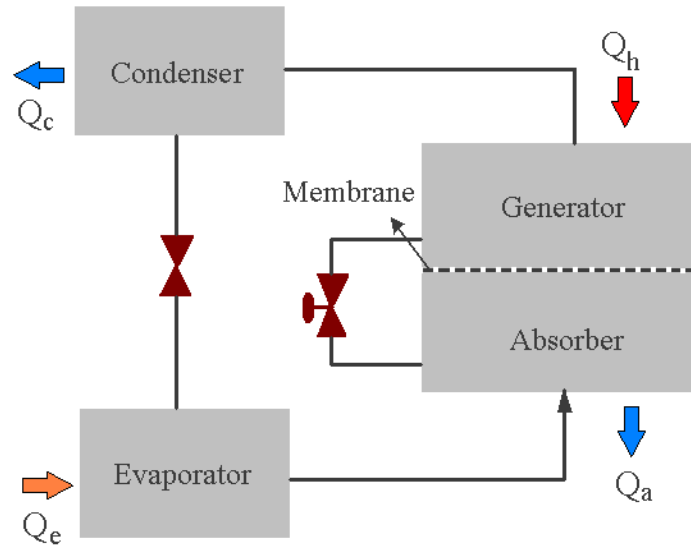


Figure 5: Absorption refrigeration cycle proposed by Zerweck [63]

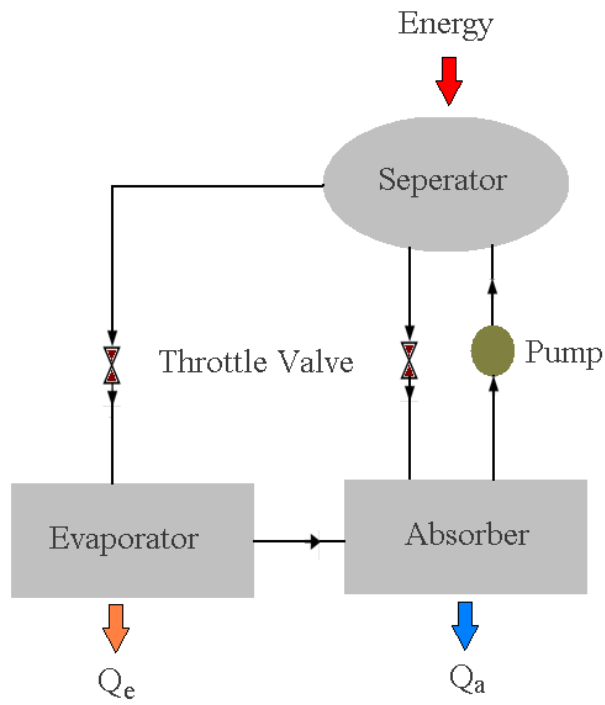


Figure 6: Absorption refrigeration cycle proposed by Riffat and Su [60]

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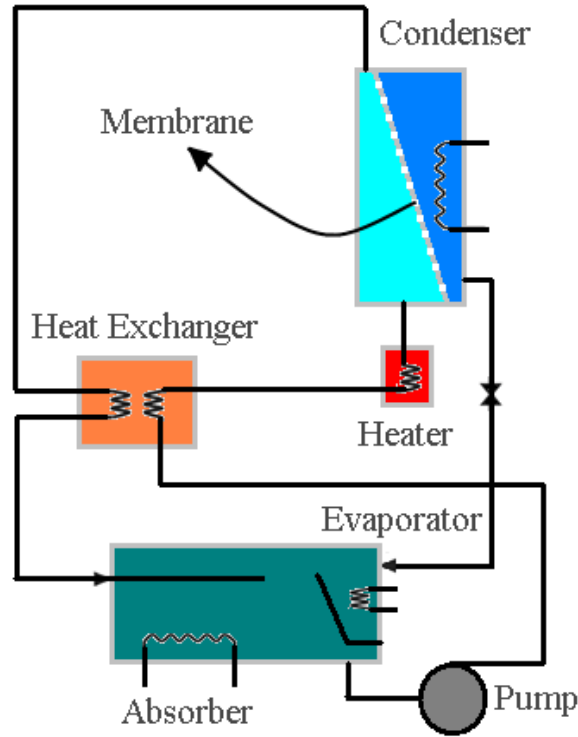


Figure 7: Absorption refrigeration cycle proposed by Riffat et al. [3]

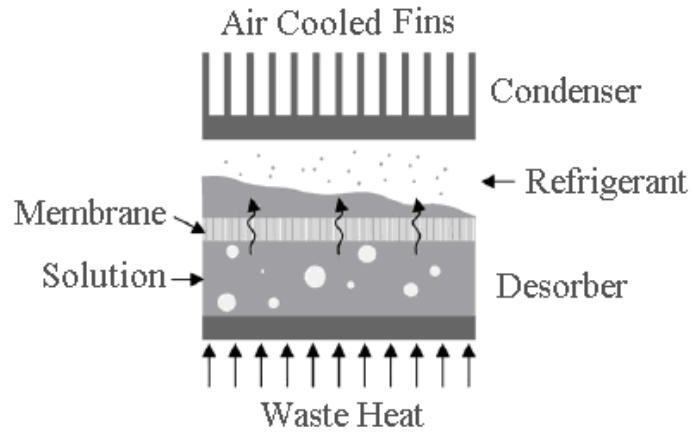


Figure 8: Absorption refrigeration cycle proposed by Kim et al. [62]

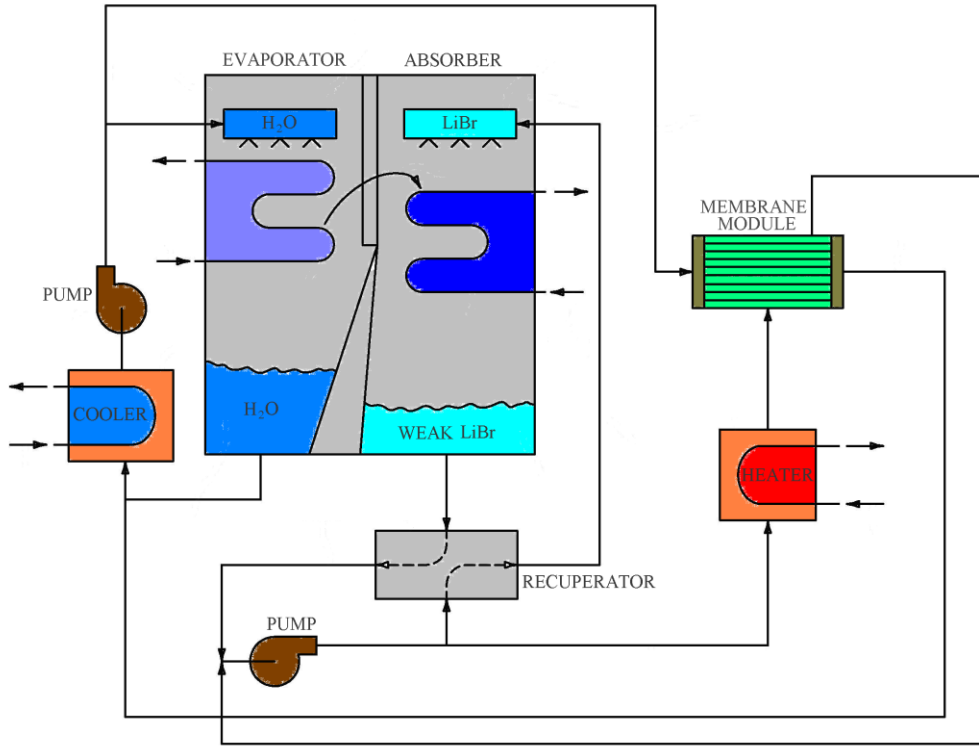


Figure 9: Absorption refrigeration cycle proposed by Zidu [22]

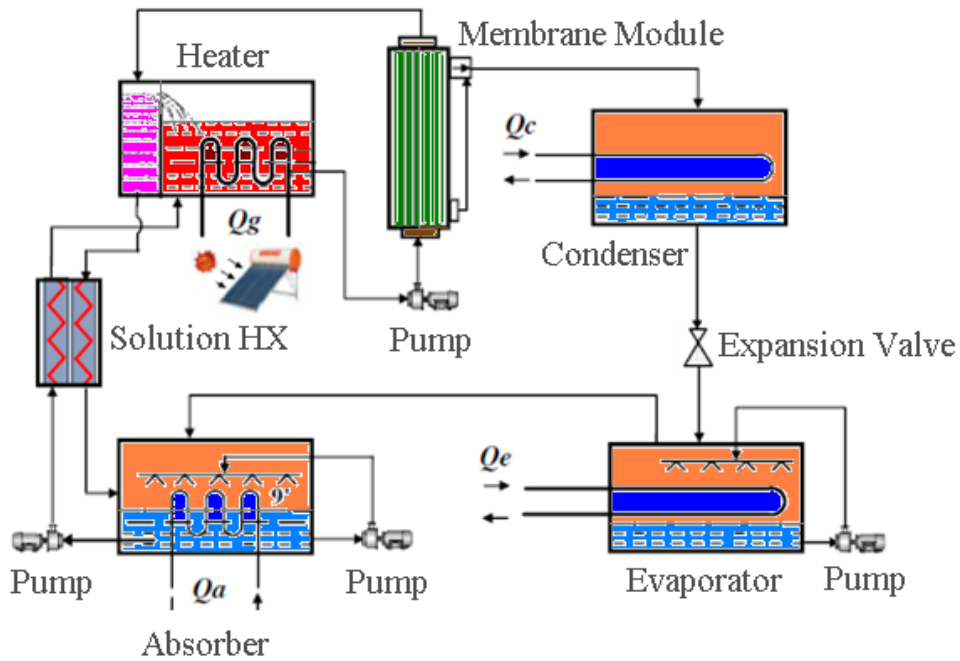


Figure 10: Absorption refrigeration cycle proposed by Wang et al. [6]

List of Tables

Table 1: Characteristics of membrane contactors reported in the investigations reviewed in this work

Table 2: Operating conditions and crystallization limit of the working fluid mixtures reported in the investigations reviewed in this work

Table 3: Geometric dimensions and parameters of the plate-and-frame membrane modules reported in the investigations reviewed in this work

Table 4: Geometric dimensions and parameters of the hollow fiber membrane modules reviewed reported in the investigations in this work

Table 5: Summary of the operating conditions of membrane based components reported in the investigations reviewed in this work

Table 6: Operating conditions of absorption refrigeration cycles using membrane based components reported in the investigations reviewed in this work

Table 1: Characteristics of membrane contactors reported in the investigations reviewed
in this work

Reference	Membrane Material	Porosity	Pore size (μm)	Thickness (μm)	Membrane Type
Schaal et al. [4]	Polypropylene	NA	0.04	40	Hydrophobic
Wang et al. [6]	Polyvinylidene Fluoride	0.85	0.16	150	Hydrophobic
Ali and Schwerdt [7, 15]	Polytetrafluoroethylene	0.64 – 0.75	0.20 – 0.45	65 - 175	Hydrophobic
Isfahani et al. [9]	Polytetrafluoroethylene	NA	0.45	50	Hydrophobic
Isfahani and Moghaddam [10]	NA	0.80	1.0	NA	Hydrophobic
Bigham et al. [11]	Polytetrafluoroethylene	0.60	1.0	20	Hydrophobic
Yu et al. [16]	NA	0.50 – 0.80	0.40 – 6.00	20 – 100	Hydrophobic
Ali [49]	Polytetrafluoroethylene	0.75	0.45	60	Hydrophobic
Chen et al. [53]	NA	0.40	0.03	30	Hydrophobic

Table 2: Operating conditions and crystallization limit of the working fluid mixtures reported in the investigations reviewed in this work

Working Fluid Mixture	Crystallization Limit	Operating Pressure	Cooling Temperature Requirement
NH ₃ /H ₂ O	No	Above atmospheric pressure	-40 °C to +5 °C
NH ₃ /Ionic Liquid [38–40]	No	Above atmospheric pressure	-40 °C to +5 °C
NH ₃ /LiNO ₃ [37, 47]	Above 0.72 mass fraction of LiNO ₃ at 50 °C	Above atmospheric pressure	-40 °C to +5 °C
NH ₃ /(LiNO ₃ +H ₂ O)	Crystallization risk is lower than NH ₃ /LiNO ₃ for same absorbent composition at 50 °C	Above atmospheric pressure	-40 °C to +5 °C
H ₂ O/LiBr [46]	Above 0.65 mass fraction of LiBr at 50 °C	Under vacuum condition	Above 7 °C
H ₂ O/(LiBr + LiI + LiNO ₃ + LiCl) [48]	Above 0.68 mass fraction of (LiBr + LiI + LiNO ₃ + LiCl) at 50 °C	Under vacuum condition	Above 7 °C
H ₂ O/(LiBr + LiI + LiNO ₃) [37]	Above 0.69 mass fraction of (LiBr + LiI + LiNO ₃) at 36.65 °C	Under vacuum condition	Above 7 °C
H ₂ O/Ionic Liquid [38–40]	No	Under vacuum condition	Above 7 °C

Table 3: Geometric dimensions and parameters of the plate-and-frame membrane modules reported in the investigations reviewed in this work

Reference	Length (mm)	Width (mm)	Depth (mm)	Solution Channel Thickness (mm)	Wall Thickness (mm)	No. of Channels
Thorud et al. [5]	58	29	NA	0.170 – 0.745	NA	NA
Isfahani et al. [8, 10]	38	203	1	0.160	NA	NA
Yu et al. [16]	20	NA	NA	0.05 – 0.20	NA	NA
Ali [49]	400	388	300	2.0	1	50
Kim et al. [62]	100	100.3	0.3	0.5	0.3	125

Table 4: Geometric dimensions and parameters of the hollow fiber membrane modules reported in the investigations reviewed in this work

Reference	Outer Diameter (μm)	Inner Diameter (μm)	Wall Thickness (μm)	Shell Inside Diameter (cm)	Effective Fiber Length (cm)	No. of Fibers
Schaal et al. [4]	NA	170	40	2.0 – 2.2	11	2100
Wang et al. [6]	NA	800	150	4.2	40	300
Chen et al. [53]	300	240	30	5.55	20	5000
Wang et al. [57]	1100	800	150	4.2	80	600

Table 5: Summary of the operating conditions of membrane based components reported in the investigations reviewed in this work

Reference	Membrane Module	Working Fluid	Component	Operating Conditions			
				Temperature (°C)	Pressure (kPa)	Absorbent Concentration in Solution (kg/kg)	Solution Flow Rate (kg/s)
Schaal et al. [4]	Hollow Fiber	NH ₃ /H ₂ O	Absorber	20.0	534.8	0.52 mol./mol.	NA
Thorud et al. [5]	Plate-and-Frame	H ₂ O/LiBr	Desorber	Saturation Temperature (T _s)	33.5	0.316 – 0.502	5.33 10 ⁻⁵
Wang et al. [6]	Hollow Fiber	H ₂ O/LiBr	Desorber	65.0 – 88.0	5.0 – 15.0	0.500	40 – 120 lit./h
Isfahani et al. [8]	Plate-and-Frame	H ₂ O/LiBr	Desorber	70.0	23.0	0.500	6.94 10 ⁻⁴
Isfahani et al. [8]	Plate-and-Frame	H ₂ O/LiBr	Absorber	25.0	1.1	0.600	1.67 10 ⁻⁴
Isfahani et al. [9]	Plate-and-Frame	H ₂ O/LiBr	Desorber	50.0 – 125.0	13.0 – 30.0	0.550	2.08 10 ⁻⁴ – 9.03 10 ⁻⁴
Isfahani and Moghaddam [10]	Plate-and-Frame	H ₂ O/LiBr	Absorber	25.0 – 35.0	0.8 – 1.8	0.540 – 0.600	1.67 10 ⁻⁴ – 5.83 10 ⁻⁴
Bigham et al. [11]	Plate-and-Frame	H ₂ O/LiBr	Absorber	35.5	0.87	0.600	Solution Mean Velocity 0.05 m/s
Bigham et al. [12]	Plate-and-Frame	H ₂ O/LiBr	Desorber	60.0 – 103.0	23.0 – 30.0	0.48 – 0.53	6.94 10 ⁻⁴
Yu et al. [16]	Plate-and-Frame	H ₂ O/LiBr	Absorber	55.0	0.87	0.550 – 0.640	Solution Mean Velocity 0.009 – 0.036 m/s
Ali [49]	Plate-and-Frame	H ₂ O/LiBr	Absorber	35.5	0.81	0.578	5.89 10 ⁻²
Chen et al. [53]	Hollow Fiber	NH ₃ /H ₂ O	Absorber	77.9	480.0	0.733	9.78 10 ⁻³
Wang et al. [57]	Hollow Fiber	H ₂ O/LiBr	Solution Heat Exchanger	HFI = 99.8 °C CFI = 40 °C	NA	SS = 0.550 WS = 0.500	4.26 10 ⁻²
Kim et al. [62]	Flat Sheet	H ₂ O/LiBr	Desorber	90.0	12.34	0.403	2.96 10 ⁻⁴

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Table 6: Operating conditions of absorption refrigeration cycles using membrane based components reported in the investigations reviewed in this work

Reference	Operating Conditions					COP
	Absorber Temperature / Heat Duty	Desorber Temperature / Heat Duty	Condenser Temperature / Heat Duty	Evaporator Temperature / Cooling Capacity	Pressure Ratio (P_{High}/P_{Low})	
Riffat et al. [3]	30 °C	75 °C	30 °C	10 °C / 140 W	NA	0.060
Schaal et al. [4]	20 °C / 28.7 kW	78 °C / 22 kW	20 °C / 28.7 kW	6 °C / 6.7 kW	3.32	0.305
Ali [49]	35 °C / 7.1 kW	75 °C / 7.35 kW	34.5 °C / 5.3 kW	4 °C / 5 kW	6.74	0.680
Chen et al. [53]	45 °C / 10.54 kW	145 °C / 10.36 kW	51.42 °C / 7.16 kW	10 °C / 6.18 kW	4.31	0.596
Kim et al. [62]	35 °C / 110 W	87.5 °C / 135 W	38.9 °C / 125 W	23.6 °C / 100 W	4.24	0.740