Stellingen

1. Het lineariseren van de temperatuurprofielen bij het ontwerpen van een warmtepomp werkend met een mengsel als koudemedium, kan desastreuze gevolgen hebben voor de COP en de verwarmingscapaciteit.
   The linearisation of the temperature profiles when designing a heat pump using a refrigerant mixture may have disastrous consequences for the COP and the heating capacity.
   La linéarisation des profils de température lors de la conception d’une pompe à chaleur utilisant un mélange de réfrigérants peut avoir des conséquences désastreuses sur le COP et sur la puissance de chauffage.

2. De vloeistofring compressor is niet geschikt voor warmtepomp of koelmachine toepassingen.
   The liquid-ring compressor is not suitable for heat pump or refrigeration applications.
   Le compresseur à anneau de liquide n’est pas adapté à l’utilisation dans les pompes à chaleur ou dans les machines frigorifiques.

3. In een goed georganiseerd nationaal energiesysteem, is er weinig plaats voor de verwarmingsketel, ook als het een hoog rendement ketel betreft.
   In a well organized national energy system, there is little place for the space heating boiler, even if it is a high efficiency boiler.
   Un système énergétique bien organisé au niveau national laisse peu de place au chauffage par chaudière, même s’il s’agit d’une chaudière à haut rendement.

4. Nucleaire energie is duurzaam, nucleair afval ook.
   Nuclear energy is sustainable, but so is nuclear waste.
   L’énergie nucléaire est durable, les déchets nucléaires aussi.

5. Natuurlijke klimaatveranderingen zijn bedreigender dan door menselijke activiteit veroorzaakte klimaatveranderingen.
   Natural climate changes are more threatening than climate changes induced by human activities.
   Les changements climatiques naturels sont plus menaçants que ceux induits pas les activités humaines.

6. De wereldwijde homogenisatie van de productie en gebruik van energie is een grotere uitdaging dan de reductie daarvan.
   The homogenisation of energy production and use on a global scale is a greater challenge than the reduction of its production and use.
   L’homogénéisation de la production et de l’utilisation de l’énergie au niveau mondial constitue un défi plus grand que leur réduction.

7. De huidige discussie over de maatschappelijke relevantie van wetenschappelijk onderzoek maakt duidelijk dat wetenschap op zich maatschappelijk niet relevant gevonden wordt.
   The present discussion about the social pertinence of scientific research makes clear that science in itself is not seen as being socially relevant.
   La discussion actuelle sur la pertinence sociale de la recherche scientifique indique que notre société ne considère pas la science comme socialement pertinente.

8. Het feit dat men gemiddeld beter scoort op de IQ testen dan 50 jaar geleden zegt meer over de IQ testen als maatstaf voor intelligentie, dan over de evolutie van de intelligentie zelf.
   The fact that on average people obtain a higher score on the IQ-tests than 50 years ago, says more about IQ-tests as a criterion for intelligence than about the evolution of intelligence.
Le fait que l'on réussisse en moyenne mieux les tests du QI qu'il y a 50 ans, en dit plus sur les tests du QI comme critère d'intelligence, que sur l'évolution de l'intelligence.

9. Tenzij als zodanig herkend, wordt een vooroordeel altijd bevestigd.
   Unless it is recognized as being a prejudice, a prejudice will always be confirmed.
   A moins d'être reconnu comme tel, un préjugé est toujours confirmé.

10. Als het huidige immigratiebeleid voortgezet wordt, zal de bevolking van Europa over enkele jaren verdeeld zijn tussen mensen met rechten en mensen zonder rechten.
    If the current immigration policy is continued, in a few years the population of Europe will be divided into those who have rights and those who have no rights.
    Si la politique actuelle de l'immigration est poursuivie, l'Europe sera dans quelques années partagée entre ceux qui ont des droits et ceux qui n'en n'ont pas.

11. De arbeidsparticipatie van vrouwen is meer gebaat bij economische noodzaak dan bij emancipatiebeleid.
    Women participation in labour is served more by economic necessity than by emancipation policies.
    La participation des femmes au travail est favorisée davantage par la nécessité économique que par les politiques d'émancipation.

12. Te vaak luisteren naar Postbus 51 doet geloven dat onsterfelijkheid een kwestie van gezond leven is.
    Listening too often to public health campaigns makes people believe that immortality is a question of healthy living.
    A écouter trop souvent les campagnes de santé publique, on croirait que l'immortalité est une question de santé.

    Because of all the campaigns against sexuel harassment, Dutch people gradually reach the stage where they need cuddle-therapy.
    Par suite de toutes les campagnes contre l'intimidation sexuelle, les Hollandais commencent à être mûrs pour la thérapie des câlins.

    The humming of Glenn Gould when he plays Bach makes the difference between perfection and genius.
    Grâce au fredonnement de Glenn Gould quand il joue Bach, on passe de la perfection au génie.

15. Over wie je lief hebt, kan je geen stellingen maken.
    It is impossible to make a logical proposition about a loved one.
    Sur ceux que l'on aime, il est impossible d'émettre une proposition logique.

16. Kennis is geen bron van zekerheid.
    Knowledge is not a source of certainty.
    La connaissance n'est pas source de certitude.


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Natte Compressie-Resorptie Warmtepomp Cycli: Thermodynamische Analyse en Ontwerp.

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
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in het openbaar te verdedigen ten overstaan van een commissie,
door het College voor Promoties aangewezen,
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"On a l'impression qu'au fond les hommes ne savent pas très exactement ce qu'ils font. Ils bâtissent avec des pierres et ils ne voient pas que chacun de leurs gestes pour poser la pierre dans le mortier est accompagné d'une ombre de geste qui pose une ombre de pierre dans une ombre de mortier. Et c'est la bâtisse d'ombre qui compte."

"Que ma joie demeure", Jean Giono, 1935.
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Abstract

This thesis is devoted to the thermodynamic analysis and design of wet compression-resorption heat pump cycles. Compression-resorption heat pumps are compression systems that work with a non-azeotropic mixture. The evaporation in the desorber is incomplete, so that either dry compression (solution recirculation) or wet compression is possible. The claimed advantage of these cycles is higher efficiency than conventional pure refrigerant cycles, because of the better temperature glide matching between the heat source and sink and the refrigerant mixture. The use of a mixture also allows the achievement of higher temperatures at lower pressures and the control of the capacity by controlling the mixture concentration.

The first part of this thesis deals with the thermodynamic analysis of compression-resorption cycles and with wet compression. For pure refrigerants, wet and dry compression systems are considered theoretically. For mixed refrigerants, theoretical consideration is given to solution recirculation systems and both theoretical and experimental studies are made for systems using wet compression.

From a study of the effect of wet compression on several heat pump internal cycles, it can be concluded that for pure refrigerants with a T-s saturated vapour line with a positive slope, like R123, wet compression is always disadvantageous when considering the COP. For pure refrigerants with a saturated vapour line with a negative slope, marginal COP gains can be achieved with wet compression. An exception to this is water, for which the COP gain may be more important. However, wet compression may still be of a great interest for high temperature heat pumps, because it limits the superheating of the vapour and therefore the risks of compressor failure and of the chemical decomposition of the refrigerant or of the oil. For zeotropic refrigerant mixtures it is very important that the compressor is able to compress a saturated or two-phase suction fluid if one wants to use the full potential of these mixtures to reduce the irreversibilities due to heat exchange with the heat source and the heat sink. A thermodynamic study on the effects of mixed and separate compression of the liquid and the vapour has shown that neither of these compression modes can be considered absolutely the best, so that cycle simulations are always necessary to determine for each application whether wet compression or dry compression (solution recirculation) should be preferred.

Based on known thermodynamic properties of non-azeotropic mixtures, temperature-enthalpy diagrams are used to analyse the cycles using these mixtures. From the non-linearity of the temperature profiles in the resorber and in the desorber, it can be concluded that a comparative study of several cycles cannot be made by simply considering the internal behaviour of the cycles. This is because pinch points can exist at an arbitrary location in the resorber or in the desorber, leading to a cycle that is not able to achieve the required external conditions. In the most simple simulation model, the temperature profiles must be calculated to avoid exceeding a prescribed minimum temperature difference. A second conclusion is that the use of logarithmic mean temperatures and logarithmic mean temperature differences should be avoided, unless mixtures with a linear temperature profile are used, or when the temperature glide is small.
enough to be linearized, or when the temperature difference between the internal and external media is very large. When using NH₃/H₂O, the use of the logarithmic mean temperature method can overestimate the mean temperature difference by more than 50%. In all cases, the use of the isentropic mean temperature difference is recommended to calculate the temperature levels between which the heat pump should work. However, it is also found that the use of logarithmic mean temperatures to calculate COPs introduces errors that remain below 5%.

It is emphasized that the definition of an ideal cycle against which to assess real cycles should be based on the external conditions and not on idealized properties of the refrigerant mixture. The confusion between internal and external ideal cycles is not relevant to cycles with constant temperature sources and sinks when a pure refrigerant is used, because both the internal and external ideal cycles behave like Carnot cycles. When the heat source and the heat sink have gliding temperatures or when a refrigerant mixture is used, the ideal external cycle that matches the external conditions perfectly is the Lorenz cycle. This cannot be fitted by any ideal internal cycle. For a given application, the comparison between the COP of a cycle using a pure refrigerant and of a cycle using a refrigerant mixture cannot be made at equal internal temperature levels. Area analysis in the T-s diagram shows again that no cycle can be considered the best in principle, and that the relative COPs of cycles using pure refrigerants and mixtures are intimately related to the external conditions. However, it is shown that the lower the ratio between the temperature lift in the cycle (difference between the sink and source high temperatures) and the heat sink temperature glide, the better is the performance of the mixture refrigerant cycle in comparison with the pure refrigerant cycle. This makes compression-resorption cycles particularly suitable for industrial applications. The use of internal heat exchange between the resorber cold end and the desorber hot end has, in principle, not always advantages, but generally turns out to have a positive effect on the COP. The use of absorptive-evaporative heat exchange similar to the heat exchange used in GAX cycles is not recommended in the compression-resorption heat pump, because it reduces the heating capacity and the COP. The use of rectification should also be avoided.

Nine cases are chosen for a parametric study with NH₃/H₂O, covering a wide range of heat pump applications. All results relating to these cases can be found in this thesis. Owing to the large number of simulations necessary to optimize the cycles, the simplest black-box model compatible with the previous thermodynamic analysis is chosen. Because no assumptions are made about the heat exchange surfaces or about the heat transfer coefficients, this model allows calculation of the optimum repartition of the UA-values between the resorber and the desorber. For each application, the performances of the wet compression cycle, the solution recirculation cycle and the pure refrigerant vapour compression cycle are compared for several mixtures and assessed against the Lorenz cycle. The COP and the Specific Compressor Displacement are analysed (SCD: compressor suction volume flow rate per kW usefull heat in the resorber). With a constant minimum temperature approach and isentropic efficiency, the COP is very sensitive to the quality of the temperature glide matching between external and internal medium, and thus to the overall concentration. The maximum COP is obtained for the overall concentration for which the sum of the mean temperature differences in the resorber and in the desorber is minimal. Although it is not possible to obtain the highest COP together with the lowest specific compressor displacement, the SCD values obtained at the highest COP are not too far from the lowest SCD value.
An entropy analysis of the wet compression cycle is also conducted. This highlighted the fact that at the optimum overall concentration, the main losses arise in the compressor, which is therefore the first component to be optimized. It is shown that to bring the losses back to a reasonable level, a wet compressor with an isentropic efficiency of at least 0.75 should be used.

Although the results remain dependent on the applications, general lines can be drawn concerning the relative efficiency of the different cycles. It is shown that, even at low heat sink and source temperature glides, the compression-resorption cycles using \( \text{NH}_3/\text{H}_2\text{O} \) perform better than pure refrigerant ones by 10 to 30\%, provided that the ratio \( \Delta T_{\text{lin}}/\Delta T_{\text{glide,sink}} \) is lower than 2. At large heat sink temperature glides (>30 °C), this limitation no longer applies, at least with the mixture \( \text{NH}_3/\text{H}_2\text{O} \). As a direct consequence of the better temperature glide matching in the compression-resorption cycles, the optimum mean \( \text{UA} \)-values (heat transfer coefficient times heat transfer area) in the desorber and in the resorber are much higher (up to 4 times) than for a pure refrigerant cycle. This emphasizes the need to design high efficiency-compact heat exchangers. A comparison between the wet compression cycle and the solution recirculation cycle shows that wet compression with \( \text{NH}_3/\text{H}_2\text{O} \) always leads to higher COPs (by 2 to 13 \%).

The performances of several pairs and ternary mixtures of fluorocarbons and of hydrocarbons are studied. An analysis of the T-h diagrams shows that for mixtures belonging to the same chemical group, the higher the critical temperature difference of the mixture’s components, the higher the non-linearity of the isobars in the T-h diagram. This means that for high temperature glide applications, it is difficult to find a refrigerant mixture matching the external glide properly. From the same case-study as for \( \text{NH}_3/\text{H}_2\text{O} \), it is concluded that the behaviour of the refrigerant mixtures can be first estimated by using the two parameters \( \Delta T_{\text{glide,mix}} \) and \( \Delta T_{\text{glide,mix}}/\Delta h_{\text{ev}} \), where \( \Delta T_{\text{glide,mix}} \) and \( \Delta h_{\text{ev}} \) are the temperature difference and the enthalpy difference between the liquid and vapour saturation lines at the pressure of 1 bar and the overall concentration of 0.5 kg/kg. \( \Delta T_{\text{glide,mix}} \) should match the heat sink temperature glide of the application, or, at least, should not be a limiting factor, and \( \Delta T_{\text{glide,mix}}/\Delta h_{\text{ev}} \) should be as small as possible. According to this, propane/n-butane will generally perform very well for small heat sink temperature glide applications (≤ 15 K) at a mean heat sink temperature up to 90 °C. Propane/n-pentane will perform reasonably for almost all applications at mean heat sink temperatures up to 110 °C, except large heat sink temperature glide applications (≥ 44 K). R152a/R123 and R134a/R123 are found to perform reasonably for moderate heat sink temperature glide applications (≤ 25 K) at a mean heat sink temperature up to 110 °C. R125/R123 and R23/R123 do not usually perform well, except in the case of some very large heat sink temperature glide applications (≥ 80 K), where R23/R123 did perform well. \( \text{NH}_3/\text{H}_2\text{O} \) is found to perform very well for all applications, up to about 150 °C. However, this classification should be used to eliminate mixtures rather than to choose one because, owing to the complexity of the optimization procedure, the selection of an efficient mixture for a given application demands the use of cycle simulations. From the case-study it is concluded that the binary mixture \( \text{NH}_3/\text{H}_2\text{O} \) and the ternary blends propane/n-butane/n-pentane and R125/R152a/R123 are the less sensitive to the external conditions. For \( \text{NH}_3/\text{H}_2\text{O} \), the COP is never lower than 12 \% of the maximum COP. The results relating to the SCD are more widely spread, but \( \text{NH}_3/\text{H}_2\text{O} \) never performs really poorly. The major drawback of \( \text{NH}_3/\text{H}_2\text{O} \) is its high \( \text{UA} \)-value, in particular for large temperature glide applications. It was confirmed that for small heat sink temperature glide applications,
the pure refrigerant vapour compression cycle can be the most advantageous one in terms of COP and UA-values, in particular at large $\Delta T_{in}/\Delta T_{glide,sink}$ ratios. However, its SCD or its discharge pressure is generally much higher than that of the other cycles. Generally the wet compression cycle appears to be the best cycle, since it can lead to a COP that is up to 50% better than the COP of the solution recirculation cycle. The mean COP increase due to wet compression on the nine examples and nine mixtures studied is 14%. However, for a few application/mixture combinations, the COP of the solution recirculation cycle turns out to be better than the COP of the wet compression cycle.

The second part of this thesis is devoted to the design of a wet compression-resorption heat pump test-plant and to an analysis of the measurements. The test-plant is designed to heat a sink from 38 °C to 68 °C, with a heating capacity of 32 kW, and using a heat source at 40 °C. Technological options are chosen according to the present state-of-the-art of the required components, on the premise that the components should be commercially available. The resorber is of the plate-fin type with serrated corrugations. Co-current downflow of the solution and vapour and counter-current flows between condensing mixture and cooling water were chosen. The desorber is of the same type as the resorber, and vertically downwards co-current two-phase flow was chosen to reduce the pressure drop as much as possible. The water flow is counter-current. Rotary compressors are less sensitive to liquid injection than piston compressors and, of the rotary compressors, screw compressors may provide the best solution because their capacity, power and pressure ratio are suitable for a wide range of industrial applications. However, it was not possible to find a screw compressor adapted to NH$_4$/H$_2$O and to wet compression that was suitable for the small capacity of the test-plant. Finally, despite its very low efficiency, a liquid-ring compressor is used to test the other components of the test-plant.

Because of the use of the liquid-ring compressor, the design values could not be reached. The heat sink could only be heated to 53 °C and had a heating capacity varying between 9 and 20 kW. The liquid at the discharge side of the liquid-ring compressor is found to be subcooled and very low isentropic efficiencies are found, in consequence of which internal COPs less than 1 are found. However, the external COP based on the water side heating and cooling capacities could reach a value of 5. The analysis of the measurement data on the resorber shows that the entering liquid is much more subcooled than expected. The overall heat transfer coefficient in the resorber varies between 200 and 1200 W/m$^2$K, and is very sensitive to the vapour velocity, which should be kept high. The desorber has a very poor heat transfer coefficient of about 100-150 W/m$^2$K, probably because of the occurrence of mist flow, due to the high vapour volume flow rate at the inlet and to the poor distribution system. In both the resorber and the desorber, mean temperature differences below 8 K are observed, with minimum temperature differences down to 1 K. Reasonable agreement is found between the measured results and the results of the parametric model.

Finally recommendations for further research are outlined. Improvements must be made to the heat pump, including using a better compressor, with a lower injection volume flow rate. Fundamental research on the design of wet compressors should be initiated and research on the design of high efficiency compact heat exchangers for condensing and evaporating mixtures should be continued.
Nomenclature

\[ A \quad \text{Heat exchange area} \quad [m] \]
\[ C_p \quad \text{Specific heat} \quad [kJ/kg\cdot K] \]
\[ f_r \quad \text{Fraction of heat exchanged in absorptive-evaporative heat exchange} \quad [%] \]
\[ h \quad \text{Specific enthalpy} \quad [kJ/kg] \]
\[ H \quad \text{Enthalpy} \quad [kJ] \]
\[ m \quad \text{Mass flow rate} \quad [kg/s] \]
\[ m_i \quad \text{Liquid mass fraction (m_i + m_v = 1)} \quad [kg/kg] \]
\[ m_v \quad \text{Total mass flow rate of refrigerant circulating in a cycle} \quad [kg/s] \]
\[ m_v \quad \text{Vapour mass fraction} \quad [kg/kg] \]
\[ n_r \quad \text{Rotational speed} \quad [rpm] \]
\[ P \quad \text{Pressure} \quad [bar] \]
\[ Q \quad \text{Heat or Heat rate} \quad [kJ] \text{ or } [kW] \]
\[ R \quad \text{Ideal gas constant} \quad [8.314 \text{ J/molK}] \]
\[ s \quad \text{Specific entropy} \quad [kJ/kg\cdot K] \]
\[ S \quad \text{Entropy} \quad [kJ/K] \]
\[ SCD \quad \text{Specific compressor displacement} \quad [m^3/kJ] \]
\[ T \quad \text{Temperature} \quad [\degree C] \]
\[ T_c \quad \text{Critical temperature (Chapter 5)} \quad [\degree C] \]
\[ U \quad \text{Heat transfer coefficient} \quad [kW/m^2\cdot K] \]
\[ UA \quad \text{Heat transfer coefficient times heat exchange area} \quad [kW/K] \]
\[ V \quad \text{Specific volume} \quad [m^3/kg] \]
\[ \dot{V} \quad \text{Volume flow rate} \quad [m^3/s] \]
\[ W \quad \text{Work} \quad [kJ] \]
\[ x \quad \text{Liquid concentration in the most volatile component} \quad [kg/kg] \]
\[ x_o \quad \text{Overall concentration (x_o = m_i x + m_v y)} \quad [kg/kg] \]
\[ y \quad \text{Vapour concentration in the most volatile component} \quad [kg/kg] \]

Greek letters

\[ \alpha \quad \text{Void fraction} \quad [m^3/m^3] \]
\[ \alpha_r \quad \text{Volumetric heat transfer coefficient} \quad [kW/m^3\cdot K] \]
\[ \beta \quad \text{Performance coefficient} \quad [m^3/kW\cdot K] \]
\[ \beta_r \quad \text{Volumetric performance coefficient} \quad [m^3/kW\cdot K] \]
\[ \Delta \quad \text{Difference} \]
\[ \eta \quad \text{Isentropic efficiency compressor} \]
\[ \rho \quad \text{Density} \quad [kg/m^3] \]
\[ \gamma_i \quad \text{Infinite-dilution activity coefficient} \]

Other symbols

\[ \Delta h_{lv} \quad \text{isobaric enthalpy difference between the liquid and vapour saturation line of a mixture} \quad [kJ/kg] \]
\[ \Delta T \quad \text{Temperature difference} \quad [K] \]
\[ \Delta T_{glide} \quad \text{Temperature difference of the heat source or} \]
heat sink fluid between the inlet and outlet of an heat exchanger

\( \Delta T_{glide,mixt} \) isobaric temperature difference between the liquid and vapour saturation line of a mixture

\( \Delta T_{lip} \) Temperature difference between the desorber inlet temperature of the heat source and the resorber outlet temperature of the heat sink

\( \Delta T_q \) Temperature difference between the two fluids of an heat exchanger when a heat quantity q has been exchanged

Subscripts

\( c \) Cold side
\( comp \) Compressor
\( cond \) Condensor
\( d \) Desorber, mixture side
\( des \) Desorber, water side
\( eq \) Equilibrium
\( e.v., \ exp \) Expansion valve
\( ex, \ exch \) Internal heat exchanger
\( fill \) Filling vessel
\( gen \) Generator or Evaporator
\( h \) Hot side
\( inj \) Injection
\( l \) Liquid
\( L \) Lorentz
\( los \) Heat losses
\( lr \) Liquid ring
\( mean \) Average value
\( meas \) Measured value
\( min \) Minimum value
\( mixt \) Mixture
\( net \) Netto (work)
\( o \) Overall or total value
\( out \) Outlet
\( PR \) Pure refrigerant
\( r \) Resorber, mixture side
\( res \) Resorber, water side
\( simul \) Value obtained by simulation
\( sink \) Heat sink
\( sour \) Heat source
\( tot \) Total value
\( w \) Wet compression in Chapter 1 and 2; water or heat transfer fluid in other chapters

Abbreviations

\( COP \) Coefficient of performance (ratio of the resorber heating capacity and of the compressor work)

\( CLMF \) Constant Liquid Mass Fraction Model
Definitions

Carnot cycle: Ideal cycle for constant temperature heat sink and heat source, perfectly matching the external conditions, see Section 3.4.2.

Lorenz cycle: Ideal cycle for arbitrary heat sink and heat source, perfectly matching the external conditions, see Section 3.4.1.

Pure refrigerant cycle: Ideal internal cycle for a pure refrigerant (equivalent to a Carnot cycle), see Section 3.4.3.

Mixture cycle: Ideal internal cycle for a refrigerant mixture (not equivalent to a Lorenz cycle), see Section 3.4.3.

Oesenbrück cycle: Compression-resorption cycle with separated vapour compression and liquid pumping, see Section 1.2.1.

Solution recirculation cycle: See Oesenbrück cycle.

Vapour compression cycle: In this thesis, Rankine cycle used with a pure refrigerant.

Wet compression cycle: Compression-resorption cycle where vapour and liquid are compressed together.
Chapter 1

Introduction

1.1 Why use heat pumps

1.1.1 Saving energy with heat pumps

The distribution of the total primary energy consumption of the European Union (see Figure 1.1) is such that about 82% of the energy is used in buildings and industries. About 47% of this energy is used to heat buildings and as industrial process heat (Zegers [1987]). It is estimated (NREL [1991]) that about 30% of the energy used by the process industry is still released at temperatures and in quantities which would make re-use feasible. This represents about 12% of the total primary energy consumption.

Heat pumps are devices which can upgrade low temperature energy to high temperature levels. They can currently provide heat up to temperatures of about 120 °C. For heating in buildings, heat is needed at temperatures lower than 90 °C, which means that heat pumps could provide for the entire building heating market, which represents more than 26% of the total primary energy use. Heat sources for these heat pumps may be natural sources (air, ground water, sea water, geothermal and solar energy), or industrial waste heat. The process industry has a high heat demand of up to 400 °C (food, paper, textile industries) and also between 1200 and 1600 °C (iron, aluminium, ceramic and glass industries) (Zegers [1987]). Because of the limit on the temperature that heat pumps can achieve, only less than 2% of the total industrial process heat demand could be covered by heat pumps. An increase in the temperature limit to 400 °C could increase the potential
market to about 8 %, which represents about 2 % of the total energy consumption. Together with the savings in the heating of buildings and the fact that heat pumps are 30 to 50 % more efficient than conventional systems, heat pumps could save between 8 and 14 % of the total primary energy use. However, this estimate should be tempered by three remarks. First, the values cited above are based on approximate performance and economic and marketing data. Secondly, for high temperature applications (400 °C), sources of at least 200 °C should be available so that the heat pump efficiency will be high enough to compete with other systems. Such high temperature waste heat could probably be better used in heat exchangers (Berntsson [1987]). It is indeed known from pinch technology (Linnhof [1988]) that heat pumps must be placed across the process pinch point and not above or below. Since the temperature pinch point in most industries lies between 80 and 120 °C, sources at 200 °C should not be used, except in special cases of high temperature pinch point industries. Thirdly, heat pumps must be able to compete with cogeneration, which at present is often more competitive from an economic point of view, but has the environmental disadvantage that it does not re-use existing waste heat.

1.1.2 Environmental aspects

Although it has still not been strictly proved, it is now believed that because of an increase of greenhouse gases like CO₂, due to human activities, an important rise in the earth’s mean surface temperature may occur. Short term solutions for this problem are not likely to exist, but, from a long term perspective, a rapid and intensive reduction in the emission of greenhouse gases is necessary.

Although most heat pumps are electrically driven, thus increasing the use of electricity, they will still reduce the total consumption of fossil fuel, when used to replace
conventional systems. How heat pumps will reduce CO₂ emissions will depend, therefore, on the technology that heat pumps replace and on their source of drive energy.

If the drive energy is electricity, this reduction will depend on how the electricity is generated. When electricity is not generated by fossil fuel energy, a drastic reduction of CO₂ emissions is expected but even for electricity generated by fossil fuel energy, heat pumps could still reduce the CO₂ emissions by about 30% when compared with fossil fuel fired boilers (Bouma [1993]).

If the heat pump drive energy is a fossil fuel, a reduction up to 50% in the CO₂ emissions could be expected, mainly because of the much lower energy consumption than conventional systems require. The potential of heat pumps to reduce the total CO₂ emissions is believed to be around 9%. The contribution of power stations and heat pumps to the production of other greenhouse gases like methane, NOₓ, and CFCs is believed to be negligible.

However, these data on the positive environmental effects of heat pumps must be approached with caution (for instance, the generation of electricity by non-fossil fuel energy (nuclear) is not necessarily cleaner than its generation by fossil fuel energy) and some evident disadvantages should be named; some refrigerants may indeed contribute to significant greenhouse gas emissions by leakage or at the end of the life cycle of the equipment (Bouma [1993]), which could seriously reduce the claimed reduction potential. NOₓ is also produced by diesel and gas engines, and last, but not least, some refrigerants like CFCs and HCFCs, still used in heat pumps, attack the ozone layer when they are released into the atmosphere.

Despite these reservations it is evident that if one wants to use the full potential of heat pumps, research should be orientated in the following directions:

1. finding new environmentally friendly refrigerants, (no ozone depleting potential, no contribution to the greenhouse effect), which are also safe for human beings (low toxicity and flammability).
2. increasing the efficiency of heat pumps by employing new cycles, new refrigerants and optimized components.
3. developing heat pumps for high temperature applications.
4. finding an optimum balance between the quality of the equipment (to limit leakages and to increase life time and safety) and the pay-back time.

1.1.3 Types of heat pumps for different applications

Heat pumps have a good potential at different temperature levels. The process industry illustrates the high temperature case. In the process industry there is a high heat demand up to 400 °C, with a peak between 120 and 160 °C (Zegers [1987], Berntsson [1987]). Waste heat is usually available at temperatures between 50 and 110 °C. The low temperature case, for which most of heat pumps have been developed to date, is that of manufacturing industry and building heating, where heat is needed at temperatures
between 60 and 100 °C, and where most waste heat sources are between 20 and 60 °C, (Berntsson [1987]) or lower, when natural sources are involved.

Four types of heat pumps are normally considered for industrial and building heating applications: the vapour recompression and open cycle heat pumps, the compression heat pumps, the absorption heat pumps and the compression-resorption heat pumps (see for instance Berghmans [1980] and Brodowicz [1993] for general accounts of these types of heat pumps).

**Vapour recompression and open cycle heat pumps:** These are interesting because of their high COPs and low investment costs, which is the reason why nowadays they are widely applied in industry. However, the lower limit of the evaporation temperature for steam is 80 - 100 °C, mainly because of the specific vapour volume becoming too high. Because a lot of industrial sources have a lower temperature, other types of heat pump are also required to use the full potential of waste heat.

**Compression heat pumps:** These are usually electrically driven. It is possible to achieve high temperatures by using multi-stage systems, but they are complex and necessitate high investment costs. Thus, the crucial problem is to find fluids for condensing temperatures above 120 °C. The use of non-azeotropic mixtures can contribute to the solution and sometimes also allows a higher efficiency. Heat pumps driven by diesel or natural gas combustion engines are preferable to electrically driven ones only when the electricity price is two or three times higher than that of the fuel. As electricity prices for industry are generally kept low, their application at the present time is limited.

**Absorption heat pumps:** For practical reasons, the heat sink temperature of absorption heat pumps of type I is maximized at about 100 °C, which limits their use in high temperature applications. Heat pumps of type II, called heat transformers, can achieve high temperatures, up to 150 °C, however they give quite a low temperature lift (about 40 °C), which results in the same heat source problem as for the vapour recompression and open cycles. A second restriction is that the heat source must be much larger than the heat sink. They do have the advantage of using only cost-free energy (waste heat), at least when they are not directly fired and of being free of moving parts.

**Compression-resorption heat pumps:** These are still in an experimental stage, but are quite promising because they combine the advantages of absorption and compression systems. They could achieve high temperature levels, up to 180 °C, with quite high temperature lifts, and with relatively high COPs. Harmless refrigerant mixtures can also be used. Compression-resorption heat pumps are at present a particularly attractive research subject, since three of the four research directions mentioned in the previous section are combined. This justifies the choice of this research subject.
1.2 Compression-resorption heat pumps

1.2.1 Definition

The compression/resorption heat pump, sometimes called hybrid heat pump, is a compression system working with a non-azeotropic mixture. The evaporation in the desorber is incomplete, so that solution recirculation between the desorber and the resorber is possible. When all the solution is recirculated (Figure 1.2.a), the cycle is called the Osnabrück cycle, after its inventor. The name total wet compression cycle is used for those cycles for which all the solution is sent to the compressor, avoiding the use of a solution pump (Figure 1.2.b). Every possible intermediate stage between these two types of cycle can be used. The total variation scale between these two cycles can be used, where only a part of the solution is sent to the compressor, and the rest is pumped into the resorber.

![Diagram of compression-resorption heat pump with a) solution recirculation (Osnabrück cycle) b) total wet compression.](image)

The claimed advantages (Ziegler [1989]) of the compression-resorption heat pumps are numerous. First, since non-azeotropic mixtures do not condense or evaporate at constant temperature because of the changing liquid concentration during these processes, the choice of an adequate overall concentration could contribute to decrease the process irreversibilities by improving the matching between the mixture temperature glide and the heat source and sink temperature glides. This is of primary importance when the source and the sink are not at constant temperatures. Secondly, the use of non-azeotropic mixtures also allows the achievement of higher temperatures at lower pressures, because the addition of an absorbent produces a vapour pressure decrease. Thirdly, changing the mixture concentration at constant source and sink temperatures creates an additional way to control the capacity (Vakil [1983]) (the traditional way is to control the compressor...
inlet capacity). Finally, under certain conditions, a higher COP can be achieved than with pure refrigerants.

### 1.2.2 Historical background and literature

The principle of the Osenbrück cycle has been known since 1895 (Osenbrück [1895]). One then has to wait till 1950 to find other theoretical publications on this topic by Altenkirch ([1950], [1954]), using the mixture NH$_3$/H$_2$O. This subject was forgotten again till the eighties, probably because no one knew how to solve the technical problems around the compressor that must be able to withstand wet compression, and also perhaps because of a lack of interest in reducing the energy consumption of machines.

However, it must be remembered that mixtures have already been used since 1963 in vapour compression plants, using a Rankine cycle with freon mixtures (Chaikovsky [1963], Arora [1967], Garcia [1983], Blaise [1987], Camporese [1987] Ambrosino [1989]). In these plants the mixture is totally evaporated in the desorber, so that there is no solution recirculation. When the correct mixture concentration is chosen some COP and/or capacity increase is reported.

The compression-resorption cycles may be superior to the above mentioned Rankine cycle for different reasons. First, the desorber surface can be reduced because of incomplete evaporation. Secondly, the vapour superheating can be reduced, which can be favourable for high temperature applications. Thirdly, as the temperatures depend on the evaporation degree they can be adapted to the external conditions. Lastly it is possible to adapt the mixture concentration to variable external conditions (Lotz [1981]).

Since 1987, seven plants have been built and tested. The Osenbrück cycle was used in three laboratory test-plants (Stokar ([1986], [1987]), Rane [1989], Kawada [1991]) and in an industrial plant of 1 MW (Mucic [1989], [1990]). NH$_3$/H$_2$O was used in all plants, except in that of Kawada, who used TFE/E181. At the same time, the derivative of this cycle using total or partial wet compression has been used in two industrial plants of respectively 800 and 890 kW (Malewsky [1988] and Bergmann [1990]) and in one laboratory test-plant (Torstensson [1991]), with the working pair NH$_3$/H$_2$O. Of the industrial plants, only that of Mucic is still working. The exploitation of the plants of Malewski and Bergmann has stopped, mainly because of financial problems. In the plants of Kawada, Malewski, Bergmann and Torstensson, problems were reported with the lubrication and sealing of the compressor, which almost always turns out to be the bottle neck of the plant. Indeed, if a wet vapour is to be compressed, the use of an oil-lubricated compressor can lead to problems in the compressor because of the oil being removed by the solution, causing compressor failure. The resorption and desorption processes can also be disturbed by the oil. A reliable method is to use an oil-free compressor (Stokar, Malewski, Bergmann, Rane), but this is often costly. In Malewski’s plant, the bearings and gland seal were lubricated by the solution itself, but this led to critical corrosion problems, after which grease lubrication was tried. Torstensson used an oil-lubricated compressor without oil recovery, but the oil used did not seem to be very suitable. No further information about the problems he faced has been published. Finally, Kawada and Mucic
used an oil-lubricated compressor with oil separators. Little is known about the plant of Kawada, but the third version of Mucic’s plant seems to work without problems.

Little is known concerning the performances of the desorber and resorber, with the exception of the detailed measurements of Stokar. Stokar, Kawada and Mucic used falling film resorbers. Bergmann and Malewski have used shell and tube heat exchangers and Torstensson a co-axial tube. According to Kawada, the presence of oil does not affect seriously the desorber performances with TFE/E181. However, the desorber and resorber design remains a strategic point because the performances of the plants strongly depends on the heat transfer coefficients. Perfect counter-current must be used, phase equilibrium must be approached as closely as possible and maldistribution must be avoided. System fluctuations also have an important influence on the COP. Rane emphasized that the temperature glides in the resorber and desorber should be optimized first. For all these plants, important COP gains, up to 22%, are claimed when comparisons are made with pure refrigerant systems. The COP enhancement is greater for heat sources and heat sinks with high temperature glides, but can still be significant for temperature glides as low as 5 K. A detailed review of these plants can be found in Åhlby [1990] and Itard [1992].

Other authors have looked at the theoretical behaviour of the compression-resorption cycles. Theoretical studies of the Osenbrück cycle have been made by Åhlby ([1987a,b], [1989], [1991]). She has especially concentrated on the choice of a suitable mixture, studying the performances of the cycle as a function of the properties of the refrigerant and of the solvent. On this basis, the pair NH₃/H₂O appeared to be the most promising for high temperature applications. The performances of different cycles for a NH₃ concentration of 80% were also studied and compared with the performances of pure refrigerant cycles. For optimized cycles, the performances were always better for the compression-resorption cycle. The need for internal absorber temperature glide optimization was stressed. Pourreza [1986] and Herold [1991] have also studied the internal behaviour of different compression-resorption cycles with respectively R22/DEGDME and LiBr/H₂O. In Rademacher [1986], the need for cycle optimization in terms of refrigerant concentration was also underlined.

In a number of papers ([1987], [1988a,b], [1989], [1990a,b]), Bergmann and Hivessy have studied the total wet compression cycle with NH₃/H₂O for a very large temperature glide of the heat sink and a high cycle temperature lift. The chosen NH₃ concentration was about 80%. An improvement of 10% was obtained when compared with fully separated compression. In addition the effect of internal heat exchange on the wet compression cycle was also studied.

Lastly, the works of Alefeld [1982] and Ziegler [1989], who have made extensive studies of different configurations of resorption-compression cycles and compressor boosted absorption cycles, are cited.
1.3 The thesis

As most authors have concentrated on the study of a single type of cycle for a specific application and for a specific mixture, there was a need for a comprehensive thermodynamic study of the compression-resorption cycles specifically focused on the differences between the solution recirculation cycle and the wet compression cycle, and at the correct comparison of these cycles with others. Therefore, in the first part of this thesis (Chapters 2 to 5) a general analysis of the compression-resorption cycles is performed, whereas the second part (Chapter 6 and 7) is devoted to the design and the testing of the experimental plant.

Chapter 2 deals with the comparative advantages of wet and dry compression for cycles using pure refrigerants and cycles using mixed refrigerants, and in particular with the thermodynamic comparison between the compression-resorption cycles with solution circuit and with total wet compression.

Some aspects of compression-resorption cycle modelling are quite different from the usual aspects of modelling classical compression systems. These differences have sometimes led authors to erroneous conclusions. Chapter 3 is therefore devoted to the considerations that must be taken into account when modelling and designing compression-resorption cycles and when comparing them with other cycles.

The general model for the analysis of the wet compression cycle is treated in Chapter 4. A first and second law analysis of the cycle behaviour with the working pair NH₃/H₂O is made for very different external conditions, and for the entire range of possible concentrations and pressures. From this extensive analysis and from the comparison with the solution recirculation cycle, general conclusions are drawn concerning the behaviour and the possible applications of the compression-resorption cycles.

In Chapter 5, the same extensive analysis is given, but this time to determine the best mixtures for specific applications. Several fluorocarbon pairs, normal paraffin pairs and also ternary blends are studied.

Chapter 6 deals with the design of a wet compression test-plant for a case similar in temperatures to a low temperature district heating application. The chosen technical options are presented, as well as the problems faced. The measurement and control procedures are also described.

The results of a three month measurement campaign are presented in Chapter 7. The performances of the test-plant are analyzed and a comparison with the model used in Chapter 4 is presented.

Finally, recommendations for further research are presented in Chapter 8.
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Chapter 2

Wet compression against dry compression

2.1 Introduction

Heat pumps that use non-azeotropic mixtures as a working medium can be placed in three categories. In the first one, the desorption process is total, so that a saturated or superheated vapour leaves the desorber and the compression therefore takes place in the superheated region. This first category is similar to the classical vapour compression cycle (Rankine cycle). The second category is that of heat pumps with solution recirculation. This time, the desorption process is not completed, so that liquid remains in the desorber. This liquid is separated from the vapour and pumped into the resorber, after being heated in an internal heat exchanger. In the third category, liquid and vapour are not separated, but are sent together to the compressor, which therefore also acts as a pump. An extended bibliography concerning these three types is given in Chapter 1.

The first step in this investigation was therefore to decide what kind of heat pump should be studied, modelled and built. To do this it was necessary to consider whether dry compression or wet compression should be applied and to determine the comparative advantages of heat pumps using solution recirculation (category 2) and total wet compression (category 3). Another question then naturally arises: if wet compression is advantageous when using non-azeotropic mixtures, why should it not also be so for pure refrigerants?

Section 2.2 of this chapter therefore deals with the question of whether and when wet compression should be applied to pure refrigerants. Examples using the refrigerants R12,
R123 and NH₃ are given. The choice of R12 is debatable, since its use has been forbidden, but in this context it must be seen as a typical example of a series of refrigerants. Section 2.3 is devoted to non-azeotropic mixtures. An example using NH₃/H₂O (80 % - 20 %) is given. The conclusions are finally drawn in section 2.4.

2.2 Pure refrigerants

2.2.1 Statement of the problem

From classical thermodynamics it is known that the highest possible efficiency for a heat pump cycle working between the temperatures Tₑ and Tₙₑ is given by the Carnot cycle. Present vapour-compression heat pump cycles are Rankine cycles, which to a certain extent approach the upper value. An ideal Rankine cycle (isentropic expansion and compression) is drawn in Figure 2.1 (1-2-3-3'4). One can see that, for a cycle working between Tₑ and Tₙₑ, compression inside the wet vapour region would transform the ideal Rankine cycle into a Carnot-like cycle (1-2'-3'-4) and would therefore increase the efficiency.

![Figure 2.1 Ideal vapour compression (1-2-3-4) and wet compression (1-2'-3'-4) cycles.](image)

However, for real cycles, neither the expansion nor the compression is isentropic. Before going on, it is necessary to recall some basic definitions:

1. The COP of a heat pump cycle is the ratio between the heat released into the condenser and the work furnished to the cycle.

\[
COP = \frac{|Q_{\text{cond}}|}{W_{\text{net}}} \tag{2.1}
\]
2. When the expansion is isentropic, the expansion process creates work which can be reused by the compressor via a turbine. When the expansion is isenthalpic, there is no work creation, so the compressor needs more external work than in the case of isentropic expansion ($W_{\text{comp}} = W_{\text{net}}$).

3. Since $dQ = TdS$ for a reversible transformation, the heat furnished or released by such a reversible transformation from some point 1 to some point 2 in a T-s diagram, is the area under the curve linking points 1 and 2.

4. The nett work needed by a heat pump or refrigeration cycle is

$$W_{\text{net}} = W_{\text{comp}} - W_{\text{exp}} = |Q_{\text{cool}}| - |Q_{\text{gen}}|.$$

The behaviour of the COP for wet compression and for dry compression will be studied in the following sections, first for an ideal cycle (section 2.2.2), second for a cycle with isenthalpic expansion (section 2.2.3), third for a cycle with non-isentropic compression (section 2.2.4), and fourth, for the real cycle (section 2.2.5). The behaviour of the internal cycle will be studied, thus without taking the heat source and the heat sink into account.

### 2.2.2 Ideal cycle: isentropic expansion and isentropic compression

#### 2.2.2.1 The wet vapour region: evolution of the COP with the vapour quality.

*Figure 2.2.a* shows a cycle with a high vapour quality (cycle 1-2'-3'-4), while *Figure 2.2.b* shows a low vapour quality cycle (cycle 1-2''-3''-4). From definitions 3 and 4 of the previous section, it can be deduced that the nett work of these cycles is the area of the cycles themselves. The COPs of the heat pump cycles, COP$_a$ and COP$_b$, can therefore be defined as follows:

![Diagram](image)

*Figure 2.2: Comparison of the COP of an ideal wet compression cycle for a) a high vapour quality and b) a low vapour quality.*
\[ \text{COP}_a = \frac{\text{area}_{0^{-3^{-4}}}^{0^{-2^{-3^{-4}}}}} \]

\[ \text{COP}_b = \frac{\text{area}_{0^{-3^{-4}}}^{0^{-2^{-3^{-4}}}}} \]

As can be deduced from Figure 2.2, these two ratios are equal, which leads to the well-known feature of a Carnot cycle, that the COP depends only on the temperature levels:

\[ \text{COP}_a = \text{COP}_b = \text{COP}_{\text{Carnot}} = \frac{T_h \Delta S}{(T_h - T_c) \Delta S} = \frac{1}{1 - \frac{T_c}{T_h}} \]

The COP of an ideal wet compression heat pump cycle therefore remains constant and equal to the Carnot COP throughout the wet vapour region.

5.2.2.2 Comparison of the COP for the wet and dry compression cycles

Refrigerants with a negative saturated vapour line slope: These are classical refrigerants for which the T-s diagrams exhibit a more or less bell-shaped saturation line, as shown in Figures 2.1, 2.2 and 2.3. The condenser heat and the nett work of a dry compression cycle (1-2-3-4) are represented in Figure 2.3, and comparison with the wet compression cycle (1-2-3'), reveals that their ratio is smaller for dry compression than for wet compression. This is because the inequality (2.5) is always true when A, B, x are positive and A is larger than B (A represents area_{0^{-3^{-4}}}^{0^{-2^{-3^{-4}}}} B area_{1^{-2^{-3^{-4}}}}^{2^{-3^{-4}}} and x area_{3^{-4}}^{3^{-4}}).

\[ \square \text{Qcond} \quad \square \text{Wnet} \]

**Figure 2.3:** COP comparison between the wet and dry compression cycles.

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\[
\frac{A+x}{B+x} < \frac{A}{B}
\] (2.5)

From a thermodynamic point of view, wet compression is therefore advantageous. Nevertheless, this advantage appears to be quite minimal, since in most cases the supplementary work introduced by dry compression (3'-3'‘-O’‘) is very small (see R12 and NH3 in section 2.2.2.4).

Whether the COP of the superheated cycle (1-2-2s-3s-3'-4) is better than that of the cycle without superheating (1-2-3-3’-4) (see Figure 2.4) depends on the relative values of the areas (3’-O3-3s) and (2-O2-2s), as will be subsequently demonstrated.

![Figure 2.4: Comparison between the dry compression cycles with and without superheating.](image)

The COP of the cycle without superheating is \( \text{COP}_{w} = \frac{(A+x)}{(B+x)} \) and the COP of the cycle with superheating is \( \text{COP}_{s} = \frac{(C+w)}{(D+w-z)} \). It is known that \( A/B = C/D \) and that \( (A+x)/(B+x) < A/B \) (Equation 2.5). Furthermore, \( C/D < (C+w)/(D+w-z) \) is always true when \( (w-z) < 0 \) and implies that \( w/(w-z) > C/D \) when \( (w-z) > 0 \). This means that for refrigerants for which the area 3’-O3-3s is lower or equal to the area 2-O2-2s, the cycle with superheating will be favourable. In all other cases, the cycle with superheating will be favourable only when \( C/D < w/(w-z) \). However, as \( z \) is generally much smaller than \( w \), superheating is seldom profitable.
Refrigerants with an positive T-s saturated vapour line slope: Some refrigerants with a heavy molecular weight show a positive slope on a part of their saturated vapour line in the T-s diagram. This, for instance, is the case for R123 and n-butane. A detailed analysis of this phenomenon is made in Plank [1956] and Morrisson [1994]. In Figure 2.5, the saturation line for such a refrigerant has been drawn, as well as the wet and dry compression (1-2'-2-3-4) cycles. Following the same area analysis as previously, it is obvious that the dry compression cycle will now have a slightly (the area 2-2'-O' is quite small) better efficiency than the Carnot cycle (see R123 in section 2.2.2.4). At first sight, this could be a violation of the second law of thermodynamics, but it is not, because owing to the superheating in the dry compression cycle the two cycles are not working between the same mean temperatures.

The analysis and the conclusions concerning the effects of superheating are the same as for a refrigerant with a bell-shaped saturation line.

![Figure 2.5: Comparison between the COP of the wet and dry compression cycles for a vapour saturation line with a positive slope.](image)

2.2.2.3 Conclusions and examples

Wet compression is interesting for an ideal cycle, except for refrigerants with a T-s vapour saturation line with a positive slope. Table 2.1 gives values that have been calculated with the program REFPROP of the NIST for R12, NH, and R123. These values have been calculated for a heat pump working between the refrigerant temperatures 10 °C and 60 °C. For the cycles with superheating it is assumed that the superheating takes place in the evaporator, using free energy available at the desired temperature. Liquid line/suction line heat exchange was not studied, because compared to the former at constant evaporation temperature, the latter has only unfavourable effects.

For NH₃, the use of the wet compression cycle instead of the ideal Rankine cycle increases the heat pump performances by 8.1 %, while for R12 the increase is only 1.5 %. The theoretical advantage of dry compression for R123 is hardly discernible, so that wet compression neither decreases nor increases the COP.
<table>
<thead>
<tr>
<th></th>
<th>R12</th>
<th>NH₃</th>
<th>R123</th>
</tr>
</thead>
<tbody>
<tr>
<td>wet compression</td>
<td>6.7</td>
<td>6.7</td>
<td>6.67</td>
</tr>
<tr>
<td>ideal Rankine</td>
<td>6.6</td>
<td>6.2</td>
<td>6.7</td>
</tr>
<tr>
<td>cycle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 K superheating</td>
<td>6.6</td>
<td>6.1</td>
<td>6.7</td>
</tr>
<tr>
<td>20 K superheating</td>
<td>6.6</td>
<td>6.0</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Table 2.1: COP of a ideal heat pump (isentropic expansion and compression) working between 10 and 60 °C for several refrigerants.

2.2.3 First deviation from ideality: isenthalpic expansion

In this section, the expansion is assumed to be isenthalpic, whereas the compression remains ideal, that is isentropic.

2.2.3.1 The wet vapour region: evolution of the COP with the vapour quality.

Such a wet compression cycle is represented in Figure 2.6 (1-2’-3’-4). Isenthalpic expansion has a dramatic effect on the COP in the wet vapour region, because it introduces a new part of compressor work (O-O’-1-1’) which remains constant whatever the quality of the vapour. The poorer the quality, the more important the relative part of this work on the total work, thus the lower the COP. As shown by Figure 2.6.b, the COP finally decreases to 1, because the compressor work becomes equal to the condenser heat.

![Figure 2.6](image)

*Figure 2.6: Comparison of the COP of a wet compression cycle with isenthalpic expansion for a) a high vapour quality and b) a low vapour quality.*
In the wet vapour region, the COP is therefore maximum for the maximum value of the compressed vapour quality.

2.2.3.2 Comparison of the COP for the wet and dry compression cycles

Refrigerants with a negative saturated vapour line slope: One can perform the same area analysis as that done previously. This leads to the conclusion that whether or not the dry compression cycle is advantageous depends on the relative values of the different areas. To go further, a cycle analysis in the \( \ln(p) \)-h diagram is performed, that gives a practical criterion against which the relative performances of both the cycles can be assessed.

The Rankine cycle and the wet compression cycle are now drawn in a \( \ln(p) \)-h diagram (Figure 2.7). Isenthalpic expansion and isentropic compression are assumed in both cases.

![Figure 2.7: Rankine cycle (1-2-3-4) and wet compression cycle (1-2'-3'-4) in a \( \ln(p) \)-h diagram.](image)

The COPs for the wet compression cycle and the Rankine cycle are given in Equations 2.6 and 2.7 respectively:

\[
COP_w = \frac{|Q_{4,3}^w|}{W_{3,2}^w} = \frac{h_3 - h_4}{h_3 - h_2} \quad (2.6)
\]

\[
COP_r = \frac{|Q_{4,3}|}{W_{3,2}} = \frac{h_3 - h_4}{h_3 - h_2} \quad (2.7)
\]

A simple and logical way to compare the performances of different cycles is to consider constant heating capacity (Bergmann [1990]), which implies different mass flow rates.

From \( Q_{3,4} = Q_{3,4} \), one gets Equation 2.8:
\[ m_w (h_x - h_4) = \dot{m}_R (h_3 - h_4) \]  

(2.8)

As \((h_x - h_4)\) is always lower than \((h_3 - h_4)\), the inequality (2.9) is always true:

\[ \frac{\dot{m}_R}{m_w} < 1 \]  

(2.9)

Using Equation 2.8, Equation 2.6 becomes:

\[ \text{COP}_w = \frac{\dot{m}_R}{m_w} \frac{h_3 - h_4}{h_3 - h'_2} \]  

(2.10)

The ratio of the COPs is then given by Equation 2.11:

\[ \frac{\text{COP}_w}{\text{COP}_R} = \frac{\dot{m}_R}{m_w} \frac{h_3 - h_2}{h_3 - h'_2} \]  

(2.11)

Therefore, \(\text{COP}_w > \text{COP}_R\) implies Equation 2.12:

\[ \frac{h_3 - h_2}{h_3 - h'_2} < \frac{\dot{m}_R}{m_w} < 1 \]  

(2.12)

If the isentropes were convergent or parallel, the ratio \((h_3 - h_2)/(h_3 - h_4)\) would be higher than or equal to 1, thus wet compression would be always unfavourable. However, isentropes in the \(\text{Ln}(p)-h\) diagram are always divergent, thus wet compression will be advantageous only if Equation 2.13 is true.

\[ \frac{h_3 - h_2}{h_3 - h'_2} \leq \frac{\dot{m}_R}{m_w} \]  

(2.13)

It is therefore necessary to make calculations for each case. For a given working medium, the result may also be different at different temperature levels. Examples are given in Table 2.2 of Section 2.2.3.3. Wet compression appears to be unfavourable for R12, for which dry compression increases the COP by 2.0 %, and to be favourable for \(\text{NH}_3\), as it increases the COP by 3.6 %.

Note that Equation 2.12 is valid for the comparison of the Rankine and wet compression.
cycles, but has also a more general validity. For instance, it can just as well be used to compare different degrees of evaporator superheating or different degrees of vapour quality in wet compression.

**Refrigerants with a positive T-s saturated vapour line slope:** Performing an area analysis in the T-s diagram (Figure 2.8 and below) leads to the conclusion that the dry compression cycle is always more efficient than the wet compression cycle.

![Figure 2.8: Comparison between the COP of the wet and dry compression cycles for a vapour saturation line with a positive slope.](image)

In Figure 2.8, the COPs (with subscripts w and R for wet and dry compression respectively) are written as function of the areas A, B, C, D, E, F, defined as follows:

\[
A = \text{area}_{O-O''-3'-4} \quad B = \text{area}_{1'-2'-3'-4} \\
C = \text{area}_{O-O''-1'-1'} \quad D = \text{area}_{O''-O''-3'-3'} \\
E = \text{area}_{2'-02-3'-3'} \quad F = \text{area}_{2'-02-2}
\]

\[
\text{COP}_w = \frac{A}{B+C} \quad \text{COP}_R = \frac{A+D}{B+C+E-F} \tag{2.14}
\]

Because all terms are positive and \(A/B = D/E\), one gets

\[
\frac{A}{B+C} < \frac{D}{E} \tag{2.15}
\]

\[
\frac{A}{B+C} < \frac{A+D}{B+C+E} \tag{2.16}
\]

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As all terms are positive, it is evident that

\[
\frac{A+D}{B+C+E} < \frac{A+D}{B+C+E-F}
\]

(2.17)

Combining Equations 2.16 and 2.17 leads to the result \( \text{COP}_w < \text{COP}_R \). However, since \( F \) is very small, \( \text{COP}_w \approx \text{COP}_R \). This is illustrated in Table 2.2 by the behaviour of R123, for which the use of dry compression has no effect on the COP.

Whether or not superheating is useful can be determined for both negative and positive saturated vapour line slopes by using Equation 2.13 in the same way as previously. Because of a certain regularity in the slope of the isentropes, one can say that if the Rankine cycle is more efficient than the wet compression cycle, a small degree of superheating will increase the efficiency even more. Conversely, if the Rankine cycle is less efficient than the wet compression cycle, superheating will decrease the COP further. As can be seen from Table 2.2, 20 °C superheating will increase the COP by 1.9 % for R12 and by 3.6 % for R123, whereas for \( \text{NH}_3 \), it will decrease the COP by 3.6 %.

2.2.3.3 Conclusions and examples

Isenthalpic expansion has such an effect on the performances of the wet compression cycle, that only a wet compression cycle with a maximum vapour quality can be considered acceptable. Whether dry compression is better than wet compression depends on the refrigerant itself and on the chosen temperature levels. Table 2.2 gives the calculated COP values for R12, \( \text{NH}_3 \), and R123. In each case the values for the wet compression cycle have been calculated for the maximum vapour quality. The superheating is assumed to take place either in the evaporator, or by liquid line/suction line heat exchange, which, for isenthalpic expansion does not change anything at the COP, when considering constant evaporation temperature and availability of the source at the desired temperature level.

<table>
<thead>
<tr>
<th></th>
<th>R12</th>
<th>( \text{NH}_3 )</th>
<th>R123</th>
</tr>
</thead>
<tbody>
<tr>
<td>wet compression</td>
<td>5.1</td>
<td>5.8</td>
<td>5.6</td>
</tr>
<tr>
<td>ideal Rankine cycle</td>
<td>5.2</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>10 K superheating</td>
<td>5.2</td>
<td>5.5</td>
<td>5.7</td>
</tr>
<tr>
<td>20 K superheating</td>
<td>5.3</td>
<td>5.4</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 2.2: COP of a non-ideal heat pump (isenthalpic expansion and isentropic compression) working between 10 and 60 °C for several refrigerants.
2.2.4 Second deviation from ideality: non-isentropic compression

In this section, the compression is assumed to be non-isentropic, whereas the expansion is ideal, that is isentropic.

Non-isentropic compression also has a dramatic effect on the COP in the wet vapour region, because it introduces a new part of work ((3-2'-O''-O') in Figure 2.9), which does not tend to zero when the vapour quality decreases and which is not counterbalanced by the increasing condenser heat. Although this supplementary work slightly decreases when the vapour quality decreases because of the divergence of the isentropic lines in the Ln(p)-h diagram, it is easy to see that the poorer the quality, the more important the relative part of this work to the total work, thus the lower the COP. As shown by Figure 2.9.b, the COP finally decreases to 1, as in the case of isenthalpic expansion.

![Diagram showing COP comparison for high and low vapour quality](image)

\textbf{Figure 2.9: Comparison of the COP of a wet compression cycle with non-isentropic compression for a) a high vapour quality and b) a low vapour quality.}

The conclusions concerning the COP behaviour in the dry and superheated region are the same as for isenthalpic expansion. The Rankine cycle is more efficient than the wet compression cycle by 2.0 % for R12. For R123 the COPs of both the cycles are equal. For isenthalpic expansion (previous section), the improvements were also 2.0 % and 0.0 % respectively. When the wet compression cycle is more favourable than the Rankine one for isenthalpic expansion, it will be even more favourable for non-isentropic compression (For NH$_3$, the efficiency increases by 3.6 % and 6.3 % respectively). This is because the supplementary work introduced by non-isentropic compression decreases in the wet region (as opposed to isenthalpic expansion, where it remains constant), due to the decreasingly slanting isentropes in the Ln(p)-h diagram.

These data are summarised in Table 2.3, where an isentropic efficiency of 75 % was chosen. In Table 2.3 as in Table 2.1, the superheating takes place in the evaporator. For the wet compression cycle, the given value corresponds to a maximum quality of the compressed vapour.
<table>
<thead>
<tr>
<th></th>
<th>R12</th>
<th>NH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>R123</th>
</tr>
</thead>
<tbody>
<tr>
<td>wet compression</td>
<td>4.9</td>
<td>5.1</td>
<td>5.1</td>
</tr>
<tr>
<td>ideal Rankine</td>
<td>5.0</td>
<td>4.8</td>
<td>5.1</td>
</tr>
<tr>
<td>cycle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 K superheating</td>
<td>4.9</td>
<td>4.7</td>
<td>5.1</td>
</tr>
<tr>
<td>20 K superheating</td>
<td>4.9</td>
<td>4.6</td>
<td>5.1</td>
</tr>
</tbody>
</table>

*Table 2.3: COP of a non-ideal heat pump (compression isentropic efficiency of 75 %, isentropic expansion) working between 10 and 60 °C for several refrigerants.*

### 2.2.5 Real cycle: isenthalpic expansion and non-isentropic compression

In a real heat pump cycle, the effects of isenthalpic expansion and non-isentropic compression are combined. This means that the COP fall in the wet vapour region will be even more rapid than when only one of the two departures from ideality occurs (this COP decrease is also in accordance with the known fact that refrigerants for compression machines should have an evaporation heat as high as possible). For R12, the Rankine cycle is 2.5 % better than the wet compression cycle while it was only 2.0 % better for isentropic compression (section 2.2.4) and for isenthalpic expansion (section 2.2.3). For R123, as in the former cases, there is no increase. For NH<sub>3</sub>, the COP of the wet compression cycle is better by 4.5 % instead of 6.3 % and 3.6 % respectively. The values for the real cycle are given in *Table 2.4*. Using a figure similar to *Figure 2.9a*, it can be shown that the COP of the real cycle in the wet region, is given by *Equation 2.18*, where \( \eta_{r} \) is the isentropic efficiency of the compressor and \( COP_{r} \) the COP of the cycle with isentropic compression and isenthalpic expansion, as given in *Table 2.2*.

\[
COP = \eta_{r} \cdot COP_{r} + (1 - \eta_{r})
\]

*Equation 2.18*

<table>
<thead>
<tr>
<th></th>
<th>R12</th>
<th>NH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>R123</th>
</tr>
</thead>
<tbody>
<tr>
<td>wet compression</td>
<td>4.0</td>
<td>4.6</td>
<td>4.5</td>
</tr>
<tr>
<td>ideal Rankine</td>
<td>4.1</td>
<td>4.4</td>
<td>4.5</td>
</tr>
<tr>
<td>cycle</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>10 K superheating</td>
<td>4.2</td>
<td>4.4</td>
<td>4.5</td>
</tr>
<tr>
<td>20 K superheating</td>
<td>4.2</td>
<td>4.3</td>
<td>4.6</td>
</tr>
</tbody>
</table>

*Table 2.4: COP of a real heat pump (compression isentropic efficiency of 75 %, isenthalpic expansion) working between 10 and 60 °C for several refrigerants.*
2.2.6 Conclusions

The values from Tables 2.1 to 2.4 are plotted in Figures 2.10 to 2.12, to give a general view of the evolution of the COP when irreversibilities are introduced into the cycle. R12 and NH₃ are both refrigerants with a bell-shaped T-s saturation line, but show different behaviour, whereas R123 is a refrigerant with a positive saturated vapour line slope.

\[ \text{R12} \]
\[ T_c = 10 \, ^\circ\text{C}, \, T_h = 60 \, ^\circ\text{C} \]

\[ \text{NH3} \]
\[ T_c = 10 \, ^\circ\text{C}, \, T_h = 60 \, ^\circ\text{C} \]

**Figure 2.10**: Behaviour of the COP for a heat pump using R12 and working between 10 and 60 °C.

**Figure 2.11**: Behaviour of the COP for a heat pump using NH₃ and working between 10 and 60 °C.
**Figure 2.12:** Behaviour of the COP of a heat pump using R123 and working between 10 and 60 °C.

It has been shown that for refrigerants with a positive T-s vapour saturation line slope, like R123, wet compression is always disadvantageous. If wet compression is always favourable for the ideal cycle of T-s bell-shaped saturation line refrigerants, this advantage decreases drastically as soon as the irreversibilities are taken into account and turns into a disadvantage for some refrigerants, like R12. For some others, like NH₃, at constant isentropic efficiency, wet compression is slightly more efficient than dry compression. This small increase in efficiency can only be gained at a very high technological cost so the use of wet compression must generally be considered impractical, with the exception of the applications listed below:

- when the refrigerant is water, the COP increase when using wet compression instead of dry compression is almost 30 %, for a heat pump working between 10 and 60 °C. In this case, it is worth applying wet compression (see also Ozaki [1990]).

- although the COP gain, when it exists, is generally low, the use of wet compression with pure refrigerants may become interesting when developing high temperature heat pumps. Indeed, too high a superheating should in that case be avoided, because of the risks of mechanical failure of the compressor and of chemical or thermal instabilities of the oil and the refrigerant.

### 2.3 Non-azeotropic refrigerant mixtures

#### 2.3.1 Introduction

Unlike that of pure refrigerants, evaporation and condensation at constant pressure of a
non-azeotropic mixture takes place at non-constant temperature. The introduction of a supplementary species (mixture of two refrigerants instead of a pure refrigerant) leads to a supplementary degree of freedom in the system. A pure refrigerant system in the two-phase region has only one degree of freedom: the temperature is a function of the pressure only. A non-azeotropic mixture possesses two degrees of freedom: the temperature is a function of the pressure and of the liquid concentration. Since, during the evaporation, the liquid becomes poorer in the most volatile component, the temperature will change. Some examples of this variation can be seen in an Ln(p)-h diagram in Camporese [1987] and in a T-h diagram in Bergmann [1987]. In Chapter 3 these diagrams will be considered in greater detail. A T-h diagram for a mixture of water and ammonia with 80 % mass ammonia is given in Figure 2.13. The thermodynamic properties have been calculated with the Trepp-Ziegler equation (Ziegler [1982]).

**Figure 2.13: T-h diagram for the mixture NH₃/H₂O (80% - 20%).**

### 2.3.2 Rankine cycle against wet compression cycles

*Equation 2.13* could also be used to determine whether wet compression is preferable to dry compression. However, this is of little interest, because it merely overshadows the main advantage of using mixtures, which is the free choice of the temperature levels for a given pressure and is thus related to a Second Law analysis. Using a Rankine cycle with a refrigerant mixture indeed has the disadvantage of limiting the degrees of freedom by fixing the temperature limits, which therefore cannot be optimized in relation to the external conditions.

A simple illustration of this is provided by the example of an NH₃/H₂O (80 % - 20 %) heat pump for which the heat sink enters the resorber at 75 °C, and the heat source enters the desorber at 60 °C. Furthermore it is assumed that the heat exchangers are ideal.
counter-current ones with an infinite heat exchange area and no zero-pinch point
temperature difference, that the expansion is isenthalpic and the compression isentropic.
Three possible cycles are drawn in Figure 2.13; cycle A, the Rankine cycle, cycle B, a
wet compression cycle where the compressed vapour quality (= vapour mass fraction, see
Equation (3.3)) is 0.750, and cycle C, with the compressed vapour quality of 0.575.

Since at the end of the resorber all vapour must be absorbed, the representative point of
the cold end of the resorber on Figure 2.13 should be on the saturation line. Its
temperature is known (75 °C), thus the pressure in the resorber is fixed: 29.3 bar. In the
same way, since the vapour quality and the temperature of the compressed vapour are both
known, the suction pressure can be determined and has a different value for the three
different cycles. On the assumptions of isentropic compression and isenthalpic expansion,
the entire cycle is thus fixed. The numerical values are given in Table 2.5.

<table>
<thead>
<tr>
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<th>T_h = 75 °C</th>
<th>T_c = 60 °C</th>
<th>p_h = 29.3 bar</th>
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<tr>
<td></td>
<td>dry</td>
<td>wet</td>
<td></td>
</tr>
<tr>
<td>compression</td>
<td>compression</td>
<td>compression</td>
<td></td>
</tr>
<tr>
<td>cycle A</td>
<td>m_c = 75 %</td>
<td>m_c = 57%</td>
<td></td>
</tr>
<tr>
<td>T_end</td>
<td>compression</td>
<td>compression</td>
<td></td>
</tr>
<tr>
<td>compression</td>
<td>°C</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>T_end</td>
<td>-26</td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>compression</td>
<td>°C</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>T_end</td>
<td>-26</td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>expansion</td>
<td>°C</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>p_1 (bar)</td>
<td>0.90</td>
<td>3.40</td>
<td>10.70</td>
</tr>
<tr>
<td>p_2/p_1</td>
<td>32.6</td>
<td>8.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Q (kW/kg)</td>
<td>2218</td>
<td>1149</td>
<td>663</td>
</tr>
<tr>
<td>W (kW/kg)</td>
<td>799</td>
<td>279</td>
<td>87</td>
</tr>
<tr>
<td>COP</td>
<td>2.8</td>
<td>4.1</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Table 2.5: Pressure ratio, compressor work, heating capacity and COP for dry and
wet compression with NH\(_3\)/H\(_2\)O (80 % - 20 %).

It is easy to see that the higher the compressed vapour quality, the higher the pressure
ratio and also the higher the mean temperature in the resorber and the lower the mean
temperature in the desorber. Thus, the higher the vapour quality, the higher the
temperature lift the heat pump must overcome and therefore the lower the efficiency of
the cycle.

The choice of the cycle will therefore depend on the temperature one wants to achieve in
the resorber. For instance, if the heat sink must be heated from 75 °C to 100 °C, and if the
heat exchangers are assumed to be ideal and no pinch points occur, it is evident that cycle
C should be chosen. But if the heat sink must be heated to 140 °C, cycle B offers the best
solution. Finally it must be noted that for mixtures with a lower degassing width than
\( \text{NH}_3/\text{H}_2\text{O} \) (see for instance R12/R11 in Camporese [1987]), the Rankine cycle might provide the best solution when the desired temperature glide in the resorber is of the same magnitude as the temperature glide across the saturation curve at constant pressure.

This generalised reasoning shows why wet compression is so interesting for mixtures. Nevertheless, the values given in Table 2.5 are not entirely reliable because, as will be shown in detail in Chapter 3, often the external and internal temperature profiles do not match each other, creating pinch points in the resorber and desorber. Because of these pinch points, it is always preferable to take into account the external conditions, instead of comparing only the internal refrigerant cycles. This means that the second law must be taken into account from the very beginning of the design process.

2.3.3 Total wet compression against solution recirculation

A widely accepted practical means to achieve wet compression, has been to recirculate the solution remaining from the incomplete desorption process by pumping it into the resorber. The saturated vapour which has been separated from the solution is then sent to the compressor. A saturated vapour enters the compressor, but leaves it in a superheated state, which brings less technological problems than when the vapour remains wet throughout the compression path. Figure 2.14a shows a cycle with solution recirculation (Osenbrück cycle), and Figure 2.14b shows a total wet compression cycle.

![Diagram](image)

**Figure 2.14:** a) Heat pump with solution recirculation (Osenbrück cycle) b) Total wet compression heat pump.

2.3.3.1 Analysis of the solution recirculation cycle

In the case of the total wet compression cycle C, the temperature varies from 75 to 100 °C in the resorber, and from 60 to 37 °C in the desorber. The temperatures and pressures given for cycle C in Table 2.5, together with the ln(p)-h diagram, or the Trepp-Ziegler
equation of state (Ziegler [1982]), give the ammonia concentration of the liquid before the compression: $x_2 = 0.5382$ and that of the vapour: $y_2 = 0.9938$.

Liquid and vapour are now separated before the compression. The vapour will be superheated in the compressor, and in the present case of isentropic compression of a vapour of concentration $y_2$, will reach a temperature of 144 °C. The temperature of the pumped liquid will hardly increase. Usually an internal heat exchanger is used to limit the irreversibilities in the resorber. Nevertheless, even if the internal heat exchanger is perfect, the temperature of the liquid entering the resorber will never exceed the resorber cold end temperature of 75 °C.

**Solution line/resorber heat exchange:** In order to bring the liquid nearer to its saturation temperature, and in this way to improve the resorber performances, (Altenkirch [1950], Stokar [1986], Pourreza-Djournari [1986]), the liquid line is usually brought in counter-current heat exchange with the resorber itself. The consequence of this is to reduce the useful resorber heat by a quantity $m_h(h_{32} - h_{31})$. In Table 2.6, where case C is treated for the solution recirculation cycle (with the assumption of adiabatic pumping of the liquid), the values of the resorber heating capacity are given for both the extremes: in the first column, there is no internal heat exchanger, so that $T_{31} = T_{4} = 60$ °C. In the second column, the heat exchanger is assumed to be ideal, so that $T_{31} = T_{4} = 75$ °C. In both cases, the temperature $T_{32}$ is assumed to be the saturation temperature at the liquid concentration $x_2$ and the resorber pressure, that is $T_{32} = 105$ °C. If $T_{31}$ is higher than $T_{32}$, adiabatic absorption is assumed until the saturation temperature is achieved. The resorber heating capacity is calculated as follows:

$$Q_{res} = m_h h_{3v} + m_h h_{12} - h_4 - m_i (h_{12} - h_{31})$$  \hspace{1cm} (2.19)

<table>
<thead>
<tr>
<th></th>
<th>without int. heat exchanger</th>
<th>ideal int. heat exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{3v}$ (°C)</td>
<td>144</td>
<td>144</td>
</tr>
<tr>
<td>$T_{3L}$ (°C)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>$T_{31}$ (°C)</td>
<td>60</td>
<td>75</td>
</tr>
<tr>
<td>$T_{32}$ (°C)</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>$W_{comp-pump}$ (kW/kg)</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>$Q$ (kW/kg)</td>
<td>670</td>
<td>700</td>
</tr>
<tr>
<td>COP</td>
<td>7.2</td>
<td>7.5</td>
</tr>
</tbody>
</table>

**Table 2.6:** Temperatures, work, heating capacity and COP of cycle C with solution recirculation and isentropic compression, for the mixture NH$_3$/H$_2$O (80%-20%).
**Solution line/vapour line heat exchange:** A preheater is sometimes used (Mucic [1989]) to preheat the solution to its saturation temperature by means of heat exchange with the superheated vapour coming from the compressor. This brings it closer to its saturation temperature. This has the advantage of reducing the irreversibilities in the resorber by reducing the temperature mismatch with the external medium introduced by the superheated vapour. However, the external conditions are not taken into account in the present analysis, and, because the superheated vapour is cooled from a heat quantity \( m_i(h_i - h_0) \), the absorber heating capacity is also given by Equation 2.17 and the results concerning the work, the heating capacity and the COP are exactly the same as in the case of suction line/resorber heat exchange.

**2.3.3.2 Comparison with the total wet compression cycle**

The comparison between the COP of the total wet compression cycle (7.6, cycle C, Table 2.4) and the COP of the solution recirculation cycle shows that total wet compression increases the COP by 1.3% in the case studied. However, this does not have general validity. Whether the wet compression cycle is better than the solution recirculation cycle depends on the relative compressor work and on the relative resorber heating capacity of both these cycles.

A necessary condition for lower compressor work in the wet compression cycle than in the solution recirculation cycle is that the higher specific work needed in the solution recirculation cycle (due to the higher entropy of point 2 before compressor) is not compensated by the lower mass flow rate \( m_i \) instead of 1. When it is not compensated, the isentropic compression takes place at a higher entropy level for the solution recirculation cycle than for the wet compression cycle, thus the work done on compression is higher. It can be expected that the higher the temperature lift during the compression, the lower will be the wet compression work in comparison with the dry compression work.

In cases where the solution line/resorber or solution line/vapour line heat exchange allows both \( T_{3,4} \) and \( T_{3,2} \) to reach the same temperature as in the wet compression cycle, the specific heating capacities will be equal for both the cycles. When the vapour mass fraction of its temperature is high enough, after separated compression and internal heat exchange the vapour will remain superheated, thus the heating capacity (after adiabatic absorption) will be higher than in the case of wet compression. This effect can be expected to be stronger at high temperature lift and for refrigerants with a small slope of the isentropic lines in the T-h diagram. Since the use of wet compression instead of solution recirculation can result in a decrease in both the compressor work and the heating capacity, it is not possible to draw conclusions about the respective values of the COP. In order to determine which cycle must be used, calculations must be made for each application.

The COP gains are also dependent on how close to perfection "total wet compression" will really be. There is no a-priori evidence that perfect wet compression could be achieved in a real compressor. The compression process is a very rapid one, so that it is doubtful whether equilibrium between the phases will be reached at the end of the compression. If this is not the case, the compressor will deliver a subcooled liquid and a superheated vapour (Bergmann [1990]), which will be brought near the equilibrium by adiabatic
resorption into the liquid-vapour pipe from the compressor to the resorber. In the most unfavourable case, the total wet compression cycle will therefore behave like the solution recirculation one, with the advantage of avoiding the use of a solution pump and of a solution heat exchanger. However it seems reasonable to expect that the wet compression will take place at an intermediate state between separate compression and equilibrium.

Taking into account the isentropic efficiency of the compressor does not change the previous conclusions, if it is assumed that both the dry and the wet compressors have the same isentropic efficiency. However, nothing is known about the comparative isentropic efficiencies of a given compressor in the dry region and in the wet region. If the first turns out to be higher than the second, the positive influence of wet compression could be reduced to zero, whereas if the opposite is true, it could be enhanced.

2.4 Conclusions

In this chapter the author has shown that wet compression has few advantages when used with pure refrigerants. For a limited number of pure refrigerants, all having a T-s bell-shaped saturated vapour line, a gain in COP can be achieved, but at present this gain generally does not compensate for the technological problems encountered. However, for high temperature applications, where vapour superheating must be avoided, wet compression can offer a good solution.

For non-azeotropic mixtures, the wet compression cycle can lead to higher COPs than the solution recirculation cycle, but this advantage, when present, could be eliminated if ideal wet compression cannot reasonably be approached in the compressor, or if the isentropic efficiency of wet compression is too low. These uncertainties on the performances of the wet compression cycle were the reason why it has been investigated both theoretically and experimentally in this research project.

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Chapter 3

Considerations when modelling compression-resorption cycles

3.1 Introduction

The second step in the present investigation was to establish a good basis for the further analysis of the compression-resorption cycles. Thermodynamic considerations will be the basis of attempts to answer questions automatically arising when dealing with these cycles. Although the idea is not new, the use of T-h and T-s diagrams will be worked out in Section 3.2 because it forms the basis of a proper modelling of the wet compression-resorption cycle. For the same reasons, in Section 3.3 the emphasis will be put on the non-linearity of the temperature profiles. Although it has been known for a long time that the temperature profiles were not linear, all the consequences of this were not appreciated. Section 3.4 deals with the correct way of comparing the wet compression cycle with the pure refrigerant cycle. It will be clear that the Second Law should be taken into account at the very beginning of the analysis. Finally, the usefulness of internal heat exchange will be treated.

3.2 The use of T-h or T-s diagrams in the representation of compression-resorption cycles.

In the field of absorption heat pumps, Dühring diagrams (Ln p-1/T) and enthalpy-concentration (h-x) diagrams are commonly used to represent the cycles. These diagrams do not allow for rapid calculation of the total enthalpies and entropies at the different
points of the cycle when equilibrium is involved. Indeed, in a h-x diagram, the enthalpy of the liquid is easily read, as well as that of the vapour, but the liquid mass fraction \( m_l \) has to be calculated separately to get the total enthalpy \( h \) of the system, given by Equation (3.1), where \( m_v = 1 - m_l \). A similar relation is used for the calculation of the total entropy (Equation (3.2)).

\[
h = m_l h_l + m_v h_v
\]

(3.1)

\[
s = m_l s_l + m_v s_v
\]

(3.2)

As already proposed by Bergman [1987], it should be easier to use the same kind of T-s diagrams as are used for pure components (Figure 3.1a), since all important thermodynamic data can be read directly.

![Figure 3.1: Temperature - entropy diagrams for a) a pure refrigerant and b) a mixture with the overall concentration \( x_o \).](image)

When considering a liquid mixture with a certain concentration \( x_o \) (\( x_o \) will be referred as overall concentration), it is possible to draw such a diagram (Figure 3.1b): according to the phase rule, a two-phase two-component mixture at equilibrium has 2 degrees of freedom, which means that only two parameters are needed to determine all other thermodynamic properties. The construction of such a diagram is therefore as follows:

1. On the bubble line, all the refrigerant is still in the liquid phase, thus \( x = x_o \). For a given pressure \( p \), \( T_l \) and \( s_l \) (as well as \( h_l \)) can be determined from the data \( x = x_o \).

2. On the dew line, all the refrigerant is in the vapour phase, thus \( y = x_o \). For a given
pressure $p$, $T_v$ and $s_v$ (as well as $h_v$) can be determined from the data $y=x_v$.

3. For temperatures $T$ between $T_1$ and $T_v$, $x$, $y$, $s$, $s_v$ (as well as $h_v$, $h_c$) can be determined from the pair $(p, T)$. The liquid mass fraction is then given by Equation (3.3) and $s$ and $h$ are calculated by Equation (3.1) and (3.2).

$$m_l = \frac{x - y}{x - y} \tag{3.3}$$

Although the T-s diagram is very useful to the understanding and description of the thermodynamic cycles, the ln(p)-h diagram is more widely used for compression cycles with pure refrigerants, because it allows for direct reading of the enthalpies. It is also possible to construct ln(p)-h diagrams for mixtures with fixed concentration, in exactly the same way as previously described. However, as will be shown later in this chapter, when using mixtures, the temperature glides in the desorber and resorber are of primary importance, since they will determine for a large part the cycle’s efficiency and possible pinch points in the resorber and in the desorber. The use of temperature-enthalpy diagrams instead of ln(p)-h diagrams has thus been preferred, because it allows for direct visualisation of the temperature profiles in the desorber and the resorber. The T-s and T-h diagrams for the pair NH$_3$/H$_2$O are given in Appendix A for the entire range of concentrations. The Trepp/Ziegler equation (Ziegler [1982]) has been used to calculate the thermodynamic properties of the mixture.

Figures 3.2 and 3.3 also give two examples of T-h diagrams for the mixture NH$_3$/H$_2$O for two different ammonia overall concentrations, respectively 30 and 80 %. The change in the shape of the isobars between these two concentrations is remarkable and the temperature changes during the evaporation are the highest when the liquid reaches an ammonia concentration between 60 % and 30 %.

An ideal wet compression cycle is represented, with the assumptions of isentropic compression, isenthalpic expansion and no pressure drops in the resorber and desorber. The overall concentration $x_o$ is in fact the concentration of the (subcooled) liquid after completion of the resorption process (point 4). The numbers refer to the cycle as described in Figure 3.4. In its ideal version (isentropic expansion), this cycle will be referred in this thesis as the "mixture" cycle.

When a representation of the Osenbrück cycle (see Figure 2.14a of the previous chapter) is desired, some precautions must be taken because of the separation of the two phases before the compression. The compression of the vapour takes place as if the overall concentration were the NH$_3$ concentration of the vapour at the inlet of the compressor, and the pumping of the liquid takes place as if the overall concentration were the NH$_3$ concentration of the liquid at the inlet of the solution pump, so that the line between points 2 and 3 represents neither the real transformation of the pumped and heated liquid, nor that of the vapour. In this case it would be better to draw line 2-3 in Figure 3.3 with a dashed line.

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Figure 3.2: $T$-$h$ diagram for the two-phase zone of the NH3/H2O mixture for $x_o = 0.3$ kg/kg.

Figure 3.3: $T$-$h$ diagram for the two-phase zone of the NH3/H2O mixture for $x_o = 0.8$ kg/kg.

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Some general remarks can be made concerning Figures 3.2 and 3.3, all of which have an influence on the modelling of the compression-resorption cycles:

1. When the overall concentration $x_o$, the suction pressure $p_s$, and the temperatures $T_3$ and $T_4$ are fixed, the entire ideal wet compression cycle is determined, i.e. the discharge pressure $p_d$ and the temperatures $T_5$ and $T_6$ are functions of the former parameters only.

2. For an isobaric transformation (ideal condensation and evaporation of the mixture), the shape of the temperature-enthalpy curves strongly depends on the overall concentration, thus the first variable to be optimized for a given application should be $x_o$.

3. The isobars in the T-s diagram are neither linear (as stated in Morawetz [1989] and Kawada [1991]) nor exponential. This will be discussed in section 3.3.

### 3.3 Temperature profiles

For heat exchangers working with constant specific heat media, the temperature profile is linear i.e. the temperature is a linear function of the exchanged heat (see Figure 3.5a) For counter current heat exchangers, the minimum temperature difference between the streams, $\Delta T_{\text{min}}$, is located either at the cold or at the hot end, depending on the relative values of $\text{m.c}_p$ for the two streams. In ideal heat exchangers, and assuming there is no superheating, when one of the streams is an evaporating pure component, $\Delta T_{\text{min}}$ is located at the cold side, whereas when the stream is condensing, $\Delta T_{\text{min}}$ is located at the hot side.
When the specific heat of a stream is not constant throughout the temperature course of the medium, the temperature profile is no longer linear. This happens when the medium is a condensing or evaporating non-azeotropic mixture (Scharfe [1986], Bell [1990]). This can be easily seen from the T-h diagram of Figure 3.2. The nonlinearity is a consequence of the changing concentration in the liquid and gas phases and may lead to unfeasible temperature profiles, as represented in Figure 3.5b. This is because the external fluid usually has a different temperature profile, namely a linear one. Depending on the temperature levels, on the chosen mixture and on its concentration, the minimum temperature difference between the streams can be located at any point on the curve. The choice of a minimum temperature difference at one of the extremities of the heat exchangers is not sufficient to ensure a feasible temperature profile. Note that, depending on the mixture components and on the overall concentration, the curvature of the mixture temperature profile could also be the other way round, thus leading to problems with the desorber.

![Figure 3.5: Temperature profiles for a) a condensing pure refrigerant b) a condensing mixture](image)

The first conclusion is that models based on only the specification of the highest ($T_3$) and lowest ($T_4$) temperatures at which heat is rejected into the heat sink (Pourcza-Djousshari [1986], Rademacher [1986], Herold [1991]), fall short because they usually cannot predict between which temperatures the heat sink will be heated, which is of primary importance in a heat pump application. Indeed, since the external medium (heat sink) is not taken in account and since the temperature profiles are not calculated, the existence and the
location of a possible pinch point are not determined. This would lead to problems except in the case of mixtures with a linear heat rejection profile, or when the temperature glide is small. Generally speaking, even when using a "minimal model" for the heat exchangers, like a simple black box model, a minimum temperature between the two streams should be specified (see also Didion [1987]). The complete temperature profiles of the two streams should be calculated, in order to find the location of a possible pinch point that will be closely related to the chosen concentration and temperature levels. In other words, a preliminary series of iterations is necessary to calculate the refrigerants mixture temperature level at the hot side of the heat exchanger. This means that the interactions between the heat source or sink and the refrigerant mixture should be taken into account from the very beginning of the analysis, by using a quality factor (minimum temperature difference for instance), thus by integrating the Second Law of Thermodynamics in the analysis.

The second conclusion, arising directly from point 3 of the previous section, is that the assumption that the temperature course of the mixture follows that of the external medium, as stated in Åhly [1989], is not valid. To achieve this perfect matching, an ideal mixture (with a linear temperature-heat rejection profile) would be necessary.

Thirdly, the logarithmic mean temperature difference method, used in Mc Linden [1987] and Åhly [1991], must be avoided because, as already pointed out in section 3.2, the temperature of the condensing (or evaporating) streams does not follow an exponential function of the entropy, which is a necessary condition for using this method. Only for mixtures with a quasi-linear profile or when the mixture temperature glide is very small, or when the temperature difference between the streams is very large, can the LMTD method be applied without introducing unacceptably high errors. When working with small driving temperature differences, as is usually the case with highly efficient heat exchangers, the error introduced by using the LMTD method for the heat exchanger considered as one lump may be really significant: overestimates of the mean temperature difference by 50 % are not unusual for the NH₃/H₂O mixture. This difficulty may be overcome by dividing the heat exchanger into as many parts as are necessary to obtain a linear temperature profile for each of the lumps, or by using the mean temperature difference defined in Equation (3.4). This ΔT<sub>mean</sub> will be referred as isentropic mean temperature difference, by analogy to the isentropic mean temperature as defined by Alefeld [1987].

\[
\Delta T_{\text{mean}} = \frac{\Delta Q}{\int_{T_0}^{T_\infty} \frac{dQ}{\Delta T}}
\]  

(3.4)

Finally, although this method is theoretically not exact, the use of the logarithmic mean temperature for calculating the COP does not introduce such large errors, because the error in the temperature is quite small compared to the cycle temperature lift. The error introduced into the COP by the LMT method depends on the chosen mixture, its concentration and the temperature levels. In all the cases considered, the error remained small for the NH₃/H₂O mixture, being within 5 %, provided that the cycle's temperature levels were well chosen. This is because the use of a mean temperature, no matter whether
logarithmic or isentropic, makes invisible the presence of a possible pinch point, which would affect the choice of the mixture temperature levels, as will be seen in the next section.

3.4 Lorenz, Carnot, pure refrigerant and mixture cycles

3.4.1 Introduction

Representations like those given in Figure 3.6 have been used by Bergmann [1988], Morawetz [1989], Mucic [1990], Didion [1990], Kawada [1991], Lottin [1996] and others, to compare the Lorenz and Carnot cycles or to show that for cycles working between the same minimum and maximum temperatures the COP of a compression-resorption cycle is always better than the COP of a pure refrigerant cycle. Although this is true for refrigerating machines, there are three reasons why this approach is limited when dealing with heat pumps. First, the work to be furnished to the compression-resorption cycle (cycle’s area in Figure 3.6) is indeed less than for a pure refrigerant cycle, but as the heating capacity (area under the upper curves of the cycle in Figure 3.6) is also lower, no general conclusion can be drawn. Second, the external conditions are not taken into account, which makes this comparison unsuitable when employed to compare the two heat pump cycles for a given application (see previous section). This section shows that a correct comparison between cycles leads to a less advantageous image of the compression-resorption cycle.

![Diagram](image)

**Figure 3.6:** Classical comparison between the compression-resorption and the pure refrigerant cycles or between the Lorenz and Carnot cycles

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3.4.2 Lorenz cycle

The task to be achieved (external conditions) in a heat pump application can be specified by different combinations of the inlet and outlet temperatures of the heat source and sink and of their flow rates. It seems evident that the inlet temperatures of the source and sink are always known. Since heat pumps are concerned, the desired outlet temperature of the heat sink is also known, as well as its flow rate (or, which is the same, the desired heating capacity). The outlet temperature of the heat source is usually unimportant, since the heat is just rejected as waste heat, but its flow is a more restrictive factor because the source may be available only in a limited rate. That is the reason why in this thesis the external conditions chosen for the heat sink are the mass flow rate $m_{\text{sink}}$ and its inlet and outlet temperatures $T_{w2}$ and $T_{w3}$, and, for the heat source, the mass flow rate $m_{\text{source}}$ and its inlet temperature $T_{w2}$ (see solid lines in Figure 3.7).

If one wants to make high efficiency cycles, i.e. cycles producing as less a possible entropy, every cycle that could be used to achieve a certain task should be compared to an ideal cycle, unequivocally defined. An unequivocally definition of an ideal cycle can only be made by defining an ideal cycle that perfectly fits the desired external conditions (Bergmann [1991]).

The Lorenz cycle (Plank [1959]) consists of two isentropic and two polytropic lines (the only constraint on a polytropic transformation is mechanical reversibility, see Smith [1988]), the latter having an equal entropy difference between the beginning and the end. They must always refer to the external conditions and must fit them perfectly (see solid and dashed lines in Figure 3.7). The entropy differences for the source and the sink should be equal and also equal to the entropy difference of the polytropic transformation in the Lorenz cycle, as given in Equation (3.5):

$$m_{\text{sink}}(s_{w1}-s_{w2}) = m_{\text{source}}(s_{w2}-s_{w1}) = m_{L}(s_{2L}-s_{4L}) = m_{L}(s_{2L}-s_{1L})$$ (3.5)

When, as in the present case, $T_{w2}$ and $m_{\text{source}}$ are fixed, Equation (3.5) determines the entropy at point 1, and therefore the temperature $T_{1L}$. When $T_{w1}$ is an input date instead of $m_{\text{source}}$, as it is very often the case in the literature, the mass flow rate of the source will be fixed in the same way by Equations (3.5). If both the two mass flow rates and the four temperature levels of the source and sink were fixed, the cycle formed in this way would usually not be a Lorenz cycle because Equation (3.5) would not be satisfied - except by coincidence.

Equation (3.5) allows for the determination of $S_{1L}$, and the temperature at this point, $T_{1L}$, is then fixed by the polytropic equation. When the specific heat of the external media remains constant, which is usually the case, the variations in the temperature as a function of the entropy are exponential, and the polytropic equation becomes Equation (3.6):

$$T_{1L} = T_{w2} e^{rac{-m_{\text{sink}}(s_{w1}-s_{w2})}{m_{\text{source}}T_{w1}}}$$ (3.6)

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Because $T_{\text{w}1}$ is the only free variable, the external cycle fits to the Lorenz one only if $T_{\text{w}1}$ equals $T_{\text{II}}$, as drawn in Figure 3.7. However, as the real internal cycle will never be the Lorenz one (different temperature levels to allow for heat exchange and/or different temperature-entropy variations of the internal and external media), as will be seen in Section 3.4.5, the real evolution of the source will be such that the temperature at point 1, $T_{\text{w}1}$, will never reach $T_{\text{II}}$ (or, if $T_{\text{w}1}$ is fixed, $S_{\text{II}}$ will never be reached).

### 3.4.3 Carnot cycle

The Carnot cycle is only a special case of the Lorenz cycle in which the temperatures of the external media remain constant, as in the case of steam production. As the Carnot cycle is a particular case of the Lorenz cycle, care has to be taken that well-known properties of the Carnot cycle are not abusively generalized to the Lorenz one.

### 3.4.4 Differences between the properties of the Carnot and Lorenz cycles

Theoretically, a Carnot cycle can be realized by an ideal heat engine working with a pure refrigerant, because a pure refrigerant evaporates and condenses at constant temperatures. The term "ideal heat engine" should be understood to indicate that isentropic compression in the wet vapour region is possible (see Section 2.2.1). On this assumption, the COP of an ideal pure refrigerant cycle (internal COP) is equal to the COP of the Carnot cycle (referring to the external media), which explains the confusion between the two terms. Moreover, these COP are independent of the external media, as well as of the chosen refrigerant and depend only on the temperature levels. Because wet compression is still difficult to realize, the vapour is in superheated state after the compression, so that the temperature in the first part of the condenser is no longer constant. In fact, the ideal
internal COP is therefore the COP of the Rankine cycle, which depends on the chosen refrigerant.

Even theoretically, in its general form, a Lorenz cycle cannot be realized by an ideal engine working with a mixture. Indeed, the temperature-entropy curves for a mixture are certainly not exponential, as already emphasized in sections 3.2 and 3.3, and therefore cannot follow the variations of the external media. This means that, even when wet compression is assumed, the COP of an ideal "mixture cycle" is never equal to the COP of the Lorenz cycle (except in cases when the Lorenz cycle is a Carnot cycle). Furthermore, the COP of the ideal mixture cycle always depends on the chosen mixture. Generally speaking, the COP of the Lorenz cycle depends on the external media, but when the specific heats of the source and the sink are constant in their temperature course, which is often the case, the Lorenz COP is then only a function of the logarithmic mean temperatures.

To conclude, whereas the confusion between internal and external ideal COPs does not affect cycles with constant temperature sources and sinks, it leads to many problems in the case of gliding temperatures. To avoid confusion, the words "Carnot" and "Lorenz" should be reserved for the external ideal cycles, i.e. the best cycles one can devise to achieve a given task. The names "pure refrigerant" and "mixture" cycles, are used by the author to refer to the best cycles one can devise to achieve a given task with a specific pure refrigerant and a specific mixture, respectively. The wet compression-resorption cycle is the non-ideal version of the mixture cycle, i.e. the end and begin point of the expansion process have the same enthalpy.

### 3.4.5 Comparison between the different cycles

A Lorenz cycle should not be compared with a Carnot cycle, because the temperature of the external media is either constant or variable, but not both. The right formulation of the problem is to ascertain whether a pure refrigerant or a mixture should be used for a specific purpose.

Let the input data be $T_{w3}$, $T_{w4}$, $T_{w2}$, $m_{sink}$, and $m_{sour}$. As already shown in section 3.4.1, the temperature $T_{hl}$ is then determined for the Lorenz cycle. In the ideal case, where the heat transfer coefficient or the heat transfer area is infinite and thus no temperature difference is needed between the streams of the heat exchangers, the source will reach the temperature $T_{w1} = T_{hl}$ (Figure 3.7).

To achieve the intended result with a pure refrigerant (i.e. to heat a fluid with a mass flow rate $m_{sink}$ from $T_{w4}$ to $T_{w3}$, using a fluid of mass flow rate $m_{sour}$ at a temperature $T_{w2}$), in the ideal case a constant temperature $T_{3} = T_{w3}$ is needed at the refrigerant side of the resorber. The cycle is represented in Figure 3.8a in a T-S diagram, where $S$ is the total entropy, in kJ/K. The quantity of heat exchanged is the area under the curves ($dQ = TdS$) and should be equal for the two streams of the resorber, which results in the equality of the areas $A_e$ and $A_{pr}$.
Assuming that the desorber temperature at the refrigerant side is $T_1 = T_{IL}$ (see Figure 3.8a), the heat taken by the refrigerant must again be equal to the heat given by the external medium, so the areas under the two curves should be equal, i.e. $B_e$ is equal to $B_{pr}$. The external medium will therefore only reach the temperature $T_{w1}$ indicated in Figure 3.8a, instead of $T_{IL}$, and the temperature difference between the streams will be greater than zero. This produces an artificial decrease of the COP. To approach the Lorenz cycle more closely, it is better to let the pure refrigerant work at a higher temperature, $T_{IPR}$, defined so that $T_{IPR} = T_{w1}$ and $B_p = B_e$, as represented in Figure 3.8b. The COP of the ideal pure refrigerant cycle should thus be calculated between the temperature $T_{w3}$ and $T_{IPR}$ instead of $T_{w3}$ and $T_{IL}$.

When the working fluid is a mixture, an additional problem has to be solved, according to section 3.3. Also in the ideal case, the appropriate temperatures $T_1$ and $T_2$ allowing for heat exchange have to be found by iterations, with the condition of $T_1$ being on the liquid line. The way these iterations must be made will be described in Chapter 4. However, depending on the relative slopes of the temperature profiles of the external and internal medium in the T-h diagram, different configurations are possible. Two of these are shown in Figures 3.9a and 3.10. In Figure 3.9a the isobars for the mixture are much steeper than that of the external medium, whereas they are flatter in Figure 3.10. As shown in section 3.3, the slope of these curves depends on the mixture itself, on the chosen overall concentration and on the temperature levels. The temperature of the external medium at point 1, $T_{w1, mix}$, is determined in the same way as for a pure refrigerant ($B_e = B_{mix}$), but, in the ideal case, $T_{w1, mix}$ is not necessarily equal to $T_1$ (as it was the case for pure refrigerants), because the pinch point can be located somewhere else (see Figure 3.9a). Figure 3.10 is constructed in the same way as Figure 3.9a.
Figure 3.9: a) Choice of the temperature levels for a mixture cycle. b) Comparison between the mixture and the pure refrigerant cycles.

Figure 3.10: Second case of comparison between a mixture and a pure refrigerant cycle.
The comparison between the pure refrigerant and the mixture cycles must be made with constant external conditions (with the exception of $T_{w3}$), which generally implies different temperatures of the internal media: in the case of Figure 3.9b, the refrigerant mixture must work in the resorber at a higher temperature than $T_{w3}$, because of a pinch point located between the resorber inlet and outlet, whereas it will reach a quite low temperature in the desorber. In the case of Figure 10, it is possible to work with a lower refrigerant mixture temperature $T_3$ in the resorber, and a higher temperature in the desorber.

Since, by construction, the heat output at the resorber is the same for all the cycles, the comparison of the work furnished to the cycles - i.e. the area of the cycles - is sufficient to compare the COPs, that are given in the Equations (3.7):

$$COP_L = \frac{Q_{res}}{W_L}, \quad COP_{PR} = \frac{Q_{res}}{W_{PR}}, \quad COP_{mixture} = \frac{Q_{res}}{W_{mixture}}$$  \hspace{1cm} (3.7)

In Figure 3.9b, the work of the mixture cycle is clearly higher than the work of the pure refrigerant cycle (A>B), therefore $COP_{mixture}$ is lower than $COP_{PR}$. From the point of view of efficiency, in this application it would be better to use a pure refrigerant than a mixture with the T-S curve represented on Figure 3.9. In Figure 3.10, it is exactly the opposite (A<B), thus the use of the specific mixture refrigerant with the T-S curve of Figure 3.10 should be recommended.

It should be noted that the comparison made in these section was for ideal cycles and its aim was only to describe the correct methodology for the comparison of the cycles and to indicate that there is no evidence that a mixture should always perform better than a pure refrigerant: it is not possible to make a general prediction about whether a mixture cycle is more efficient than a pure refrigerant cycle. Calculations must be made for each set of external conditions and each mixture. However, when the external medium has a constant heat capacity, the more linear the heat rejection profile of the mixture refrigerant, the closer the approach to the Lorenz cycle. Nevertheless, in a comparison between real cycles, one should also take into account the irreversibilities of the cycles, i.e. the isenthalpic expansion and the non-isentropic compression, as well as the fact that for many pure refrigerants, a Rankine cycle would have a better efficiency that the wet compression one, when the irreversibilities are taken into account (see Chapter 2). This does not affect the methodology described above, but would bring variations in the comparative efficiency of the cycles, as will be described in Chapter 4.

It should also be noted that the method proposed here to compare the different cycles takes into account the heat transfer between the fluids only by the means of a minimum temperature difference between the streams. In the previous figures, this minimum temperature was set at zero, but allowing for a non-zero temperature difference changes neither the reasoning nor the results. One has to remember that the heat transfer areas are not the same in the two cycles, because the fluids do not have the same heat transfer coefficients and the mean temperature differences between the streams are not the same. This method of comparing the minimum approach temperatures is very suitable for design studies, as no data on the heat transfer equipment and on the heat transfer coefficients are needed. Other methods which are less easy to study on a T-S diagram and require more
information on the equipment could be used, but they are more suitable for the comparison of a pure refrigerant and a mixture for a given heat pump equipment. One of these methods is comparison at constant mean temperature difference, which implies that the heat transfer coefficient times the heat transfer area is kept constant. This method also requires the specification of a minimum approach temperature to avoid unfeasible temperature profiles. On the assumption of an almost constant heat transfer coefficient, an approximation of the necessary heat transfer areas is possible. However, the heat transfer coefficients are not usually constant throughout all heat transfer area, and are not equal for different mixtures and pure refrigerants. It would therefore be better to make a more detailed model of the heat transfer processes in the plant and to make a direct comparison at constant heat transfer area, taking into account the real heat transfer coefficients, as made in Mc Linden [1987], or, even better, also taking into account the transport properties. However, a comparison at constant heat transfer area is not the aim of a primary design study, and at this stage a minimum approach temperature comparison is sufficient. This subject will be treated more extensively in Chapter 4, where the set up of the model is described.

3.5 Internal heat exchange

The usefulness of internal heat exchange in the solution recirculation cycle is evident: to approach the equilibrium at the inlet of the resorber, which is necessary to reject heat on the full scale of the temperature glide, the liquid must be heated so that its temperature becomes closer to the equilibrium temperature. At the same time, the cooling of the condensate after the resorber decreases the throttling losses. Solution line/resorber heat exchange or solution line/vapour line heat exchange is also generally applied. In fact, it has the effect of rectifying the vapour and to bring the liquid closer to its saturation temperature. According to Equation 2.18, this rectification has no direct effect on the resorber heat balance. Applying rectification of the vapour without using the heat coming free to heat the liquid would, of course, have a negative effect.

In conventional compression heat pumps, liquid line/suction line heat exchange is sometimes used (Vakil [1983], Domanski [1992]), as represented in Figure 3.11a with the assumptions of isentropic compression and isenthalpic expansion. At constant heating capacity and pressure ratio it produces an increase of the COP only for refrigerants for which Equation (3.8) is verified.

\[
h_{3c} - h_{2c} \leq \frac{\dot{m}}{\dot{m}_c} (h_{3e} - h_{2e}) \tag{3.8}
\]

where \( \dot{m}, h_{3c}, h_{3e} \) refer to the cycle without internal heat exchange and \( \dot{m}_c, h_{2c}, h_{2e} \) to the cycle with heat exchange. In other words, whether the COP increases or decreases depends on the relative slopes of the isentropic lines in the superheated region: for R12 the COP increases, but for NH₃ it decreases (see also Chapter 2). However, it should be noticed that in cases where liquid line/suction line heat exchange decreases the pressure ratio, an extra COP gain may be achieved.
Figure 3.11: Classical compression system: a) Liquid line - suction line heat exchange (4-4e/2-2e). b) Evaporative heat exchange (4-4e/2-2e).

Figure 3.12: Hybrid wet compression cycle: a) Evaporative heat exchange (4e-4ee/2-2e). b) Absorptive/evaporative heat exchange (4eb-4ee/2-2e).

In evaporative heat exchange, the heat released by subcooling the liquid coming out the condenser, (line 4-4e in Figure 3.11b), is used to achieve a part of the evaporation process (line 2-2). Theoretically, this kind of heat exchange would have no effect on the COP or the temperature and pressure levels (Vakil [1983]). The conclusion is quite different in the case of the total wet compression cycle, where evaporative heat exchange (between 4e-4ee and 2-2e in Figure 3.12a) is the only kind of internal heat exchange that can be applied. As represented in Figure 3.12a, to minimize the losses, the heat exchanger should be
positioned between the cold end of the resorber and the hot end of the desorber (the cycle1-2-3-4 is the cycle without heat exchange and 1-e-2-3-e-4-e represents the cycle with heat exchange). If the desorber capacity is kept free, one can see that internal heat exchange has the effect of reducing the discharge pressure when working at $T_e$ constant (Bergmann [1987]) and therefore of increasing the compressor efficiency. Furthermore, the desorber heat output is higher in the cycle with heat exchange (\( h_{1e} - h_{4e} \)) whereas the compressor work remains almost constant (\( h_{3e} - h_{4e} \approx h_{3} - h_{4} \)), which produces a COP increase. However, how the compressor work remains constant depends on the relative slopes of the isentropic lines, and one cannot exclude the possibility that for some refrigerants, the compressor work increases in such a way that internal heat exchange would have a negative influence on the COP. Moreover, the external conditions were not taken into account in the previous considerations, whereas they might have a considerable effect on the claimed COP gain. Indeed, although $T_3$ is equal to $T_{3e}$, the mixture temperature glide is increased ($T_{3e} < T_3$), which can lead to an unfeasible temperature profile. In the latter case, the cycle with internal heat exchange should work at a temperature $T_{3e}$ higher than $T_3$, leading to a considerably reduced COP gain. However, internal heat exchange will turn out to be positive for the NH$_3$/H$_2$O mixture (see Chapter 4).

Absorptive-evaporative heat exchange (cycle 1-e-2-e-3-e-4-e-4-e in Figure 3.12b), where the heat released by the subcooling and a part of the resorption process is used to achieve a part of the desorption process, as represented in Figure 3.12b, (4-e-4-e / 2-2-e), has also been proposed by Bergmann [1987] for the compression-resorption cycle. It was studied under the name GAX cycle by Sharfe [1986] and Herold [1991] for absorption heat pumps, where it has the effect of increasing the efficiency of the thermal compressor. The main advantage of absorptive-evaporative heat exchange in the compression-resorption refrigerating cycle is to further reduce the pressure ratio. However, in heat pumping mode, this is, as in the case of simple evaporative heat exchange, no guarantee of a better COP because the heating capacity per kg mixture will probably decrease if the pressure ratio can not be decreased enough because of the temperature profiles (the condition for an heating capacity increase it that \( h_{1e} - h_{3} \)) is higher than \( h_{1e} - h_{3} \)). It will appear (see Chapter 4) that when working with small driving temperature differences between the streams, for NH$_3$/H$_2$O it is almost impossible to further reduce the pressure ratio, and to achieve a COP gain by means of absorptive-evaporative heat exchange.

3.6 Conclusions

The problems that arise when modelling compression-resorption heat pumps have been surveyed. The use of temperature-enthalpy diagrams for the mixtures shows that the temperature profiles in the desorber and resorber are strongly dependent upon the overall concentration and are not linear, at least for NH$_3$/H$_2$O. A direct consequence of this is that the external conditions should always be taken into account, because if the temperature levels of the compression-resorption cycles are not chosen with care, the design can be disturbed by unfeasible temperature profiles. Another consequence is that, except when working with approximately linear temperature glides or with high driving temperature differences, the logarithmic mean temperature difference method cannot be applied.
Because all comparisons between cycles must be based on the application, the different cycles must often be compared at different temperature levels. Because the behaviour of the mixture cycle depends on the chosen mixture, and on its concentration and temperature levels, no general conclusions can be drawn concerning the relative efficiencies of the mixture and pure refrigerant cycles. The benefits of internal heat exchange are also subject to the same uncertainties.

References


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Chapter 4

Model for the design of the cycle and simulations for the pair NH$_3$/H$_2$O

4.1 Introduction

4.1.1 Choice of the model

Besides the choice of an optimal working medium, which will be the subject of Chapter 5, the optimization of the performances of a heat pump cycle for a given application implies the choice of thermo-physical data like overall concentration, temperature and pressure and the choice of the cycle’s components and of their size. These optimization variables are not independent, since the physical size of the chosen components affects the optimal concentration, temperatures and pressures. Conversely, the choice of the concentration and of the temperature and pressure levels has consequences on the choice and the sizing of the cycles’s components. The first case is related to the simulation of an existing test-plant in order to optimize its thermo-physical working parameters or to retrofit it with other refrigerants. The second case is the design case for which components must be developed to achieve a given performance for a given application. The model discussed in this chapter is of the second type and therefore deals with the optimal design of a wet compression-resorption heat pump for given applications. The values to be optimized are the COP in heating mode, the specific compressor displacement (SCD), defined as the compressor inlet volumetric capacity per kW useful heat in the resorber, since it gives a measure of the compressor size and, finally, the entropy losses in each of the devices, to allow for a second law analysis of the heat pump cycle.
When a heat pump is to be designed for a given application, that is when the external conditions are fixed, the heat transfer between the internal fluid (refrigerant) and the external fluids (source and sink) must be taken into account in the model. The way this is done can range from the detailed modelling of the heat and mass transfer in the resorber and the desorber to a minimum temperature approach. In the most generalized steady state model, partial differential equations are used, based on the heat, mass and momentum balance equations and the equation of state for the boundary conditions corresponding to the resorber or desorber geometry. Generally, the momentum equation can be decoupled from the others and a given velocity profile is assumed (Pato [1986], Wassenaar [1994]). This model is a more complete one and gives accurate results but its major drawback in design applications where a lot of different configurations must be simulated, is its large time consumption.

Models using ordinary differential equations come one step below on the complexity scale: the model based on assumed temperature, concentration and velocity distributions (Perez-Blanco [1988], Wassenaar [1992]) requires more a-priori knowledge of the processes in the resorber, and is therefore very sensitive to erroneous assumptions. According to Wassenaar [1992], the model based on the Nusselt and Sherwood numbers (Grossman [1983], Wassenaar [1992]) is the optimal model for absorber design, since it gives acceptable results with a relatively low computational time requirement. However, its performances appear to be poor in the domain of interest for industrial absorbers.

In the most simple model, the resorber is considered as one lump for which overall heat and mass balances are written. It does not take into account the resorber geometry. The transport processes are also neglected, or taken into account only by means of a specified temperature deviation from the equilibrium (Grossman [1994]). The heat transfer between internal and external fluids is taken into account by means of Equation (4.1)

\[ Q = UA\Delta T_{\text{mean}} \]  

(4.1)

where \( \Delta T_{\text{mean}} \) can be any suitable mean temperature difference: the logarithmic mean temperature difference when the temperature profiles are linear or the isenthalpic mean temperature difference as defined in Chapter 3 when the profiles are not linear. Another method, often used when designing compact heat and mass exchangers, is to divide the resorber into as many lumps as necessary to obtain a linear temperature profile on each of the lumps (PFSG [1990]). The LMTD or the NTU methods can then be applied to each of the lumps. According to Wassenaar [1992], at constant heat exchange area, this simple model when applied to the resorber could introduce errors of more than 20% when comparing its outputs with those of the model with partial differential equations.

For the objective of this model, which is first to optimize the thermo-physical working parameters for given external conditions, at least two parameters must be varied (see section 4.2). The concentration should be studied in the range 0 to 100% with quite small step changes, because the shape of the isobars in the T-h diagrams for the mixture \( \text{NH}_3/\text{H}_2\text{O} \) suggests that the variations will be quite fast. To accurately study the effects of the chosen parameters one can estimate that the cycle should be calculated for about 50 different overall concentrations and 4 different suction pressures (as will be seen later in
section 4.2, the temperature levels are a function of these two parameters). If the effect of internal heat exchange is also to be studied, about 400 cycle simulations are necessary for one set of external conditions. Under these conditions, the computational time the model requires becomes of great importance. Furthermore, in the first two types of models, different kinds of resorber and desorber geometry should be tested to optimize the process, which further increases the computational time. From this point of view, and if one remembers to be more interested in the study of the overall performance of the cycle than in the detailed modelling of one of the components, black box models for all components of the cycle seem to provide the optimal solution. The validations of a simulation model for absorption heat pumps based on a black box model carried out by Grossman [1985], have shown that the COP was predicted within 10%, which is acceptable for a design study. The use of a black box model will also allow the prediction of the optimum UA-values and of their optimum distribution between the resorber and the desorber.

4.1.2 Mean temperature difference versus minimum temperature difference

Two different kinds of problems are generally encountered when modelling heat exchangers. In the rating problem, the geometry of the heat exchanger and its surface A are known, as well as the inlet temperatures of both the fluids and their mass flow rates. The quantity of exchanged heat and the outlet temperatures of both fluids are required. In the sizing problem, the quantity of heat exchanged, the inlet temperatures and the mass flow rates are known and outlet temperatures and heat exchange area are required.

In the design study of a heat pump cycle, the problem not only involves the design of a resorber, but also the optimization and design of the entire cycle. The consequence is that more data are fixed than in the usual sizing problem. According to Section 3.4.2, the given external conditions are the inlet and outlet temperatures $T_{w_1}$ and $T_{w_2}$ of the sink and its mass flow rate $m_{sink}$, and the inlet temperature $T_{x_2}$ of the source and its mass flow rate $m_{x_2}$. Counter current heat exchangers are assumed. As described in Chapter 3.2 and illustrated in Figure 3.2, once one has chosen a given concentration $x_s$ and a given suction pressure $p_x$, the choice of $T_2$ and $T_1$ defines the entire cycle, assuming isenthalpic expansion and known isentropic efficiency, and that point 4 must be on the saturation line or subcooled by a known amount of degrees. Therefore, when considering the resorber, not only the temperatures at the sink side are known, but also both the inlet and outlet temperatures at the refrigerant side. This makes the solving of the heat balances straightforward: the refrigerant mass flow rate necessary to achieve the desired heating capacity is directly calculated from the heat balance at the refrigerant side. As all temperatures are known, $\Delta T_{mean}$ can be calculated as well as $U_{A_r}$. Conversely, for the desorber, since $T_1$, $T_2$ and the refrigerant mass flow rate are known, the outlet temperature of the source is calculated directly from the heat balance at the source side.

Whatever kind of model is chosen, the remaining problem in designing the cycle is to select the right $T_2$ and $T_1$. When considering the resorber, firstly one can assume a constant heat transfer area (McLinden [1987], Webb [1989]): as $T_i$ is known for each
iteration on the discharge pressure, $T_1$ arises from the value of $\Delta T_{\text{mean}}$ calculated by 
Equation (4.1) (after calculation of the overall heat transfer coefficient). Secondly, one can assume a constant UA value (Högberg [1993], Grossman [1994]), which is equivalent to assuming a constant mean temperature difference because of the heat transfer Equation (4.1). The calculation of the temperature profiles by iterations on the discharge pressure will allow the adjustment of $T_1$ to the chosen $\Delta T_{\text{mean}}$. The last option is to assume a minimum temperature difference between the streams. In the same way as previously, the calculation of the temperature profiles will allow the adjustment of $T_1$ to the chosen $\Delta T_{\text{min}}$ (Högberg [1993], Grossman [1994]). The first case is of interest when comparing the performances of different refrigerants in a given plant. The second case is also suitable for this purpose, because the approximation of a constant $U$-value leads to a constant heat exchange area. However, it may introduce non-negligible errors because $U$ depends strongly on the operating conditions and on the refrigerant. In the third case, the heat exchange area is no longer kept constant and becomes an output of the model. It is therefore more adapted to design applications. However, since the $\Delta T_{\text{mean}}$ method is currently used in heat exchanger design, it is necessary to look carefully at how it differs from the $\Delta T_{\text{min}}$ method.

First it should be noted that in order to avoid unfeasible temperature profiles, a minimum temperature difference must be specified, even when using the $\Delta T_{\text{mean}}$ method (equivalent to the UA method) and whatever the type of refrigerant - pure or mixed. Of course $\Delta T_{\text{mean}}$ will always be higher than, or equal to $\Delta T_{\text{min}}$ in the most favourable case of perfectly matching temperature profiles (see Section 3.3).

In our simulations the main function to be optimized is the coefficient of performance. For a pure refrigerant the COP depends on the two temperature levels at which the heat pump operates; the greater the temperature difference between the two mean temperature levels, the lower the COP. To optimize the COP it is therefore necessary to ensure that the mean temperature differences in the resorber and in the desorber are as small as possible. However these $\Delta T_{\text{mean},r}$ and $\Delta T_{\text{mean},d}$ are always limited by the existence of a minimum temperature difference necessary to make heat exchange possible. For a pure refrigerant, the choice of a $\Delta T_{\text{min}}$ that really represents a minimum temperature beyond which no heat exchange is possible, gives the optimal values of $\Delta T_{\text{mean},r}$ and $\Delta T_{\text{mean},d}$. These two mean temperature differences are not necessarily equal, since they depend on the relative heat source and heat sink mass flow rates. The choice of any other value of $\Delta T_{\text{mean},r}$ or $\Delta T_{\text{mean},d}$ leads to a lower COP, because either the cycle must overcome a higher temperature lift ($\Delta T_{\text{mean},r}>\Delta T_{\text{mean},r}^{\text{opt}}$ or $\Delta T_{\text{mean},d}>\Delta T_{\text{mean},d}^{\text{opt}}$) or heat transfer will stop at a certain location of the resorber or of the desorber ($\Delta T_{\text{mean},r}<\Delta T_{\text{mean},r}^{\text{opt}}$ or $\Delta T_{\text{mean},d}<\Delta T_{\text{mean},d}^{\text{opt}}$). In the latter case, neither the required heating capacity nor the required temperature levels will be achieved. However, for a pure refrigerant and with constant external conditions, $\Delta T_{\text{mean}}^{\text{opt}}$ is an increasing function of $\Delta T_{\text{min}}$ only. This is no longer true in the case of a mixture, since at fixed $\Delta T_{\text{max}}$, $\Delta T_{\text{mean}}$ depends on both the overall concentration and on the pressure. Because the isobars are parallel at constant overall concentration, the pressure is not expected to have a lot of influence. However, the effect of the overall concentration on $\Delta T_{\text{mean}}$ is expected to be strong, owing to the rapidly changing shape of the isobars in the T-h diagram (see Appendix D), when $x_0$ varies. The above mentioned reasoning which applies to a pure refrigerant, can also be applied in the case of a mixture. The difference is that $\Delta T_{\text{mean}}^{\text{opt}}$ is no longer a function of $\Delta T_{\text{min}}$ only, but also depends on $x_0$ and $p_1$. With constant external conditions, the optimal UA-values distribution between the resorber and
the desorber is therefore a function of $\Delta T_{\text{min}}$, $x_o$ and $p$.

In a design phase it is therefore of primary importance to use a model with a minimum temperature difference instead of mean temperature difference. This will make it possible to obtain the optimal $\Delta T_{\text{mean}}$ in the resorber and in the desorber and therefore the optimal UA values on which the surface choice and the sizing of the desorber and resorber will be based. Once the overall heat transfer coefficient has been calculated, or if it has been assumed to be constant, this allows to study the costs inherent in a COP increase, in terms of heat exchange area.

In short, as highlighted by Högborg [1993], the method of the $\Delta T_{\text{min}}$ is not suitable for the simulation of a specific installation, since there is no reference to the real heat transfer area. Moreover, the $\Delta T_{\text{min}}$ method is not suitable for the comparison of the performances of different refrigerants or refrigerant mixtures for a given heat transfer area. However, the $\Delta T_{\text{min}}$ method can be recommended as a design method, because at the design stage it is important to assess the heat exchange surface needed to achieve a given COP.

Chapter 4 presents the black box model based on the minimum temperature approach which has been developed to select the thermo-physical parameters of the wet compression-resorption cycle. After the description of the model, the results of the simulations of nine cases representative of situations often met in industrial or district heating environments are analyzed in terms of both first and second laws. For given compressor efficiency and minimum temperature differences, the overall ammonia concentration, the suction pressure and the size of the internal heat exchange are varied in order to find the optimum working conditions in relation to the COP, to the specific compressor displacement and to the entropy losses in each of the devices. Their influence on the discharge pressure and on the internal temperature levels is also studied. Finally, the performances of the wet compression-resorption cycle, of the solution recirculation cycle and of the pure refrigerant cycle are compared in terms of COP, SCD and UA-values.

4.2 Description of the model

The wet compression-resorption cycle that was studied is represented in Figures 4.1 and 4.2. When no internal heat exchange is applied, point 4 coincides with point 4e and point 2 with point 2e. Point 4 is located on the saturation line, except when absorptive heat exchange is applied. In this case, part of the resorption heat is used to further heat the desorber via the internal heat exchanger and point 4 slides on the isobar on the right, into the two-phase zone (see Section 3.5).

All calculations are effected by a simulation program, using the function's library of the program DOTHERMO (Itard [1994]). In this program, the thermodynamic properties of the NH$_3$/H$_2$O mixture are calculated with the Trepp-Ziegler equation (Ziegler [1982]). For a mixture of two components, two parameters are needed to calculate all thermodynamic properties at the equilibrium. Knowing a third parameter (overall concentration $x_o$, as defined in Section 3.2 for instance) permits the calculation of the total thermodynamic
Figure 4.1: Layout of the wet compression-resorption cycle.

NH₃ overall concentration \( x_0 = 0.3 \)

Figure 4.2: Representation of the wet compression-resorption cycle in the \( T-h \) diagram for an overall NH₃ concentration of 30%.
functions (liquid + vapor) at a given point. An overview of the functions that can be obtained from DOTHERMO is given below.

- \( \text{titre}(p, T) \) calculates the equilibrium concentration at the pressure \( p \) and the temperature \( T \).
- \( \text{psat}(x_o, T, n) \) calculates the saturation pressure of the liquid (\( n = 1 \)) or the vapor (\( n = 2 \)) corresponding to the overall concentration \( x_o \) and the temperature \( T \).
- \( \text{tsat}(x_o, p, n) \) calculates the saturation temperature of the liquid (\( n = 1 \)) or the vapor (\( n = 2 \)) corresponding to the overall concentration \( x_o \) and the pressure \( p \).
- \( \text{h}(x_o, p, T) \) calculates the total enthalpy corresponding to the overall concentration \( x_o \), the pressure \( p \) and the temperature \( T \).
- \( s(x_o, p, T) \) calculates the total entropy corresponding to the overall concentration \( x_o \), the pressure \( p \) and the temperature \( T \).
- \( \text{thho}(x_o, p, h) \) calculates the temperature corresponding to the overall concentration \( x_o \), the pressure \( p \) and the total enthalpy \( h \).
- \( \text{tsso}(x_o, p, s) \) calculates the temperature corresponding to the overall concentration \( x_o \), the pressure \( p \) and the total entropy \( s \).
- \( \text{pthho}(x_o, T, h) \) calculates the pressure corresponding to the overall concentration \( x_o \), the temperature \( T \) and the total enthalpy \( h \).
- \( \text{pssso}(x_o, T, s) \) calculates the pressure corresponding to the overall concentration \( x_o \), the temperature \( T \) and the total entropy \( s \).

As already emphasized, all these functions are nonlinear. A succinct description of the optimization model will be given in Sections 4.2.1 to 4.2.6. In this model, the overall concentration \( x_o \) represents the concentration of the saturated liquid (no vapor present) leaving the resorber (point 4).

### 4.2.1 Input parameters

The input data for the heat sink are:

- \( T_{w1} \), inlet temperature
- \( T_{w3} \), outlet temperature
- \( m_{w3} \), mass flow rate

The input data for the heat source are:

- \( T_{w2} \), inlet temperature
- \( m_{w3} \), mass flow rate

The following data concerning the mixture are needed:

- the values of the suction pressure \( p_1 \) for which calculations are desired
- the maximum pressure allowed in the cycle
- the minimum temperature difference allowed between the two streams of each
of the heat exchangers, $\Delta T_{\text{mix}}$, for the resorber, $\Delta T_{\text{mix,d}}$ for the desorber and $\Delta T_{\text{mix,e}}$ for the internal heat exchanger.

- the isentropic efficiency of the compressor

The heat sink and the heat source are assumed to be water. Furthermore it is assumed that the heat pump is perfectly insulated and that the pressure drop on line can be neglected.

### 4.2.2 Output variables

For each value of $p_1$ and each overall concentration, the output variables are:

- the temperatures of the mixture at the inlet and outlet of each component, as well as the enthalpies, entropies, liquid and vapour concentrations and vapour mass fractions.
- the discharge pressure $p_2$
- the outlet temperature of the heat source $T_w$
- the capacity of the heat exchangers and the compression work
- the COP, the SCD and the entropy losses in each of the components
- the COP of the Lorenz and pure refrigerant cycle corresponding to the external conditions
- the temperature profiles in the heat exchangers
- the mean temperature differences in the heat exchangers and their UA-values.

### 4.2.3 Compressor model

In the compressor model an ideal wet compressor has been assumed; the liquid is assumed to enter the compressor via the suction port, in equilibrium with the vapour. There is no liquid injection at a pressure intermediate between the suction and the discharge pressures. The liquid and vapour phases are assumed to be in thermodynamic equilibrium at the beginning and at the end of the compression. The internal losses are taken into account by means of a given isentropic efficiency $\eta_s$. This means that the model does not take the variations of the isentropic efficiency with the pressure ratio into account. This is because the equations describing these variations depend on the chosen compressor, on the chosen refrigerant and on the chosen oil and therefore are not easy to integrate into a general model. Moreover, there are no data available on compression efficiency when wet compression is involved.

The input data are the overall concentration $x_o$, the suction pressure $p_1$, the inlet temperature $T_2$, the isentropic efficiency $\eta_s$ and the discharge pressure $p_2$. The outputs are the discharge temperature $T_3$ and the compressor work, $W$, for one kg refrigerant. The suction pressure is assumed to be equal to the desorber pressure. The calculations are made as follows:

The total entropy at point 2, which is a function of the input value $x_o$, $p_1$ and $T_2$ only is
calculated:

\[ s_2 = s(x_o, p_1, T_2) \quad (4.2) \]

Since for isentropic compression \( s_2 \) is equal to \( s_3 \), the discharge temperature corresponding to isentropic compression is calculated from

\[ T_{3i} = tiss(x_o, p_2, s_2) \quad (4.3) \]

The total enthalpy corresponding to isentropic compression is calculated by

\[ h_{3is} = h(x_o, p_2, T_{3i}) \quad (4.4) \]

The real total enthalpy is then calculated, using the definition of the isentropic efficiency:

\[ h_3 = \frac{(h_{3is} - h_2)}{\eta_is} + h_2 \quad (4.5) \]

The discharge pressure is then given by Equation (4.6):

\[ T_3 = ttho(x_o, p_2, h_3) \quad (4.6) \]

The specific compressor work is given by Equation (4.7):

\[ W = h_3 - h_2 \quad (4.7) \]

where

\[ h_2 = h(x_o, p_1, T_2) \quad (4.8) \]

### 4.2.4 Expansion valve model

The expansion is assumed to be isenthalpic. At the outlet of the valve, the vapour produced by flashing is in equilibrium with the liquid. The input data are the overall concentration \( x_o \), the inlet temperature \( T_{4i} \), the resorber pressure \( p_2 \) (assumed to be equal to the discharge pressure), and the suction pressure \( p_1 \). The output is the temperature at the desorber inlet \( T_1 \).

The enthalpy at point 4 is calculated directly from the pressure and temperature:
\[ h_4 = h(x_o, p_2, T_{w4}) \]  

(4.9)

Since \( h_4 \) is equal to \( h_1 \), the temperature at point 1 follows from \textit{Equation (4.10)}:

\[ T_1 = thho(x_o, p_1, h_4) \]  

(4.10)

### 4.2.5 Resorber, desorber and internal heat exchanger model

Counter-current flow is assumed and the pressure drop is neglected. When two phases are in contact, they are assumed to be in equilibrium.

**Resorber:** The input data are \( T_{w3}, T_{w4}, m_{\text{sink}}, T_3, p_1 \) and \( x_o \). The output data are \( T_4, m_n \), the temperature profiles and the minimum temperature difference between the streams. When no absorptive heat exchange is used, point 4 is located on the saturation line and \( T_4 \) is calculated using \textit{Equation (4.11)}.

\[ T_4 = tsat(x_o, p_2) \]  

(4.11)

When absorptive heat exchange is used, the user must input the fraction \( f_r \) of resorber heat used for internal heat exchange, where \( f_r \) is defined by

\[ f_r = \frac{h_3 - h_{\text{sat}}}{h_1 - h_4} \]  

(4.12)

where \( h_{\text{sat}} \) is the saturated liquid enthalpy at the pressure \( p_2 \). In this case, the temperature \( T_4 \) at the resorber outlet is then given by:

\[ T_4 = thho(x_o, p_2, h_4) \]  

(4.13)

The resorber capacity is known from the sink data:

\[ Q_{\text{res}} = m_{\text{sink}} c_p (T_{w3} - T_{w4}) \]  

(4.14)

The refrigerant mass flow rate follows from \textit{Equation (4.15)}:

\[ m_n = \frac{Q_{\text{res}}}{h_3 - h_4} \]  

(4.15)

In order to calculate the temperature profiles, the heating capacity is divided into \( n \) lumps (50 per default or any other user-given value) and the outlet temperatures of the lumps are calculated for both the refrigerant and the sink. The minimum temperature is calculated from these \( (n+1) \) temperature values.

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**Desorber:** The input data are $T_1$, $T_{2e}$, $m$, $x_o$, $p_1$, $T_{w2}$ and $m_{\text{sink}}$. The output data are $T_{w1}$, $Q_{\text{des}}$, the temperature profiles and the minimum temperature difference between the streams. The desorber capacity is directly calculated by Equation (4.16):

$$Q_{\text{des}} = m(h_{2e} - h_1)$$  \hspace{1cm} (4.16)

where

$$h_{2e} = h(x_o, p_1, T_{2e})$$  \hspace{1cm} (4.17)

$$h_1 = h(x_o, p_1, T_1)$$  \hspace{1cm} (4.18)

The temperature then $T_{w1}$ follows from Equation (4.19):

$$T_{w1} - T_{w2} = \frac{Q_{\text{des}}}{m_{\text{w1}} c_p}$$  \hspace{1cm} (4.19)

The temperature profiles and the minimum temperature difference are calculated in the same way as for the resorber.

**Internal heat exchanger:** The input data are $T_1$, $T_2$, $m_o$, $x_o$, $p_1$, $p_2$ and $\Delta T_{\text{min,e}}$. Internal heat exchange is applied between the cold side of the resorber and the hot side of the desorber and is possible only if

$$T_4 > T_2 + \Delta T_{\text{min,e}}$$  \hspace{1cm} (4.20)

The output data are the temperature $T_{4e}$ and $T_{2e}$ and the capacity of the internal heat exchanger $Q_{\text{ex}}$. A first estimation of $T_{4e}$ is made by Equations (4.21) and (4.22): They are

$$T_{2e} = T_{w2} - \Delta T_{\text{min,d}}$$  \hspace{1cm} (4.21)

$$T_{4e} = T_{2e} + \Delta T_{\text{min,e}}$$  \hspace{1cm} (4.22)

The heating capacity is calculated at the hot side of the heat exchanger by

$$Q_{\text{ex}} = m_o(h_1 - h_{4e})$$  \hspace{1cm} (4.23)

where

$$h_4 = h(x_o, p_2, T_4)$$  \hspace{1cm} (4.24)

$$h_{4e} = h(x_o, p_2, T_{4e})$$  \hspace{1cm} (4.25)

$T_{2e}$ is then calculated by Equations (4.26) and (4.27):
\[ h_{2e} = h_2 - \frac{Q_{ex}}{m_o} \]  
(4.26)

\[ T_{2e} = \text{thho}(x_o, p_1, h_{2e}) \]  
(4.27)

Depending on the value of \( T_{a4e} - T_{2e} \), the variable \( T_{a4e} \) is then increased step by step or decreased from \( dT \) and Equations (4.23) to (4.27) are repeated. The iteration process is stopped when:

\[ T_{a4e} - T_{2e} = \Delta T_{\text{min},e} \]  
(4.28)

The fact that for the internal heat exchanger, the pinch point is always located at the cold end arises from the relative slopes of the isobar at \( p_1 \) (heating from \( T_{2e} \) to \( T_2 \)) and of the liquid saturation line (cooling from \( T_4 \) to \( T_{2e} \)); as can be seen in Figure 4.2, the slope of the latter is always much higher than the slope of the former.

### 4.2.6 Set-up of the model

As can be deduced from observation of the diagrams given in Appendix D for \( \text{NH}_3/\text{H}_2\text{O} \), the lower the overall concentration at constant pressure, the higher the temperature on the saturation line. Since the only temperature data being limited by a maximum value is \( T_{2e} \), the temperature at the end of the desorption process, the highest possible value of \( T_{2e} \), i.e. \( T_{w2} - \Delta T_{\text{min},d} \), gives the lowest possible value of the overall concentration \( x_{\text{min}} \) for a given suction pressure \( p_1 \). For each \( p_1 \) and each concentration between \( x_{\text{min}} \) and 1, the cycle is calculated as follow:

A first estimate of \( T_2 \) and \( T_3 \) is made using the equations

\[ T_2 = T_{2e} = T_{w2} - \Delta T_{\text{min},d} \]  
(4.29)

\[ T_3 = T_{a4} + \Delta T_{\text{min},r} \]  
(4.30)

Point 3 is then calculated according to the compressor calculations of Section 4.2.3. After this, point 4 is calculated as described in Section 4.2.5 (resorber), as well as the temperature profiles of both the internal and external media. If the calculated minimum temperature difference between the fluids differs from \( \Delta T_{\text{min},d} \) by more then 0.2 K, a new estimate of \( T_3 \) is made and the compressor and resorber calculations are repeated until the calculated minimum temperature difference and \( \Delta T_{\text{min},r} \) differ by less than 0.2 K.

When the difference between the calculated minimum temperature difference and \( \Delta T_{\text{min},r} \) is smaller than 0.2 K, the internal heat exchanger is calculated as described in Section 4.2.5. The points 4e and 2e are then known and point 1 is then calculated as described in Section 4.2.4. The desorber and temperature profiles calculations are made according to...
Figure 4.3: Succinct flow-chart of the simulation program.

Section 4.2.5. If the calculated minimum temperature difference between the streams differs from $\Delta T_{\text{min,d}}$ by more than 0.2 K, a new estimate of $T_3$ is made and the complete procedure is repeated until the calculated minimum temperature difference and $\Delta T_{\text{min,d}}$ differ by less than 0.2 K. A succinct flow-chart of the program is given in Figure 4.3.
4.3 Comparison with cycles using a pure refrigerant

The comparison is achieved by referring to the application in the way described in Chapter 3, Section 3.4.5, i.e. at constant resorber heat output and not at constant temperature levels. Wet compression with the same compressor efficiency as for the wet compression-resorption cycle is assumed, and the COP is calculated using Equation (2.18). In this equation COP, is the COP of the pure refrigerant cycle with isentropic compression and isenthalpic expansion and therefore depends on the chosen refrigerant. To give a quick idea of the performance of a pure refrigerant cycle, the COP will however be calculated using the COP, corresponding to the cycle with isentropic compression and isentropic expansion, that is by using the Carnot COP, independent of the chosen refrigerant. This implies that the calculated COP of the pure refrigerant cycle is always overestimated and must be seen as an upper limit of what can be achieved with a pure refrigerant. Calculations of the real performance of vapour compression cycles with different pure refrigerants will be performed in Chapter 5.

4.4 Choice of the simulated cases

Because this study is not aimed at a particular application, but has been developed for the purpose of getting a broad view of the behaviour of the wet compression-resorption heat pump and its applicability domain, it is necessary to cover the entire scope of applications as efficiently as possible. As emphasized in Chapter 1, most existing heat pumps have been developed for low temperatures, that is for cases where heat is needed at temperatures below 100 °C, but nowadays there is a strong potential demand for heat pumps that could produce heat at temperatures far above 100 °C. However, although a high temperature level has consequences on the choice of the refrigerant mixture itself (high boiling point, stability and pressure considerations), it has no direct consequence on the COP calculation method: in this regard, a high temperature heat pump behaves like a low temperature one.

Intuitively two data are important for the COP of the heat pump ideal cycle. The first is the temperature glide of the heat sink (T_{w3}-T_{w4}): the better the refrigerant or refrigerant mixture can approach the external temperature glide in the resorber, the closer will be the cycle to the Lorenz cycle, and the higher will be the COP. However, the relative values of the temperature glide of the heat sink (T_{w3}-T_{w4}), and of the heat pump temperature lift (T_{w3}-T_{w2}) must also be taken into account as illustrated in Figure 4.4. A cycle with a low temperature lift has been drawn in Figure 4.4a, with its corresponding pure refrigerant cycle, at constant resorber heat output. Since area A is lower than area B, the cycle using the mixture gives a better COP than the cycle using the pure refrigerant (see Chapter 3). In Figure 4.4b, a cycle with exactly the same resorber temperature glide as in 4.4a has been drawn, but this time, with a high temperature lift. Since area A becomes higher than area B, the cycle using the pure refrigerant will be the best. Therefore, applications have been chosen in relation to their heat sink temperature glide and to their ratio ΔT_{lift}/ΔT_{glide} between temperature lift and heat sink temperature glide. From an extensive literature study concerning heat pump applications in recent years, it appears that heat sink
For the sake of clarity, the applications are placed in three categories: the applications for which the ratio of the temperature lift and of the temperature glide is lower or equal to 1, the applications for which $1 < \Delta T_{\text{lift}}/\Delta T_{\text{glide}} \leq 2$ and the applications for which $\Delta T_{\text{lift}}/\Delta T_{\text{glide}} > 2$. Each of these three categories has also been divided into three sub-classes: low heat sink temperature glide ($0 \leq \Delta T_{\text{glide}} \leq 15$ K), medium temperature glide ($15 < \Delta T_{\text{glide}} \leq 30$ K) and large temperature glide ($>30$ K). In the first category, where the ratio between the temperature lift and the temperature gap is lower than 1, there is always an overlap between the inlet temperatures of the source and of the sink, because direct heat exchange between the source and the sink could not be defended from an economic point of view, because of a too low driving temperature. From all the cases studied one application has been selected per subclass and is presented in Tables 4.1 to 4.3. Note that the applications labelled * were not found as they are in the reference mentioned, but have been adapted to fit into our classification. Since no real data for the compressor isentropic efficiency are available, an arbitrary value was chosen for each case. The influence of this parameter will be studied in section 4.5.5. For all cases, a minimum temperature difference of 5 K was chosen and internal heat exchange was applied when possible.

### 4.5 First law analysis

In this section, the optimization curves for the COP are discussed for the applications described in Tables 4.1 to 4.3. Three examples are given in Figure 4.5 and all other
<table>
<thead>
<tr>
<th></th>
<th>small $\Delta T_{\text{glide}}$ example 1.1</th>
<th>medium $\Delta T_{\text{glide}}$ example 1.2</th>
<th>large $\Delta T_{\text{glide}}$ example 1.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>inlet sink, $T_{\text{ws}}$ (°C)</td>
<td>10</td>
<td>46</td>
<td>15</td>
</tr>
<tr>
<td>outlet sink, $T_{\text{wo}}$ (°C)</td>
<td>15</td>
<td>65</td>
<td>85</td>
</tr>
<tr>
<td>inlet source, $T_{\text{w}}$ (°C)</td>
<td>12</td>
<td>49</td>
<td>25</td>
</tr>
<tr>
<td>$\dot{m}_{\text{sink}}$ (kg/s)</td>
<td>23.92</td>
<td>11.18</td>
<td>3.42</td>
</tr>
<tr>
<td>$Q_{\text{res}}$ (MW)</td>
<td>0.5</td>
<td>0.88</td>
<td>1</td>
</tr>
<tr>
<td>$\dot{m}_{\text{sour}}$ (kg/s)</td>
<td>42.72</td>
<td>8</td>
<td>9.21</td>
</tr>
<tr>
<td>$\eta_{\text{is}}$</td>
<td>0.80</td>
<td>0.7</td>
<td>0.67</td>
</tr>
<tr>
<td>$\Delta T_{\text{min,r}}$ (K)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$\Delta T_{\text{min,d}}$ (K)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$\Delta T_{\text{min,e}}$ (K)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$\Delta T_{\text{lift}}$ (K)</td>
<td>3</td>
<td>16</td>
<td>60</td>
</tr>
<tr>
<td>$\Delta T_{\text{glide}}$ (K)</td>
<td>5</td>
<td>19</td>
<td>70</td>
</tr>
<tr>
<td>$\Delta T_{\text{lift}}/\Delta T_{\text{glide}}$</td>
<td>0.6</td>
<td>0.84</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 4.1: Simulated applications for $\Delta T_{\text{lift}}/\Delta T_{\text{glide}} \leq 1$. 
(‘: example modified)

Optimization curves can be found in Appendix A. The COP of the Lorenz cycle corresponding to the application is given in the title form and the COP of the corresponding pure refrigerant cycle is given in the graph as a horizontal line. A rapid survey of these figures highlights different behaviours of the COP, depending on the application and, to a lesser extent on the pressure. For some applications, the COP decreases with the ammonia concentration (Figures 4.5c) whereas for other applications, there is clearly an optimum that can be either very sharp (Figure 4.5b) or very flat (Figure 4.5a). The parameters having an effect on the COP will be discussed in the next section.
<table>
<thead>
<tr>
<th>1 &lt; ΔT_{lift}/ΔT_{glide} ≤ 2</th>
<th>small ΔT_{glide} example 2.1</th>
<th>medium ΔT_{glide} example 2.2</th>
<th>large ΔT_{glide} example 2.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>inlet sink, T_{w,d} (°C)</td>
<td>60</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>outlet sink, T_{w,3} (°C)</td>
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<td>90</td>
<td>140</td>
</tr>
<tr>
<td>inlet source, T_{w,2} (°C)</td>
<td>55</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>m_{sink} (kg/s)</td>
<td>23.90</td>
<td>11.96</td>
<td>17.94</td>
</tr>
<tr>
<td>Q_{res} (MW)</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>m_{sour} (kg/s)</td>
<td>23.90</td>
<td>11.96</td>
<td>17.94</td>
</tr>
<tr>
<td>η_{ie}</td>
<td>0.70</td>
<td>0.85</td>
<td>0.7</td>
</tr>
<tr>
<td>ΔT_{min,r} (K)</td>
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<td>5</td>
<td>5</td>
</tr>
<tr>
<td>ΔT_{min,d} (K)</td>
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<td>5</td>
<td>5</td>
</tr>
<tr>
<td>ΔT_{min,ex} (K)</td>
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<td>5</td>
<td>5</td>
</tr>
<tr>
<td>ΔT_{lift} (K)</td>
<td>15</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>ΔT_{glide} (K)</td>
<td>10</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>ΔT_{lift}/ΔT_{glide}</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 4.2: Simulated applications for 1 < ΔT_{lift}/ΔT_{glide} ≤ 2.
(‘*: example modified)

4.5.1 Limits of the curves

The lowest possible concentration is given by the combination of two constraints:

1. As shown in Section 4.2.6, the highest possible value of T_{2e} (T_{w,2} - ΔT_{min,d}) gives the absolute lowest possible value of the overall concentration.

2. The lowest value of the overall concentration is further limited by the fact that point 3 (end compression) at the lowest possible value of T_{3} (T_{w,1} + ΔT_{min,r}) must be in the two-

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<table>
<thead>
<tr>
<th>[\Delta T_{\text{glide}}\text{ example 3.1}]</th>
<th>[\Delta T_{\text{glide}}\text{ example 3.2}]</th>
<th>[\Delta T_{\text{glide}}\text{ example 3.3}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food processing plant</td>
<td>Chemical plant</td>
<td>drying plant</td>
</tr>
<tr>
<td>\text{inlet sink, } T_{\text{w4}} \ (\circ C)</td>
<td>52</td>
<td>110</td>
</tr>
<tr>
<td>\text{outlet sink, } T_{\text{w3}} \ (\circ C)</td>
<td>60</td>
<td>130</td>
</tr>
<tr>
<td>\text{inlet source, } T_{\text{w2}} \ (\circ C)</td>
<td>31</td>
<td>70</td>
</tr>
<tr>
<td>\dot{m}_{\text{sink}} \ (kg/s)</td>
<td>14.90</td>
<td>21.53</td>
</tr>
<tr>
<td>\dot{Q}_{\text{res}} \ (MW)</td>
<td>0.5</td>
<td>1.8</td>
</tr>
<tr>
<td>\dot{m}_{\text{sour}} \ (kg/s)</td>
<td>40.00</td>
<td>21.53</td>
</tr>
<tr>
<td>\eta_{\text{in}}</td>
<td>0.70</td>
<td>0.85</td>
</tr>
<tr>
<td>\Delta T_{\text{min,c}} \ (K)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>\Delta T_{\text{min,d}} \ (K)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>\Delta T_{\text{min,ex}} \ (K)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>\Delta T_{\text{lift}} \ (K)</td>
<td>29</td>
<td>60</td>
</tr>
<tr>
<td>\Delta T_{\text{glide}} \ (K)</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td>\Delta T_{\text{lift}}/\Delta T_{\text{glide}}</td>
<td>3.6</td>
<td>3</td>
</tr>
</tbody>
</table>

*Table 4.3: Simulated applications for \[2 < \Delta T_{\text{lift}}/\Delta T_{\text{glide}} \leq 4\].
\(^{(*)} \text{example modified}\)*

phase zone and not in the subcooled region, which can occur at low concentrations, when point 2 is too close to the liquid saturation line.

The highest possible concentration is also determined by two constraints:

1. Point 3 should be in the two-phase zone and not in the superheated vapour region.

2. The cycle’s high pressure (point 3) should be lower than the maximum pressure allowed in the cycle.

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4.5.2 The COP as a function of the overall concentration

Usually, the COP first increases with the ammonia concentration, reaches a maximum and then decreases with the overall ammonia concentration. However, depending on the possible overall concentration range, only parts of this general profile can be present. The COP of the system is affected by two parameters: the pressure ratio, since it is determining for the compressor work, and the way the temperature profiles of the internal and external media are matching each other. Although the latter is related to a Second Law analysis of the cycle (see Section 4.10), it has direct consequences on the pressure ratio. Because the isobars in the T-h diagram are almost parallel, and if a closest temperature approach has been chosen, poorly matching temperature glides will imply either a lower suction pressure, or a higher discharge pressure than in the case of perfectly matching temperature profiles, thus in all cases a higher pressure ratio. To illustrate this, the pressure ratios, for example 2.3, are given as a function of the overall concentration in Figure 4.6. Comparison with Figure 4.5b makes clear that a maximum COP corresponds to a minimum pressure ratio. In Figure 4.8 the temperature profiles at different concentrations around the optimal value are given for the resorber and the desorber respectively. At the optimal overall concentration, the temperature profiles match each other almost perfectly. In the example examined above (example 2.3), the temperature profiles of the source and of the sink are parallel because their specific heats are almost the same, and because the same mass flow rates have been chosen. Together with the fact that at constant overall concentration, the isobars in the T-h diagram are also almost parallel, this leads to the conclusion that the best glide matching in the desorber and in the resorber occurs at identical overall concentrations. This is illustrated by Figure 4.7 where the mean temperature difference between the streams, calculated with Equation (3.4) is drawn as function of the overall concentration. At constant minimum temperature difference, the mean temperature difference between the stream is indeed a direct measure of the glide matching.

However, when heat sink and heat source media are not identical, or when their mass flow rates are different (see example 1.3 for instance), the best glide matching will not occur for the same overall concentration in the resorber and in the desorber. This is illustrated in Figure 4.9, where it also can be seen that the lowest pressure ratio is achieved at the overall concentration which minimizes the sum of $\Delta T_{\text{mean},r}$ and $\Delta T_{\text{mean},d}$. Figure 4.10 represents the temperature profiles for different overall concentrations and gives a good illustration of a nonlinear temperature profile at the mixture side and of a pinch point occurring in the middle of the resorber, for $x_o = 0.749$.

4.5.3 The COP as a function of the suction pressure

The increase of the suction pressure has always the effect of moving the curves towards higher overall concentrations. This is because, at fixed overall concentration and temperature, the higher the suction pressure, the closer point 2 to the liquid saturation line and the more chance there is for point 3 to be in the subcooled region. To avoid this, a higher overall concentration must be taken (see Section 4.5.1). The shape of the curve can
Tw2 = 25°C, Tw4 = 15°C, Tw3 = 85°C
\( \text{n\text{res}} = 3.42 \text{ kg/s}, \ \text{n\text{des}} = 9.21 \text{ kg/s}, \ \text{COP}_L = 9.09 \)
\( n_{\text{bs}} = 0.67, \ \Delta T_{\text{min}} = 5 \text{ K} \)

Figure 4.5: COP optimization curves for a) case 1.3 b) case 2.3 and c) case 3.2.
**Figure 4.6:** Variations of the pressure ratio with $x_s$ for example 2.3.

**Figure 4.7:** Mean temperature difference between the streams of the resorber and of the desorber for example 2.3 at $p_1 = 4$ bar.
Figure 4.8: temperature profiles, for example 2.3, at several overall concentrations and for a suction pressure $p_s = 4$ bar.
also be affected in that for some suction pressures, the curve can have an optimum, and for others, be only a decreasing or an increasing function of $x_o$ (see Figure 4.5). However, the optimum COP is not severely affected by the choice of the suction pressure when the curves for these suction pressures all show a maximum. The COP variation at the optimal concentration then remains within 10%. The choice of the suction pressure is therefore less important than the choice of the overall concentration pressure which can easily be explained by the pseudo-parallelism of the isobars in the T-h diagram. However, since a COP gain of 10% is never negligible, it is always advisable to perform a suction pressure optimization.

**4.5.4 The effect of $\Delta T_{\text{min}}$ on the COP**

The evolution of the COP curves with the minimum temperature difference, in example 2.3 at a suction pressure of 3 bar, are represented in Figure 4.11. When $\Delta T_{\text{min}}$ increases, the curves are shifted to the higher overall concentration range. Indeed, working with a lower desorber end-temperature at a constant suction pressure means that point 2 shifts to the left on the T-h diagram and comes nearer to the saturation line. Because a higher resorber inlet temperature is also needed when $\Delta T_{\text{min}}$ increases, point 3 has more chance of falling in the subcooled liquid region, which in turn means that a higher overall concentration must be chosen. The variations of the maximum COP with $\Delta T_{\text{min}}$ are represented in Figure 4.12 for example 2.3, at a suction pressure of 3 bar. The maximum
Figure 4.10: Temperature profiles, for example 1.3, at several overall concentrations and for a suction pressure $p_i = 2$ bar.
COP always varies linearly with $\Delta T_{\text{min}}$, for all the cases where a real maximum exists (therefore not for cases like example 3.2 (see Figure 4.5c) or example 1.1 for $p_1 < 3$ bar (see Figure A.1a, Appendix A). This can easily be explained if one remembers that at the optimal concentration, the mean temperature difference is almost equal to the minimum temperature difference (see Figure 4.13), which means that the mean temperature at the resorber and desorber refrigerant side is an almost linear function of $\Delta T_{\text{min}}$. The COP, that is strongly related to the ratio of the resorber mean temperature (refrigerant side) with the difference between the resorber and desorber mean temperatures (refrigerant side), is therefore also an almost linear function of $\Delta T_{\text{min}}$. In cases where $\Delta T_{\text{min,r}}$ and $\Delta T_{\text{min,d}}$ are not identical, it is obvious that the maximum COP varies linearly with $\Delta T_{\text{min,r}}$ or $\Delta T_{\text{min,d}}$ only if these two variables increase proportionally.

Because the maximum COP corresponds to the overall concentration giving the best glide matching, the mean temperature difference at that point is very close to the minimum temperature difference (see Figure 4.13), at least for those cases where the heat sink and heat source temperature profiles are similar. In efficient modern heat exchangers of the corrugated plate-fin type for instance, minimum temperature differences of 1 K are acceptable, but a mean temperature difference of 1 K is not, because it implies a heat exchange area that is not economically justifiable. In the design study, the COP curves should therefore always be used together with the $\Delta T_{\text{mean}}$ curves. Take, for instance, the curves of Figure 4.11 for $\Delta T_{\text{min}} = 5$ K and $\Delta T_{\text{min}} = 1$ K. The maximum COP (3.9) at $\Delta T_{\text{min}} = 5$ K is achieved at a concentration of 0.44, corresponding to $\Delta T_{\text{mean,r}} = 5.7$ K and $\Delta T_{\text{mean,d}} = 5.2$ K. For $\Delta T_{\text{min}} = 1$ K, the COP will be higher than 3.9 for the concentration range 0.40 - 0.48. At the limits of this range, the COPs of the two curves are equal.

![COP diagram](image)

**Tw$_2$ = 80 °C, Tw$_4$ = 100 °C, Tw$_3$ = 140 °C
\[\text{rres} = 17.94 \text{ kg/s, rdes} = 17.94 \text{ kg/s, COP} = 6.86 \]
\[n_{1s} = 0.70, p_1 = 3 \text{ bar} \]

**Figure 4.11:** Effect of $\Delta T_{\text{min}}$ on the COP curves, for example 2.3, at $p_1 = 3$ bar.
Figure 4.12: Maximal COP as a function of $\Delta T_{\text{min}}$ for example 2.3, at $p_1 = 3$ bar.

Figure 4.13: Evolution of $\Delta T_{\text{mean,cd}}$ with the overall concentration for two different minimum temperature differences.
looking at the corresponding mean temperature differences in Figure 4.13, it appears that these limits correspond to a desorber mean temperature lower than 3.5 K and a resorber mean temperature lower than 4 K. If a mean temperature difference of 2.5-4 K is considered reasonable, it would be better to work at an overall concentration of 0.46 (COP = 4.0) that will produce $\Delta T_{\text{mean}, r} = 3.6$ K and $\Delta T_{\text{mean}, d} = 2.5$ K at a $\Delta T_{\text{min}}$ of 1 K. However, if a mean temperature difference of 5-6 K is necessary, it would be better to work at $x_0 = 0.44$ and $\Delta T_{\text{min}} = 5$ K (COP = 3.9) than at $x_0 = 0.38$ and $\Delta T_{\text{min}} = 1$ K (COP = 3.4). Both will produce the same mean temperature differences in the resorber and in the desorber ($\Delta T_{\text{mean}, r} \approx 6$ K, $\Delta T_{\text{min}, d} \approx 5$ K), but because the glide fitting is better in the former case than in the latter, better performances are achieved.

### 4.5.5 The effect of $\eta_{is}$ on the COP

The evolution of the COP with the isentropic efficiency is shown in Figure 4.14 for example 2.2. The isentropic efficiency does not have very much effect on the optimal concentration. As can be seen in Figure 4.15 the curve of the COP plotted against the isentropic efficiency follows accurately Equation (2.18), that was established for pure refrigerants, but has a more general validity. It was expected from Bergmann [1990] that at a lower isentropic efficiency the cycle (i.e. the temperature $T_1$) could be achieved at a lower discharge pressure (see Figure 4.16). This was not confirmed by our simulations, that show that the isentropic efficiency has absolutely no effect on the discharge pressure $p_2$, but does affect the discharge temperature $T_1$ (see Figure 4.17). This is because Bergmann did not take into account the external conditions. When taking them into account, it appears that a lower discharge pressure also means, at constant $T_1$, a lower temperature profile ($T_4$ decreases) and therefore leads to a mean temperature difference lower than the prescribed one. Thus generally, the temperature $T_1$ must be increased in order to satisfy the condition on the temperature approach, so that no reduction of the pressure ratio can be expected.

![Figure 4.14:](image)

*Figure 4.14: Evolution of the COP curves with $\eta_{is}$, for example 2.2, at $p_1 = 2$ bar.*
Tw2 = 60 °C, Tw4 = 70 °C, Tw3 = 90 °C
\( \dot{m}_{\text{res}} = 11.96 \text{ kg/s}, \dot{m}_{\text{des}} = 11.96 \text{ kg/s}, \text{COR} = 12.10 \)
\( \Delta T_{\text{min}} = 5 \text{ K}, p_1 = 2 \text{ bar} \)

**Figure 4.15:** Comparison between the calculated COP and the COP predicted by Equation (2.18), for two different overall concentrations.

\[ \text{COP} = n_\text{is}(\text{COP}_{n\text{-is}} - 1) + 1 \quad x_0 = 0.396 \quad x_0 = 0.616 \]

**Figure 4.16:** Effect of the isentropic efficiency on the pressure ratio and on the resorber temperature profile when the discharge temperature \( T_3 \) is constant.

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Tw2 = 60 °C, Tw4 = 70 °C, Tw3 = 90 °C

\[ \text{\(\dot{m}_{\text{res}} = 11.96 \text{ kg/s, } \dot{m}_{\text{des}} = 11.96 \text{ kg/s, } \text{COP}_{\text{a}} = 12.10\)} \]
\[ \Delta T_{\text{min}} = 5 \text{ K, } p_1 = 2 \text{ bar} \]

T3 (°C)

\[ x_0 = 0.396 \quad x_0 = 0.616 \]
\[ p_2 = 20.0 \text{ bar} \]
\[ p_2 = 8.4 \text{ bar} \]

**Figure 4.17:** Evolution of the discharge temperature \( T_3 \) and pressure \( p_2 \) with the isentropic efficiency for two different overall concentrations.

### 4.5.6 The effect of the source and sink mass flow rates on the COP

Although the heat source and heat sink mass flow rates are fixed for each application, it is interesting to notice how they influence the shape of the COP curve. The COP curves for several heat source mass flow rates are drawn in **Figure 4.18**, at constant heat sink mass flow rate. Of course the COP decreases with \( m_{\text{des}} \), since it implies a decreasing \( T_1 \), and the heat pump must therefore overcome a higher temperature lift. The greater the difference between the heat source mass flow rate and the heat sink mass flow rate, the broader becomes the bell-shaped curve. As already indicated in Section 4.5.2, this arises directly from a mismatch between the overall concentrations ensuring a minimal \( \Delta T_{\text{mean}} \) in the desorber and in the resorber. This is clearly illustrated in **Figure 4.19**. In **Figure 4.19a**, the resorber has a minimum \( \Delta T_{\text{mean, in}} \) at \( x_\alpha = 0.62 \), whereas \( \Delta T_{\text{mean, d}} \) reaches its minimum only at \( x_\alpha = 0.72 \), which explains the broad shape of the COP curve. In **Figure 4.19b**, where the heat sink and heat source mass flow rates are equal, the \( \Delta T_{\text{mean}} \) curves are well matched, and reach their minimum at \( x_\alpha = 0.40 \), which explains the sharp shape of the COP curve. In **Figure 4.19c**, a broader shape would be expected for the same reasons as in **Figure 4.19a**. This does not occur because \( \Delta T_{\text{mean, d}} \) has no minimum value, because the overall concentration limit is reached before. In that case, the optimum COP depends only on the location of the resorber minimum \( \Delta T_{\text{mean, in}} \).
4.5.7 The effect of internal heat exchange on the COP

Internal heat exchange of the evaporative type, where the heat released by subcooling the liquid at the end of the resorption process is used to further heat the desorber (heat exchange between 4-4e and 2e-2 in Figure 4.2), always has a positive effect on the COP, at least when the external conditions and the chosen $\Delta T_{\text{min}}$ allow for its use. The COP increase is illustrated in Figure 4.20 for example 3.1 and in Figure 4.22 for example 1.3. The reasons for this positive effect have already been studied in Section 3.5. Figures 4.21 and 4.23 show that the COP increase corresponds to a decrease of the pressure ratio, owing to the fact that point 2 shifts toward the higher vapour quality and therefore makes the achievement of a lower $T_1$ possible at a lower discharge pressure. At the same time, the resorption width (line 3-4) increases, allowing for a lower refrigerant mixture mass flow rate. This contributes to a further decrease of the compressor work and thus to an increase of the COP.

Reservations concerning the use of absorptive-evaporative heat exchange for heat pump applications have already been expressed in Section 3.5, but we now briefly return to this subject. In this kind of heat exchange, part of the resorption heat is used together with the subcooling heat, to further heat the desorber. Two calculations have been made for each of the 9 examples studied. In the first case 10 % and in the second case 25 % of the resorber heat (without subcooling by internal heat exchange) is used together with the subcooling heat in internal heat exchange. In example 3.1 (Figure 4.20), where there is no overlap between the resorber and desorber temperatures, a decrease of the COP is observed, as compared to the COP of the cycle with simple evaporative heat exchange. In example 1.3 (Figure 4.22), where there is a broad temperature overlap between

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**Figure 4.18:** Effect of the relative values of the mass flow rates of the heat source and of the heat sink on the COP, for example 2.2, $p_1 = 2$ bar.
Figure 4.19: Mean temperature differences in the desorber and in the resorber for different values of the heat source mass flow rate, for example 2.2, $p_1 = 2 \text{ bar}$. 

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**Figure 4.20:** Effect of internal heat exchange on the COP, for example 3.1, $p_1 = 6$ bar.

**Figure 4.21:** Effect of internal heat exchange on the pressure ratio, for example 3.1, $p_1 = 6$ bar.

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Figure 4.22: Effect of internal heat exchange on the COP, for example 1.3, \( p_1 = 2 \text{ bar} \).

Figure 4.23: Effect of internal heat exchange on the pressure ratio, for example 1.3, at \( p_1 = 2 \text{ bar} \).
desorber and resorber, the COPs are equal. No COP gain is achieved, but the pressure ratios in both cases are decreasing when absorptive heat exchange is applied. That this decrease in pressure ratio does not result in a COP increase could be due to the fact that the increase in resorption width and the decrease in work do not compensate the 10 or 25% heat lost in internal heat exchange, which leads to an increase in the refrigerant mass flow rate. However, it is observed that in all cases, the mass flow rate decreases. The real explanation must be found – as already explained in Section 3.5 - in the even lower slope of the isentropic line in the T-h diagram, when point 2 shifts to the right. The lower the slope of the isentropic line, the higher the compressor work and, at a certain point, the increase in compressor work is no longer compensated by the refrigerant mass flow rate decrease. Equation (3.8) is no longer verified and the COP decreases.

4.5.8 Evolution of the cycle’s temperatures

In order to make clear the behaviour of the wet compression-resorption cycle, the evolution of the cycle’s temperatures are shown in Figure 4.24 for example 2.3 at a suction pressure of 3 bar. The same kind of curves are observed in all examples. At lower concentrations, the resorber pinch point is located at the hot end (see Figure 4.8), \( T_3 \) therefore remains constant and the overall concentration increase has only the effect of reducing the pressure ratio (see Figure 4.6), at the same time decreasing \( T_4 \), the resorber cold end temperature. Since \( p_1 \) is fixed, an increase in the overall concentration means a lower temperature course in the desorber. The pinch point is located at the desorber cold end, which makes possible to work at a higher \( T_3 \). However, from a given value of the overall concentration, the shape of the isobars becomes nonlinear (see appendix D), making the resorber pinch point shift towards the resorber cold end and thus \( T_3 \) becomes higher and higher. The same happens in the desorber, where the pinch point shifts towards the hot end with the consequence of an even lower \( T_1 \). One can also observe that for overall concentrations higher than the optimal one, the heat sink outlet temperature \( T_{w1} \), which is not fixed in this model, remains almost constant, owing to the small variations of \( Q_{des} \) (see Figure 4.25). In Figure 4.24, the temperature \( T_{in} \) achieved by the Lorenz cycle is represented, as well as the water temperature at point 1 in the case where a pure refrigerant is used (\( T_{w1PR} \)).

4.5.9 The compressor work and the heat exchangers capacities

The compressor work, as well as the resorber, desorber and internal heat exchanger heating or cooling capacities are represented in Figure 4.25. Of course the resorber capacity remains constant and the optimal overall concentration corresponds to a minimal compressor work, and therefore, according to the first law of thermodynamics, to a maximal desorber capacity. The evolution of the internal heat exchanger capacity is remarkable, since at low concentrations, more heat is spent in internal heat exchange, than is made useful. This high internal heat exchanger rate is to be explained by the relatively high \( T_4 \) temperature, that allows considerable boosting of the desorption process towards higher temperatures.

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**Figure 4.24:** Evolution of the cycle’s temperatures, for example 2.3, \( p_1 = 3 \text{ bar} \).

**Figure 4.25:** Evolution of the compressor work and of the desorber and heat exchanger capacities, for example 2.3, \( p_1 = 3 \text{ bar} \).
4.6 Specific compressor displacement analysis

The specific compressor displacement is defined as being the compressor inlet volumetric capacity necessary to achieve 1 kW heating capacity at the resorber. It is expressed in m³/kJ or in m³/s/kW, and in fact is the volume flow rate at point 2 divided by the resorber capacity. Two calculations have been achieved; the first one taking into account the vapour volume flow rate only, and the second one both the vapour and liquid volume flow rates. For the latter, the calculations have been achieved by using a zero-slip flow model: the total density of the two-phase flow is calculated by Equation (4.31), where the void fraction \( \alpha \), equal to the phase volume fraction (Oliemans [1990]) is given by Equation (4.32).

\[
\rho_2 = \alpha \rho_{l2} + (1 - \alpha) \rho_{v2}
\]  
\[\tag{4.31}\]

\[
\alpha = \frac{V_{l2}}{V_{l2} + V_{v2}}
\]  
\[\tag{4.32}\]

The total refrigerant volume flow rate is then:

\[
\dot{V}_2 = \frac{m_v}{\rho_2}
\]  
\[\tag{4.33}\]

However, the results of the two calculations (vapour only and zero-slip flow) are very similar. The result of the SCD calculated by taking into account the liquid as well as the vapour is slightly higher than for the calculation with the vapour only, but the difference never exceeds 5%. This is because the difference between liquid and vapour density is such that even a high liquid mass flow rate (>50%) produces a negligible liquid volume flow rate. There is therefore no real compressor capacity decrease to be expected when applying wet compression - at least when no extra liquid injection is needed to seal and/or cool the compressor.

**Behaviour of the SCD:** the SCD curves, as function of the overall concentration and of the suction pressure for example 2.3, are presented in Figure 4.26. As expected, the higher the overall NH\(_3\) concentrations, the lower the SCD, because the proportion of the lighter component increases. Optimizing the SCD comes down to choosing the highest possible overall concentration, which is contrary to optimizing the COP. However, if the SCD decrease is rapid at low concentration, its variations become rather slow once the optimal overall concentration with regard to the COP is passed. In this way, optimizing the COP will not lead to an inadequate SCD. The shape of the SCD curves is closely related to that of the total refrigerant mass flow rate, that is represented in Figure 4.27. Indeed, the lower
the overall concentration, the smaller the resorption width and the higher the refrigerant mass flow rate needed to achieve the required heating capacity. However, at higher concentrations (see Appendix D), the resorption width grows more slowly and so does the mass flow rate. The influence of the mass flow rate is combined with that of the density and that of the vapour quality at point 2: the higher the suction pressure at constant mass flow rate, the lower the SCD. However, at constant suction pressure the influence of the density is limited, since $T_2$ remains almost constant. The overall concentration and the mass flow rate have the most effect on the SCD.

**Effect of the internal heat exchange on the SCD:** It is interesting to notice that evaporative heat exchange has a positive impact not only on the COP, but also on the SCD, as illustrated in Figure 4.28, for example 3.1. The explanation can be found in the related mass flow rate decrease. However the application of absorptive-evaporative heat exchange produces an increase of the SCD. This is due to the fact that both the vapour quality and the vapour density at point 2 increase in such a way (with internal heat exchange, point 2 shifts to the right in the T-h diagram) that it counter-balances the decrease in total mass flow rate. For the SCD as for the COP, evaporative heat exchange is therefore to be recommended, whereas absorptive-evaporative heat exchange should usually be avoided.

![SCD figure](image)

**Figure 4.26:** Evolution of the SCD with the overall concentration and the suction pressure, for example 2.3.
Tw2 = 80 °C, Tw4 = 100 °C, Tw3 = 140 °C
\( \dot{m}_{\text{res}} = 17.94 \text{ kg/s}, \dot{m}_{\text{des}} = 17.94 \text{ kg/s}, \text{COP}_t = 6.86 \)
\( n_{\text{is}} = 0.70, \Delta T_{\text{min}} = 5 \text{ K} \)

**Figure 4.27:** Evolution of the total mixture mass flow rate with the overall concentration and the suction pressure.

Tw2 = 31 °C, Tw4 = 52 °C, Tw3 = 60 °C
\( \dot{m}_{\text{res}} = 14.90 \text{ kg/s}, \dot{m}_{\text{des}} = 40.00 \text{ kg/s}, \text{COP}_t = 12.49 \)
\( n_{\text{is}} = 0.70, \Delta T_{\text{min}} = 5 \text{ K}, p_1 = 6 \text{ bar} \)

**Figure 4.28:** Effect of the internal heat exchange on the SCD, for example 3.1, \( p_1 = 6 \text{ bar} \).

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4.7 Second law analysis

4.7.1 Reasons for an entropy analysis

The COP analysis is often termed the First Law analysis because it is primarily based on the first law Equation (4.34). However, full account is taken of the Second Law of thermodynamics when calculating the COP because all cycle’s irreversibilities must be compensated for in terms of a supplementary work input. The First Law does indeed say that the sum of the internal energy difference of each of the components of the cycle is zero, that is, for a heat pump cycle with isenthalpic expansion:

\[ W = Q_{res} \times Q_{doc} \]  \hfill (4.34)

The entropy being a state function, the sum of the entropy difference of each of the components of the cycle is also zero. Therefore, total entropy production of the heat pump system, considered as being the internal cycle together with the heat source and the heat sink, is the sum of the entropy production at the heat sink and of the entropy production at the heat source:

\[ \Delta S_{total} = \dot{m}_{sink}(s_{s,1} - s_{in}) + \dot{m}_{source}(s_{s,1} - s_{in}) \]

\[ - \int_{1}^{2} \frac{dQ_{res}}{T} - \int_{2}^{1} \frac{dQ_{des}}{T} \]  \hfill (4.35)

Since points w3, w4, w2, as well as \( \dot{m}_{sink} \) and \( \dot{m}_{source} \) are the fixed external conditions, only point w1 can change as result of changes in the internal cycle (concentration or pressure variations, irreversibilities). For the Lorenz cycle, point w1 is such that \( \Delta S_{total} = 0 \). For any other cycle, the irreversibilities will lead to a higher entropy at point 1 (see Chapter 3), thus to a higher \( \Delta S_{total} \), and therefore to a lower desorber cooling capacity (right term of Equation (4.35)). This in turn leads, via Equation (4.34), to a higher compressor work.

However, although the COP reflects the total irreversibilities of the cycle, it says nothing about the location of these irreversibilities and their relative values. The Second Law analysis is the right tool to obtain this information, which is of great importance when optimizing the components. Referring to Figures 4.1 and 4.2, the total entropy increase is defined by Equation (4.36):

\[ \Delta S_{total} = \dot{m}_{sink}(s_{2e} - s_{1}) + (s_{2o} - s_{2e}) + (s_{1} - s_{2}) + (s_{4} - s_{3}) +
\]

\[ (s_{4e} - s_{4}) + (s_{1} - s_{4e})] + \dot{m}_{sink}(s_{s,1} - s_{in}) + \dot{m}_{source}(s_{s,1} - s_{in}) \]  \hfill (4.36)
where the sum between the square brackets (entropy difference sum on the complete internal cycle) is equal to zero. The equation can be rearranged to form (Equation 4.37):

$$\Delta S_{total} = \Delta S_{res} + \Delta S_{des} + \Delta S_{ex} + \Delta S_{comp} + \Delta S_{e.v.}$$  \hspace{1cm} (4.37)$$

with

$$\Delta S_{res} = \dot{m}_{o}(s_4 - s_3) + \dot{m}_{sol}(s_{w1} - s_{w4})$$  \hspace{1cm} (4.38)$$

$$\Delta S_{des} = \dot{m}_v(s_{2e} - s_1) + \dot{m}_{wur}(s_{w1} - s_{w2})$$  \hspace{1cm} (4.39)$$

$$\Delta S_{ex} = \dot{m}_v [(s_{4e} - s_4) + (s_2 - s_{2e})]$$  \hspace{1cm} (4.40)$$

$$\Delta S_{comp} = \dot{m}_v (s_3 - s_2)$$  \hspace{1cm} (4.41)$$

$$\Delta S_{e.v.} = \dot{m}_s (s_1 - s_{4e})$$  \hspace{1cm} (4.42)$$

Therefore, it is easy to calculate the entropy losses of each component of the cycle, since only simple entropy balances are needed. At the refrigerant side, all entropies can be calculated from the Gibbs energy, which is made in the subroutines of DOTHERM. The same program can be used at the source and sink sides if water or steam is concerned, or Equation (4.43) may be used if the specific heat can be considered as constant in the desired temperature interval.

$$\Delta S_{\Delta B} = \dot{m}c_p \ln \frac{T_B}{T_A}$$  \hspace{1cm} (4.43)$$

Finally, a few words about the choice of the entropy-based analysis instead of the exergy-based analysis, which is often preferred in the refrigerating world. By definition (see, for instance, Townsend [1980]), the exergy is the potential of a process to produce work at a certain reference temperature. This raises two problems. The first one is that in a heat pump or refrigerating machine application, the quantity of work that could be produced by a heat exchanger is not relevant. The problem is to know whether heat is produced in the most effective way. The second problem is the arbitrary choice of the reference temperature. Should it be the inside or outside air temperature, the inlet temperature of the heat sink, the inlet or outlet temperature or the mean temperature of the heat source? The right choice of this reference temperature is crucial since the exergy is a semi-state function i.e the entropy losses are independent of the path followed by the transformation.
but not independent of the reference temperature. The entropy analysis leads to unambiguous results, because no arbitrary temperature is used. This subject has been addressed in detail by Alefeld [1987], Alefeld [1989] where a method for calculating the COP from the Second Law is also proposed. This subject has been very recently treated again by van der Ree [1997] and Infante Ferreira [1997], who demonstrates that to obtain consistent results in the exergy analysis of a heat pump, the reference temperature should be chosen as the logarithmic mean temperature of the heat source.

4.7.2 Distribution of the entropic losses

The entropic losses of each component, calculated with Equations 4.37 to 4.42 are represented as a function of the overall concentration, for example 1.3 (Figure 4.29), 2.3 (Figure 4.30) and 1.1 (Figure 4.31). The right axis shows the total entropy losses. Of course, the total entropy losses vary inversely with the COP (see Figure 4.5 or Appendix A); at a minimum $\Delta S_{\text{total}}$ there is a corresponding maximum COP. It also appears that the variations of $\Delta S_{\text{total}}$ are largely controlled by the entropic losses in the compressor, when its efficiency is not very high (see Figures 4.29, 4.30 and 4.33). However, the resorber and desorber losses can be high enough to strongly influence the total entropy losses (see Figure 4.31 and Section 4.7.3). It should also be remembered that minimum entropic losses of a component do not necessarily mean that the specific entropy difference for this component is minimum; the influence of the external conditions via the total refrigerant mass flow rate can be dominant in such a way that a minimal mass flow rate can create minimum entropic losses at non-minimum specific entropic losses.

As expected, the losses in the desorber and in the resorber show the same evolution as that of the mean temperature difference (compare Figure 4.9 with Figure 4.29 and Figure 4.7 with Figure 4.30): the better the internal and external temperature profiles matches, the lower the isentropic losses, thus the lower the compressor work and the higher the COP (see also Section 4.7.4). The entropic losses in the internal heat exchanger always decrease with the overall concentration, which can be explained from the evolution of the temperature at point 4 and point 2 (see Figure 4.24) and thus from the glide matching between the two streams. The $\Delta T_{\text{mean}}$ curve for the heat exchanger in example 1.3 is given in Figure 4.32 and is to be compared with the heat exchanger irreversibilities in Figure 4.29.

The entropic losses in the expansion valve show several behaviours: the loss may remain almost constant (Figure 4.29), increase with the overall concentration (Figure 4.30), or decrease (Figure 4.31), depending on the relative temperatures and pressures at points 4c and 1 and on the slope of the isentropic lines in the T-h diagrams at each overall concentration.

Lastly, it should be noted that the contribution of each component to the cycle's irreversibilities strongly depends on the overall NH$_3$ concentration. At low concentrations, the irreversibilities in the internal heat exchanger may be as high as the irreversibilities of the compressor, whereas they become almost negligible at high concentrations. In some
Figure 4.29: Entropy generation of each component of the cycle, for example 1.3, $p_1 = 2$ bar.

Figure 4.30: Entropy generation of each component of the cycle, for example 2.3, $p_1 = 3$ bar.
Figure 4.31: Entropy generation of each component of the cycle, for example 1.1, $p_1 = 4$ bar.

Figure 4.32: Evolution of the the mean temperature difference in the internal heat exchanger, for example 1.3.
Figure 4.33: Contribution of each component to the cycle’s irreversibilities for the studied applications, at the optimal $x_i$, corresponding to the chosen suction pressure.
cases (see Figure 4.29), the relative contributions of the desorber and resorber are reversed from a certain value of the overall concentration.

In Figure 4.33 the distribution of the entropic losses for the optimal overall concentration (at a given suction pressure) of each of the nine examples, is given. As indicated above, the general trend is that, as with conventional pure refrigerant compression systems (see for instance Alefeld [1987]), the greater part of the irreversibilities comes from the compressor. Depending on the compressor isentropic efficiency, this represents 20 to 55% of the total losses. Example 1.1 (Figure 4.33a) is an exception that will be explained in Section 4.7.3. In all cases, the desorber and resorber irreversibilities are very close to each other, sometimes a little bit higher in the desorber, sometimes a little bit higher in the resorber. This similarity is due to the fact that, with the exception of the mass transfer, which is not taken into account in this model, these two devices work in a similar way and at the refrigerant side their temperature glides are comparable. The degree of irreversibility then depends on whether the best glide matching is achieved in the desorber or in the resorber. The irreversibilities due to the expansion valve are rather important, as they can represent up to 25% of the total entropic losses and be as high, or even higher than, the losses in the resorber and in the desorber. The effect of the liquid subcooling via the internal heat exchanger will be studied in Section 4.7.5. As logically expected, the higher the ratio $\Delta T_{\text{inh}}/\Delta T_{\text{glide}}$, the higher the losses introduced by the internal heat exchange (compare a, b and c in Figure 4.33), because the mean temperature difference between the two streams of the internal heat exchanger increases. This explains the limits of the use of an internal heat exchanger.

### 4.7.3 Effect of $\eta_{\text{inh}}$ on the entropic losses

According to Figure 4.33, in most cases the main losses arise in the compressor, which is therefore the first component that should be optimized. Indeed, gaining 10% on the resorber losses has little effect if the compressor losses are 5 or 6 times higher than the losses in the other components. A first step in optimizing the cycle should be to reduce the compressor isentropic losses to about the size of the losses in the other components by increasing the isentropic efficiency. The variation in the entropic losses with compressor isentropic efficiency are shown for example 1.1 in Figure 4.34 and for example 3.1 in Figure 4.35, at the point of optimal concentration. The isentropic efficiency necessary to reduce the compressor losses to the size of those of the other components depends on the application and particularly on the heat pump temperature lift, since, together with the minimum temperature difference, this controls the pressure ratio. At constant compressor isentropic efficiency, the lower the temperature lift, the lower the entropic losses. This explains that in example 1.1 ($\Delta T_{\text{inh}} = 3$ K), Figure 4.33a, the irreversibilities in the compressor with $\eta_{\text{inh}} = 0.8$ are less than in the desorber and resorber, whereas in examples 2.2 and 3.2, which have higher isentropic efficiency ($\eta_{\text{inh}} = 0.85$), the compressor irreversibilities remain higher than in the resorber and desorber, because of the much higher $\Delta T_{\text{inh}}$ (30 and 60 K respectively). Note that the optimal concentration can vary slightly with $\eta_{\text{inh}}$. As explained above, in the case of example 1.1, an isentropic efficiency of 0.7 is enough to have comparable irreversibilities in the compressor, resorber and desorber. In example 3.1, as in all other applications presented in this chapter, an
Tw$_2$ = 12 °C, Tw$_4$ = 10 °C, Tw$_3$ = 15 °C  
\( \dot{n}_{\text{res}} = 23.92 \text{ kg/s}, \dot{n}_{\text{des}} = 42.72 \text{ kg/s}, \text{COP} = 151.5 \)  
\( \Delta T_{\text{min}} = 5 \text{ K}, p_1 = 4 \text{ bar} \)

\( \Delta S \) (kW/K)

\[ \begin{array}{c}
0.6 \\
0.55 \\
0.5 \\
0.45 \\
0.4 \\
0.35 \\
0.3 \\
0.25 \\
0.2 \\
0.15 \\
0.1 \\
0.05 \\
0 \\
0.1 \\
0.2 \\
0.3 \\
0.4 \\
0.5 \\
0.6 \\
0.7 \\
0.8 \\
0.9 \\
1 \\
\end{array} \]

nis

\[ \begin{array}{c}
0 \\
0.1 \\
0.2 \\
0.3 \\
0.4 \\
0.5 \\
0.6 \\
0.7 \\
0.8 \\
0.9 \\
1 \\
\end{array} \]

Figure 4.34: Variations of the irreversibilities with \( \eta_{\text{op}} \) for example 1.1, \( p_1 = 4 \text{ bar} \), at the optimal \( x_{\text{op}} \).

Tw$_2$ = 31 °C, Tw$_4$ = 52 °C, Tw$_3$ = 60 °C  
\( \dot{n}_{\text{res}} = 14.90 \text{ kg/s}, \dot{n}_{\text{des}} = 40.00 \text{ kg/s}, \text{COP} = 12.49 \)  
\( \Delta T_{\text{min}} = 5 \text{ K}, p_1 = 6 \text{ bar} \)

\( \Delta S \) (kW/K)

\[ \begin{array}{c}
0.6 \\
0.55 \\
0.5 \\
0.45 \\
0.4 \\
0.35 \\
0.3 \\
0.25 \\
0.2 \\
0.15 \\
0.1 \\
0.05 \\
0 \\
0.1 \\
0.2 \\
0.3 \\
0.4 \\
0.5 \\
0.6 \\
0.7 \\
0.8 \\
0.9 \\
1 \\
\end{array} \]

nis

\[ \begin{array}{c}
0 \\
0.1 \\
0.2 \\
0.3 \\
0.4 \\
0.5 \\
0.6 \\
0.7 \\
0.8 \\
0.9 \\
1 \\
\end{array} \]

Figure 4.35: Variations of the irreversibilities with \( \rho_{\text{op}} \) for example 3.1, \( p_1 = 6 \text{ bar} \), at the optimal \( x_{\text{op}} \).
Figure 4.36: Contribution of each component to the cycle’s irreversibilities for $\eta_i = 0.85$, at the optimal $x_v$.

isentropic efficiency of at least 0.75 is necessary. Of course, the more efficient the resorber and desorber (that is, the lower the mean temperature difference between the streams), the higher should be the compressor isentropic efficiency. The new distribution of the losses at an isentropic efficiency of 0.85 is given for a few examples in Figure 4.36, for the optimal concentration. To conclude this section, one can say that if one wishes to avoid creating unreasonable losses in the compressor, a wet compressor with an isentropic efficiency of at least 0.75 should be developed.

However, the effect of increasing the isentropic efficiency decreases as the isentropic efficiency increases, because the irreversibilities introduced by the other components of the cycle form an even larger proportion of the total entropy losses. Therefore, above a compressor isentropic efficiency of about 0.75, it becomes of interest to optimize the other components also.

4.7.4 Effect of $\Delta T_{\text{min}}$ on the entropic losses

One way of reducing the irreversibilities is to reduce $\Delta T_{\text{min}}$ in the resorber and desorber. Section 4.5.4 implies that this happens linearly (linear variations of the COP with $\Delta T_{\text{min}}$ in Figure 4.12). As can be seen in Figure 4.37, this is indeed the case, because at the optimal $x_v$, the mean temperature difference is almost equal to the minimum temperature.
Tw2 = 80 °C, Tw4 = 100 °C, Tw3 = 140 °C
Φres = 17.94 kg/s, Φdcs = 17.94 kg/s, COP = 6.86
n_{is} = 0.70, p1 = 3 bar

△S (kW/K)

△ T_{min} (K)

**Figure 4.37:** Variations of the entropy losses with △T_{min} for example 2.3, p1 = 3 bar, at the optimal x_{ro}.

difference. The fact that the temperature profiles do not match each other perfectly is illustrated by the fact that the isentropic losses in the desorber at △T_{min} = 0 K are not zero. In the present example, the match in the resorber is almost perfect.

The variations of the entropy losses in the internal heat exchanger are not linear because △T_{mean} depends not only on △T_{min} but also on the temperatures at point 4 and 2c. However, the way in which one can reduce the irreversibilities in the heat and mass exchangers is intrinsically limited by the driving temperature difference necessary to allow for heat exchange. In current high efficiency heat exchangers, minimum temperature differences of less than 1 K are achieved, but for economic reasons, a mean temperature difference under the limit of 3 to 5 K is not acceptable.

### 4.7.5 Effect of the internal heat exchange on the entropic losses

As already emphasized in Section 3.5 and in Section 4.5.7, one of the effects of internal heat exchange is to reduce the throttling losses by subcooling the high pressure liquid. **Figures 4.37 and 4.38** show that internal heat exchange indeed drastically reduces the entropic losses in the expansion valve - by 23 % in example 3.1 and 37 % in example 1.3. However it introduces a new irreversibility, due to the presence of the internal heat exchanger. When evaporative heat exchange only is applied, the sum of the heat exchanger
$Tw_2 = 31 \degree C, Tw_4 = 52 \degree C, Tw_3 = 60 \degree C$

$n_{res} = 14.90 \text{ kg/s}, \dot{m}_{des} = 40.00 \text{ kg/s}, \text{ COP}_{L} = 12.49$

$n_{is} = 0.70, \Delta T_{min} = 5 \text{ K}, p_1 = 6 \text{ bar}$

$\Delta S \text{ (kW/K)}$

0.1

0.09

0.08

0.07

0.06

0.05

0.04

0.03

0.02

0.01

0

no heat exchanger

evaporative H.E.

absorptive H.E. (10%)

absorptive H.E. (25%)

Figure 4.38: Influence of the internal heat exchange on the entropic losses distribution, for example 3.1, $p_1 = 6 \text{ bar}$, optimal $x_o^\circ$

$Tw_2 = 25 \degree C, Tw_4 = 15 \degree C, Tw_3 = 85 \degree C$

$n_{res} = 3.42 \text{ kg/s}, \dot{m}_{des} = 9.21 \text{ kg/s}, \text{ COP}_{L} = 9.09$

$n_{is} = 0.67, \Delta T_{min} = 5 \text{ K}, p_1 = 2 \text{ bar}$

$\Delta S \text{ (kW/K)}$

0.25

0.225

0.2

0.175

0.15

0.125

0.1

0.075

0.05

0.025

0

no heat exchanger

evaporative H.E.

absorptive H.E. (10%)

absorptive H.E. (25%)

Figure 4.39: Influence of the internal heat exchange on the entropic losses distribution, for example 1.3, $p_1 = 2 \text{ bar}$, optimal $x_o^\circ$
and expansion valve irreversibilities remains lower than when no internal heat exchange is applied, which has a positive influence on the COP (see Figures 4.20 and 4.22). However, when absorptive-evaporative heat exchange is applied, the throttling losses do not decrease much in comparison with simple evaporative heat exchange because points 4e and 1 remain more or less constant. But because absorptive heat exchange considerably increases the quantity of heat exchanged, the internal heat exchanger irreversibilities also increase considerably, in such a way that the gain resulting from the liquid subcooling is totally canceled by the losses introduced by the heat exchanger, with the known consequences on the COP. One can observe in Figures 4.38 and 4.39 that internal heat exchange also has repercussions on the desorber and resorber entropic losses. In both the applications that are represented, internal heat exchange decreases the desorber irreversibilities, because it allows better glide matching, whereas the opposite happens in the resorber.

4.8 Comparison with the solution recirculation cycle and the pure refrigerant cycle

In this section, the comparative advantages of the wet compression cycle, of the solution recirculation cycle and of the pure refrigerant cycle will be studied in terms of COP and UA values, as well as in terms of second law efficiency. The analysis has been performed for the maximal achievable COP of each of the cycles, within the limits of the suction pressure being higher than atmospheric pressure and of the discharge pressure being lower than 25 bar, to avoid the use of high pressure equipment. Only in example 3.3, was it impossible to remain within these limits and the discharge pressure reached the level of 26.7 bar for the wet compression cycle and the level of 37.5 bar for the solution recirculation cycle.

Appendix B deals with the solution recirculation model and with the comparison between the COP = f(x_v) curves of the wet compression and solution recirculation cycles. When calculating the solution recirculation cycle, the same data set was used as for the wet compression cycle (thus same minimum temperature differences and same compressor isentropic efficiency). The liquid pump efficiency was supposed to be 0.7 in all cases.

4.8.1 COP comparison

Figure 4.40 gives the maximum COP of each of the three cycles, for each application studied. Of course, the COP depends strongly on the external temperature lift to be overcome and is, within each $\Delta T_{\text{lift}}/\Delta T_{\text{glide}}$ class, a decreasing function of it. In all cases the solution recirculation cycle has lower performances than the wet compression cycle. The pure refrigerant cycle, calculated as described in Section 4.3, appears to have lower performances than both the compression -resorption cycles, except for examples 3.1 to 3.3, which have the highest ratio $\Delta T_{\text{lift}}/\Delta T_{\text{glide}}$ (3 to 4). This is in agreement with the analysis described in Section 4.4. Figure 4.41 gives a more detailed comparison of the relative COP increase which is achieved when using a $\text{NH}_3/\text{H}_2\text{O}$ wet compression-resorption cycle.
instead of a pure refrigeration cycle. For each temperature glide class, the COP gain one can expect from using a NH\textsubscript{3}/H\textsubscript{2}O wet compression-resorption decreases strongly as the ratio $\Delta T_{\text{lift}}/\Delta T_{\text{glide}}$ increases. For large values of this ratio, the use of a pure refrigerant cycle can become the most efficient solution. However, the COP gain is not only a function of this ratio. The temperature glide of the heat sink also plays a role, in that the larger this glide, the more beneficial the compression-resorption cycle. This is because the pair NH\textsubscript{3}/H\textsubscript{2}O is better able to fit large temperature glides than small ones, due to its large boiling point temperature difference. To summarise, the compression-resorption cycle has the best potential (as compared with a pure refrigerant cycle) in the case of large temperature glides and low ratios $\Delta T_{\text{lift}}/\Delta T_{\text{glide}}$. COP improvements as high as 30 % (and probably higher because the calculation method overestimates the COP of the pure refrigerant cycle, see Section 4.3) can be achieved. For low and medium resorber temperature glides ($\Delta T_{\text{glide}} \leq 30$ K), it is always advisable to also study a pure refrigerant cycle when the ratio $\Delta T_{\text{lift}}/\Delta T_{\text{glide}}$ is higher than 2.

In Figure 4.42, the relative COP increase that can be achieved when using a wet compression cycle instead of a solution recirculation cycle, has been plotted against the ratio $\Delta T_{\text{lift}}/\Delta T_{\text{glide}}$ and against the temperature lift. Within each ratio class, the higher the temperature lift, the higher the COP of the wet compression cycle in comparison with the COP of the solution recirculation cycle. However, a given temperature lift can produce very different COP improvements, depending on the other cycle’s conditions, making the use of simulations unavoidable. This is in accordance with the analysis of Section 2.3.3.2. The main conclusion of the present section is that a COP increase up to 14 % can be achieved by using wet compression instead of solution recirculation.
Figure 4.41: Relative COP gain when using a NH3/H2O wet compression-resorption cycle instead of a pure refrigerant cycle.

Figure 4.42: Relative COP gain when using a wet compression-resorption cycle instead of a solution recirculation cycle.

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4.8.2 UA-values comparison

The UA-values for the resorber, the desorber, the internal heat exchanger and the desuperheater are given for all the cases studied in Figure 4.43. They have been calculated by using Equation (3.4) for both the compression-resorption cycles, and using the logarithmic mean temperature difference for the pure refrigerant cycle. As a direct consequence of the better external temperature glide fitting by the compression-resorption cycles (lower mean temperature difference between the streams), these cycles have much higher UA-values than the pure refrigerant cycle. This important increase is especially visible at temperature glides of about 40 °C (examples 2.3 and 3.3), which correspond to the temperature interval the NH₃/H₂O mixture can fit the best. The strong gain in COP must be paid for in terms of UA-values, that is in terms of heat exchange coefficient or in terms of heat exchange surface. However, this does not mean that at constant UA-value, the use of the compression-resorption cycle does not bring any COP gain, although this gain will be reduced strongly in comparison with the present analysis. This subject has been treated many times in the literature (see for instance Webb [1989] and Vakil [1983]). Furthermore, the boiling and condensing heat transfer coefficients of mixtures are known to be lower than those of the pure components, because of the extra mass transfer resistance and because of their poorer thermophysical properties. This implies that unless means are found to greatly increase the heat transfer, the increase in heat transfer surface needed to get the full potential of the compression-resorption cycles will be much greater.

![UA-values corresponding to the maximum COPs](image)

*Figure 4.43: UA-values corresponding to the maximum COPs.*
than the increase in UA-value described in Figure 4.43. The design of high efficiency heat exchangers which will be sold at competitive prices is therefore of primary interest. For low temperature slides (\( \leq 15 \) K, examples 1.1, 2.1, 3.1), the resorber and desorber UA-values of the wet compression-resorption cycle are less than 1.5 times higher than for the pure refrigerant cycle, whereas at medium temperature glides (between 15 and 30 K, examples 1.2, 2.2, 3.2) they are about twice as high, increasing to 3 to 4 times higher for high temperature glides (> 30 K, examples 1.3, 2.3, 3.3). Getting the maximum potential of the wet compression-resorption cycle with the same heat exchange area as for the pure refrigerant cycle implies an increase in the boiling and condensing heat transfer coefficients of the mixture in the same proportions as described above. This can be difficult, especially in the case of high temperature glides. Using special heating surfaces (rough, structured), with special shapes or producing artificial nucleation sites (Stephan [1995]) might provide a means to improve the boiling heat transfer. Although the heat transfer coefficient for film condensation is much lower for mixtures than for pure components, according to Stephan [1995], it seems that the assumption of film condensation does not hold for condensing mixture vapours at small driving temperature difference. In such cases, stream and/or drop condensation occurs and the heat transfer coefficient can be up to four times greater than that of film condensation.

Lastly it should be observed that in all cases the contribution of the desuperheater in the solution recirculation cycle is negligible. These is partly due to the high mean temperature difference between the streams of this component (superheated vapour/subcooled liquid).

4.8.3 Second law efficiency

The second law efficiency, defined as being the ratio of the cycle’s COP and of the Lorenz’ COP, has been plotted in Figure 4.44, for the wet compression cycle, the solution recirculation cycle and for the pure refrigerant cycle, with the assumption of isentropic compression. All three cycles show the same behaviour: in the same glide class the higher the ratio \( \Delta T_{\text{lift}}/\Delta T_{\text{glide}} \), the better the efficiency. When assuming isentropic compression, the departure from the Lorenz cycle has three main causes: the chosen minimum temperature difference, which is the same for the three cycles; the bad glide matching and the expansion losses. It is evident that the effect of poor glide matching is reduced when the temperature lift increases because the relative work increase due to this poor matching then becomes an even smaller part of the work necessary to achieve the temperature lift (see also Figure 4.4). As expected, and as already observed in Figure 4.41, at high ratios \( \Delta T_{\text{lift}}/\Delta T_{\text{glide}} \) and for moderate temperature glides, the pure refrigerant cycle has a better efficiency than the compression-resorption cycles. However, one must keep in mind that the expansion losses have not been taken into account in the pure refrigerant cycle, whereas they have been in the compression-resorption cycle.

Furthermore it can be observed that within the same \( \Delta T_{\text{lift}}/\Delta T_{\text{glide}} \) class, the increase in the second law efficiency with the temperature glide is more rapid for the wet compression cycle than for the solution recirculation cycle or for the pure refrigerant cycle. This is due to the fact that at large temperature glides the wet compression cycle allows for a better glide matching.

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4.9 Conclusions

The black box model discussed in this chapter has been based on a minimum temperature approach rather than on a constant UA value or on a constant heat exchange area, because this choice permits the calculation of the optimal energy performances of the cycle as well as the corresponding optimal distribution of the UA values. The results of this model emphasise the importance of optimizing for each set of external conditions, the overall concentration, and to a lesser extent, the suction pressure. At the concentration corresponding to the maximum COP, the pressure ratio is at its minimum and the temperature profiles in the resorber and in the desorber are optimized, which does not mean that the glide matching is optimal in both of them (see Figure 4.9). From Appendix A it can be concluded that the general trend is that for heat source temperatures lower than 40 °C, the optimal overall concentration is higher than 0.75; for temperatures between 40 and 65 °C, the optimal concentration is between 0.45 and 0.75; for temperatures higher than 65 °C, the optimal overall concentration is lower than 0.45.

The COP varies linearly with the chosen minimum temperature difference, in so far as ΔT_{min,r} and ΔT_{min,d} vary proportionally. An increase of ΔT_{min} produces an increase in the optimal overall concentration. In a design study, the COP curves should always be used together with the ΔT_{mean} curves to provide an economic parameter. Sometimes a poorer glide matching (ΔT_{mean} > ΔT_{min}) at a lower minimum temperature difference should be
preferred to a better glide matching \( \Delta T_{\text{mean}} = \Delta T_{\text{min}} \) at a higher minimum temperature difference. Internal heat exchange of the evaporative type, where the heat released by subcooling the liquid at the end of the resorber is used to further heat the desorber, always has a positive effect on the COP - when it can be applied. This is not the case for evaporative-absorptive heat exchange, where part of the resorber heat is used together with the subcooling heat to further heat the desorber. This kind of heat exchange has been found to be always disadvantageous for the working pair NH\(_3\)/H\(_2\)O.

The Specific Compressor Displacement (SCD) does not show any maximum, but still decreases with the overall concentration at a rate which is strongly related to the refrigerant mass flow rate. Optimizing the COP together with the SCD is therefore not possible. However, at the optimal concentration with regard to the COP, the SCD is observed to have values not too far from that of the minimal SCD.

The entropy analysis has shown that for a compressor isentropic efficiency lower than about 0.75, the entropy losses in the compressor form the main part of the total entropy losses and are then much higher than the losses in the other components. Minimal entropy losses in the desorber and in the resorber correspond to a minimal mean temperature difference in these components, and the minimal total losses corresponds to the point where the sum of the desorber losses and of the resorber losses is minimal. The irreversibilities due to the expansion valve are rather large, up to 20\% of the total losses and may even be as high as the losses in the resorber and in the desorber. If no internal heat exchanger is used, the losses increase dramatically.

A comparison between the NH\(_3\)/H\(_2\)O wet compression-resorption cycle and the pure refrigerant cycle has shown that the former has the best potential in the case of large heat sink temperature glides (> 30 K) and low ratios \( \Delta T_{\text{lift}}/\Delta T_{\text{glide}} \) (< 2). COP improvements as high as 30\% can then be achieved. At low heat sink temperature glides and high ratios \( \Delta T_{\text{lift}}/\Delta T_{\text{glide}} \), the wet compression-resorption cycle should be thoroughly compared with the pure refrigerant cycle, since the latter could lead to a better COP. A comparison between the wet compression-resorption cycle and the solution recirculation cycle leads to the conclusion that the COP can be improved up to 14\% by using wet compression. At a constant \( \Delta T_{\text{lift}}/\Delta T_{\text{glide}} \) ratio, the COP improvement is an increasing function of the temperature lift.

A comparison of the UA values of these three cycles for the optimal concentration leads to the conclusion that if one wants to use the full potential of the compression-resorption cycles, increased UA values are needed. These UA values may be up to 4 times that of the pure refrigerant cycle at high temperature glides, because of the better glide fitting. This emphasizes the necessity to develop high efficiency compact heat exchangers.

References


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Chapter 5

Comparison between the efficiency of several cycles and refrigerant mixtures

5.1 Introduction

In Chapter 4 the importance of cycle optimization was illustrated by the use of the mixture \( \text{NH}_3/\text{H}_2\text{O} \). For each application, a mixture composition that will provide the closest possible match with the external temperature glides of both the heat source and the heat sink must be selected. However, the quality of the glide matching also depends on the choice of the components of the mixture. Research on the use of zeotropic mixtures to increase the efficiency of the vapour compression cycle started several decades ago. Table 5.1 lists the main authors of publications on this subject, together with the refrigerant pairs they used, most of which are based on R12 or R22. Since the Montreal Protocol, there has been a great increase in the research on non-ozone depleting and environmentally safe refrigerants, and the potential of binary and ternary mixtures of HFCs to replace R22 and R502 has been recognized. However, with the exception of a blend like R407c (R32/R125/R134a), most of these refrigerants are azeotropic or near-azeotropic mixtures. For more information, see Godwin [1994] and Stuij [1995]. Much work has also been done in the field of natural working fluids (see for instance Proceedings IIR (B2) [1994] and [1996]) and notably on hydrocarbon blends for refrigerating (propane/isobutane) and heat pumping applications.

Less attention has been paid to the compression-resorption cycle, since this system is used much less frequently than the vapour compression cycle. However, those researching on mixtures for the compression-resorption cycle can easily take advantage of the results achieved for both the absorption (see for instance Plank [1959], Iedema [1984], Bokelmann [1986], Ruiter [1990] and Nowaczyk [1992]) and compression cycles. Table
<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haselden</td>
<td>1957</td>
<td>propane/n-butane</td>
</tr>
<tr>
<td>Chaikovsky</td>
<td>1963</td>
<td>R13/R12, R22/R12</td>
</tr>
<tr>
<td>Arora</td>
<td>1967</td>
<td>R22/R114</td>
</tr>
<tr>
<td>Garcia</td>
<td>1983</td>
<td>R12/R114</td>
</tr>
<tr>
<td>Camporese</td>
<td>1987</td>
<td>R12/R11</td>
</tr>
<tr>
<td>McLinden</td>
<td>1987</td>
<td>R22/R11, R22/R114</td>
</tr>
<tr>
<td>Webb</td>
<td>1989</td>
<td>R22/R114</td>
</tr>
<tr>
<td>Ambrosino</td>
<td>1989</td>
<td>R22/R11, R23/R22</td>
</tr>
</tbody>
</table>

*Table 5.1: Work on refrigerant mixtures for the vapour compression cycle before 1989.*

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pourreza-Djourshari</td>
<td>1986</td>
<td>R22/DEGDME&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Hodgett</td>
<td>1987</td>
<td>R12/E181&lt;sup&gt;2&lt;/sup&gt;, R22/E181, R12/NMP&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Rademacher</td>
<td>1987</td>
<td>R22/R113</td>
</tr>
<tr>
<td>George</td>
<td>1989</td>
<td>R22/DMF&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>Åhlby</td>
<td>1989</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;OH/LiBr</td>
</tr>
<tr>
<td>Herold</td>
<td>1991</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O/LiBr</td>
</tr>
<tr>
<td>Kawada</td>
<td>1991</td>
<td>R22/E181, TFE&lt;sup&gt;5&lt;/sup&gt;/NMP, TFE/E181</td>
</tr>
<tr>
<td>Högb erg</td>
<td>1993</td>
<td>R22/R114, R22/R142b</td>
</tr>
<tr>
<td>Groll</td>
<td>1995</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;/acetone</td>
</tr>
</tbody>
</table>

<sup>1</sup>: Diethylene glycol dimethyl ether (C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>);<sup>2</sup>: TEGDME = DTG = tetracyclohexyl glycol dimethyl ether (C<sub>24</sub>H<sub>38</sub>O<sub>2</sub>);<sup>3</sup>: N-Methylpyrrolidone (C<sub>4</sub>H<sub>11</sub>NO);<sup>4</sup>: Dimethylformamide;<sup>5</sup>: Tri-fluorethanol (C<sub>3</sub>F<sub>6</sub>OH)

*Table 5.2: Overview of mixtures other than NH<sub>3</sub>/H<sub>2</sub>O used in or proposed for compression-resorption cycles.*

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5.2 gives an overview of the mixtures studied or tested in compression-resorption cycles. It should be noted that the use of ternary mixtures is also being extensively investigated for absorption machines since they can produce an increase in the thermodynamic efficiency by linearisation of the temperature profile or by intensification of the heat transfer, or offer better protection against corrosion. NH₃/H₂O mixed with a salt like LiBr was studied by Kawada [1991], Keller [1990] and Peters [1995], the mixture H₂O/LiCl/LiNO₃ by Iyoki [1995] and LiBr/LiI/LiCl/LiNO₃ by Nishiyama [1995].

Much work has also gone into the proposal of methods and strategies to select refrigerants for specific cycles. Alefeld [1987] uses a second law analysis of the vapour compression cycle to reduce the necessary knowledge of the refrigerant properties to a single non-dimensional parameter cT/r where c is the specific heat capacity, r the heat of vaporization and T the evaporator temperature. McLinden [1988] has investigated the performances of the vapour compression cycle using reduced refrigerant properties in the Carnahan-Starling-DeSantis equation of state. The most important factor appears to be the critical temperature. A high critical temperature (T_{cond}/T_c ≈ 0.7) yields a high COP but a low volumetric heating capacity, while a low critical temperature (T_{cond}/T_c ≈ 0.9) yields a high volumetric heating capacity but a moderate COP. The volumetric capacity increases at higher condenser temperature owing to higher pressures and thus higher vapour densities. The COP decreases because of the higher irreversibilities associated with the superheating of the compressor and the expansion process. At low to moderate ideal gas heat capacity, a high critical pressure appears to be favourable to both the COP and the capacity. These desirable properties are usually achieved for refrigerants with small molecules of low molecular weight.

Fundamental work on the choice of refrigerant mixtures for absorption heat pumps has been carried out by Jedema [1984]; he indicates that the heat of evaporation should be as high as possible to minimize the irreversible losses, which are proportional to the refrigerant mass flow rate; the mixture should show a negative deviation from Raoult’s law in order to minimize the recirculation ratio; and finally, the specific heat capacity of the mixture should be as low as possible since it does not contribute to the heat pump performances.

Hodgett [1987] and Åhlby [1989] use the same kind of analysis, this time applied to the solution recirculation heat pump. Similar results were obtained, with the exception that for the cycle in question, the heat of mixing should also be exothermic and as high as possible. The work of the compressor must also be minimized, which implies a low pressure ratio, and thus also a strong negative deviation from Raoult’s law, a small ratio of the specific heat of the mixture’s components and a low compressibility factor Z. Since it is also desirable that the specific compressor displacement should be as low as possible, the solution should have the smallest possible specific volume.

This chapter does not aim to make a fundamental analysis of the desired properties of the refrigerant or to investigate totally new pairs. The analysis of the performances of several mixtures in the wet compression cycle, in the solution recirculation cycle and in the vapour compression cycle is based only on properties like critical temperature and temperature-enthalpy diagrams. First the choice of the mixtures to be studied and the equation chosen to calculate the thermodynamic properties of the mixtures will be explained. The temperature-enthalpy diagrams for the selected mixtures will be given, and
based on this, preliminary conclusions concerning their applicability domain will be presented. Finally, the results relating to the COP, the SCD and the UA-values obtained from the simulations will be presented and discussed.

5.2 Choice of the studied mixtures

A first estimate of potential working media can be based on thermodynamic data like the normal boiling point temperature and the critical point, together with safety and environmental impact data. The working fluids must be as harmless as possible to the environment in general and to human beings in particular, which implies that they should have a near-zero ozone depleting potential, a very low greenhouse warming potential and low toxicity and flammability. The refrigerant mixture must be able to achieve the temperature range common in heat pump practice and more or less covered by the nine case-studies defined in Chapter 4. To avoid the need for expensive vacuum and high pressure equipment, the working pressures must be within the common limits of 1 and 25 bar. Finally, the viscosity and heat transfer properties should be as close as possible to those of commonly used refrigerants. The choice of the mixture was based on an investigation by Höberg [1989] on possible working fluids for high temperature heat pumps (that is with heat sink temperatures of about 70 °C). This investigation is devoted to fluorocarbons and hydrocarbons. Of course, depending on the application, other working pairs could have been chosen, but it was not our aim to define the best pair for a given application (if it exists), but rather to come to general criteria by comparison of the performances of a specific mixture in several applications.

5.2.1 Fluorocarbons

The most environmentally acceptable substances within the group of fluorocarbons are the chlorine-free hydrofluorocarbons (HFCs). The use of this group of chemicals is relatively new for refrigeration and heat pump applications, however, research is in progress and a limited number of HFCs is already available on the market, in particular R23, R125, R134a, R152a. Table 5.3 lists some properties of these substances (see McLinden [1990] and Calm [1994]).

Due to the relatively low values of their normal boiling points and of their critical temperatures, it does not seem reasonable to consider mixtures based solely on these refrigerants for heat pump applications. A mixture for the compression-resorption heat pump requires a less volatile component which has higher normal boiling and critical temperatures. It has been reported by Devotta [1994], that such HFCs (e.g. R347ccd, R338eea, R245fa and R245ca) are now under investigation. Devotta [1994] also suggests that hydrofluorinated ethers (HFEs) like HFE245fa, HFE245cb, HFE143 and HFE254cb could be used in the future. Some properties of these high temperature HFCs and HFEs are listed in Table 5.4. However, the research is in the first stage (stability, compatibility tests, etc.), and no thermodynamic data are available for these substances. In spite of their environmental disadvantages, at present the appropriate high boiling point component must
be one of the group of HCFCs (see Table 5.5, from McLinden [1990] and Calm [1994]). In view of their normal boiling points, the choice is restricted to only R123 or R141b, which are both moderately toxic. Since R123 has lower ODP and GWP values than R141b, it was chosen as the non-volatile component of the mixtures. The following fluorocarbon mixtures were therefore taken into consideration: R23/R123, R125/R123, R134a/R123, and R152a/R123.

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>M</th>
<th>NBT °C</th>
<th>Tc °C</th>
<th>Flam.</th>
<th>Tox.</th>
<th>ODP</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>R23</td>
<td>70.01</td>
<td>-82.0</td>
<td>25.6</td>
<td>non-fl.</td>
<td>1000</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>R125</td>
<td>120.02</td>
<td>-48.5</td>
<td>66.3</td>
<td>non-fl.</td>
<td>1000</td>
<td>0</td>
<td>0.84</td>
</tr>
<tr>
<td>R134a</td>
<td>102.03</td>
<td>-26.5</td>
<td>100.6</td>
<td>non-fl.</td>
<td>1000</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>R152a</td>
<td>66.00</td>
<td>-24.7</td>
<td>113.5</td>
<td>3.9-16.9</td>
<td>1000</td>
<td>0</td>
<td>0.03</td>
</tr>
</tbody>
</table>

M: Mol. weight (kg kmol⁻¹); NBT: normal boiling temperature; Tc: critical temperature; Flam: % vol refriger. in air; Tox: ppm; ODP: ozone depleting potential, relative to that of R12 (1); GWP: greenhouse warming potential relative to that of R11.

Table 5.3: Some properties of commercially available HFCs.

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>M</th>
<th>NBT °C</th>
<th>Tc °C</th>
<th>Flam.</th>
<th>Tox.</th>
<th>ODP</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>R347ceed</td>
<td>184.02</td>
<td>15.1</td>
<td>144.2</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>R338sea</td>
<td>202.02</td>
<td>25.4</td>
<td>148.6</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>R245fa</td>
<td>134.00</td>
<td>15.3</td>
<td>157.5</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0.089</td>
</tr>
<tr>
<td>R245ca</td>
<td>134.00</td>
<td>25.0</td>
<td>178.4</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>HFE245fa</td>
<td>150.05</td>
<td>23.8</td>
<td>198.4</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>HFE245cb</td>
<td>150.05</td>
<td>34.06</td>
<td>171.0</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>HFE143</td>
<td>100.00</td>
<td>30.06</td>
<td>186.83</td>
<td>fl.</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>HFE254cb</td>
<td>132.0</td>
<td>36.44</td>
<td>189.44</td>
<td>fl.</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.4: Some properties of high boiling point temperature HFCs and HFES.
<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>M</th>
<th>NBT °C</th>
<th>T_\text{c} °C</th>
<th>Flam.</th>
<th>Tox.</th>
<th>ODP</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>R22</td>
<td>86.47</td>
<td>-40.8</td>
<td>96.15</td>
<td>non-fl.</td>
<td>1000</td>
<td>0.055</td>
<td>0.36</td>
</tr>
<tr>
<td>R123</td>
<td>152.93</td>
<td>27.9</td>
<td>185.0</td>
<td>non-fl.</td>
<td>100</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>R141b</td>
<td>116.95</td>
<td>32.0</td>
<td>210.3</td>
<td>7.3-16.0</td>
<td>100</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>R142b</td>
<td>100.5</td>
<td>-9.8</td>
<td>137.1</td>
<td>6.7-14.9</td>
<td>1000</td>
<td>0.065</td>
<td>0.42</td>
</tr>
<tr>
<td>R124</td>
<td>136.48</td>
<td>-11.0</td>
<td>122.2</td>
<td>non-fl.</td>
<td>500</td>
<td>0.022</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Table 5.5: Some properties of commercially available HCFCs.*

### 5.2.2 Hydrocarbons

The advantages of hydrocarbons are well known: they are quite stable; they do not have any effect on the atmospheric ozone layer; they have an insignificant greenhouse warming potential - about 2% of the greenhouse warming potential of R134a. However, because of the flammability of the normal paraffins, they are less commonly used as working fluids for refrigeration and heat pump systems than the fluorocarbons. The traditional attitude towards the use of hydrocarbons as refrigerants started to change once it was understood that there is no existing ideal refrigerant, that matches all criteria. The general expert opinion is that the need for the safety measures required might not be prohibitive and that current technologies could mitigate the need for such measures. In view of these new developments, it seems reasonable to consider the use of normal paraffin mixtures as working fluids for the compression-resorption heat pump. Propane is the most commonly used hydrocarbon refrigerant (see Table 5.6, from Edminster [1983]) so here mixtures based on propane are considered. As the normal boiling point of propane is far below 0 °C, and its critical temperature is not high enough for heat pump applications, propane may be used as a component in a mixture with some less volatile hydrocarbon, for instance, n-butane or n-pentane. The list of possible substances could be extended to include less volatile ones such as hexane or heptane, but the less volatile the component, the greater is its viscosity. This may create problems with regard to equipment design, particularly the design of heat exchangers. For this reason the following mixtures were taken into consideration: propane/n-butane and propane/n-pentane.

### 5.2.3. Ternary mixtures

As the present research is focused on the thermodynamic aspects, ternary mixtures are considered from this viewpoint. Compared to a binary mixture, a ternary mixture possesses an additional degree of freedom and this makes possible a better approximation of the ideal Lorenz cycle. Two ternary mixtures were taken into consideration: R125/R152a/R123 and R290/R600/pentane.
<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>M</th>
<th>NBT °C</th>
<th>T_e °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>16.04</td>
<td>-161.5</td>
<td>-82.5</td>
</tr>
<tr>
<td>Ethane</td>
<td>30.07</td>
<td>-88.8</td>
<td>32.2</td>
</tr>
<tr>
<td>Propane (R290)</td>
<td>44.10</td>
<td>-42.1</td>
<td>96.8</td>
</tr>
<tr>
<td>n-Butane (R600)</td>
<td>58.12</td>
<td>-0.5</td>
<td>152.1</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>72.15</td>
<td>36.1</td>
<td>196.5</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>86.18</td>
<td>68.7</td>
<td>234.3</td>
</tr>
</tbody>
</table>

*Table 5.6: Some properties of hydrocarbons.*

5.3 Calculation of the thermodynamic properties

The use of the program CYCLE 11 of the National Institute of Standards and Technology (Domansky [1992]), based on the refrigerant database REFFROP was considered. This program is intended to calculate vapour compression cycles using a mean temperature difference approach. The fact that a minimum approach temperature was chosen in our previous work on the compression-resorption cycle using ammonia and water, would make the comparisons ambiguous. Another programme that is widely used when modelling heat pumps, in particular absorption cycles, is ABSIM (Grossmann [1994]). However, since it was not possible to simulate the wet compressor correctly (a problem also encountered with the simulations for NH₃/H₂O), it was decided to set up a specific program. This was done by V. Fedotov [1994], who calculated the thermodynamic properties of several mixtures, and used the results of these calculations to calculate the wet compression cycle.

The Trepp-Ziegler equation (Ziegler [1982]), which is based on the Schulz equation (Schulz [1971]), was used for the calculation of the thermodynamic properties of NH₃/H₂O, (see Chapter 4). For the vapour phase, the virial equation was used, in which the series stops at the second virial coefficient: pv = RT + B(T)p, see Equation (C.12) in Appendix C. For the liquid phase, an equation of state of the type v = a₁ + a₂p + a₃T + a₄T² was chosen, where the coefficients were fitted on pure liquid, pure gas and vapour liquid equilibrium (VLE) data. However, this set of equations of state cannot be extended to other mixtures. Since we intended to test HCFCs and HFCs mixtures as well as mixtures of hydrocarbons, it was necessary to find an equation of state valid for these components and for both the liquid and vapour phases. A review of the existing equations of state which has formed the basis for the choice of a suitable equation, the Starling-Han equation of state (Fedotov [1994]), is proposed in Appendix C. The Starling-Han equation was therefore implemented in the calculation cycle for the wet compression cycle, the solution recirculation cycle and the vapour compression cycle.
5.4 The T-h and T-s diagrams

5.4.1 Particularities of the diagrams

Using the principles described in Chapter 3, the temperature-enthalpy and temperature-entropy diagrams have been calculated by using the Starling-Han equation of state. The diagrams for R23/R123, R125/R123, R134a/R123, R152a/R123, propane/n-butane and propane/n-pentane are presented in Appendix D, with their estimated critical temperature (calculated with REPROP), for the overall mass concentrations 0.1, 0.2, 0.4, 0.6, 0.8 and 0.9. Contrary to expectations, some of the mixtures have a critical temperature that is not the maximum temperature of the system. This is clearly the case, for instance, for the mixture R23/R123 at overall concentrations of 0.4 and 0.6. This is actually a well-known phenomenon when the critical temperatures of the mixture’s components are very far from each other. In such cases it is impossible to make a linear approximation of the critical pressure between the critical points of the two pure components (see for instance Smith [1987]) and the critical point may be located at a point where neither the pressure nor the temperature are maximum. This phenomenon has been extensively treated by Sage [1939] for hydrocarbons; for instance, the system methane/n-pentane exhibits a maximum critical pressure in excess of about 100 bar on that of pure methane. To illustrate this a p-T diagram for the mixture R23/R123 with an overall concentration of 0.5 has been drawn in Figure 5.1. For pressures above 52 bar, the program fails because the pressure becomes too close to the critical pressure and the algorithm is not able to find a suitable initial value. The critical points for R23 and R123 have also been drawn and one can see that the pseudo critical pressure (linear approximation) is far from the estimated critical pressure (above 60 bar). One can also see that the temperature of the saturated vapour line can exceed the critical temperature of the 50/50 mixture (78.9 °C) by a large amount.

\[ \text{R23/R123} \times_0 = 0.5 \]

![Figure 5.1: P-T diagram for the mixture R23/R123 with the overall mass concentration 0.5.](image)

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<table>
<thead>
<tr>
<th>Mixture</th>
<th>$\Delta NBT$ (K)</th>
<th>$\Delta T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R23/R123</td>
<td>109.9</td>
<td>159.1</td>
</tr>
<tr>
<td>R125/R123</td>
<td>76.4</td>
<td>118.7</td>
</tr>
<tr>
<td>R134a/R123</td>
<td>54.4</td>
<td>84.4</td>
</tr>
<tr>
<td>R152a/R123</td>
<td>52.6</td>
<td>71.5</td>
</tr>
<tr>
<td>prop/n-pent</td>
<td>78.2</td>
<td>99.7</td>
</tr>
<tr>
<td>prop/n-but</td>
<td>42.6</td>
<td>55.3</td>
</tr>
<tr>
<td>NH$_3$/H$_2$O</td>
<td>133.0</td>
<td>343.0</td>
</tr>
</tbody>
</table>

*Table 5.9: Normal boiling and critical temperature differences for the mixtures studied.*

In *Table 5.9* the differences between the normal boiling temperatures and between the critical temperatures of the mixture's components are reviewed. For mixtures belonging to the same chemical group (mixtures HFCs/HCFCs and mixtures of hydrocarbons), the higher the critical temperature difference, the higher the non-linearity of the isobars in the T-h and T-s diagrams. This means that for high temperature glide applications it will probably be difficult to find a refrigerant mixture closely matching the external glide. When comparing HFCs/HCFCs mixtures with hydrocarbons mixtures (see Appendix D), it is obvious that for comparable temperature glides, the hydrocarbons mixtures are more linear than the HFCs/HCFCs mixtures, and thus they will probably perform better. It can be deduced from *Table 5.9* that an analysis on the basis of the critical temperatures is almost identical to an analysis on basis of the normal boiling temperatures, the only exception being the relative place of propane/n-pentane and R125/R123.

### 5.4.2 First classification of the mixtures in view of their application

Besides the temperature levels of the application, two main parameters have been shown to be of importance in predicting the performances of a cycle: the temperature glide in the resorber and the temperature lift. In *Figure 5.2*, the temperature-enthalpy diagrams for the seven mixtures studied at an overall concentration of 0.5 have been drawn on a fixed scale to allow easy comparison. In this figure the importance of the heat of evaporation is immediately apparent. For the same mixture temperature glide, the higher this evaporation width, the more efficient the cycle, because the mass flow rate needed for a given application decreases, and therefore the irreversibilities of the cycle also decrease. This means that the criterion that a fluid should have isentropic lines as vertical as possible in the T-h diagram in order to limit the compressor work is not a good one. It is of importance only if the same mass flow rates are needed for both the fluids and if this is not the case, a lower mass flow rate can definitely compensate for an isentropic line with a smaller slope. From that point of view the major advantages of NH$_3$/H$_2$O over the other
Figure 5.2: Comparison of the T-h diagrams for the studied mixtures at $x_i = 0.5$.

122 - Comparison between cycles and mixtures
<table>
<thead>
<tr>
<th>Mixture</th>
<th>T range (°C)</th>
<th>$\Delta T_{\text{glide,mix}}$ (K)</th>
<th>$\Delta T_{\text{lift,mix}}$ (K)</th>
<th>$\Delta T_{\text{glide,mix}}/\Delta h_{ev}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R23/R123</td>
<td>-25 / 54</td>
<td>79.9</td>
<td>80.9</td>
<td>0.318</td>
</tr>
<tr>
<td>R125/R123</td>
<td>-14 / 99</td>
<td>43.7</td>
<td>106.5</td>
<td>0.214</td>
</tr>
<tr>
<td>R134a/R123</td>
<td>-5 / 109</td>
<td>24.9</td>
<td>110.4</td>
<td>0.118</td>
</tr>
<tr>
<td>R152a/R123</td>
<td>-9 / 103</td>
<td>21.0</td>
<td>132.2</td>
<td>0.080</td>
</tr>
<tr>
<td>prop./n-pen.</td>
<td>-10 / 110</td>
<td>43.5</td>
<td>150.2</td>
<td>0.092</td>
</tr>
<tr>
<td>prop./n-but.</td>
<td>-24 / 93</td>
<td>15.4</td>
<td>113.8</td>
<td>0.036</td>
</tr>
<tr>
<td>NH$_3$/H$_2$O</td>
<td>39 / 147</td>
<td>86.5</td>
<td>109.1</td>
<td>0.049</td>
</tr>
</tbody>
</table>

Table 5.10: Some characteristic properties of the studied mixtures at $x_0 = 0.5$.

Pairs that have been studied are very clearly illustrated by Figure 5.2. An estimation of the compared performances of the refrigerants may be based on four figures: the achievable temperature range, the achievable temperature glide $\Delta T_{\text{glide,mix}}$, the mean temperature lift between 1 and 25 bar $\Delta T_{\text{lift,mix}}$, and the ratio $\Delta T_{\text{glide,mix}}/\Delta h_{ev}$ that should be as small as possible for a given $\Delta T_{\text{glide,mix}}$. These values have been calculated for an overall mass concentration of 0.5; $\Delta T_{\text{glide,mix}}$ and $\Delta h_{ev}$ were calculated at 1 bar. The lowest temperature of the temperature range was calculated as the arithmetic mean temperature between the saturated liquid temperature and the saturated vapour temperature at 1 bar and the highest temperature as the arithmetic mean temperature between the saturated liquid temperature and the saturated vapour temperature at 25 bar. The results for the different mixtures are given in Table 5.10. As already emphasized, the factor determining the quality of the cycle is the ratio $\Delta T_{\text{glide,mix}}/\Delta h_{ev}$. Supposing an application for which all above described mixtures could be applied from the viewpoints of their temperature range, their $\Delta T_{\text{glide,mix}}$ and their $\Delta T_{\text{lift,mix}}$, the classification of the mixtures (from the highest COP to the lowest one) would be the following: propane/n-butane, NH$_3$/H$_2$O, R152a/R124, propane/n-pentane, R134a/R123, R125/R123 and finally R23/R123. In view of the $\Delta T_{\text{glide,mix}}/\Delta h_{ev}$ value, it can be expected that NH$_3$/H$_2$O and propane/n-butane will give similar performances and that the pairs propane/n-pentane, R152a/R123 and R134a/R123 will have also close COPs. Of course, because the cycle is not calculated and the concentration is not optimized, no absolute results can be expected from this analysis. The general trends in the applicability domain of the considered mixtures on their temperature range as defined in Table 5.10 are listed below, although it is possible that there may be some exceptions:

1. Propane/n-butane will perform very well for low heat sink temperature glide applications ($\leq 15$ K).
2. NH$_3$/H$_2$O will perform very well for all applications.
3. R152a/R123 and R134a/R123 will perform reasonably for heat sink temperature glide applications that are not too high ($\leq 25$ K).
4. Propane/n-pentane will perform reasonably for almost all applications (with the
exception of very high heat sink temperature glide applications (≥ 44 K).
5. R125/R123 will not usually have very good performances.
6. R23/R123 will also not perform very well, except for some high heat sink
   temperature glide applications (∼ 80 K).

Based on this general trends, a classification of the mixtures for the nine applications
described in Chapter 4 (Tables 4.1, 4.2 and 4.3) has been made. This classification will
be compared with the results obtained by simulation.

Example 1.1 (T_{w_1} = 10 °C, T_{w_2} = 15 °C, T_{w_3} = 12 °C): for this example, T_{mean,rs} = 12.5 °C,
ΔT_{glide} = 5 K and ΔT_{lift} = 3 K. Because none of these data is close to the limits described in
Table 5.10, one can expect all mixtures to have similar COP performances, although it
is probable that the pair R23/R123 does not perform well.

Example 1.2 (T_{w_1} = 46 °C, T_{w_2} = 65 °C, T_{w_3} = 49 °C): for this example, T_{mean,rs} = 55.5 °C,
ΔT_{glide} = 19 K and ΔT_{lift} = 16 K. In view of the limitations on T_{mean,rs} and on ΔT_{glide}, it is
probable that neither R23/R123 nor propane/n-butane will perform well.

Example 1.3 (T_{w_1} = 15 °C, T_{w_2} = 85 °C, T_{w_3} = 25 °C): for this example, T_{mean,rs} = 50 °C,
ΔT_{glide} = 70 K and ΔT_{lift} = 60 K. Probably a low ΔT_{glide,max} mixture like propane/n-butane
will perform poorly, but it is also a possible that it (or R152a/R123 or R134a/R123) will
perform better than a mixture like R23/R123, which has a high ΔT_{glide,max} but a low
ΔT_{glide,max}/Δh_{ev} value.

Example 2.1 (T_{w_1} = 60 °C, T_{w_2} = 70 °C, T_{w_3} = 55 °C): for this example, T_{mean,rs} = 65 °C,
ΔT_{glide} = 10 K and ΔT_{lift} = 15 K. The pair R23/R123 can be expected to have a poor
performance. Because the pair propane/n-butane matches well ΔT_{glide} and has a very good
ΔT_{glide,max}/Δh_{ev}, it can be expected to perform very well.

Example 2.2 (T_{w_1} = 70 °C, T_{w_2} = 90 °C, T_{w_3} = 60 °C): for this example, T_{mean,rs} = 80 °C,
ΔT_{glide} = 20 K and ΔT_{lift} = 30 K. It is therefore likely that R23/R123 and propane/n-butane
will not perform very well.

Example 2.3 (T_{w_1} = 100 °C, T_{w_2} = 140 °C, T_{w_3} = 80 °C): for this example, T_{mean,rs} = 120
°C, ΔT_{glide} = 40 K and ΔT_{lift} = 60 K. For this high temperature application, the low
temperature range mixtures like R23/R123 and propane/n-butane can be expected to
perform poorly, although the high ΔT_{glide,max} of R23/R123 could also allow for a reasonable
performance. Small ΔT_{glide,max} pairs like propane/n-butane, R152a/R123 and R134a/R123
are expected to perform poorly and NH3/H2O should be one of the best solutions.

Example 3.1 (T_{w_1} = 52 °C, T_{w_2} = 60 °C, T_{w_3} = 31 °C): for this example, T_{mean,rs} = 56 °C,
thus the pair R23/R123 will probably not perform well, ΔT_{glide} = 8 K and ΔT_{lift} = 29 K.
In view of the low ΔT_{glide} value, all others mixtures are expected to perform reasonably.

Example 3.2 (T_{w_1} = 110 °C, T_{w_2} = 130 °C, T_{w_3} = 70 °C): for this example, T_{mean,rs} = 120
°C, ΔT_{glide} = 20 and ΔT_{lift} = 60 K. Low temperature range mixtures like R23/R123 and
propane/n-butane are not expected to perform well. Because of the moderate ΔT_{glide} all
other mixtures could be considered, however NH3/H2O will probably be one of the best.
Example 3.3 \((T_w = 100 \, ^\circ\text{C}, \, T_{w1} = 140 \, ^\circ\text{C}, \, T_{w2} = 50 \, ^\circ\text{C})\): for this example \(T_{\text{mean,t}} = 120 \, ^\circ\text{C}, \, \Delta T_{\text{g1}} = 40 \, \text{K}\) and \(\Delta T_{\text{g2}} = 90 \, \text{K}\). Since \(\Delta T_{\text{g2}}\) does not appear to be very important in determining the potential mixtures, the conclusions are the same as for example 2.3.

## 5.5 Results of the simulations for several applications

In this section the simulations of the applications described in Table 4.1 to 4.3 are described and analyzed. The program for the wet compression cycle has already been described in Chapter 4 and the program for the solution recirculation cycle in Appendix B. The only difference is that these programs are now using the database DOTHERMO instead of DOTHERMO (used for \(\text{NH}_3/\text{H}_2\text{O}\) only). For both these cycles, an optimization has been made and all values and curves presented in Figure 5.3 and in Appendix E correspond to the optimized overall concentration and suction pressure. In Chapter 4 results were presented for an ideal pure refrigerant cycle. Although the compressor efficiency was included in the results presented the comparison of the different cycles would be more accurate if the real vapour compression cycle was calculated. This calculation follows that same principle as both the other cycles, using a specified closest-approach temperature in the heat exchangers and a specified compressor isentropic efficiency. For each application of this cycle, the evaporator superheating was optimized as well as the temperature limits of the internal heat exchanger (if present) between the liquid line after the condenser and the suction line before the compressor. Refrigerants with a high critical temperature, namely R123, n-butane, n-pentane, \(\text{H}_2\text{O}\) and \(\text{NH}_3\), were chosen for the simulations. The analysis presented here is based on the COP, SCD and UA-values of the respective cycles at the optimized working point. The bar-charts for application 2.3 are given in Figures 5.3 to illustrate the results and all others are given in Appendix E. The constraints applied when determining the maximal COP of the cycles were a suction pressure higher than 1 bar and a discharge pressure lower than 25 bar. When these criteria were not satisfied, a star' on the diagram indicates that the suction pressure was lower than or equal to 1 bar and a double star'' indicates that the discharge pressure was higher than or equal to 25 bar.

### 5.5.1 Low \(\Delta T_{\text{liq}}/\Delta T_{\text{g1}}\) applications

Example 3.1 \((T_w = 10 \, ^\circ\text{C}, \, T_{w1} = 15 \, ^\circ\text{C}, \, T_{w2} = 12 \, ^\circ\text{C})\): the graphics are given in Figure E.1. Generally the wet compression cycle has a COP which is only very slightly better than the COP of the solution recirculation cycle (about 3 %), except for the ternary blends for which the advantage can increase to 25 % and for R23/R123 (increase by 37 %). The COPs for the vapour compression cycle do not differ very much from the value calculated with the method given in Chapter 4. As expected, R23/R123 does not perform well, in fact less well than all other pure refrigerants in the vapour compression cycle. All other mixtures perform reasonably, with the ternary mixture R125/R152a/R123 performing the best in the wet compression cycle, closely followed by propane/n-butane, R134a/R123, \(\text{NH}_3/\text{H}_2\text{O}\) and propane/n-pentane. It should be noticed that this classification changes for the solution recirculation cycle, since the ternary blends in that cycle have a
Figure 5.3: Optimum COP and corresponding SCD and UA-values for example 2.3
\(T_{\text{w1}} = 100\, ^{\circ}\text{C}, T_{\text{w1}} = 140\, ^{\circ}\text{C}, T_{\text{w2}} = 80\, ^{\circ}\text{C}\).
lower COP than propane/butane for instance. The advantages in terms of SCD when using a mixture are highlighted by the second diagram in Figure E.1. With an almost constant COP, the SCD of the mixture R125/R123 is more than 10 times lower than that of pure R123. This is certainly not the case for pure ammonia and its mixtures with water, because NH₃ has a much lower specific volume than H₂O. The differences between the refrigerant mixtures in terms of UA-values are limited and therefore this criterium will not be decisive in the choice of an appropriate mixture.

Example 1.2 \( (T_{w4} = 46 \, ^\circ C, \ T_{w3} = 65 \, ^\circ C, \ T_{w2} = 49 \, ^\circ C) \): the graphics are given in Figure E.2. As expected, propane/n-butane and R23/R123 perform poorly. In one case (propane/n-butane) the solution recirculation cycle gives better COP performances than the wet compression cycle. Here also the predictions for the vapour compression cycle are close to the predictions of Chapter 4. Both the ternary blends R125/R152a/R123 and propane/n-butane/n-pentane perform better than R134a/R123, NH₃/H₂O and propane/n-pentane. However, the pair R152a/R123 yields the highest COP, although the latter is only slightly higher than that of the ternary mixtures. Except for propane/n-butane, the solution recirculation cycle achieves a COP lower than the COP of the wet compression cycle by 2 to 10 %, but it has a very favourable SCD, that can be 50 % lower than the SCD of the wet compression cycle, which makes possible to work with a much smaller compressor while achieving a reasonable COP.

Example 1.3 \( (T_{w4} = 15 \, ^\circ C, \ T_{w3} = 85 \, ^\circ C, \ T_{w2} = 25 \, ^\circ C) \): the graphics are given in Figure E.3. Most pairs, with the exception of NH₃/H₂O, do not perform much better than the pure ammonia vapour compression cycle. Without any doubt, the best solution in terms of COP and SCD is the NH₃/H₂O mixture. However, its UA-value is very high (2.5 times that of pure ammonia). Finally it should be mentioned that the use of the ternary blends is not recommended since at a COP comparable to that of the NH₃ vapour compression cycle, they have SCD and UA-values that are almost twice as high.

5.5.2 Medium \( \Delta T_{\text{lift}}/\Delta T_{\text{glide}} \) applications

Example 2.1 \( (T_{w4} = 60 \, ^\circ C, \ T_{w3} = 70 \, ^\circ C, \ T_{w2} = 55 \, ^\circ C) \): the graphics are given in Figure E.4. As expected from section 5.4.2, the mixture propane/n-butane performs very well in the wet compression cycle (better than NH₃/H₂O by about 12 %) and the mixture R23/R123 has a very poor COP. Their performances are also clearly better than those of the vapour compression cycle. The best COP is achieved by the ternary blend propane/n-butane/n-pentane, closely followed by propane/n-butane and then by the ternary blend R125/R125a/R123, and by R152a/R123 and R134a/R123, all three of which have a similar COP. As previously observed, the classification for the solution recirculation is different, since the best pair for this cycle is R152a/R123. In view of the SCD values, propane/n-butane is better than its ternary mixture with n-pentane, and they furthermore have very close UA-values.

Example 2.2 \( (T_{w4} = 70 \, ^\circ C, \ T_{w3} = 90 \, ^\circ C, \ T_{w2} = 60 \, ^\circ C) \): the graphics are given in Figure E.5. As predicted in section 5.4.2, the pairs R23/R123 and propane/n-butane have a low COP. At equal COPs, the ternary mixture propane/n-butane/n-pentane has a UA-
value lower by more than 19% in comparison to the UA-value of R152a/R123. For this application the ternary mixture should therefore be preferred.

**Example 2.3** ($T_{w_4} = 100 \, ^\circ C$, $T_{w_1} = 140 \, ^\circ C$, $T_{w_2} = 80 \, ^\circ C$): the graphics are given in Figure E.6 and 5.3. As predicted in section 5.4.2, the pairs propane/n-butane, R152a/R123 and R134a/R123 perform very poorly. In fact, it was not possible to calculate the cycle for the mixture propane/n-butane. The NH$_3$/H$_2$O pair has a much higher COP than all others (34% better than propane/n-pentane), with a reasonable SCD, but at the expense of the UA value, which is 73% higher than that of propane/n-pentane. It is typical that in some cases (R23/R123 and R134a/R123) the wet compression cycle could be calculated, but not the solution recirculation cycle (the reverse can also happen, see Section 5.5.3). This usually happens for mixtures for which either the temperature range or the $\Delta T_{\text{glide,mix}}$ are not well suited to the application. Because of the differences in pressure and temperature levels between the wet compression and the solution recirculation cycles, it may happen that one of these cycles can be calculated and the other cannot.

**5.5.3 High $\Delta T_{\text{lift}}/\Delta T_{\text{glide}}$ applications**

**Example 3.1** ($T_{w_4} = 52 \, ^\circ C$, $T_{w_1} = 60 \, ^\circ C$, $T_{w_2} = 31 \, ^\circ C$): the graphics are given in Figure E.7. As expected R23/R123 performs poorly and all other mixtures (with the exception of R125/R123) have COP close to each other. The vapour compression cycle performs very well because of the high $\Delta T_{\text{lift}}/\Delta T_{\text{glide}}$ ratio and because of the small temperature glide of the heat sink. However, at constant COP performance, the mixtures can have a much lower SCD than the pure refrigerants. For instance, R152a/R123 in the wet compression cycle, which has a COP very close to that of pure R123, exhibits an SCD which is more than four times lower than the SCD of R123. When considering the three parameters COP, SCD and UA-value together, the pure ammonia vapour compression cycle should be preferred because of its high COP, low SCD and low UA value. Its only drawback is its high discharge pressure that exceeds 25 bar (28.4 bar).

**Example 3.2** ($T_{w_4} = 110 \, ^\circ C$, $T_{w_1} = 130 \, ^\circ C$, $T_{w_2} = 70 \, ^\circ C$): the graphics are given in Figure E.8. The same comments as those given in example 2.3 can be made. As predicted in section 5.4.2, R23/R123 and propane/n-butane have a poor COP or cannot be calculated. If the SCD is considered to be more critical than the UA-value, the ternary mixture R125/R152a/R123 should be chosen. However, if the UA-value is a more critical parameter, the use of NH$_3$/H$_2$O in the wet compression cycle should be recommended (SCD higher by 113% but UA-value lower by 19%).

**Example 3.3** ($T_{w_4} = 100 \, ^\circ C$, $T_{w_1} = 140 \, ^\circ C$, $T_{w_2} = 50 \, ^\circ C$): the graphics are given in Figure E.9. In view of the COP and of the SCD, NH$_3$/H$_2$O used in the wet compression cycle should be the best option, but shows a very high UA-value (69% higher than the UA-value of R23/R123, which has a COP lower by 34%). For this high temperature application, the advantages of a vapour compression cycle using water become more obvious: its COP is only 1.2 times lower than the COP of NH$_3$/H$_2$O and its UA-value is almost 3 times lower. The main drawback, of course, is the excessive SCD. 28 times
higher than the SCD of NH_{3}/H_{2}O.

5.6 Conclusions

The first conclusion of this case study is that neither a cycle nor a mixture can be said to be the best, although the relative performances of the binary mixture NH_{3}/H_{2}O and of the ternary blends propane/n-butane/n-pentane and R125/R152a/R123 in the wet compression cycle are less sensitive to the external conditions. For NH_{3}/H_{2}O, for instance, the COP is never lower than 12% of the maximum COP. The results of the SCD are more spread but NH_{3}/H_{2}O never performs really poorly. The major drawback concerning NH_{3}/H_{2}O can be its high UA-value, in particular for high temperature glide applications (see examples 1.3, 2.3 and 3.3). However, for lower temperature glide applications the UA-values do not differ too much from those of the other mixtures.

As already highlighted in Chapter 4, for the low temperature glide applications the vapour compression cycle is interesting in terms of COP and UA-values, in particular for high ΔT_{lfd}/ΔT_{glide} ratios (example 3.1). However, a disadvantage of the vapour compression cycle is formed by its high specific compressor displacement, with the exception of pure ammonia which has a low specific volume and usually shows an SCD equivalent to the SCD of NH_{3}/H_{2}O, with the disadvantage of a discharge pressure exceeding 25 bar. With pure n-butane, this maximum pressure is not exceeded and although the SCD value is not very good, it remains acceptable.

In the comparison between the wet compression cycle and the solution recirculation cycle, generally the wet compression cycle appears to be the best cycle, since it can lead to a COP that is up to 50% better than the COP of the solution recirculation cycle. The mean COP increase due to wet compression in the nine examples and nine mixtures studied is 14%, included the seven cases where the COP decreases due to wet compression. It appears that for both the ternary blends and NH_{3}/H_{2}O, the wet compression cycle is always better than the solution recirculation one. For the mixtures R23/R123, R125/R123, R134a/R123 and propane/n-pentane, the solution recirculation cycle is better in one case of the nine, generally (but not always) at high temperature lift. For the mixtures R152a/R123 and propane/n-butane, the share increases to two or three cases. However, for NH_{3}/H_{2}O the COP of the wet compression is never better by more than 13%, whereas for R125/R123 it can be better by 65%. Therefore, the pattern remains too vague for a general conclusion to be drawn other than that simulations are necessary in all cases.

Generally the UA-values for the wet compression cycle and for the solution recirculation cycle do not differ very much. It is remarkable that one of these cycles may have the highest COP while also having the lowest UA-value, whereas the COP could be expected to be high because of a better glide matching, yielding a higher UA-value. However, a better resorber glide matching in the solution recirculation cycle can have no visible effect on the COP if the compressor work for this cycle is too high in comparison to the compressor work needed for the wet compression cycle.

From this case-study it can be confirmed that at constant ΔT_{glide,mix} (almost equivalent to a constant normal boiling temperature difference between the mixture's components), the
mixture that is the more linear will perform the best (see section 5.4.1). The perfect example for this behaviour is propane/n-pentane ($\Delta T_{\text{glide,mix}} = 43.5$ K) and R125/R123 ($\Delta T_{\text{glide,mix}} = 43.7$ K). In all examples, propane/n-pentane has a higher COP (sometimes only by a small amount) than R125/R123, as shown by its more linear isobars in the T-h diagram. However, the $\Delta T_{\text{glide,mix}}$ of different mixtures are seldom identical, so prediction of the behaviour of the HFC/HCFC mixtures in comparison with the hydrocarbons mixtures remains difficult and very dependent on the application.

As shown in section 5.4.2, the predictions of the performance of a mixture can best be related to the $\Delta T_{\text{glide,mix}}$ of the mixture and to the ratio $\Delta T_{\text{glide,mix}}/A h_{\text{ev}}$ (at $x_0 = 0.5$ and $p = 1$ bar). The first of these should match the heat sink temperature glide of the application, or at least should not be a limiting factor, and the second should be as small as possible. Of course the $\Delta T_{\text{glide,mix}}$ value is closely related to the normal boiling temperature difference or to the critical temperature difference of the mixture’s components, thus, in the absence of other thermodynamic data, a first selection can be based on the normal boiling point or on the critical point. For low heat sink temperature glide applications ($\leq 10$ K), mixtures with a low critical (or normal boiling) temperature difference between the components can be selected (propane/n-butane, R152a/R123 and R134a/R123). For medium heat sink temperature glide applications (between 10 and 20 K), mixtures with a medium critical temperature difference between the components should be selected (R152a/R123, R134a/R123, propane/n-pentane). For high heat sink temperature glide applications, mixtures with a high critical temperature should be chosen (R125/R123, R23/R123, NH$_3$/H$_2$O). This first selection gives qualitative indication of the performance of the selected mixtures. A better estimation of the suitability of a mixture for a given application can the best be made by calculating the ratio $\Delta T_{\text{glide,mix}}/A h_{\text{ev}}$, which gives then the following classification:

1. Propane/n-butane will perform very well for low heat sink temperature glide applications ($\leq 15$ K), at a mean heat sink temperature up to 90 °C.
2. NH$_3$/H$_2$O will perform very well for all applications (up to about 150 °C).
3. R152a/R123 and R134a/R123 will perform reasonably for moderate heat sink temperature glide applications ($\leq 25$ K), at a mean heat sink temperature up to 100-110 °C.
4. Propane/n-pentane will perform reasonably for almost all applications, with the exception of very high heat sink temperature glide applications ($\geq 44$ K), at mean heat sink temperatures up to 110 °C.
5. R125/R123 will usually not have very good performances.
6. R23/R123 also will not perform very well, with the exception of some high heat sink temperature glide applications ($\approx 80$ °C).

However, this classification should be used to eliminate mixtures rather than to choose one. Due to the complexity of the optimization procedure, the selection of an effective mixture demands the use of cycle simulations.
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Chapter 6

Design of a laboratory wet compression-resorption heat pump

6.1 Introduction

The test-plant has been designed to serve two goals, the first one being the validation of the model and calculations made in the theoretical part of this work. The second objective is to find solutions to the problems inherent to the compression-resorption principle (heat and mass exchangers with a high heat exchange area and a high thermal efficiency because of the small driving mean temperature difference) and to the wet compression (the compressor must withstand liquid and operate near the equilibrium conditions). The experimental wet compression-resorption heat pump test-plant will be described in this chapter. First the choice of the design characteristics will be explained and then the different components of the heat pump will be described, particular attention being paid to the compressor, the resorber and the desorber. The measurement and control system will also be presented, as well as the complete lay-out of the test-plant.

6.2 Choice of the design characteristics

In Chapters 4 and 5 it has been shown that the wet compression cycle with NH$_3$/H$_2$O brings most advantages for heat sinks with high temperature glides when the ratio $\Delta T_{in}/\Delta T_{glide}$ is close to one. This is typical of industrial or district heating situations, where one stream of waste heat can be used partly as a heat source, thus being cooled to a
temperature close to that of the environment, and partly as a heat sink, being upgraded to a temperature at which it can be useful for the process. A waste heat temperature of 40 °C was assumed, since it corresponds to the mean temperature of the waste heat rejections in the manufacturing industry and also to the lower temperature limit of the waste heat rejection in the process industry. Because one of the few compressors suitable for a laboratory test-plant was an air compressor (see section 6.5) that could not support temperatures exceeding 80 °C, it was decided to avoid the field of high temperature applications. The maximum temperature of the NH₃/H₂O solution was fixed at 75 °C, that should have allowed for heating the heat sink from 40 °C to 70 °C, which is a typical value for low temperature district heating or hot water installations. Unfortunately, the choice of the design characteristics has been made at the very beginning of this project, and the cycle was not correctly analyzed at that time. The minimum temperature approach in these conditions turned out to be too small (Schneider [1991]) and since it was not possible to increase the refrigerant mixture temperature because of concerns about the safety of the compressor, the water temperature level was reduced from 40 - 70 °C to 38 - 68 °C. The inlet temperature of the heat source was fixed at 40 °C. This small temperature overlapping range between source and sink may appear strange, but it is better to take advantage of it in the heat pump, since direct heat exchange makes no sense in view of the very small temperature difference between the two flowing streams (2 K).

The basic lay-out of the test-plant is given in Figure 6.1. The intention was to test the heat pump for several internal and external conditions, thus the design of the cycle’s components was based on both a design value and an allowed variation range. The design data for the resorber, the desorber, the internal heat exchanger and the compressor are given in Tables 6.1 to 6.4.

Figure 6.1: Simplified lay-out of the wet compression-resorption heat pump test-plant.

136  ·  Test-plant design
### Table 6.1: Design data for the resorber.

<table>
<thead>
<tr>
<th>Data</th>
<th>Design value</th>
<th>Variation range</th>
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</tr>
<tr>
<td>$\dot{m}_d$ (kg/s) - $\dot{v}_d$ (m³/s)</td>
<td>$0.0540 - 7.0 \times 10^{-5}$</td>
<td>$0.0105 \leq \dot{m}_d \leq 0.0532$</td>
</tr>
<tr>
<td>$\dot{m}_4$ (kg/s) - $\dot{v}_4$ (m³/s)</td>
<td>0 - 0</td>
<td>-</td>
</tr>
<tr>
<td>$\dot{m}_3$ (kg/s) - $\dot{v}_3$ (m³/s)</td>
<td>$0.0355 - 4.3 \times 10^{-5}$</td>
<td>$0.0110 \leq \dot{m}_3 \leq 0.0450$</td>
</tr>
<tr>
<td>$\dot{m}_v$ (kg/s) - $\dot{v}_v$ (m³/s)</td>
<td>$0.0185 - 3.42 \times 10^{-3}$</td>
<td>$0.0079 \leq \dot{m}_v \leq 0.0183$</td>
</tr>
<tr>
<td>$h_4$ - $h_3$ (kJ/kg)</td>
<td>-29.5 - 557.4</td>
<td></td>
</tr>
<tr>
<td>$s_4$ - $s_3$ (kJ/kgK)</td>
<td>0.479 - 2.257</td>
<td></td>
</tr>
</tbody>
</table>

### Table 6.2: Design data for the compressor.

<table>
<thead>
<tr>
<th>Data</th>
<th>Design value</th>
<th>Variation range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_{is}$ (kW)</td>
<td>4.4</td>
<td>4.4 ... 8.0</td>
</tr>
<tr>
<td>$p_1$ - $p_2$ (bar)</td>
<td>2 - 8.67</td>
<td>6.38 $\leq p_2 \leq 9.32$</td>
</tr>
<tr>
<td>Discharge temp. $T_3$ (°C)</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>Suction vol. $\dot{v}_{2i}$ (m³/h)</td>
<td>54.9 (s = 0.14 m³/h)</td>
<td>45.9 ... 68.5</td>
</tr>
<tr>
<td>Discharge vol. $\dot{v}_{3i}$ (m³/h)</td>
<td>12.5 (s = 0.16 m³/h)</td>
<td>9.1 ... 24.9</td>
</tr>
<tr>
<td>Data</td>
<td>Design value</td>
<td>Variation range</td>
</tr>
<tr>
<td>------</td>
<td>--------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>$Q_{des}$ (kW)</td>
<td>27.3</td>
<td>22 ... 36</td>
</tr>
<tr>
<td>$T_{w1}$ (°C)</td>
<td>10</td>
<td>-10 ... 27</td>
</tr>
<tr>
<td>$T_{w2}$ (°C)</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>$T_i$ (°C)</td>
<td>6.52</td>
<td>-16 ... 22</td>
</tr>
<tr>
<td>$T_{2e}$ (°C)</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>$p_i$ (bar)</td>
<td>2.00</td>
<td>-</td>
</tr>
<tr>
<td>$m_{wd}$ (kg/s) - $v_{wd}$ (m$^3$/s)</td>
<td>0.218 - 2.18 10$^{-4}$</td>
<td>1.7510$^{-4}$ ≤ $v_{wd}$ ≤ 6.6710$^{-4}$</td>
</tr>
<tr>
<td>$x_1$ - $y_1$ (kg/kg)</td>
<td>0.5439 - 0.9991</td>
<td>0.4337 ≤ $x_1$ ≤ 0.8883</td>
</tr>
<tr>
<td>$x_{2e}$ - $y_{2e}$ (kg/kg)</td>
<td>0.3605 - 0.9858</td>
<td>-</td>
</tr>
<tr>
<td>$m_{l1}$ (%)</td>
<td>87.7</td>
<td>-</td>
</tr>
<tr>
<td>$m_{l2e}$ (%)</td>
<td>61.7</td>
<td>-</td>
</tr>
<tr>
<td>$m_{ll}$ (kg/s) - $v_{ll}$ (m$^3$/s)</td>
<td>0.0473 - 5.7 10$^{-5}$</td>
<td>0.0094 ≤ $m_{ll}$ ≤ 0.047</td>
</tr>
<tr>
<td>$m_{lv}$ (kg/s) - $v_{lv}$ (m$^3$/s)</td>
<td>0.0067 - 4.44 10$^{-3}$</td>
<td>0.0011 ≤ $m_{ll}$ ≤ 0.0067</td>
</tr>
<tr>
<td>$m_{2el}$ (kg/s) - $v_{2el}$ (m$^3$/s)</td>
<td>0.0333 - 3.8 10$^{-5}$</td>
<td>0.0014 ≤ $m_{2el}$ ≤ 0.0413</td>
</tr>
<tr>
<td>$m_{2ev}$ (kg/s) - $v_{2ev}$ (m$^3$/s)</td>
<td>0.0207 - 1.522 10$^{-2}$</td>
<td>0.0091 ≤ $m_{2ev}$ ≤ 0.0207</td>
</tr>
<tr>
<td>$h_1$ - $h_{2e}$ (kJ/kg)</td>
<td>-29.5 - 475.3</td>
<td>-</td>
</tr>
<tr>
<td>$s_2$ - $s_{2e}$ (kJ/kgK)</td>
<td>0.527 - 2.257</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.3: Design data for the desorber.

The chosen design conditions are very favourable to the wet compression-resorption system since the heat sink temperature glide is high (30 K) and the ratio $\Delta T_{flu}/\Delta T_{glide}$ is low (0.93). This can be verified in Figure 6.2, where the calculated performances (COP and SCD) of the wet compression-resorption cycle, the solution recirculation cycle and the vapour compression cycle are given for several binary and ternary mixtures for the set of external conditions described in Table 6.5. The mixture NH$_3$/H$_2$O is well suited in terms of COP: only R290/n-pentane and the ternary blend R290/R600/pentane could achieve slightly higher COP (by 3% and 6% respectively). In regard to the specific compressor displacement, mixtures like R125/R123 and R290/pentane would have been respectively about 36 and 20 % better, at almost equal COP performances. Compared with the pure refrigerant cycles under the same conditions of isentropic efficiency and minimum temperature approach, the COP increase is more than 50 %, whereas the SCD decreases by 39 % (R600). Calculations of the solution recirculation cycle under the same conditions
### Internal heat exchanger

<table>
<thead>
<tr>
<th>Data</th>
<th>Design value</th>
<th>Variation range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{exc}}$ (kW)</td>
<td>2.2</td>
<td>2 ... 7.5</td>
</tr>
<tr>
<td>$T_{2e}$ (°C)</td>
<td>32.1</td>
<td>26.7 ... 33</td>
</tr>
<tr>
<td>$T_2$ (°C)</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>$T_{4e}$ (°C)</td>
<td>35</td>
<td>30 ... 35</td>
</tr>
<tr>
<td>$T_4$ (°C)</td>
<td>43.86</td>
<td>-</td>
</tr>
<tr>
<td>$p_{2-2e} - p_{4-4e}$ (bar)</td>
<td>2.00 - 8.67</td>
<td>6.38 $\leq p_{4-4e} \leq$ 9.32</td>
</tr>
<tr>
<td>$x_{2e}$ (kg/kg)</td>
<td>0.3766</td>
<td>0.3716 ... 0.4079</td>
</tr>
<tr>
<td>$x_2$ (kg/kg)</td>
<td>0.3605</td>
<td></td>
</tr>
<tr>
<td>$x_4 = x_{4e}$ (kg/kg)</td>
<td>0.6000</td>
<td>0.5 ... 0.9</td>
</tr>
<tr>
<td>$m_{1,2e} - m_{1,2}$ (%)</td>
<td>63.5 - 61.7</td>
<td></td>
</tr>
<tr>
<td>$m_{1,4} = m_{1,4e}$ (%)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$\dot{m}<em>{2e}$ (kg/s) - $\dot{V}</em>{2e}$ (l/min)</td>
<td>0.0338 - 2.34</td>
<td>2.34 $\leq \dot{V}_{2e} \leq$ 3.14</td>
</tr>
<tr>
<td>$\dot{m}<em>{2e}$ (kg/s) - $\dot{V}</em>{2e}$ (l/min)</td>
<td>0.0194 - 848.4</td>
<td>359.8 $\leq \dot{V}_{2e} \leq$ 848.4</td>
</tr>
<tr>
<td>$\dot{m}<em>{2l}$ (kg/s) - $\dot{V}</em>{2l}$ (l/min)</td>
<td>0.0333 - 2.30</td>
<td>-</td>
</tr>
<tr>
<td>$\dot{m}<em>{4l}$ (kg/s) - $\dot{V}</em>{4l}$ (l/min)</td>
<td>0.0207 - 913.2</td>
<td>-</td>
</tr>
<tr>
<td>$\dot{m}<em>{4l} = \dot{m}</em>{4e}$ (kg/s)</td>
<td>0.0540</td>
<td></td>
</tr>
<tr>
<td>$\dot{V}_{4l}$ (l/min)</td>
<td>4.1</td>
<td>4.0 ... 4.2</td>
</tr>
<tr>
<td>$h_{2e} - h_2$ (kJ/kg)</td>
<td>434.6 - 475.3</td>
<td></td>
</tr>
<tr>
<td>$h_{4e} - h_4$ (kJ/Kg)</td>
<td>-70.1 ... -29.4</td>
<td></td>
</tr>
<tr>
<td>$s_{2e} - s_2$ (kJ/kgK)</td>
<td>2.124 - 2.257</td>
<td></td>
</tr>
<tr>
<td>$s_{4e} - s_4$ (kJ/kgK)</td>
<td>0.349 - 0.480</td>
<td></td>
</tr>
</tbody>
</table>

*Table 6.4: Design data for the internal heat exchanger.*

(with a liquid pump efficiency of 0.7 and a minimum temperature difference of 4.5 K in the heat exchanger and in the desuperheater) show that a COP increase of 10% can be achieved when using wet compression, assuming the latter is perfect. In Table 6.5 the results of the simulations for the wet compression cycle using NH$_3$/H$_2$O are given for the overall concentration leading to a maximal COP. The optimal overall concentration in Table 6.5, as well as the data of all other cycles data is different from that given in Table 6.1 to 6.4, because the latter data on the resorber and desorber correspond to a different
Figure 6.2: COP and SCD for several mixtures and cycles for the design case (W.C.: wet compression; S.R.: solution recirculation).

<table>
<thead>
<tr>
<th>$T_{w4}$ = 38 °C</th>
<th>$T_{w3}$ = 68 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{w2}$ = 40 °C</td>
<td>$Q_{\text{res}}$ = 31.4 kW</td>
</tr>
<tr>
<td>$\dot{m}_{or}$ = 0.25 kgs$^{-1}$</td>
<td>$\dot{m}_{wd}$ = 0.22 kgs$^{-1}$</td>
</tr>
<tr>
<td>$\Delta T_{\text{min}}$ = 3.3 K</td>
<td>$\Delta T_{\text{mind}}$ = 4.2 K</td>
</tr>
<tr>
<td>$\Delta T_{\text{mixe}}$ = 2.0 K</td>
<td>$\eta_{\text{ls}}$ = 0.85</td>
</tr>
<tr>
<td>$Q_{\text{des}}$ = 26.6 kW</td>
<td>$Q_{\text{ex}}$ = 1.1 kW</td>
</tr>
<tr>
<td>$W_c$ = 4.8 kW</td>
<td>$x_s$ = 0.5961</td>
</tr>
<tr>
<td>$\dot{m}_l$ = 0.0495 kgs$^{-1}$</td>
<td>$T_{w1}$ = 11.1 °C</td>
</tr>
<tr>
<td>$T_1$ = 5.9 °C</td>
<td>$T_{2c}$ = 35.8 °C</td>
</tr>
<tr>
<td>$T_2$ = 37.5 °C</td>
<td>$T_1$ = 77.3 °C</td>
</tr>
<tr>
<td>$T_4$ = 42.7 °C</td>
<td>$T_{4c}$ = 37.8 °C</td>
</tr>
<tr>
<td>$p_1$ = 2 bar</td>
<td>$p_2$ = 8.29 bar</td>
</tr>
<tr>
<td>COP = 6.54</td>
<td>SCD = 4.610$^{-4}$ m$^3$s$^{-1}$/kW</td>
</tr>
<tr>
<td>$\Delta T_{\text{mea}}$ = 4.4 K</td>
<td>$U_{A_r}$ = 7.2 kW/K</td>
</tr>
<tr>
<td>$\Delta T_{\text{meawd}}$ = 6.2 K</td>
<td>$U_{A_d}$ = 4.3 kW/K</td>
</tr>
<tr>
<td>$\Delta T_{\text{meane}}$ = 3.3 K</td>
<td>$U_{A_{\text{ex}}}$ = 0.3 kW/K</td>
</tr>
</tbody>
</table>

Table 6.5: Input data (bold letters) of the simulation program and results for the optimal NH$_3$ overall concentration.
minimum temperature approach ($\Delta T_{\text{min,r}} = 3.40$ K, $\Delta T_{\text{min,d}} = 3.48$ K) and to a different cycle calculation ($\eta_\text{in} = 1$ and no internal heat exchanger).

6.3 The resorber

6.3.1 General design considerations

Most of the thermodynamic advantages of compression-resorption heat pumps can be attributed to the good glide matching between the heat transfer fluid and the internal fluid. To achieve the best possible glide matching, perfect counter-current flow is necessary as well as a small mean temperature difference between the fluids. This implies that a large heat exchange surface area and/or a high heat transfer coefficient are needed. As seen in Chapter 4, the resorber UA-values are higher in the case of the optimized compression-resorption system than in the case of the vapour compression system. Since it is also known that the heat transfer coefficient for condensing mixtures is lower than the condensation heat transfer coefficient of the pure refrigerant (see for instance Collier [1994], Didion [1990], Koyama [1990] (R22/R114), Murphy [1988] (R114/R12)), a larger heat transfer surface is required than is necessary for pure refrigerant condensation. Plate-fin heat exchangers, which consist of a stack of alternate flat plates and corrugations brazed together as a block (see Figure 6.3) provide a good solution because of their large heat transfer surface per unit volume (typically 1000 m$^2$/m$^3$, compared with about 300 m$^2$/m$^3$ for a conventional shell and tube heat exchanger). Plate-fin heat exchangers also afford the advantage of true counter-current flow (see HTFS [1990]) and of a very close temperature approach (1-6 K) - although the latter can now also be achieved with shell-and-tube heat exchangers.

Another way to keep the heat exchange surface within limits while still having a low temperature approach is to use methods that increase the heat transfer coefficients. Besides active enhancement methods like stirring, vibrations or electric fields (Tanasawa [1994]), several passive methods can be applied: enhanced surfaces (special shapes, roughness, coatings), use of additives and use of inserts (Webb [1994]). Because plate-fin heat exchangers usually operate in the laminar or transition region, the enhancement method must be efficient at low Reynolds numbers. Therefore enhancement techniques in plate-fin heat exchangers generally use special shapes (see Figure 6.4) to ensure mixing of the liquid film (wavy fin) and repeated growth and destruction of the boundary layer (offset strip - also called serrated, or perforated fins). Serrated corrugations are usually recommended for condensation at low Reynolds numbers whereas, because of their decreasing friction coefficient (HTFS [1990]), wavy corrugations are recommended at high Reynolds numbers. The serrated corrugations have a much higher Colburn J Factor than the other corrugations, thus a higher heat transfer coefficient, at the expense of a higher friction coefficient (see Figure 6.5). This is not necessarily a problem in single-phase heat transfer, but in two-phase heat transfer (boiling or condensing), pressure losses lead to a decrease in the condensation temperature that makes the use of a small temperature approach impossible. However, when downwards flow is used, the friction losses can be
Figure 6.3: Counter-current plate fin heat exchanger with two corrugation types.

a) Wavy fin

b) Perforated fin

c) Serrated fin

Figure 6.4: Enhanced corrugations for plate-fin heat exchangers.

compensated by the momentum and gravitational gains.

In the present case, the resorber has characteristics of a condenser (condensation of a mixture) and characteristics of an absorber since not only is vapour fed, but also liquid in which the condensed vapour will be absorbed (see later in this section). This differs from traditional absorbers in that the liquid that is entering is not (or only slightly) subcooled while the vapour that is entering vapour is not (or only slightly) superheated thus the absorption process takes place nearer to the equilibrium conditions. In falling film
Figure 6.5: Colburn J factor and friction coefficient for single-phase flow for several corrugations (HTFS [1990]).

absorbers, the vapour is often introduced at the bottom of the absorber because of the difficulty of distributing the liquid and the gas simultaneously at the top. This design advantage may, however, be offset by flooding problems and by the fact that the pressure drop will be higher than in the case of co-current down flow. In the present design, vapour and liquid are separated after passing the compressor (see Section 6.6) in order to make safe operation of the compressor possible, but in a later stage of research, there will be no more need for separation. Due to this and to the lower pressure drop, the co-current down flow design is preferred. In this design, enhanced condensation will probably take place at the top of the resorber, because the draining of the condensate film will be improved due to the high interfacial shear stress caused by the vapour velocity. The condensation rate will probably decrease with the resorber length, because convective condensation is less at the bottom owing to the low (or zero) vapour velocity.

Another technique for improving the condensation of a pure refrigerant is to use droplet condensation instead of film condensation. Very high heat transfer coefficients are achieved, these being 4 to 20 times higher than for film condensation. To achieve droplet
condensation it is necessary to use additives or coatings (Teflon, noble metals) to inhibit surface wetting. For the condensation of refrigerants with a high surface tension (steam for instance), additives that increase the surface tension like oleic acid are used. No good additives have been found for low surface tension refrigerants (Webb [1994]). Because the efficiency of the additives decreases quite rapidly by depletion or surface contamination, coatings seem to be more promising, although they introduce an additional heat transfer resistance. Because of the difficulty of achieving drop condensation, condensers generally use film condensation. In film condensation any technique yielding film mixing, a reduced film thickness and a good draining of the condensate will improve the condensation heat transfer. As mentioned above, special geometries can improve the film mixing. Reduced film thickness and appropriate draining are intimately related. The film can be drained by gravity (vertical down flow), by shear stress forces (co-current vapour flow) and by surface tension (special shapes like fluted tube, Webb [1994]). With regard to the latter, a simple plain corrugation (extended surface) also acts as an enhanced surface because of the surface tension forces confining the condensate in the concave parts of the surface, i.e. between the corrugations and the separation plate. The condensate is drained and a thin film remains on the flat plate region between the corrugations (see Figure 6.6).

![Figure 6.6: Surface tension drainage yielding a thin film on the cooled wall.](image)

Less is known about the enhancement techniques for the absorption of vapour into a binary mixture or for binary mixture condensation. In the case of absorption of a pure vapour into a binary mixture (absorption of water into a LiBr/H₂O mixture or absorption of pure ammonia into a NH₃/H₂O solution), it is very important to avoid dry patches on the absorber walls, where the vapour cannot be absorbed. Contrary to what occurs in pure refrigerant condensation, the wettability of the surface must be increased, for instance by using surfactants to lower the surface tension. However, the most effective additives are those that enhance the mass transfer processes by creating surface convection - the so-called Marangoni effect (Setterwall [1991], Kim [1993], Jung [1993], Möller [1996]). The case where a binary vapour is being absorbed into a binary liquid (as in the case if the NH₃ vapour is not rectified) or condensed, is different because the vapour may also be condensed (and thus the outlet liquid enriched) when dry patches are present (see next alinea. According to Stephan [1995], binary mixture condensation can take place as film
condensation, as streamer condensation, or as drop condensation or, in the mixed forms, as film-streamer or streamer-drop condensation. In the case of non-film condensation, heat transfer coefficients higher by a factor of 4 than those for pure film condensation are observed. Non-film condensation could therefore compensate for the lower heat transfer coefficients of mixtures. According to Stephan [1995], the occurrence of non-film condensation is related to the instability of the condensate film, that occurs when \( \Delta \sigma/\Delta T < 0 \), where \( \sigma \) is the surface tension of the liquid in equilibrium with the vapour at the temperature \( T \). There are no experimental data for the surface tension of \( \text{NH}_3/\text{H}_2\text{O} \), so it was therefore estimated by using the calculation program of Wassenaar [1996], based on the equation of Tamura [1955] and described in Reid [1977]. Calculation under the resorber conditions \( (p = 8.67 \text{ bar}) \) show that \( \Delta \sigma/\Delta T > 0 \) for \( x < 0.5 \) and \( \Delta \sigma/\Delta T < 0 \) for \( x > 0.5 \). This means that in the first part of the absorber, non-film condensation could occur with higher heat transfer coefficient than in the bottom part of the absorber, where film-wise condensation occurs.

Stephan [1995] also introduces the concept of hyper-total condensation; if the bulk of the vapour is subcooled, which can happen when the temperature difference between wall and vapour is high, fog formation occurs. When the condensation is not total, the condensed droplets will flow out with the excess vapour. The condensing vapour has a higher concentration than initially, producing a condensate of a higher concentration than the expected concentration \( x_e \) (see Figure 6.7). This phenomenon was observed experimentally by Hershkovits [1992]. The same phenomenon may occur when no equilibrium can be maintained between the vapour and the liquid, that is in a case where dry patches or dry channels exist on the absorber wall. However with total condensation - which is desired in the present design - if the condensate coming from the different paths or channels is well mixed at the outlet, the concentration of the condensate leaving the absorber will be equal to the overall concentration \( x_{\text{e}} \), but the efficiency and the capacity of the condenser will be reduced. Total condensation will occur if the temperature approach is high enough.

When, as in the present case, a small temperature approach is wanted, dry channels may lead to non-total condensation (see Figure 6.8). In this case some of the vapour is not condensed, which also leads to poorer performances. From this analysis it can be concluded that for condensing mixtures it is very important that, if droplet condensation cannot be achieved, the vapour remains in contact with the condensate film in all channels. The distribution problem will be all the more important, since not solely vapour at the concentration \( x_e \) is introduced at the resorber top, but a vapour at the concentration \( y = x_i \) and a liquid at the concentration \( x_i \) (\( m_x = m_x x_i + m_y y_i \), see Figure 6.7). With regard to this, a condenser for mixtures must have the quality of an absorber rather than the qualities of a pure refrigerant condenser. Care must be taken to ensure that the condensate draining occurs without dewatering the wall (see Figure 6.6).

To conclude this section, the following options were chosen for the design of the resorber:

- plate-fin heat exchanger with serrated corrugations
- co-current down flow of the solution and the vapour
- counter-current flow between condensing mixture and cooling water
- no coatings, no additives for surface wetting or surface convection.

Coatings and additives for surface wetting and surface convection would themselves provide subject matter for a separate thesis.
**Figure 6.7:** Subcooling of the vapour \( y = x_f \) leading to fog formation and to a condensate with \( x_f > x_w \).

**Figure 6.8:** The condensation begins in the two-phase region. If vapour and liquid are not in contact: a) if cooling to \( T_{4f} \) is possible, the condensate is at \( x_f > x_w \), b) if cooling to \( T_4 \) only is possible, vapour at \( y_f \) remains.
6.3.2 Core design characteristics

The working temperature range allows the use of aluminium alloy for the plate and the corrugations instead of stainless steel which has a lower heat conductivity. Because of the presence of wet ammonia, the alloy should not contain any copper. In view of the experience of the Engineering Company Colibri with NH₃/H₂O absorption heat pumps, the alloy AlMn₁ is used for the heat exchanger core and AlMgSi₀.₅ for the headers and flanges. The rating of the resorber made by Colibri was based on the data specified in Table 6.1 and on a maximal pressure drop of 0.15 bar at the refrigerant mixture side. The plates and corrugations were salt-brazed. The serrated corrugations that are used are described in Table 6.6 and in Figures 6.9 and 6.10. The corrugations at the water side are identical to the corrugations at the NH₃/H₂O side. This is probably not the cheapest solution, but because serrated fins of low height are in a wide range of Reynolds numbers (500 to 15000), the most efficient (high ratio j/l, see Figure 6.5) they have been chosen.

The rating of the resorber by Colibri has led to a heat exchanger matrix with 15 layers on the water side and 14 on the NH₃/H₂O side, the dimensions being 1200 x 113 x 100 mm (see Figure 6.11). The heat exchange surface area is 6.39 m² at the NH₃/H₂O side, 6.58 m² at the water side and the total heat exchange area is 9.18 m². The volume of the heat exchange core is 0.01356 m³.

\[
y = (h-t)(1 + \cos(2\pi x/w))/2
\]

| h  | 3.00 x 10⁻³ m | Plate spacing   |
| w  | 7.00 x 10⁻³ m | Flow passage width |
| t  | 0.20 x 10⁻² m | Fin thickness    |
| x₁ | 2.15 x 10⁻³ m | Uninterrupted small fin length in flow |
| x₂ | 6.45 x 10⁻³ m | Direction        |
| a  | 0.45 x 10⁻³ m | Uninterrupted large fin length in flow |

\[
P_w = 1.179 \times 10^{-2} \ m
\]

\[
\Lambda_r = 9.8 \times 10^{6} \ m^2
\]

\[
D_h = 3.32 \times 10^{-4} \ m
\]

\[
n = 285.71 \text{ fin/m}
\]

\[
\beta = 1122.8 \text{ m}^2/\text{m}^3
\]

\[
\alpha = 0.406
\]

| \(P_w\) | Wetted perimeter per channel |
| \(\Lambda_r\) | Free flow cross sectional area per channel |
| \(D_h\) | Hydraulic diameter (= 4\(A_h/P_w\)) |
| \(n\) | Passage density |
| \(\beta\) | Total heat transfer area/volume between plates |
| \(\alpha\) | Fin area/total area |

Table 6.6: Specifications of the serrated corrugations.

6.3.3 Distributor design

Equal distribution of the liquid and the vapour in the channels is known to be of the greatest importance. The liquid must flow as a film along the channels, the vapour
Figure 6.9: The serrated fins used in the resorber and desorber.

Figure 6.10: Photography of the serrated corrugations
occupying the central space. In traditional absorption equipment (tubes rows) or laboratory experiments, liquid feeding is usually done by using overflow devices, a porous membrane or via a slot (see Sack [1967], Yih [1986], Westra [1990], Brunin [1995]). For film absorption inside tubes, special cone distributors that ensure that there will be film flow can also be used. However, these methods are not easily applicable to a compact heat exchanger. For compact heat exchangers using vertical downwards flow, a spray nozzle is usually used to distribute the liquid into the vapour, which is admitted above the sprinkler (instead of a sprinkler, sparge pipes may be used). Special corrugated plate distributors are used after the sprayer has been passed and at the resorber outlet in order to ensure that the path and thus the pressure drop are identical in all channels. Several distributor designs for re-mixing two-phase flow are shown in HTFS [1990]. The main

- Test-plant design
Figure 6.12: View of the upper side of the resorber and of the distribution system.

drawback when using a spray nozzle is the high pressure loss (minimal 0.2 bar). For a well designed absorption plant, this will not cause a problem because of the liquid subcooling. However the liquid being sprayed in the present case is near its saturation temperature, so flash gas will be produced and this will disturb the working of the nozzle. It was therefore decided to design an appropriate distributor with a very low (<0.03 bar) pressure loss. The liquid is distributed by a sparge pipe on a plate with a matrix of 4x4 small diameter pipes, the liquid level reaching the top of the pipes. The vapour flowing above the pipes entrains the liquid into the pipes and distributes it on the total frontal area of the channels. The design was made by DeNiet [1994] and tested with air and water. Since the metering pipes are sprayed regularly on the frontal area, the flow path and thus the pressure drop will be about the same in all channels. The only path difference comes from the outlet pipe that is located at the centre of the matrix (see
Figure 6.11). A sight-glass was placed between the distributor and the beginning of the plate in order to watch the quality of the distribution (see Figure 6.12). The material used for the distributor is stainless steel 316 L.

6.4 The desorber and the internal heat exchanger

Compact heat and mass exchangers were chosen for the same reasons as those given for the absorber. Co-current liquid and vapour flow is demanded since a two-phase flow is produced after passing the expansion valve and the use of a separation device is thermodynamically not advantageous. Upward flow is usually chosen for evaporating fluids in tubes or in plate-fin heat exchangers; the liquid is fed in at the bottom, which makes the distribution easier, and the vapour is taken away at the top of the heat exchanger. However, when a very low temperature approach is wanted, the pressure drop should be reduced as much as possible and therefore downward flow should be recommended. For vertical downward co-current two-phase flow, the liquid is generally confined to the wall and only annular or annular entrained flow is observed (Webb [1994], Collier [1994], Oliemans [1990]). Downward film evaporators are often used as reboilers, with a recirculation ratio between 2 and 4, in order to prevent possible dry-out. In the case of the present design, incomplete evaporation is desired, and although the evaporator will be used as once-through device, it has an equivalent recirculation ratio \( \frac{\dot{v}_1}{(\dot{v}_{2e} - \dot{v}_1)} \) of 3. Because of the low wall superheat (low temperature approach) and of the moderate estimated heat flux, nucleate boiling is not likely to take place, or at least can be assumed not to have a large influence when plain corrugations are used. Convective evaporation is expected to make the greatest contribution to the heat transfer coefficient, if a film is effectively formed on the wall (Robertson [1980]). At low liquid volumetric flow rates, it is possible that all the liquid is dispersed as droplets in the vapour phase, creating a dry-wall mist flow with its inherent low heat transfer coefficient. Therefore, it is as important for the desorber as for the resorber, that no dry patches occur. Since heated films tend to break easily, the velocity of the vapour should not be too high (liquid present as mist only) but also not too low, because a very thin film is needed to achieve a high convective evaporation heat transfer coefficient. Enhanced geometries for convective vaporization can promote either nucleate boiling, or convective evaporation, both these terms being superposed in convective vaporization (Chen [1966], Steiner [1992], Webb [1994]). Because surfaces that give a high single-phase heat transfer coefficient also give a high convective evaporation coefficient, the use of the serrated fin is recommended (see Figure 6.5). Surfaces enhancing the nucleate boiling component, by using perforated corrugations (see Figure 6.4) or porous coatings could also be used. However the performances of perforated plates are not as predictable as those of serrated corrugations, thus we decided to use the latter, although it will certainly be worth experimenting with perforated corrugations in a later stage.

The desorber core, rated by Colibri, consists of 17 layers at the water side and 16 layers at the NH₃/H₂O side, its dimensions being 1000 x 131 x 135 mm (see Figure 6.13). The heat exchange surface area is 7.23 m² at the NH₃/H₂O side, 7.46 m² at the water side and the total heat exchange area is 10.42 m². The volume of the heat exchange core is 0.01769 m³.
The design of the internal heat exchanger was also made by Colibri. Because of its small capacity, and thus its small dimensions, cross flow was chosen. The corrugations are the same as for the resorber and the desorber. The heat exchanger is integrated to the desorber and placed at the bottom end of it, in such a way that the two-phase NH₃/H₂O mixture always flows along the channels of the internal heat exchanger. A by-pass is installed at the side of the NH₃/H₂O solution coming from the resorber, in order to eliminate the internal heat exchange when this is needed for the validations. The heat exchanger size is 162 x 131 x 135 mm and there are 16 channels at the side of the two-phase mixture to be heated, and 17 channels at the side of the solution to be subcooled. The material used for both the desorber and the heat exchanger is aluminium alloys as described in Section 6.3.2.
Because of the very low volumetric flow rate of the liquid after passing the expansion valve (1.3% of the volumetric vapour flow rate, see Table 6.2), it was believed that the two-phase mixture would behave as a continuous vapour phase with entrained droplets. In view of this, a simple diffuser would be suitable to distribute this pseudo-continuous phase uniformly over the whole frontal area and this was implemented in the test-plant. However, it could have been predicted that because of the low volumetric liquid flow rate, it would be necessary to use a distributor to obtain a liquid film flow at the inlet of the heat exchange area, and to ensure that not too much liquid would be entrained into the vapour core since this would greatly decrease the heat transfer coefficient. Evidently, a diffuser cannot ensure that this condition is met because a simple calculation of the flow pattern (see Oliemans [1990] for instance) shows that at the inlet of the core, plug or slug flow will occur due to the large pipe diameter, causing failure of the distribution system. All measurements described in Chapter 7 were made with the diffuser. However we plan to use a distribution system similar to that of the resorber (see Section 6.3.3) for future experiments (see Chapter 8).

6.5 The compressor

Chapter 2 indicated that the compressor is of great importance in obtaining the wet compression-resorption cycle. Two extreme cases have been recognized: the first one being the case of equilibrium two-phase compression and the second one being the separate compression case in which the liquid behaves as if it was pumped separately. The vapour is then superheated and there is no heat exchange between liquid and vapour. Between these two cases a wide range of behaviour is possible, and the programme of experiments was designed to assist in gaining understanding of the wet compression process. Several possible technological options will be described. At the beginning of the design process it was necessary to make basic choices between the use of an oil-free or an oil-lubricated compressor and about the type of compressor. These choices were based on a study of the available literature, on basic technological considerations and on a study of the compressors available on the market, since the development of a new compressor was not considered within the scope of this thesis.

6.5.1 Oil-free or oil-lubricated compressor

In both the solution recirculation cycle and the wet compression cycle, the vapour to be compressed is in the saturated state. Since vapour and liquid are separated in the solution recirculation cycle, the compressor has to handle only a very small quantity of liquid. In the case of the wet compression cycle, the problems are amplified because a larger quantity of liquid is flowing into the compressor. The lubrication is more likely to decrease because of the oil forming an emulsion with the solution, or to cease because of the lubrication oil being carried away with the liquid, thus causing irreparable damage to the compressor. Furthermore, the oil taken away from the compressor could disturb the resorption and desorption processes. It is therefore recommended that when using an oil-lubricated compressor oil separators should be installed (see for instance Mucic [1990]).
Brunin [1995]). A gravity separator may be suitable for the vapour phase, but a membrane separator would be better for the liquid phase because oils have more or less the same density as the liquid phase, making gravity separation difficult. Since separation is never perfect, it can be expected that the performances of the heat pump will decrease with time, and that it will be necessary to use a thermal separation process on a regular basis to keep the oil concentration within design limits (see also Brunin [1995]). Using an oil-lubricated compressor therefore implies the installation of three separation devices, complicating the test-plant, making it more expensive, and increasing the risk of failure. Because of the greater simplicity of the plant and of the lower number of components, despite the higher cost oil-free compression seems to be a more attractive alternative. This option was therefore used for the design of the test-plant.

6.5.2 Choice of a compressor suitable for wet compression

6.5.2.1 Literature study on wet compression

When this study began (1989), there was little literature on wet compressors. However,
since 1986 an increased interest in liquid-gas compression can be observed, corresponding to an increased demand from the oil/gas pumping industry, and the demand for oil-free air production for medical purposes. Furthermore there has also been increased interest in designing high temperature heat pumps for which the compression superheat must be limited to avoid chemical instability of the refrigerant and compressor failure.

Because the oil-pumping industry is more concerned with low quality mixtures (high liquid content), pumps are generally used. These pumps are generally large (> 150 m³/h) and designed for high pressure differences (Δp > 20 bar). Rotodynamic pumps (centrifugal, radial, mixed) are used for mixtures with low gas contents (up to 15%). Positive displacement pumps are inherently capable of handling higher gas contents (Arnaudau [1988]). Of the rotodynamic pumps, radial flow pumps are preferred since they can achieve a higher pressure rise or be smaller than axial pumps. Jacobsen [1990] reports the design of a high efficiency contrarotative machine. Ashman [1988] designed a hybrid pump with the characteristics of a centrifugal pump (periphery pump) and those of a positive displacement pump (liquid ring pump) in order to handle the pressure rise caused by possible slugs. Dolan [1988] describes how to handle the pressure rise under slugging conditions and appeared to be able to handle very high gas fractions (up to 90%). Centrifugal compressors have also been widely used for steam compression in cases where the capacity is large enough and the compression ratio is relatively low. However, there is still a need for capacity up to 1000 kW and for pressure ratios above 3. This need could be satisfied by screw compressors.

Screw compressors with water injection into the suction or into the compression space can produce a reduction of the vapour superheat, absorbed by the evaporating water particles. Westphal [1978] and al. designed a water-flooded, oil-free, air, twin-screw compressor. Timing gears were used, because water could not provide adequate lubrication. Haselden [1986] tested a Mistui-Seiki monoscrew compressor. It had poor volumetric efficiency (30%), probably due to excessive clearance and losses due to heat transfer effect.

For refrigeration and closed heat pump duties, Plastinini [1986] investigated the effect of injecting liquid into a positive displacement compressor. He found that heat exchange between liquid and vapour is better with small liquid droplets and that increasing the amount of injected liquid reduces the power spent on compression, but increases the power losses in the valves and the injection line. In two-phase compression, slugging must be avoided because the incompressibility of the liquid slug could lead to cylinder pressures up to 10 times the peak pressure, damaging the valves. Singh [1986] tried to define the conditions leading to the appearance of slug flow in a reciprocating compressor and found that slugging occurs only at start-up when the mixture quality is very low (almost all liquid). A study by Liu [1994], who shows that slugging depends on the quality, on the kinematics and on the design of the compressor, leads to a similar conclusion. Assuming a homogeneous flow entering the cylinder control volume, it was shown that slugging is more likely to occur with very low mixture qualities, when the heat transfer between refrigerants and the cylinder is poor, or when the refrigerant is one that is condensed during the compression (positive saturated vapour line slope, see phase diagram in Chapter 2). It was shown that increasing the temperature gradient (dT/dα with α crank angle) by transferring heat into the refrigerant and decreasing the cylinder volume gradient (dV/dα) had a positive effect in avoiding slugging. Since scroll compressors have a compression angle of 540 °, compared to 360° for rolling piston, 300° for twin-screw and 180° for
reciprocating compressors, they should be recommended for wet compression.

It is still necessary to determine the best way of injecting the liquid. According to Habershill [1987], who considered isochoric liquid injection into a reciprocating compressor, late injection helps to decrease the discharge temperature and to increase the COP of the heat pump. The optimal location of the injection is at the point where the temperature before injection is equal to the desired temperature for the discharge. However, his results are not in agreement with the later work of Stosis [1988], Ozaki [1990] and Ayub [1992]. Stosis [1988] studied the influence of oil injection into a screw compressor. The effect of the droplet size was studied and it was found that oil and gas have the same temperature up to the droplet diameter of 500 µm, but even for droplets with a diameter as high as 1 mm, the temperature difference between oil and gas does not exceed 1.5 K. It was concluded that if the droplets are not able to reach the housing and to form an oil film, it can be assumed that oil and gas behave like a homogeneous mixture. The temperature of the injected oil, which should be as low as possible, has a strong influence on the discharge temperature and on the temperature during the cycle. This affects the energetic efficiency, but not the volumetric efficiency. The position of the injection port was shown to have a strong influence on the temperature during the cycle, but not on the discharge temperature. An optimum injection location was found between the one optimizing the volumetric efficiency and the one optimizing the energetic efficiency. Although the oil to gas ratio influences the discharge temperature, it was shown to have only little influence on the compressor performances. Ozaki [1990] studied the effect of wet compression for a refrigeration cycle using H₂O as refrigerant. Instead of using the two-phase flow coming from the evaporator, Ozaki recommended the injection of atomized liquid, since this is more practical for promoting vaporization of the liquid phase and stabilizing the system. The easiest mixing process to realize is isobaric mixing, with isenthalpic pressure drop at the atomizer. However, the mixing power is high. In view of the COP, isochoric mixing should be preferred since the required power falls between isentropic and isobaric mixing. An optimal condition for isobaric liquid injection was found, but it seemed that if the pressure drops in the atomizer and during the phase change are taken into account, the earlier the injection the better the performances, so injection should be made in the suction line. In a later experimental set-up, Ozaki [1994] studied the injection of water into steam. The temperature of the atomized water droplets was found to be very close to the saturation temperature corresponding to the working pressure, the temperature difference between the vapour and liquid phases was about 10 K, and droplets up to diameters of 10 µm were sufficiently evaporated. Ayub [1992] made a similar study on the optimum location of the injection for scroll compressors, comparing injection into the suction line, into the sealed suction pocket and into a sealed compression pocket. For R22, suction pocket injection appeared to be the best, theoretically as well as experimentally, although the capacity ratio decreased slightly. An experimental analysis of Afjei [1992] on suction line liquid injection into a scroll compressor shows that the mass flow efficiency is decreasing with decreasing suction vapour quality, but that the total energy efficiency improves due to a lower shell temperature. The absence of superheating should produce an increase in the mass flow rate, but liquid leakage reduces this by flashing into the suction chamber. However this flashing process will be limited at high speed. To ensure that this literature study covers the years when research for this thesis was in progress, the work of Dutta [1996] must be mentioned. The wet compression process was studied by using 2 models: a homogeneous one (T_v = T_i) and a droplet model (T_v < T_i) that took into account the heat transfer between vapour and liquid. The
homogeneous and droplet models gave similar results for small size droplets, producing results similar to the experimental data: the liquid enters the cylinder as a thin drop and exchanges heat with the vapour perfectly.

6.5.2.2 Compressors used in wet compression-resorption cycles

At present four test-plants using wet compression are known to the author. In a test-plant with 1.4 kW heating capacity, Torstensson [1991] used an oil-lubricated aluminium scroll compressor without any form of oil recovery. He reported problems of compatibility between the solution and the oil, but gave no data on the compressor, resorber and desorber behaviour. Malewski [1988] used in an industrial test-plant (800 kW heating capacity) a monoscrew compressor in which the bearings and gland seal were lubricated by the solution itself. This led to critical corrosion problems, after which closed grease lubrication of the bearings was applied. In this test-plant, the liquid is separated from the vapour after the desorption process, heated in an internal heat exchanger and, in order to ensure a good seal, is injected into the compressor via a nozzle at a pressure intermediate between the suction and the discharge pressures. Bergman [1990] used in an industrial plant for water heating (1000 kW heating capacity) an oil-free screw air compressor adapted to the purpose. In his test-plant, the liquid is also separated from the vapour after the desorber, pumped and injected partly in the suction line, partly in the discharge line in quantities that can be varied from total wet compression to total separate compression. The plants of both Malewski and Bergman did run but have now been shut down because of economic problems. The fourth test-plant is a laboratory plant at the Technical University of München (Sixt [1995]). It uses the mixture R22-E181 (instead of NH₃/H₂O that is used in the three others) in a four-component cycle (evaporator, generator, absorber and condenser). A Wankel compressor lubricated by a mixture of the oil and the solution itself has been used. The absorption during the compression process has been such that after passing the compressor, no vapour was available to be absorbed in the absorber.

6.5.2.3. Selection of a compressor for a first run of the test-plant

The main limitation on the choice of a compressor has been its small size (55 m³h⁻¹ inlet capacity and 4.5 kW isentropic power) combined with the use of NH₃/H₂O, because compressors suitable for use with ammonia in an oil-free design were not available below 30 kW power and 900 m³h⁻¹ inlet capacity.

Although piston compressors have been used experimentally for wet compression (see Section 6.5.2.1), it was considered that too much risk was attached to their use because of possible liquid slugs damaging discharge and suction valves, pistons and shafts. They can be used only under homogeneous flow conditions, which cannot be ensured with certainty.

Centrifugal and axial compressors are interesting in that they do not need any internal lubrication, but their blades may also be damaged by liquid slugs. An improved design might possible solve this problem (see Section 6.5.2.1). Their greatest disadvantage for the present application is that they are not available for low capacity (<250 kW) and high pressure ratios (>3). However, when a high capacity is needed they should be considered.

Rotary compressors are usually less sensitive to liquid injection because they do not have
suction and discharge valves. Rotating eccentric compressors were eliminated because they must be oil-injected. Of course, the use of suitable materials could allow the injection of a solution instead of oil, but this would entail much preliminary research. Scroll and sliding vane compressors can be used as air compressors in an oil-free design. These kinds of compressor were developed for small power, and are therefore well suited for a laboratory test-plant, but less interesting in industrial applications. When this research began, manufacturers had no experience of liquid injection, thus this option was discarded. However, according to Section 6.5.2.1, such compressors now appear to be very suitable and they are certainly worthy of consideration for small scale applications. Liquid-ring compressors may appear to offer good possibilities, since the use of a liquid is part of their working principle. Nevertheless, their very low efficiency reduces the advantages of wet compression to zero, so that they have very little future in industrial applications (see below). Screw compressors may provide the best solution, as their capacity, power and pressure ratio are suitable for a wide range of industrial applications. With a synchronizing gearwheel, the oil-free design can be easily achieved. Manufacturers have also gained experience with water injection into oil-free air screw compressors and, when appropriate materials are used, it is not even necessary to use a timing gear.

In view of the advantages of screw compressors and because compressors suitable for ammonia were not available for the test-plant design range, first a small Grass’air water injected air screw compressor was adapted to the design aims. The screws were made of a composite of synthetic material and ceramic, which permits the use of water as a lubricant, avoiding the use of timing gears. However, the synthetic material used in the screws could not withstand ammonia and began to swell when it came in contact with ammonia, preventing the running of the shaft.

In order to run the test-plant as quickly as possible, it was decided to implement a liquid-ring compressor. A two-stage Travaini water ring compressor was selected. All wetted parts are of stainless steel and the sealing is ensured by simple mechanical silicon/carbide seals. A schematic view of a single-stage liquid-ring compressor is given in Figure 6.15. Although the liquid-ring compressor was mentioned in the literature an interesting solution for wet compression in heat pumps (Stokar [1987], Sixt [1995]), it is quite easy to show that in fact liquid-ring compressors are unsuitable for this application. From liquid-ring vacuum pump technology, it is known that the capacity of these pumps reaches zero when the intake pressure has decreased to the vapour pressure of the liquid compressant (or liquid ring). At that moment, the rotor chambers and the suction chamber are filled with evaporating liquid compressant only. For liquid-ring compressors, the decrease in capacity is negligible if the intake pressure is high enough compared to the vapour pressure of the liquid compressant. This is usually the case because the chosen liquid compressants are low vapour pressure liquids, like water, oils, chlorinated hydrocarbons or alcohols. However, in the wet compression heat pump, the liquid compressant should be the high pressure solution itself. If the solution is injected into the compressor at a temperature equal to or higher than the suction temperature, the liquid compressant vapour pressure will be equal to or higher than that of the intake vapour, so that the capacity of the compressor will theoretically decrease to zero. However since a certain time is necessary to initiate the evaporation of the liquid-ring, and since the compressor is running fast, it is likely that the suction vapour will be pumped all the same, but at a very low volumetric efficiency. Decreasing the temperature of the injected liquid will allow a higher pumping capacity, at the expense of the discharge temperature, that will probably decrease.
drastically, cancelling out the heat pumping task of the compressor. The direct conclusion is that with a liquid-ring compressor using the solution itself as a liquid compressant, the design conditions could never be met, and a compromise would have to be found between the volumetric capacity and the discharge temperature. The measurements made with the liquid-ring compressor will be described in Chapter 7 and the conclusions relating to the implementation of a different compressor will be given in Chapter 8.

6.6 Ancillaries and lay-out of the test-plant

To avoid corrosion problems all parts that come into contact with NH₃/H₂O, except for the aluminium heat exchangers, are made of stainless steel. The pipe diameters of the pipes with two-phase flow have been calculated by using the Smith correlation (See Smith [1971] and DeNiet [1994]), in order to ensure that there is a vapour velocity high enough to carry the liquid, but not so high as to cause excessive pressure loss. To ensure adequate sealing of an oil-free compressor, liquid must be injected at a pressure higher than the suction pressure. To avoid separation of the liquid and vapour phases after passing the desorber, the best strategy seemed to be to inject complementary high pressure liquid from the resorber into the compressor. However, in the first stage of experimentation, the quantity of high pressure liquid needed was not yet known. Furthermore several compressors were to be used, including the liquid ring compressor which needs a high liquid injection flow rate (18 l/min), thus, in order to be able to make comparisons at constant mass flow rate and capacity conditions in the other system's components, it was decided that the compressor should be isolated from the other components of the plant. That is why a gravity separator was installed before the resorber, allowing the recovery
**Figure 6.16:** Simplified lay-out of the test-plant with measurement points (m: mass flow rate, V: volume flow rate, p: pressure, T: temperature, x: NH$_3$ concentration).
of the liquid necessary to the compressor liquid injection (see Figure 6.16 and complete lay-out in Appendix F). In order to control the temperature of the injected liquid, an heat exchanger A was placed after the separator. The compressor, which has a maximum rotational speed of 3500 rpm, is driven by a Siemens variable speed electro-motor (0-1650 rpm) coupled to a drive belt. This electromotor is used because it was already available in our laboratory and its use reduced the cost of the test-plant. However, this motor is very much too large (41 kW), so COP calculations would be unrealistic if they were based on the real electricity consumption of the motor. The expansion valve and all other valves are hand controlled needle valves. The heating of the desorber and the cooling of the resorber are achieved by two water loops. To limit energy consumption, a heat exchanger B has been introduced between these two loops. The water inlet temperatures in both the desorber and resorber are thermostatically controlled. After the hot water coming out of the resorber has been precooled in the heat exchanger B, it is cooled further by a glycol/water heat exchanger C. The cold water is then sent back to the resorber, and the glycol cooled by a cooling machine. The test-plant has been designed in such a way that no pumps are needed at the NH₃/H₂O side, except when starting the operation (see Appendix F). The pumps selected are all gear pumps with magnetic coupling. Pump 32 (see Appendix F) is used to fill the system, pump 33 pumps the liquid from the resorber to the desorber until the required high pressure is achieved and pump 34 is used to inject the liquid into the compressor until the pressure difference between suction and discharge is lower than 4 bar. Three other pumps (7, 8 and 22) are used continuously at the heat transfer fluid side to ensure that circulations in the desorber circuit, in the resorber circuit and in the cooling machine are maintained. The filling system of the installation uses a liquid storage vessel of 24 litre capacity, the pump 32 and an Anton Paar density meter (see Appendix F). The liquid storage vessel is also used when emptying the system or modifying the concentration. Figures 6.17 and 6.18 give a general view of the test-plant before insulation.

![Diagram of the test-plant](image)

*Figure 6.17: General view of the test-plant.*
6.7 Measurement and control

6.7.1 Data acquisition

A total of 76 data signals is processed on-line by a data-logger Hewlett-Packard 3497A. The accuracy of the output voltage is better than ± 5µV. The data-logger is coupled to a computer, displaying the main data on screen. A Pascal program, HWP (see Itard [1997]), controls the data acquisition. Temperatures are measured each minute (or at any other given time interval), whereas the other data are recorded every 10 seconds. The latter because the pressure can vary quite quickly in the starting phase, and can exceed the maximum value allowed in the test-plant. The pressure must be quickly controlled by carefully reducing the liquid injection temperature. A measurement value consists of an average of at least ten measurement points.

6.7.2 Temperature measurement and control

Temperatures are measured with Copper-Constantan thermocouples, placed into stainless steel wells. They are connected to the data logger, which has an electronic zero point.
compensation. The thermocouples have an absolute temperature accuracy of ± 0.1 K. The conversion of the voltage signal to an absolute temperature by the data logger has a precision of about ± 0.2 K. The systematic error due to the thermal conductivity of the probe does not exceed ± 0.1 K.

A two-phase flow is expected in the suction and discharge lines, which means that the sensors will be wetted by the droplets present in the vapour phase. Consequently the recorded temperature will be close to the saturation temperature at local pressure and concentration. Therefore, the possible superheating of the vapour and subcooling of the liquid cannot be measured. This problem affects all the thermocouples in the suction and discharge lines as well as those at the NH₃/H₂O side, and at the inlet of the resorber and of the desorber. In Chen [1977] and Hewitt [1978], different methods used to measure the vapour temperature in a vapour/droplet mixture are described, but these are not easily applicable on-line. In the compressor discharge line, the vapour and the liquid are expected to reach the saturation temperature rapidly owing to the mixing effect of the turbulence at the compressor outlet. Despite the difficulties in application, some of these methods should be applied if further investigation of the equilibrium departure in two-phase compression is necessary. On the suction side, annular flow is expected, and an attempt is made to measure the liquid phase temperature (T₂₁) and the vapour core temperature (T₂₂) separately by positioning one thermocouple in the middle of the pipe and the other close to the wall.

The correction term for the impact temperature effect due to the fluid velocity v (v²/2C_p) is negligible for liquid flow and does not exceed ± 0.1 K for vapour or two-phase flow (v < 20 m/s). Therefore, the total absolute error in the temperature measurement never exceeds 0.5 K.

Both the inlet temperatures of the source (T_w₂) and sink (T_w₁) must be controlled. T_w₂ is controlled by a West 3810 PID controller, acting on the heating resistances placed in the water vessel of the heating loop (see Figure 6.17). The temperature can be manually set at the desired value. The accuracy of the thermostat is ± 2 K. T_w₁ is controlled to an accuracy of ± 2 K, by a Spirax-Sarco thermostat, which controls the glycol flow into the water/glycol heat exchanger, by mean of a three-way valve.

At the NH₃/H₂O side, the only temperature to be controlled is that of the liquid injected into the compressor. This is accomplished by first roughly controlling the water flow into the heat exchanger A (see Figure 6.16), and then controlling the flow into heat exchanger 32 by means of a thermostatic water valve.

6.7.3 Pressure measurement

Pressures are measured with Trans Instruments strain gauge transducers. In front of and behind the resorber, type BHL 4260, with a full range 0 - 10 bar, with an accuracy of 0.15 % span, corresponding to an absolute deviation of 0.015 bar has been used. The other pressure transducers all belong to the Series 2000, with an accuracy of 0.25 % span. As the full range is also 0 - 10 bar, the absolute deviation is 0.025 bar.
6.7.4 Mass flow and concentration measurement

In front of and behind the resorber, true mass flow measurement of the liquid is preferred, because the mass flow rate is the quantity that is of direct interest in calculating the heat and mass balances. Micro-motion mass flow meters from Rosemount, working on the principle of the Coriolis or gyroscopic force, were selected (see for instance Halsell [1960] or Rosemount [1991] for a description of the principle). The medium flows into a U-tube vibrating at its natural frequency. The mass flow rate is proportional to the time $\Delta t$ between two passages of the tube on its axis and to some geometrical constants. The time $\Delta t$ is measured by two magnetic sensors placed at both sides of the tube, which to some extent isolates the measurement signals from external vibrations. The Micromotion flow meters are also built with two U-tubes, vibrating in antiphase, which makes them totally independent of line vibration.

Since the natural vibration frequency is directly proportional to the total mass of tube and medium together, the density of the medium can be measured easily, by using the same detection system as for the mass flow, and a supplementary temperature measurement. All data necessary to the concentration calculation are therefore available. The $\text{NH}_3$ concentration is calculated from the temperature and the density, using the Trepp-Ziegler equation for $\text{NH}_3/\text{H}_2\text{O}$.

The accuracy is 0.2 % of the actual flow. The density is measured to an accuracy of $\pm 2$ kgm$^{-3}$, which means that the Micromotion is too inaccurate for density measurement in the vapour phase. The pressure drop through the flow meter is about 0.2 bar.

In the filling vessel, an Anton Paar density meter, model DPR 12Y, also working on the vibrating U-tube principle, was installed. This measures the liquid density to an accuracy of $\pm 2$ kg/m$^3$.

6.7.5 Volume flow measurement and control

6.7.5.1 Primary heating and cooling loop

Accurate measurement of the flow at the heat transfer fluid side (water) is necessary to calculate the heat released and gained in the desorber and the resorber respectively, and therefore to calculate the external COP. Two COPA-XM magnetic flowmeters from Fisher & Porter were selected. The operating principle is based upon Faraday's law of induction: the voltage induced across a conductor (the fluid) moving perpendicularly through a magnetic field is proportional to the average flow velocity of that conductor and thus, to its volumetric flow rate. The electrical conductivity of the fluid must be higher than 5 $\mu$Scm$^{-1}$, which is the case for water and for ammonia, as well as for their mixtures. The accuracy is 0.5 % span. The chosen full scale is 50 l/min and the deviation is 0.25 l/min. To control the water flow into the resorber and the desorber, needle valves mounted on a by-pass are used.
6.7.5.2 Cooling loop of the compressor liquid injection circuit

Since this flow does not directly affect the COP of the heat pump, two variable area flowmeters Fisher & Porter, series 10A5400, with the accuracy of class 2.5 are used. The liquid injection flow is controlled either by a variable revolution speed pump or by means of a needle valve.

6.7.5.3 NH₃/H₂O side

Two-phase flow measurement does not provide useful information unless the void fraction is measured at the same time. Because accurate on-line void fraction measurement is difficult to achieve (Hewit [1978]), it was decided to avoid flow measurements in the two-phase region.

A volume flowmeter was installed in the injection liquid line of the compressor. Because the concentration, and therefore the viscosity and the density of the solution can change, a magnetic flowmeter which is independent of the former parameters was used. The density of the liquid, and its concentration, can be deduced from that of the liquid flowing into the resorber, possibly with a correction for the temperature. A COPA-XO from Fisher & Porter with an accuracy of 1% span was selected. The full scale is 20 l/min and the deviation is 0.2 l/min.

The mass flow rate of the vapour flowing into the resorber can be calculated from the difference between the liquid mass flow rates before and after the resorber. The presence of a volume flow meter in the vapour line then makes possible the calculation of the vapour density. As the temperature and the pressure are also measured, it is possible to calculate the real NH₃ vapour concentration with the Trepp-Ziegler equation. In this way an attempt can be made to quantify equilibrium departures. Since the flowmeter is located before the resorber, it is important to limit its pressure drop, which should not greatly exceed that of the liquid line, that is 0.2 bar. the pressure drop must be also independent of the fluid physical characteristics, as they can change strongly with the concentration. A Swirler from Fisher & Porter was selected. The operating principle is based upon the measurement of oscillations of vortices. The initially axial flow is forced into curved inlet blades, that add a tangential velocity component. The flow becomes unsteady, and a change in the direction of the rotational axis takes place when the fluid enters the enlarged section of the flowmeter. This produces velocity fluctuations, the frequency of which is proportional to the volumetric flow rate. The accuracy is 1 % of rate. The pressure drop depends on the actual density and flow, but does not exceed 0.1 bar.

6.7.6 Shaft power measurement

To calculate the COP of the heat pump it is necessary to measure the shaft power accurately. This is because it is not desirable to base the COP calculation on the power consumption of the Siemens electromotor driving the compressor, since it was greatly oversized (see Section 6.5.2.3). A Kyowa Rotary Transformer Torque Transducer, model TPN-20KMCB, using a strain gage transducer, was installed to measure the shaft torque.
The deviation does not exceed 0.5 %. A generator is used to measure the rotational speed. The output voltage is proportional to the angular torsion and therefore to the rotational speed, which is measured to an accuracy of about 3%. The shaft power is the product of the rotational speed (in ms⁻¹) and the shaft torque. The total accuracy on the shaft power measurement is about 3.5 %.

6.8 Safety measures

All safety procedures are executed via a PLC, controlling the process. Lamps on the electric board indicate the nature of the problem.

Level meters have been installed upstream of each pump. If the level is below the location of the magnetic switch mounted on the level indicator, the pumps are switched off. Furthermore, if the liquid level in the injection line is too low, the compressor is stopped. A warning lamp switches on if there is no water flow into the exchangers for the cooling of the injected liquid.

Excessive temperatures (>90 °C) can damage compressor and measuring instruments and cause excessive pressures in the system. Temperature sensors have been installed on the vapour line to the resorber, on the surface of the resorber and on its water outlet. When these temperatures exceed 85 °C, the compressor is stopped, and the cooling loop is started. The temperature in the heating loop vessel is also controlled, so that it can not exceed 55 °C.

If the pressure exceeds 11.5 bar, a spring-loaded valve opens linking the discharge and suction sides. The first pressure security level is fixed at 12 bar. If the pressure on the vapour line in front of the resorber exceeds this value, the compressor and the hot water pump are switched off. When the pressure decreases, the compressor and the pump must be restarted manually, after the alarm has been reset. As the system has been designed for a maximum pressure of 16 bar, two relief valves of the rupture-disk type have been mounted on the high pressure side of the test-plant. When the pressure reaches 13 bar, the disk bursts, causing the vapour to flow through a pipe outside the laboratory.

The directives of the CPR 13 norm concerning ammonia leakage are followed. A Dräger ammonia detection system with two measurement points is used. When an ambient ammonia concentration higher than 25 ppm is detected, ventilators are switched on. At that concentration, there is no danger to health and it is possible to continue working. When the ammonia concentration exceeds 200 ppm, a sound alarm is switched on as well as the ventilators, the compressor is stopped, and the laboratory must be evacuated.

A service instruction booklet is available. This provides a detailed description of the security measures, of the procedure to be followed when filling and emptying the installation, of how to run and shut down the installation and also of the emergency stop procedure (see Itard [1997]).
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Chapter 7

Measurements on the heat pump implemented with a liquid-ring compressor

7.1 Brief description of the measurements

Three series of measurements were carried out, each series corresponding to a specific overall ammonia mass concentration. The installation was filled with NH₃/H₂O mixtures with ammonia contents of 63%, 43% and 53% for Series 1, 2 and 3 respectively. Although the trouble shooting operations of the whole installation had been completed earlier, problems concerning the mass flow and concentration measurements were observed after completion of Series 1, making it unsuitable for the resorber and desorber analysis. However the results relating to the achievable temperature and pressure levels and to the compressor performances when the suction line is closed (see below) were reliable. Since the test-plant working point used in Series 2 and 3 was based on that achieved with Series 1, the latter will be taken into account in Section 7.2, but left aside in the subsequent sections.

In order to obtain separate information on the work spent on the liquid ring and on the influence of the injection liquid temperature on the discharge pressure and temperature, all measurements were first carried out with the compressor suction side closed. This information will be summarized in Section 7.2, were conclusions about the expected working point of the heat pump are also drawn. In Section 7.3, the working points achieved with the three series are described. In Section 7.4, the compressor and the separator are studied in greater detail. The aim of this study was not to obtain a better understanding of the two-phase compression process in the liquid-ring compressor, because this compressor was already known to be unsuitable for this application, but modelling of
the compressor and the separator was necessary to estimate the state of the two-phase fluid before the resorber. Section 7.5 deals with the resorber and Section 7.6 with the desorber and its integrated internal heat exchanger. Temperature profiles, heat transfer coefficients and liquid distribution are analysed. Section 7.7 covers the behaviour of the entire test-plant when step variations of the inlet source and sink temperatures, of the source and sink volume flow rates, of the compressor rotational speed and of the temperature and volume flow rate of the injection liquid are applied. Finally, in Section 7.8, the results will be compared with those obtained from the model used in Chapter 4.

Overall heat and mass balances are used to analyse the measurement data, since the chosen metering devices and points do not allow for more detailed modelling. After each step change or any modification of a test-plant parameter, it is necessary to wait until stationary conditions are achieved. This takes between 10 and 30 minutes. Once stationary conditions have been achieved a set of several measurements (about 10) is recorded. To reduce the effect of measuring errors, a measuring point consists of the average of the set.

7.2 Measurements with a closed compressor suction line

For these measurements, all valves before the resorber were closed, as well as valve 23 in the suction line of the compressor. In this way, the compressor and the separator were isolated from the other components of the heat pump. When stationary conditions have been achieved, the NH\textsubscript{3}/H\textsubscript{2}O two-phase mixture flows through the injection port into the compressor and, after compression, is discharged into the separator from which it returns to the injection port via the expansion valve 8\textsubscript{nj} and heat exchangers 39 en 62 (A in Figure 6.17). The three measurements series are considered in this section. All data can be found in Itard [1997] and will be summarized below.

7.2.1 Temperature and pressure levels

The discharge temperatures and discharge pressures are plotted against the injection temperature in Figure 7.1, corresponding to Series 1. They are used to estimate the temperature performance of the heat pump and to see how closely the design value can be approached. Plotting the pressure \( p_{12} \) on the suction port against the injection temperature gives an estimate of the minimum suction pressure obtained in the heat pump.

In Series 1 (\( x_{0\text{nj}} = 0.63 \)), for the medium compressor speed (speed at which the full installation will be tested later) the highest possible discharge temperature (\( T_{1j} = 53.5 \, ^{\circ}\text{C} \)) obtained without exceeding a maximum pressure of 11 bar (\( p_{2j} = 10.3 \, \text{bar} \)) is achieved for an injection temperature of 28.3 °C. Assuming that the resorber and desorber are oversized because the working point of the heat pump will be much below the design conditions, it can also be assumed that the water temperature at the outlet of the resorber is also \( T_{w1} = 53.5 \, ^{\circ}\text{C} \), instead of the 68 °C for which the test-plant was designed. Considering this new external condition, from plots similar to those of Figure 7.1, it was
Figure 7.1: Pressures and temperatures as function of the compressor rotational speed for Series 1 ($\lambda_{d,0} = 0.63$), suction line closed.
possible to estimate the injection temperature that should be used and the discharge pressure that would be achieved when working with other overall concentrations (Series 2 and 3). However, because the discharge pressure in Series 2 and 3 is far from the maximum, it would have been possible to achieve a higher discharge temperature.

The temperature and pressure data obtained with a closed suction line are summarised in Table 7.1, for the new external conditions (corresponding to Series 1) and for the maximal discharge temperature.

<table>
<thead>
<tr>
<th>Series 1</th>
<th>Series 2</th>
<th>Series 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{0\text{fil}} = 0.63$</td>
<td>$x_{0\text{fil}} = 0.43$</td>
<td>$x_{0\text{fil}} = 0.53$</td>
</tr>
<tr>
<td>$T_{31}$ (°C)</td>
<td>max $T_{31}$</td>
<td>$T_{31}$, Ser. 1</td>
</tr>
<tr>
<td>53.5</td>
<td>83.8</td>
<td>53.5</td>
</tr>
<tr>
<td>$p_{21}$ (bar)</td>
<td>10.3</td>
<td>10.8</td>
</tr>
<tr>
<td>$T_{\text{inj}}$ (°C)</td>
<td>28.3</td>
<td>57.5</td>
</tr>
<tr>
<td>$p_{12}$ (bar)</td>
<td>4.8</td>
<td>4.1</td>
</tr>
</tbody>
</table>

**Table 7.1:** Expected temperatures and pressures of the heat pump, based on the measurements with a closed suction line, where $p_{12}$ is the lowest possible suction pressure ($nc = 3100$ rpm).

Since we decided to study the cycle behaviour with constant external conditions, the reference working point was based on $T_{a3} = 53.5$ °C, which is the highest temperature achievable by the three cycles. A summary of the old and new external conditions is given in Table 7.2.

<table>
<thead>
<tr>
<th>Design external conditions</th>
<th>New external conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{a2}$ (°C)</td>
<td>40</td>
</tr>
<tr>
<td>$T_{a3}$ (°C)</td>
<td>68</td>
</tr>
<tr>
<td>$T_{w4}$ (°C)</td>
<td>38</td>
</tr>
<tr>
<td>$\dot{m}<em>{\text{wr}}$ (kg/s) - $\dot{V}</em>{\text{wr}}$ (l/min)</td>
<td>0.25 - 15.0</td>
</tr>
<tr>
<td>$\dot{m}<em>{\text{wd}}$ (kg/s) - $\dot{V}</em>{\text{wd}}$ (l/min)</td>
<td>0.22 - 13.2</td>
</tr>
<tr>
<td>$Q_{\text{res}}$ (kW)</td>
<td>31.4</td>
</tr>
</tbody>
</table>

**Table 7.2:** Expected new set of external conditions for the heat pump test-plant.

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7.2.2 Compressor work

When the suction line is closed the measured compressor work corresponds to the work done on the liquid ring. Because this work is expected to be high in comparison to the work done on the two-phase flow coming from the desorber when the suction line is open, it is important to estimate it as accurately as possible if the results are to be extrapolated to other types of compressor.

Two extreme models were tested. In the first one, it was assumed that liquid and vapour were in equilibrium at the compressor outlet and inlet (equilibrium model). In the second one the liquid mass fraction is assumed constant throughout the compression process.

**Equilibrium model:** In this model, saturated liquid at pressure $p_{ni}$, temperature $T_{ni}$ and of concentration $x_{oi} = f(p_{ni}, T_{ni})$ is injected into the suction port. Its enthalpy $h_{in}$ is easily calculated from $p_{ni}$, $T_{ni}$ and $x_{oi}$. At the discharge port, the liquid is in equilibrium with the vapour, at the pressure $p_{21}$ and the temperature $T_{31}$. Because the overall concentration $x_{oi}$ is known, the liquid mass fraction and therefore the total enthalpy of the two-phase (or possibly subcooled) flow $h_{31}$ can easily be calculated. The total work spent on the liquid ring is then $W_{tr, eq} = \dot{m}_{in}(h_{31} - h_{in}).$

**Constant liquid mass fraction model:** In this model, the conditions at the injection port are the same as for the equilibrium model, but it is now assumed that there is no evaporation or desorption of liquid during the compression process. Now there is no equilibrium at the discharge port, and liquid at the temperature $T_{31}$, the pressure $p_{21}$ and the corresponding liquid enthalpy $h_{i, 31}$ leaves the compressor (this is equivalent to assuming an unmeasured liquid subcooling). The work spent on the liquid ring is then $W_{tr, lc} = \dot{m}_{in}(h_{i, 31} - h_{i, in}).$

A comparison between the results of these two models and the measured data for several pressure ratios is given in Figures 7.2, 7.3 and 7.4 for series 1, 2 and 3 respectively. The accuracy of the calculations and of the measurements is also shown on the graphic. The heat losses from the refrigerant to the environment by convection and radiation are not taken into account in the plots of the measured work, because they were found to be negligible (far less than 0.6 % in all cases), due to the good insulation of the test-plant.

From Figures 7.2 to 7.4, it is clear that the equilibrium model considerably over predicts the measured work, especially at low pressure ratios. The decrease of $W_{tr, eq}$ with the pressure ratio in the first part of the curve is a consequence of the decreasing vapour quality at the compressor outlet (defined by the achieved pressure and temperature and by the overall concentration). From the point where the compressor outlet is in the subcooled liquid region, the work will increase with the pressure ratio.

The constant liquid mass fraction model gives more interesting results. The curve of the calculated work follows approximately the curve of the measured work. For the highest filling concentration (Series 1, $x_{oi} = 0.63$, Figure 7.2), the work is underestimated at low pressure ratios. This means that vapour probably appears at the discharge side and that the real compression takes place between the equilibrium model and the constant liquid mass fraction model. This underestimation cannot be found for the other series; at the middle
Figure 7.2: Calculated and measured work (with average deviation) spent on the liquid ring (suction line closed) for Series 1 ($x_{fill} = 0.63$).
Figure 7.3: Calculated and measured work (with average deviation) spend on the liquid ring (suction line closed) for Series 2 ($x_{fill} = 0.43$).
Figure 7.4: Calculated and measured work (with average deviation) spend on the liquid ring (suction line closed) for Series 3 ($x_{f,sl} = 0.53$).
filling concentration ($x_{\text{fill}} = 0.53$, Series 3, Figure 7.4), the calculated work fits well with the measured work at low pressure ratios, whereas at the lowest filling concentration ($x_{\text{fill}} = 0.43$, Series 2, Figure 7.3), the calculated work is overestimated. This is because the higher the overall concentration at constant pressure and temperature, the higher the vapour mass fraction. It is logical that when vapour mass fractions are too high, the constant liquid mass fraction model works less well because it is assumed that when there is no vapour in the injection line there is no vapour in the discharge line. It is remarkable that at lower filling concentrations (Figure 7.3, Series 2, $x_{\text{fill}} = 0.43$ in particular), although the calculated work follows the variations of the measured work precisely and remains at the limits of the accuracy range, it systematically over predicts the work by about 25%. The most obvious explanation for this is a departure from the measured temperature, in the form of subcooling of the liquid phase. This is because if even a very small quantity of vapour is present at the compressor outlet, the measured temperature $T_3$ will be the saturation temperature at the pressure $p_2$ and at the liquid concentration. Possible subcooling of the liquid phase therefore cannot be measured. This explanation is also consistent with the fact that the overestimation of the work only takes place at low overall concentrations, that is a low vapour mass fractions.

Based on this analysis, it was decided to use the constant liquid mass fraction model to calculate the contribution of the liquid ring on the total compressor work when the whole heat pump is in working. Since the pressure ratios will be higher than when the suction line is closed under prediction is unlikely to occur, but over prediction may do so. The model was slightly modified to allow for calculation with a subcooled liquid phase at the compressor outlet. The calculation of this subcooling will be explained in section 7.4.

### 7.3 Description of the basic working points

It was expected that the external conditions described in Table 7.2 could be achieved. All parameters of the resorber ($T_{w4}$, $T_{w3}$ and $V_{w5}$) could indeed be set up correctly but more problems were encountered with the desorber. In order to ensure that the desorber worked reasonably it was necessary to considerably increase the water flow rate (from 13.2 to 22 l/min). The temperature of the water at the desorber outlet, $T_{w1}$, was much higher than it was in the design conditions because of the combined effect of this increased flow rate and of different internal conditions. This in turn caused a higher than expected temperature $T_{w10}$ (see Figure 6.16) at the outlet of the heat exchanger $B$, i.e. higher than the desired $T_{w2} = 40$ °C. Since it is not possible to cool the liquid in the water vessel (electric resistances were installed to heat it), $T_{w2}$ could not be effectively controlled. In Series 1, which was used to determine the optimum working point, a value of about 44 °C was achieved for $T_{w2}$. In order to limit the temperature overlap between source and sink, it was then decided to increase $T_{w4}$ from 38 °C to 40 °C. The external conditions based on the optimum achieved with Series 1, are given in Table 7.3.

In this chapter all further measurements of Series 1 will be discounted, since the mass flow rates, the concentrations and $T_{w3}$ and $T_{w0}$ were not correctly measured. Only the set of external conditions described above will be used throughout the different series. For each series the injection temperature allowing for both $Q_{\text{res}} \approx 13.6$ kW and $T_{w3} \approx 53$ °C.
was experimentally determined and at a compressor rotational speed of 3100 rpm was found to be 49.5 °C for Series 2 and 45.0 °C for Series 3.

All measured data for this compressor speed are reported in Figures 7.5 and 7.6, excepting only $x_i$ and $V_{sw}$ (see Figure 6.16), which were not reliable because the swirl-meter failed to measure the vapour volume flow rate at the inlet of the resorber and because the concentration measurement of the liquid at the resorber inlet was disturbed by the presence of vapour due to the pressure drop in the concentration meter. To use this instrument correctly the liquid should be subcooled.

As already indicated, the working point described in Figures 7.5 and 7.6 is based on the optimum achieved in Series 1, and is not the optimal one for Series 2 or 3. Working points giving a higher temperature $T_{w3}$ and a higher resorber heating capacity could be achieved (See Section 7.7 and Appendix G).

The COP (based on the measured shaft work) achieved in Series 2 and 3 is lower than or equal to 1 (1 and 0.8 respectively). However, for a compressor working without liquid injection, the COP defined as $Q_{rev}/(Q_{res}-Q_{des})$, could be as high as 5.1 and 3.1 respectively.

In these working conditions, the internal heat exchanger has no effect, since $T_{4e2}$ is approximately equal to the temperature at the outlet of the desorber that cannot be precisely measured because the desorber and the heat exchanger are integrated in the same core. As anticipated in Chapter 6.3.1, the pressure drop at the refrigerant mixture side of the resorber is negligible ($p_{22}=p_{23}$).

### 7.4 Measurements on the compressor and the separator

As explained in Section 7.2.2, subcooling of the liquid at the compressor outlet is likely to occur, but cannot be measured. It could be estimated by fitting the calculated shaft work (constant liquid mass fraction model) to the measured work, but this solution is not...
Figure 7.5: Working point at fixed $T_{w1}$, $T_{w2}$, $T_{w3}$, $V_{wd}$ and $V_{wr}$ for $n_c = 3100$ rpm, $x_{o,ini}=0.43$ (Ser.2, file CS088).
Figure 7.6: Working point at fixed $T_{w1}$, $T_{w2}$, $\dot{v}_{wd}$ and $\dot{v}_{wr}$, for $n_c = 3100$ rpm, $x_{o, std} = 0.53$ (Ser.3, file s178).
very satisfying because of the role of other parameters (for instance, more or less vapour than predicted by the separated model) is not known. However, in cases that will be mentioned later, the presence of the separator permits independent estimation of this subcooling under the assumption of adiabatic separation.

7.4.1 Model used for the analysis of the data

7.4.1.1 The separator outlet

In this section, the term separator includes the separator and the liquid and vapour lines from the separator to the measurements points of $T_{3v2}$, $T_{x3}$ and $T_{x1}$ (see Figure 7.7).

As indicated in Section 7.3, neither the liquid concentration at the separator outlet $x_{3\text{slot}}$ nor the vapour volume flow rate $V_{3\text{v}}$ could be measured. The mass flow rate of the liquid $\dot{m}_{3l}$ was assumed to have been correctly measured despite of the presence of a two-phase flow, because the natural vibration frequency of the micro-motion flow meter is proportional to the total mass flow (see Section 6.7.4). Since the mass flow rate $\dot{m}_o$ and the overall concentration $x_o$ were correctly measured after the internal heat exchanger, they could be used to calculate $\dot{m}_{3v}$ and $x_{3\text{slot}}$ (Equations (7.1) and (7.2)), where $x_{3\text{slot}}$ represents the overall concentration in the liquid line, possibly present vapour included ($x_{3\text{slot}} = m_{3l}x_{3l} + (1-m_{3l})y_{3l}$).

$$\dot{m}_{3v} = \dot{m}_o - \dot{m}_{3l} \tag{7.1}$$

$$x_{3\text{slot}} = \frac{\dot{m}_o x_o - \dot{m}_{3v} y_{3v}}{\dot{m}_{3l}} \tag{7.2}$$

where $y_{3v}$ is the concentration of the saturated vapour at pressure $p_{3v}$ and temperature $T_{3v2}$. It was therefore assumed that there was no liquid in the vapour line. The specific enthalpy of the saturated vapour in the vapour line was $h_{3\text{vsat}}$, corresponding to $p_{3v}$ and $T_{3v2}$.

In the liquid line, it was assumed that vapour and liquid were in equilibrium at the pressure $p_{3v}$ and the temperature $T_{x3}$. The concentration of the vapour was $y_{3l}$, corresponding to the saturated concentration at this pressure and temperature. The liquid mass fraction and the total specific enthalpy (see Equation (7.3)) could easily be calculated from the equilibrium data.

$$h_{3l} = m_{3l} h_{3l} + (1-m_{3l}) h_{3v} \tag{7.3}$$

Since the injection liquid for the compressor leaves the separator together with the liquid going to the resorber, its overall concentration was also assumed to be $x_{3\text{slot}}$. The specific
Figure 7.7: Lay-out of the system “separator + compressor” under the assumption of separated compression (italic values are measured ones).

mass of the liquid $\rho_{\text{inj}}$ at the volume flow rate measurement point was calculated using the temperature $T_{3,3}$ ($\dot{m}_{\text{inj}} = \rho_{\text{inj}} \dot{V}_{\text{inj}}$). The specific enthalpy of the injection liquid leaving the separator is equal to that of the liquid going to the resorber, that is $h_{3,\text{out}} = h_3$. The sum of the enthalpies of the flows leaving the separator is then:

$$H_{\text{s, out}} = \dot{m}_3 h_{3v,\text{sat}} + (\dot{m}_{\text{inj}} + \dot{m}_{\text{inj}}) h_3$$  \hspace{1cm} (7.4)

To calculate the state of the mixture at the separator inlet, that is at the compressor outlet, a compressor model is required.

7.4.1.2 The compressor

For the reasons indicated in Section 7.2.2, a constant liquid mass fraction model (CLMF) is used. This implies that there is no evaporation or condensation (the respective masses of liquid and vapour remain constant) during the compression process. Furthermore the flows from the suction side and from the injection port are assumed to be compressed separately (this is only a calculation artifice).

**Two-phase suction mixture:** a mass flow rate $\dot{m}_0$ enters the compressor via the suction line, at the pressure $p_{12}$ and the temperature $T_{12}$. This two-phase flow was assumed to be in equilibrium at the concentrations $x_2$ and $y_2$ and the liquid mass fraction $\dot{m}_{\text{L}}$ corresponding to $p_{12}$, $T_{23}$ and the overall concentration $x_\text{v}$. At the compressor outlet, the measured pressure and temperature were $p_{21}$ and $T_{31}$. $T_{31}$ is a saturation temperature and was assumed to be the temperature of the out-flowing vapour that had the equilibrium
concentration $y_{31} = f(p_{21}, T_{31})$. The mass fraction of this vapour was still $(1-m_{l2})$. The outflowing liquid, with a mass fraction $m_{l2}$, had an unknown temperature $T_{sub}$ and a concentration $x_{3s}$ determined by using the mass balance expressed in Equation (7.5).

$$x_{3s} = x_2 + \frac{(1-m_{l2})(y_2-y_{31})}{m_{l2}}$$ (7.5)

**Injection line:** the same reasoning was applied to the injection flow. A mass flow rate $\dot{m}_{inj}$ entered the compressor via the injection line, at pressure $p_{inj}$ and temperature $T_{inj}$. This subcooled or two-phase flow had an overall concentration $x_{inj} = x_{3inj}$, and, in the case of two-phase equilibrium, the concentrations $x_{inj}$ and $y_{inj}$ and the liquid mass fraction $m_{l inj}$. At the compressor outlet, the outflowing vapour had the same pressure, temperature and concentration $p_{21}$, $T_{31}$ and $y_{31}$ as the vapour from the suction line, but its mass fraction was then $(1-m_{l inj})$. The outflowing liquid, with a mass fraction $m_{l inj}$, had the same temperature $T_{sub}$ as the liquid that had been compressed from the suction line, and a concentration $x_{3inj}$ determined by the mass balance expressed in Equation (7.6).

$$x_{3inj} = x_{inj} + \frac{(1-m_{l inj})(y_{inj}-y_{31})}{m_{l inj}}$$ (7.6)

### 7.4.1.3 Separator model and data at the separator inlet

At the separator inlet, as at the compressor outlet, the two phase outflowing mixture has the properties listed in Table 7.4. Although it is reasonable to assume that the separator is adiabatic, in all cases the calculations of its heat losses $Q_{loss}$ by convection and radiation were based on the mean vapour temperature. The enthalpy of the liquid at the separator inlet was then given by Equation (7.7). The temperature $T_{sub}$ was then easily calculated from $p_{21}$, $h_{31li}$ and $x_{31}$.

$$h_{31li} = \frac{H_{x_{out}} - Q_{loss} - [\dot{m}_{inj}(1-m_{inj}) + \dot{m}_{v}(1-m_{l2})]h_{31v}}{\dot{m}_{inj}m_{l inj} + \dot{m}_{v}m_{l2}}$$ (7.7)

<table>
<thead>
<tr>
<th></th>
<th>Vapour</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass flow rate</td>
<td>$\dot{m}<em>{inj}(1-m</em>{inj}) + \dot{m}<em>{v}(1-m</em>{l2})$</td>
<td>$\dot{m}<em>{inj}m</em>{l inj} + \dot{m}<em>{v}m</em>{l2}$</td>
</tr>
<tr>
<td>concentration</td>
<td>$y_{31} = f(p_{21}, T_{31})$</td>
<td>$x_{31} = (x_{3inj}m_{inj} + x_{3r}m_{l2}m_{v}) / (\dot{m}<em>{inj}m</em>{l inj} + \dot{m}<em>{v}m</em>{l2})$</td>
</tr>
<tr>
<td>temperature</td>
<td>$T_{31}$</td>
<td>$T_{sub}$</td>
</tr>
<tr>
<td>specific enthalpy</td>
<td>$h_{31v} = f(p_{21}, T_{31})$</td>
<td>$h_{31li} = f(p_{21}, T_{sub}, x_{31})$</td>
</tr>
</tbody>
</table>

*Table 7.4: Conditions at the separator inlet. The only unknown is $T_{sub}$.*
If the temperature $T_{\text{sub}}$ is such that the liquid is subcooled in relation to the saturation temperature corresponding to $(p_{21}, x_{31})$, the model of the compressor and the separator presented here is consistent. This was the case for all measurements made in Series 2. However, it is possible (measurements of Series 3) that the calculated $T_{\text{sub}}$ may correspond to the two-phase region. This means that some assumptions relating to either the compressor model or the separator model are not valid. Although it is possible that departures from equilibrium occur in the suction and injection lines, it seems reasonable to assume that some of the compressor inlet liquid is indeed vaporized, as indicated by the calculated $T_{\text{sub}}$. In such cases, $h_{31}$ corresponds to the total enthalpy of a two-phase mixture at $(p_{21}, T_{31}, y_{31}, h_{31v})$ for the vapour phase and $(p_{21}, T_{\text{sub}}, x_{\text{sub}}, h'_{31l})$ for the liquid phase, where $x_{\text{sub}}$ is the saturated liquid concentration at $(p_{21}, T_{\text{sub}})$ and replaces $x_{31}$ in Table 7.4. The mass flow rates in Table 7.4 must then be replaced by those given in Equation (7.8) and (7.9), where $m_i = (x_{31} y_{31})/(x_{\text{sub}} y_{31})$.

$$m_{\text{tor}} = (1 - m_f) (m_{\text{inf}} m_{\text{inf}} + m_f m_{12}) + m_{\text{inf}} (1 - m_{\text{inf}}) + m_f (1 - m_{12}) \quad (7.8)$$

$$m_{\text{inf}} = m_f (m_{\text{inf}} m_{\text{inf}} + m_f m_{12}) \quad (7.9)$$

Following this method, calculations of the compressor work for the measurements where $T_{\text{sub}}$ was in the two-phase region were made and all led to high overestimation of this work; the calculated work was more than 70% higher than the measured work. Variations of $T_{\text{sub}}$ within the accuracy range did not lead to an accurate enough calculation of the work. The temperature $T_{\text{sub}}$, that led to a correct compressor work also led to a highly non-adiabatic separator when $h_{31}$ was calculated as indicated in Section 7.4.1.1. Because the assumption of a non-adiabatic separator is not very realistic, the most evident explanation is that there is some degree of subcooling at the separator outlet. $T_{x3}$ is then the temperature of the saturated vapour in equilibrium with a liquid at a temperature $T_{x3l}$ lower than $T_{x3}$.

In the cases where $T_{\text{sub}}$ calculated from the separator model without subcooling at $x3$ ($T_{\text{sub}} = T_1$) was in the two-phase region, the real $T_{\text{sub}}$ temperature was estimated by using a fixed weighted average of $T_{\text{sub}} = f(p_{21}, x_{31}), T_1 = (p_{21}, x_{31}), T_3 = (p_{21}, x_{31})$, and $T_5 = (p_{21}, x_{31})$.

Once $T_{\text{sub}}$ had been calculated, $T_{x3l}$ was calculated by using the adiabatic model of the separator, described in Section 7.4.1.1.

### 7.4.1.4 Calculation of the compressor work

The compressor work is calculated by Equation (7.10):

$$W_{\text{tot}} = m_{\text{tor}} h_{31v} + m_{\text{inf}} h_{31l} - m_{\text{inf}} h_{2} (p_{12}, T_{x3}, x_{x3}) - m_{\text{inf}} h_{\text{inf}} (p_{\text{inf}}, T_{\text{inf}}, x_{\text{inf}}) \quad (7.10)$$

The separate estimate of the work spent on the liquid ring and of the work spent on the suction two-phase mixture was straightforward (Equation set (7.11)) in cases were $T_{\text{sub}}$ was
in the subcooled region.

\[
W_c = m_{iq} ((1-m_{iq}) h_{3v} + m_{iq} h(p_{21}, T_{sub}, x_{v2}) - h_{g}(p_{12}, T_{sub}, x_{2v}))
\]

\[
W_{lr} = m_{inj} ((1-m_{inj}) h_{3v} + m_{inj} h(p_{21}, T_{sub}, x_{3inj}) - h_{g}(p_{12}, T_{inj}, x_{3inj}))
\]

(7.11)

In the cases where \( T_{sub} \) was not in the subcooled region, it was assumed that \( x_{3v} = x_{3inj} = x_{sub} \), which led to (conservation of the mass) \( m_{inj} \) and \( m_{iq} \) being replaced by the expressions of Equation set (7.12).

\[
m_{p, inj} = \frac{m_{inj} x_{3inj} + (1-m_{inj}) y_{inj} - y_{31}}{x_{sub} - y_{31}}
\]

\[
m_{p, j2} = \frac{m_{ij} x_{2} + (1-m_{ij}) y_{2} - y_{31}}{x_{sub} - y_{31}}
\]

(7.12)

7.4.2. Analysis of the data

7.4.2.1 Comparison of the model with the measurements

The data obtained from Series 2 and 3 are summarised in Tables G.1 and G.2 of Appendix G. All measured and calculated data of interest are reported, as well as the degree of accuracy of the calculations and measurements. Figures 7.8 and 7.9 give an illustration of the behaviour of the calculated and measured work, as well as of the accuracy of the calculations.

For Series 2, there was no departure from the constant liquid mass fraction model. The mean deviation between calculated and measured work (the heat losses are negligible, see Tables G.1 and G.2) is -2.1 % (slight underestimation of the calculated work), with a maximum deviation of 15.8 % and a minimum of -10.3 %. With the exception of one file (s159), the accuracy of the calculated and measured work is such that the results are consistent. The subcooling of the liquid phase in the discharge line (\( T_{31} - T_{sub} \)) remained approximately constant throughout the measurements, with a mean value of 6.0 K (max: 7.4 K, min: 4.8 K).

For Series 3, there was a departure from the constant liquid mass fraction model of the separator, which makes the calculated results less reliable. This departure can be expressed as the smaller percentage of liquid than in the CLMF model, so named Dev (%) in Appendix G (mean: 1%, max: 1.5%, min: 0.7%) or as the difference \( \Delta T \) between the temperature calculated without taking into account the liquid subcooling at point x3 and the weighted estimate of the temperature, so called Dev (K) in Appendix G (\( \Delta T_{mean} = 3 \) K, \( \Delta T_{max} = 4.7 \) K, \( \Delta T_{min} = 2.6 \) K). Because of the estimate used for \( T_{sub} \), the mean deviation between the calculated and measured work is very good (-0.4 %) with a
Figure 7.8: Calculated and measured compressor work, with accuracy band, as a function of $T_{up}$, $m_{inj}$ and $n_r$, for Series 2.
Figure 7.9: Calculated and measured compressor work, with accuracy band, as a function of $T_{inp}$, $\dot{m}_{inj}$ and $n_{c}$ for Series 3.
maximum deviation of 4.9% and a minimum deviation of -10.0%. In the same way as in Series 2, the accuracy of the calculated and measured work is such that the results are consistent. The subcooling of the liquid phase in the discharge line (T_{31} - T_{inj}) remained approximately constant throughout the measurements, with a mean value of 5.2 K (max: 6.7 K, min: 4.7 K).

Although the calculation of the work done on the liquid ring and on the suction mixture using the CLMF model is not very accurate, particularly for Series 3 (see below), it can be seen from Figure 7.8 and 7.9 that about two thirds of the total work is used by the liquid ring and is therefore of no value to the heat pump system itself.

The isentropic efficiency of the compressor was calculated with and without the contribution of the liquid ring. For Series 2, the isentropic efficiency did not exceed 33% when the liquid ring was not taken into account, and remained below 10% when it was taken into account. In Series 3, as in Series 2, the overall isentropic efficiency remained below 10%. The efficiency calculated without the contribution of the liquid ring is surprisingly high and can be above 1. This value is of no significance. It is due to the fact that it is impossible to take separate account of the influence of the cooling of the vapour by the liquid, that is such that the end compression point is at a temperature below the temperature that would have been achieved by isentropic compression. In this case, the \( \eta_n \) values have been omitted in Table G.2. This highlights the fact that trying to make separate calculations of the work spent on the liquid ring and the work spent on the aspired vapour is probably not worthwhile. However, since the liquid-ring compressor is not adequate, and since the total work has been predicted correctly, a better analysis of this compressor was not carried out.

7.4.2.2 Effect of some input parameters on the compressor performances

In this section, the effects of the rotational speed of the compressor, the injection liquid mass flow rate and the injection liquid temperature on the discharge temperature, the suction and discharge pressures, the compressor work and on the suction mass flow rate are analysed. The measured data are summarised in Figures 7.8 to 7.12. In all cases, all other data than \( n_c \), \( T_{inj} \) or \( \dot{m}_{inj} \) were kept constant.

From Figures 7.8 and 7.9 it can be seen that the compressor work is rather insensitive to the injection temperature and the injection mass flow rate. The only effect of the injection mass flow rate is an increase of the relative part of the work used for the liquid ring. The compressor work is the most sensitive to the compressor rational speed \( n_c \).

The discharge temperature increases with the injection temperature as expected (Figure 7.10). The discharge and suction pressures also increase slightly. More surprising is the fact that the suction mass flow rate \( \dot{m}_s \) also increases with \( T_{inj} \) whereas a decrease was expected because of the increasing vapour pressure of the liquid ring. This means that the capacity reduction due to the liquid-ring vapour pressure is not significant and that the compressor behaves like all positive displacement compressors with a built-in compression ratio: the mass flow rate increases when the compression ratio decreases, thus when \( T_{inj} \) increases. Because of the combined effects of a decreasing pressure ratio, an increasing mass flow rate and an almost constant suction pressure, the compressor work remains approximately constant.

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Figure 7.10: Effect of the injection temperature on the compressor performances, all other parameters being constant (files s157-s168 of Series 2 and s246-s255 of Series 3)
Figure 7.11: Effect of the injection mass flow rate on the compressor performances, all other parameters being constant (files s169-s174 of Series 2 and s256-s261 of Series 3)
Figure 7.12: Effect of the rotational speed on the compressor performances, all other parameters being constant (files s145 to s156 of Series 2 and s234 to s243 of Series 3)
The discharge temperature decreases with the injection liquid mass flow rate (Figure 7.11), because more cooling is available. The suction mass flow rate decreases as expected when the injection mass flow rate increases, but because the pressures and pressure ratios are decreasing, the compressor work decreases only slightly.

The rotational speed of the compressor (Figure 7.12) is the parameter that has the greatest effect on the discharge temperature and pressure and on the suction mass flow rate. Increasing the rotational speed at constant suction pressure, increases the discharge temperature and the suction mass flow rate, thus in the present application, it is recommended that the highest possible rotational speed should be used.

7.4.3 Conclusions

A constant liquid mass fraction model of the compressor designed to calculate the internal heat balances and using an adiabatic model of the separator has been presented. This model gives reasonable results when calculating the total work done by the compressor. The estimate of the separate work spent on the liquid-ring and on the suction mixture seems reliable when the discharge liquid is subcooled. However, when the model indicates that this liquid is saturated the discharge temperature must be corrected if one wants to obtain reasonable results. This correction has two effects. First it is necessary to assume a subcooling of the liquid before the reservoir in order to obtain an adiabatic separator. As will be seen in Section 7.5, this subcooling is indeed likely to occur. The second effect is that apparent isentropic efficiencies higher than 1 can be obtained, due to the impossibility of studying the compression and cooling processes separately. From the measurements of Series 2, which seems the most reliable, it appears that an isentropic efficiency of about 30% could be expected if the liquid ring is suppressed. With the liquid ring, the isentropic efficiency remains below 10%. To obtain the highest possible discharge temperature and suction flow, the injection mass flow rate should be as small as possible. In the most favourable compressor the injection liquid line should be suppressed or, at least, the flow rate should be minimized.

The fact that the constant liquid mass fraction model makes reasonable predictions of the total work is not really an advantage, because it means that the wet compression heat pump test-plant behaves like a solution recirculation plant, the compression takes place far from equilibrium and the liquid is heated by direct heat exchange with the vapour. The development of a compressor suitable for wet compression in a heat pump should therefore take the following points into account:

- in order to allow liquid and vapour to be closer to the equilibrium state the rotational speed must be not too high.

- for the same reasons, the liquid and vapour should be fully mixed at the suction port and during the compression process. If this cannot be realized by a special internal design of the compressor, it will be worth considering separating the liquid from the vapour at the inlet port, in order to re-inject the liquid in such a way that a good phase mixing is realized.
- the presence of any injection flow (other than one coming from a separated suction flow) should be avoided, since it introduces supplementary work. If it is not possible to suppress this flow (because of lubrication problems for instance), the heat freed by the cooling of this flow after the compression process should be used, together with the resorber heat, to contribute to the heating of the heat sink and in that way to increase the COP.

7.5 Measurements on the resorber

All measurement data and calculations on the resorber are summarised in Tables G.3 and G.4 of Appendix G, with the exception of the fourteen temperature measurements inside the resorber channels (see Section 7.5.2).

7.5.1 Internal and external heat balances

The conditions at the resorber inlet are determined by those at the separator outlet (see Figure 7.7). Saturated vapour \((m_{3v}, p_{22}, T_{3v/2}, h_{3vat})\) flows at the upper side of the distribution system. A two-phase flow, with a possibly subcooled liquid phase \((m_{3l}, x_{3lot}, h_{3l}, T_{x3}, T_{x3})\), enters the distributor and is mixed adiabatically with the vapour. At the resorber outlet (point 4), the liquid is subcooled, and has the enthalpy \(h_4 = f(p_{22}, T_{4l}, x_0)\). The heating capacity of the resorber using the mixture data is then:

\[
Q_r = m_{3l} h_{3vat} + m_{3l} h_{3l} - m_0 h_4
\]

(7.13)

where Equation (7.3) is used to calculate \(h_{3l}\).

A comparison between the heating capacity measured at the water side and of the heating capacity calculated at the \(NH_3/H_2O\) side for Series 2 (see Table G.3) indicates that the latter is always overestimated by 20 to 30 %. However, since the accuracy of the calculation is not very high owing to the inaccuracy of the enthalpy calculation based on estimated temperatures and liquid mass fractions, the calculated values with their error bands are generally within the error band of the measured value. Exceptions to this are the two measurements s138 and s157, that clearly fall outside the error band.

Two different calculations were made for measurements of Series 3 (Table G.4). The first one assumed no subcooling in the liquid phase at point \(x_3\) (not consistent with the compressor-separator model) and the second one assumed a subcooling of the liquid phase at point \(x_3\), as calculated by the compressor-separator model (temperature \(T_{x3l}\) for the liquid phase and measured \(T_{x3}\) for the vapour phase). In the first case, all calculated values were consistent with the measured ones (within the accuracy bands), but, as in Series 2, always overestimated. However, the overestimation (between 10 and 20 %) is lower than for Series 3. In the second case, where the entering liquid phase is subcooled, the
measured and calculated heating capacity values are in very good agreement (see for instance Figures 7.13 and 7.14). Because of this, it seemed likely that in Series 2 also, some liquid subcooling that was not predicted by the compressor-separator model occurred at the resorber inlet. Estimation of this subcooling by fitting the calculated heating capacity on the measured one, led to subcooling by about 5 K, that is not compatible with the compressor-separator model. This was because the adiabatic separator model led to subcooling in the discharge line that, in turn, led to a very large under prediction of the compressor shaft work. This meant that the constant liquid mass fraction model of the compressor was not satisfactory. Another possible explanation for the mismatch between the heating capacities may be that the assumption of saturated vapour leaving the separator and entering the resorber distribution system was not correct; a certain amount of liquid was also transported, in that way reducing the total resorber inlet enthalpy.

Since it is not possible to quantify the respective effects of these possible mismatches in the present measurements, the most likely assumption is that they are superimposed to a certain extent. It should be possible to test the assumption of subcooling by measuring the temperature of the liquid at the separator bottom, thus before the pressure drop introduced by the concentration meter. It might also be possible to place thermocouples at the top of the resorber channels. These should be positioned precisely enough to ensure that they are within the liquid film. It would be possible to measure both the temperature of the liquid and the presence of a liquid film in that way, which would give an idea of the quality of the liquid distribution.

The calculated and measured heating capacities at constant \( m_w \) and \( T_w \) have been plotted in Figures 7.13 and 7.14 as a function of the injection temperature, the injection mass flow rate and the rotational speed of the compressor. With good agreement with the behaviour of the compressor discharge temperature and with the behaviour of the suction mass flow rate (Figures 7.10 to 7.12), the resorber heating capacity increases with the injection temperature and the compressor rotational speed and decreases with the injection mass flow rate.

### 7.5.2 Temperature profiles

As can be seen in Figure 6.11, the resorber was fitted at the NH\(_3\)/H\(_2\)O side with three thermocouples in an outer channel (numbered from top to bottom \( T_{r1} \) to \( T_{r3} \)) and three thermocouples in a middle channel (numbered from top to bottom \( T_{r21} \) to \( T_{r23} \)). Six thermocouples were mounted in the same way in the adjacent water channels (\( T_{w11} \) to \( T_{w13} \) and \( T_{w21} \) to \( T_{w23} \)). A temperature measurement was also made just before the beginning of the heat exchange surface (\( T_a \)) and just after (\( T_p \)). These data are given for Series 2 and 3 in Tables G.5 and G.6 of Appendix G. Because the thermocouples were not placed very accurately, it is doubtful whether the temperature measured is the liquid film temperature or the saturation one.

The temperature profiles for three measurement files have been drawn in Figure 7.15 for Series 2 and in Figure 7.16 for Series 3. For Series 2 (\( x_o = 0.43 \)) the resorber was overdimensioned and only half of the surface was useful which affected the calculation of the
Figure 7.13: Resorber heating capacity as a function of $T_{inj}$, $\dot{m}_{inj}$ and $n_c$ for Series 2 (files s157-s168, s169-s174 and s145-s156 respectively).
Figure 7.14: Resorber heating capacity as a function of $T_{in}$, $m_{inj}$ and $n_r$ for Series 3 (files s246-s255, s256-s261 and s234-s243 respectively).
overall heat transfer coefficient. For all measurements in this Series, a length of 0.6 m (instead of 1.2 m) was used for the heat transfer. The only exception was file s096 for which a length of 1 m is used. In Series 3 (x_e = 0.63), the useful resorber length was 1 m for files s178 to s205 and the total length (1.2 m) for all other files. A comparison between the temperature profiles in the outer channel (channel 1) and the middle channel (channel 2) led to the conclusion that more liquid was present in the outer channel than in the middle one. However, the mal-distribution was less in Files s222 and s246 (Figure 7.16). Those were also the files for which the total resorber length was used. This was related to the vapour mass flow rate at the resorber inlet (see also Section 7.5.3), which must be high enough to ensure a good distribution and a good absorption process. Although the distribution system was tested with water and air before being implemented in the test-plant, in the present application a good distribution could be disturbed by the presence of vapour in the liquid line.

The calculated temperature profiles have also been plotted in Figures 7.15 and 7.16. The calculation relies on the following assumptions: the enthalpies of the mixture corresponds to the equilibrium enthalpies at the resorber pressure, at the overall concentration x_e and at the temperatures T, between T_e and T_{41}. Since the heat exchanged by both the external and internal flow should be equal but was not, the mass flow at the NH_3/H_2O side was recalculated in order to obtain a good fitting of the calculated heating capacities on both sides. This recalculation was also made for Series 3, because the subcooled temperature T_{x31} cannot be taken into account in a calculation based on equilibrium temperatures. The percentage of the total NH_3/H_2O mass flow rate less than the measured one (m_n) is reported in Tables G.3 and G.4 under the name "mald" and can be seen as a measure of the inaccuracy of the enthalpy calculation at the resorber inlet. There is no other way to calculate the minimum and mean temperature differences that is consistent with the calculations of Chapter 4, where equilibrium was assumed and no subcooling of the liquid phase was taken into account. Since the temperature is a function of the heat exchanged (calculated temperature profiles), it was furthermore supposed that the heat transfer coefficient was constant throughout the length of the resorber, which is a very rough assumption, in particular at the transition two-phase flow/subcooled liquid. The match between the calculated and measured temperature profiles appeared to be better in channel 1 than in channel 2. For Files s222 and s246 (high vapour mass flow rate) in particular the match is quite good and shows that the condensation process takes place close to the equilibrium.

The calculated temperature profiles were used to estimate the minimum and mean temperature differences in the resorber given in Tables G.3 and G.4. Because the resorber was oversized for most of the applications studied, the minimum temperature difference was generally zero. File s222 provides a good example of a pinch point located in the middle of the resorber (ΔT_{min} = 0.6). The mean temperature differences vary from 8.2 K to 3.1 K in Series 2 and from 6.7 K to 0.9 K in Series 3. Of course, the closer ΔT_{mean} to ΔT_{min}, the better the matching of the temperature profiles of the external and internal media. Files s096 and s222 give examples of good glide matching.
Figure 7.15: Calculated and measured temperature profiles for three measurements of Series 2.
Figure 7.16: Calculated and measured temperature profiles for three measurements of Series 3.
7.5.3 Overall performances of the resorber

The heat transfer coefficient was calculated by using the heating capacity measured at the water side, the mean temperature difference obtained from the calculated equilibrium temperature profiles and the effective resorber area, as described in the previous section. In the plot of the heat transfer coefficient against the heat flux in the resorber (Figure 7.17), an important dispersion of the results is observed, in particular for measurements of Series 3. This dispersion can be explained by varying parameters such as the overall concentration (accuracy ± 0.1) and the inlet vapour mass flow rate. The heat transfer coefficient appears to be very sensitive to the vapour mass flow rate in particular (Figure 7.18). The low overall heat transfer coefficients (less than 300 W/m²K) are obtained for the very low vapour mass flow rates, whereas higher vapour flow rates produce heat transfer coefficients of about 1200 W/m²K. This is because when the vapour velocity is too low (at the limit quasi-static), the Reynolds number remains low and the film thickness is too high because of the bad drainage. The U-values are in good agreement with the values obtained in Bassols [1988] with a similar plate fin resorber. At high vapour velocity they are also similar to the U-values obtained by Stokar [1987], who used a spin-tube with outside condensation. However, the volume of his spin-tube was high (0.381 m³, instead of 0.014 m³ for our plate-fin resorber), so the volumetric heat transfer coefficient α, (see Tables G.3 and G.4) is much better in our case. The very low heat flux densities (< 3.1 kW/m³) obtained in the resorber are due in particular to the minimum temperature approaching zero.

The resorber performances in terms of effective heat transfer area per kWK as a function of the heat flux density are plotted in Figure 7.19 and of course show the inverse variations of the heat transfer coefficient. For Series 2, values of around 0.2 m²kW⁻¹K⁻¹ were obtained, whereas values of about 0.06 m²kW⁻¹K⁻¹ were obtained for Series 3.

The concentration difference over the resorber length has been plotted in Figure 7.20, as a function of the resorber heat flux density and of the inlet vapour mass flow rate. As expected, the absorption process at constant overall concentration was more efficient at high heat flux densities and at high vapour velocities.

7.5.4 Conclusions

Mismatches between the resorber heating capacity calculated at the water side and at the mixture refrigerant side have demonstrated the possible subcooling of the liquid phase at the resorber inlet, the possible presence of liquid in the inlet vapour line, and, to a limited extent, the mal-distribution of the liquid due to the presence of vapour in the liquid line that was confirmed by the plot of the temperature profiles. Mean temperature differences below 8.1 °C and as low as 0.9 °C were achieved with very low minimum temperature differences. The heat flux densities achieved in the resorber were low (< 3 kW/m²), and the overall heat transfer coefficient could reach values above 1200 W/m²K provided the vapour velocity was high enough. At low vapour velocities, the heat transfer coefficient was below 500 kW/m²K.
Figure 7.17: Resorber overall heat transfer coefficient as a function of the heat flux density, based on the effective heat transfer area.

Figure 7.18: Resorber overall heat transfer coefficient as a function of the inlet vapour mass flow rate.

Figure 7.19: Effective heat exchange area per kW as a function of the resorber heat flux density.

Figure 7.20: Liquid concentration difference on the resorber length as a function of the heat flux density.

7.6 Measurements on the desorber and on the internal heat exchanger

All measurements data and calculations on the desorber are summarised in Tables G.7 and G.8 of Appendix G, with the exception of the fourteen temperature measurements inside the desorber channels (see section 7.6.3).

7.6.1 Internal and external heat balances

After the expansion valve, it was possible to measure only temperature and pressure. The two-phase mixture will therefore be assumed to be in the equilibrium condition, thus $h_1$
\[ Q_{\text{exch}} = \dot{m}_n (h_{42} - h_{4e1}) \]  

(7.14)

\[ Q_d = \dot{m}_o (h_2 - h_1) - Q_{\text{exch}} \]  

(7.15)

Both the enthalpy at the desorber outlet and the desorber outlet temperature \( T_{2e} \) can be easily calculated.

A comparison of the heating capacities calculated at the water side and at the \( \text{NH}_2/\text{H}_2\text{O} \) side shows that both the values are in very good agreement (see Tables G.7 and G.8 and Figures 7.21 and 7.22). In Figures 7.21 and 7.22, the desorber cooling capacity has been plotted against the injection temperature, the injection mass flow rate and the compressor rotational speed. In good agreement with the behaviour of the compressor suction mass flow rate (Figures 7.10 to 7.12), the desorber cooling capacity remains constant when \( T_{\text{iq}} \) varies and increases with the rotational speed. Although the suction mass flow rate decreased with the injection flow rate, the desorber cooling capacity remains almost constant. This is because it is impossible to accurately control the temperature \( T_{w2} \), which could not be kept constant enough (variations between \( \pm 3 \text{ K} \)) and to compensate for the decreasing suction mass flow rate.

Negative values of \( Q_{\text{exch}} \) in the tables of Appendix G, show that because the internal heat exchanger was not by-passed when it should have been (temperature \( T_{41} \) lower than temperature \( T_{2e} \)), the effect of the internal heat exchanger was converse to the desired effect: the mixture coming from the desorber was slightly cooled instead of heated, and the subcooled liquid coming from the resorber was slightly heated instead of cooled. However, this effect remained marginal for all measurement points.

7.6.2 Temperature profiles

The desorber was implemented with thermocouples exactly in the same way as the resorber (see Figure 6.13 and Section 7.5.2, replacing subscript "r" by "d"). The temperature profiles for three measurement files have been drawn in Figure 7.23 for Series
Figure 7.21: Desorber cooling capacity as a function of $T_{\text{inj}}$, $\dot{m}_{\text{inj}}$, and $n$, for Series 2 (files s157-s168, s169-s174 and s145-s156 respectively).
Figure 7.22: Desorber cooling capacity as a function of $T_{\text{nop}}$, $m_{\text{ij}}$, and $n_c$ for Series 3 (files s246-s255, s256-s261, and s234-s243 respectively).
2 and in Figure 7.24 for Series 3. The mal-distribution problem appears to be more important than in the resorber, as was predicted in Section 6.4. The steeper temperature increase in channel 2 implies that there was more liquid in the middle plates than in the outer ones. There was probably no liquid film in the outer channels, so that the heat transfer coefficient decreases drastically. The equilibrium temperature profile was calculated in the same way as in Section 7.5.2, but the so called mal-distribution parameter is much lower because of the good agreement between the cooling capacities at the mixture and at the water sides (no subcooling of the liquid). In channel 1 the measured temperature profiles match the calculated one much better than those in channel 2, because of the absence of a liquid film (mist flow at the saturation temperature). An estimate of the minimum and mean temperature profiles in the desorber was made by using the calculated temperature profiles. Their values are given in Tables G.9 and G.10. The mean temperature differences vary between 7.4 K and 4.3 K in Series 2 and between 5.8 K and 4 K in Series 3, with minimum temperature differences between 5.3 - 1.2 K and 4.3 - 1.2 K respectively.

7.6.3 Overall performances of the desorber

The overall heat transfer coefficient is calculated in the same way as for the resorber, that is, based on the calculated mean equilibrium temperature difference. As can be seen in Tables G.7 and G.8 the heat transfer coefficient remains constant throughout all measurements, at a very low value, between 100 and 150 W/m²K, corresponding to a heat transfer area of about 0.2 m²/kWK. This low heat transfer coefficient is related to the very low heat flux densities in the desorber (< 1.4 kW/m²), and also to the limitation of the heat transfer caused by a probably almost static vapour phase, resulting from the design of the distributor, which reduces the vapour velocity. The limitation of the heat transfer coefficient for the desorber was clearly at the NH₃/H₂O side since calculations at the water side using the Wieting correlation (Wieting [1975], Taborek [1983]) showed that the heat transfer coefficient at the water side was generally between 1500 and 2000 W/m²K.

The concentration difference over the desorber length is plotted in Figure 7.25 as a function of the desorber heat flux and shows that the desorption process was more effective at higher heat flux density and lower overall concentration.

7.6.4 Conclusions

The external and internal desorber cooling capacity match well, but mal-distribution of the liquid and the vapour was observed. Mean temperature differences between 4 and 7.4 K were found, with minimum temperature differences down to 1.2 K. The very low heat flux densities and heat transfer coefficients (=100 W/m²K) have been imputed to the too low vapour velocity, arising from an incorrect distributor design. It is recommended that before further measurements are made on the heat pump, the diffuser should be replaced by a distributor of the same type as in the resorber in order to improve the mixing of the two-phases and to increase the vapour velocity.
Figure 7.23: Calculated and measured temperature profiles for some measurements of Series 2.
Figure 7.24: Calculated and measured temperature profiles for some measurements of Series 3.
Figure 7.25: Liquid concentration difference on the desorber length as a function of the heat flux density.

7.7 Effect of internal and external parameters on the heat pump performances

In this section, the effects of several parameters on external COP, defined as $Q_{\text{res}}/(Q_{\text{res}}-Q_{\text{des}})$ are considered. We chose to work with the external COP, because the internal COP based on the shaft work is not representative of values that could be achieved with a compressor without liquid ring or when the heating capacity of the cooled injection flow is used together with the resorber heat.

7.7.1 Internal parameters

These are the rotational speed of the compressor, the temperature and the mass flow rate of the injection liquid and the overall concentration. The COP, calculated from the resorber and desorber heating capacities given in Figures 7.14, 7.15, 7.21 and 7.22 is plotted in Figure 7.26. When other conditions were constant, the COP decreased with the injection temperature because the increase in heating capacity (Figures 7.14 and 7.15) was compensated by the cooling capacity that remained constant (Figures 7.21 and 7.22). Therefore, the increase of the injection temperature permits a higher heating capacity at
Figure 7.26: Variations of the external COP as function of $T_{\text{inj}}$, $m_{\text{inj}}$ and $n_v$. 
the expense of efficiency. For similar reasons, the COP increased slightly with the injection mass flow rate, at the expense of the heating capacity. The most favourable effect was obtained by increasing the rotational flow of the compressor. That produced an increase in the heating capacity at constant COP.

The effects of the overall concentration on the COP and on the heating and cooling capacities have been given in Figure 7.27, all other parameters, with the exception of \( T_{\text{inj}} \) being kept constant; it would have been more interesting to unite Series 2 and Series 3 into one curve, but this was not possible because different injection temperatures were used in both Series (\( T_{\text{inj}} = 49.5 \, ^\circ\text{C} \) in Series 2 and \( 45.0 \, ^\circ\text{C} \) in Series 3). However, for both the Series, an increase in the overall concentration produced an increase in both the COP and the heating capacity. When comparing the series with each other, it appears that an overall concentration of about 0.5 produced a higher COP and a lower heating capacity than an overall concentration of about 0.61. Because of the lack of data for other concentrations and of the non-linear behaviour of the COP (see Chapter 4), these trends cannot be generalized.

### 7.7.2 External parameters

In this section the behaviour of the heat pump under varying external conditions is considered. The COP and the heating and cooling capacities are plotted for Series 2 and 3 in Figure 7.28 as a function of \( T_w2 \), \( T_w4 \), \( m_w \), and \( m_w2 \). The results relating to the COP are rather surprising since it was anticipated that the variations would be the converse of those shown by the four curves. This inverted trend is due to the fact that some internal parameters of the cycle, in particular \( T_w2 \) (see also Section 7.8.2), could not be kept constant. The effect of the internal heat exchanger could not be studied because the temperature levels did not permit its use.

![COP, Q_res, Q_des for Series 2 (x_o = 0.50, T_inj = 49.5 °C) and Series 3 (x_o = 0.61, T_inj = 45 °C).](image)

Figure 7.27: COP, \( Q_{\text{res}} \) and \( Q_{\text{des}} \) for Series 2 (\( x_o = 0.50, T_{\text{inj}} = 49.5 \, ^\circ\text{C} \)) and Series 3 (\( x_o = 0.61, T_{\text{inj}} = 45 \, ^\circ\text{C} \)).

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Figure 7.28: Effects of the external parameters on the COP and the heating and cooling capacities.
7.8 Comparison of the results with the model

The objective of the model described in Chapter 4 is a design study, not the simulation of a test-plant. This makes comparison difficult, but it is worth trying to validate the computer simulation by using the results obtained in the test-plant. For this a few measurement files have been selected and the input data needed by the program has been be taken from these files.

7.8.1 Determination of the input parameters

The external parameters $T_{w1}$, $T_{w3}$, $T_{w2}$, $m_{w}$, and $m_{w0}$ of each chosen measurement file serve as input to the program. For the suction pressure, the arithmetic mean of $p_{11}$ and $p_{12}$ has been taken and the calculation has been made at the measured overall concentration $x_0$. The minimum temperature differences in the resorber, given in Tables G.3 and G.4 were based on the equilibrium temperatures between $T_{w}$ and $T_{41}$. Since in all measurements the point 4 is in the subcooled liquid region, this $\Delta T_{\text{min}}$ cannot be used in the program, that makes calculations assuming that point 4 is on the saturated liquid line. A $\Delta T_{\text{min}}$ calculated between $(T_{w4}/T_{w3})$ and $(T_{4}/T_{4,\text{sat}})$ has been be used as input data, where $T_{4,\text{sat}}$ is the saturation temperature corresponding to the pressure $(p_{22}+p_{23})/2$ and the overall concentration $x_0$. Because the subcooling cannot be taken into account in the program, the calculated total mass flow rate $m_w$ will be higher than in the measurements. There are no such problems for the minimum temperature difference in the desorber, and the values calculated between $(T_{w2}/T_{w1})$ and $(T_{1}/T_{3,\text{v}})$ and given in Tables G.7 and G.8 have been used. The isentropic efficiency must also be specified. To be consistent with the computer program, the compressor efficiency should calculated without taking into account the liquid ring. However, it was seen in Section 7.4.2.1 that apparent efficiencies higher than 1 can be found, because of the cooling of the vapour by the liquid. In fact, there is no way to estimate the isentropic efficiency accurately enough, thus in all calculations an arbitrary value of $\eta_{is}$ has been used, namely 0.85.

7.8.2 Comparison with the measurements

A comparison of the simulations and of the measurements for the file s178 (Series 3, Figure 7.6) is given in Table 7.6. For the measured values, the pressure $p_2$ was taken as the arithmetic mean of $p_{23}$ and $p_{22}$ and the temperature $T_3$ as the arithmetic mean of $T_{x3}$ and $T_{3,\text{v2}}$. The measured UA values (kW/K) are based on the heating or cooling capacity measured at the water side and the mean temperature as given in Appendix G. The input parameters, extracted from the measurements, are given in Table 7.5.

For the reasons previously mentioned, the matching of the measured and calculated values is not perfect, but does give a reasonable approximation. The temperature and pressure matches at points 2 and 3 are quite good. The difference between the temperatures at point 4 arises from the absence of subcooling in the simulations. Because $T_4$ is higher in the
Table 7.5: Input data for the simulation program.

<table>
<thead>
<tr>
<th>$x_o$ kg/kg</th>
<th>$T_{w_2}$ °C</th>
<th>$T_{w_4}$ °C</th>
<th>$T_{w_3}$ °C</th>
<th>$\eta_{is}$</th>
<th>$\dot{m}_{wd}$ kg/s</th>
<th>$\dot{m}_{wr}$ kg/s</th>
<th>$\Delta T_{m_{inat}}$ K</th>
<th>$\Delta T_{m_{ind}}$ K</th>
<th>$p_1$ bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>s178</td>
<td>.6039</td>
<td>44.1</td>
<td>40.1</td>
<td>52.7</td>
<td>0.85</td>
<td>.3642</td>
<td>.2474</td>
<td>6.8</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Table 7.6: Results of the simulations and of the measurements for the file s178.

<table>
<thead>
<tr>
<th>$p_2$ bar</th>
<th>$T_1$ °C</th>
<th>$T_2$ °C</th>
<th>$T_3$ °C</th>
<th>$T_4$ °C</th>
<th>$T_{w_3}$ °C</th>
<th>$m_a$ kg/s</th>
<th>$Q_{res}$ kW</th>
<th>$Q_{des}$ kW</th>
<th>COP</th>
<th>$U_A_r$</th>
<th>$U_A_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>s178</td>
<td>9.61</td>
<td>32.4</td>
<td>41.7</td>
<td>60.9</td>
<td>39.3</td>
<td>38.3</td>
<td>.0428</td>
<td>13.0</td>
<td>8.8</td>
<td>3.1</td>
<td>2.4</td>
</tr>
<tr>
<td>meas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>s178</td>
<td>9.92</td>
<td>30.6</td>
<td>41.7</td>
<td>59.7</td>
<td>48.2</td>
<td>36.2</td>
<td>.0483</td>
<td>13.0</td>
<td>12.0</td>
<td>12.9</td>
<td>1.8</td>
</tr>
<tr>
<td>simul</td>
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</tr>
</tbody>
</table>

Simulations, it would be expected that the temperature after the expansion process will also be higher. This is not the case because the complete expansion process in the test-plant cannot be considered as an adiabatic one: between the resorber and the expansion valve, there is about 3 m upwards pipe that is very close to the hot water line of the desorber. It is therefore possible that, due to on-line pressure drop, the expansion process before the expansion valve takes place isothermally, in consequence of which there would be a higher temperature after the expansion valve itself. Because of the lower $T_1$ temperature in the simulations, the simulated water temperature $T_{w_3}$ will be lower and the desorber heating capacity higher than in the measurements, leading to a higher COP as well. The results relating to the total mass flow rate $m_a$ are consistent with the resorber analysis of section 7.5: because the subcooling is not taken into account in the simulations, a constant heating capacity would imply a higher mass flow rate in the simulations than in the measurements. However, the advantage of the subcooled liquid at the resorber outlet is counterbalanced by the subcooled liquid flow at the resorber inlet, so that, at constant heating capacity, the total mixture mass flow rate finally may or may not be higher in the measurements than in the simulations. The differences in the $U_A$ values for the resorber are caused by the variations in the mean temperature difference, that is higher for the simulations (no subcooling) than for the measurements. For the $U_A$ values of the desorber, both the cases are possible since a higher $Q_{des}$ in the simulations can be compensated by a higher $\Delta T_{m_{meas}}$ because of the lower $T_1$.

Finally, it is worth mentioning that the trends of the measured variations of the COP and the heating and cooling capacities with $T_{w_4}$, $T_{w_2}$, $\dot{m}_{wr}$ and $\dot{m}_{wd}$ (Figure 7.28) were also found in the simulations. Figure 7.29 gives an example for the variations of $T_{w_4}$. The behaviour of both the measured and the simulated cycles is illustrated in Figure 7.30.
Figure 7.29: Measured and simulated variations of the COP and of the heating and cooling capacities for Series 3.

NH3 / H2O

NH3 overall mass concentration: 60%

Figure 7.30: Simulated cycle (solid line) and measured one (dashed line) for the file s178.
7.9 Conclusions

The measurements made on the heat pump test-plant were described. Because the liquid-ring compressor was used the design values could not be reached. The heat pump was therefore tested at lower discharge temperature and capacity. The liquid-ring compressor was studied separately, with a closed suction line, in order to estimate the part of the compressor work used for the liquid ring. The liquid ring appeared to behave as if liquid and vapour was being separately compressed. The liquid at the discharge side was found to be subcooled. The calculation of the total compressor shaft work with internal balances was consistent with the measurements but it was not possible to safely predict the part of compression work spent on the suction mixture. Very low isentropic efficiencies were found. The analysis of the internal and external heat and mass balances of the resorber has shown that the entering liquid was probably more subcooled than was indicated by the constant liquid mass fraction model. The distribution of the liquid is probably not ideal because of the presence of vapour in the liquid line. It is also possible that liquid is transported in the vapour line. The resorber heat transfer coefficient varied between 200 and 1200 W/m²K and was very sensitive to the vapour velocity (that should be kept high). The external and internal heat balances of the desorber matched well, but the desorber had a very poor heat transfer coefficient due to a bad liquid distribution and a vapour velocity that was too low. In both the resorber and the desorber mean temperature differences below 8 °C were observed, with minimum temperature differences down to 1 °C. A comparison between the measurement results and results from the model used in Chapter 4 has shown a reasonable agreement, within the limits of the model’s assumptions. For further experiments with the test-plant, it is recommended that the distributor of the desorber should be replaced by one similar to that of the resorber. The liquid subcooling at the resorber inlet and in the compressor discharge line should be measured. The compressor should be replaced by one with a higher efficiency which can minimize or suppress the liquid injection flow rate. If such a compressor cannot be found or designed, the use of the injection liquid cooling heat together with the resorber heat should be recommended, although the irreversibilities introduced will remain higher than when no injection liquid is used.

References


Chapter 8

Recommendations for further research

In the opinion of the author, further research on the wet compression-resorption heat pump should follow the three directions listed below.

Further improvements must be made to the heat pump test-plant, including changing of the distribution system of the desorber in order to suppress the mist or slug flow. The vapour velocity at the resorber inlet should be increased and the liquid subcooling reduced. This can only be achieved by using a better compressor, with a lower injection volume flow rate. If this is not possible, it will be worth using the heat released by the cooling of the injection liquid, together with the resorber heat, in order to increase the COP.

A fundamental study of the design of oil-free wet compressors should be initiated to find methods to thoroughly mix the liquid and vapour phases during the compression, and to reduce or eliminate the injection flow. Although in some particular applications COP gains of more than 50 % can be achieved by using wet compression, it could be argued that this is not worthwhile because wet compression in a heat pump generally leads to moderate COP gains (≤ 14 %). However, for large heating capacity applications, there is still a significant gain in primary energy use. Furthermore, for the reasons listed in Chapter 1, the development of industrial heat pumps will be increasingly aimed at high temperature applications. Wet compression may be the only way to reach these high temperatures, since it limits the superheating of the compressed vapour, and in that way, may avoid possible compressor failure and refrigerant or oil decomposition. Another reason to conduct such a fundamental study is that the applications of wet compression are not restricted to the heat pump systems, but are also of great interest for fields like air compression for medical purposes and oil pumping.
Finally, fundamental research on the resorber and on the desorber should be continued to further the design of lowcost, high-efficiency, compact heat exchangers for condensing and evaporating mixtures. At present the condensation and evaporation of zeotropic mixtures are subjects that are gaining in importance, because these mixtures are increasingly used in refrigeration or heat pumping applications. Since condensation of these mixtures is more closely involved with the absorption of a binary vapour into a binary liquid mixture, than with pure refrigerant condensation, the fundamental works on this subject by Wassenaar [1995] and Lottin [1996] should serve as basis for future study.

References


Appendix A

COP optimization curves for the case study
Figure A.1: COP for $\Delta T_{\text{inf}}/\Delta T_{\text{glide}} \leq 1$; a) ex. 1.1, small $\Delta T_{\text{glide}}$; b) ex. 1.2, medium $\Delta T_{\text{glide}}$; c) ex. 1.3, large $\Delta T_{\text{glide}}$. 

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Tw2 = 55°C, Tw4 = 60°C, Tw3 = 70°C
\[ \dot{m}_{\text{res}} = 23.90 \text{ kg/s}, \dot{m}_{\text{des}} = 23.90 \text{ kg/s}, \text{COP_r} = 22.87 \]
\[ \eta_k = 0.70, \Delta T_{\text{min}} = 5 \text{ K} \]

\[ \text{COP} \]

\[ \begin{array}{c}
\text{a}
\end{array} \]

Tw2 = 60°C, Tw4 = 70°C, Tw3 = 90°C
\[ \dot{m}_{\text{res}} = 11.96 \text{ kg/s}, \dot{m}_{\text{des}} = 11.96 \text{ kg/s}, \text{COP_r} = 12.10 \]
\[ \eta_k = 0.85, \Delta T_{\text{min}} = 5 \text{ K} \]

\[ \begin{array}{c}
\text{b}
\end{array} \]

Tw2 = 80°C, Tw4 = 100°C, Tw3 = 140°C
\[ \dot{m}_{\text{res}} = 17.94 \text{ kg/s}, \dot{m}_{\text{des}} = 17.94 \text{ kg/s}, \text{COP} = 6.86 \]
\[ \eta_k = 0.70, \Delta T_{\text{min}} = 5 \text{ K} \]

\[ \begin{array}{c}
\text{C}
\end{array} \]

\[ \text{p_1 = 1 bar, p_2 = 2 bar, p_1 = 3 bar, p_1 = 4 bar Pure refrigerant} \]

Figure A.2: COP for \( l<\Delta T_{\text{tip}}/\Delta T_{\text{glide,r}} \leq 2 \); a) ex. 2.1, small \( \Delta T_{\text{glide,r}} \), b) ex. 2.2, medium \( \Delta T_{\text{glide,r}} \), c) ex. 2.3, large \( \Delta T_{\text{glide,r}} \)
Figure A.3: COP for $2 < \Delta T_{liq}/\Delta T_{glide,r} < 4$; a) ex. 3.1, small $\Delta T_{glide,r}$; b) ex. 3.2, medium $\Delta T_{glide,r}$; c) ex. 3.3, large $\Delta T_{glide,r}$

$Tw_2 = 31 \, ^\circ C$, $Tw_4 = 52 \, ^\circ C$, $Tw_3 = 60 \, ^\circ C$
$r_{in} = 14.90 \, kg/s$, $r_{in} = 40.00 \, kg/s$, COP$_{L} = 12.49$
$\eta_{S} = 0.70$, $\Delta T_{min} = 5 \, K$

COP

$Tw_2 = 70 \, ^\circ C$, $Tw_4 = 110 \, ^\circ C$, $Tw_3 = 130 \, ^\circ C$
$r_{in} = 21.53 \, kg/s$, $r_{in} = 21.53 \, kg/s$, COP$_{L} = 6.71$
$\eta_{S} = 0.85$, $\Delta T_{min} = 5 \, K$

COP

$Tw_2 = 50 \, ^\circ C$, $Tw_4 = 100 \, ^\circ C$, $Tw_3 = 140 \, ^\circ C$
$r_{in} = 17.94 \, kg/s$, $r_{in} = 17.94 \, kg/s$, COP$_{L} = 4.58$
$\eta_{S} = 0.70$, $\Delta T_{min} = 5 \, K$

COP
Appendix B

The solution recirculation cycle

B.1 The model

Since this cycle has been studied extensively in the literature (see Chapter 1), only the basic assumptions and a lay-out of the calculation procedure are given here. Figure B.1 gives the lay-out of the cycle studied.

*Compressor model:* The compressor model is similar to the model described in Section 4.2.3, with the exception of the overall concentration \( x_o \), that is no longer an input data. Because the compressor is now a dry one, \( x_o \) must be replaced in *Equations (4.2) to (4.8)* by the ammonia concentration of the suction vapour \( y_2 \).

*Solution pump model:* The input variables are \( p_1, p_2, T_{31} (= T_{3v} = T_2) \), \( x_2 \) and the pump efficiency \( e_{fp} \). The pump is assumed to be adiabatic. The output variable \( T_{3p} \) is calculated by *Equations (B.1) and (B.2).*

\[
h_{3p} = h_{2l} + \frac{h(x_2, p_2, T_{3l}) - h_{2l}}{e_{fp}} \tag{B.1}\]

\[
T_{3p} = \text{thho}(x_2, p_2, h_{3p}) \tag{B.2}\]
Expansion valve model: This is the same model as that described in Section 4.2.4.

Resorber and desorber model: These are the same models as described in Section 4.2.5. For the resorber, however, first the input variable $T_3$ must be calculated. Adiabatic absorption is assumed between the entering vapour and liquid (points 3v and 3l respectively) until equilibrium is reached (point 3). $T_3$ is calculated using Equations (B.3) and (B.4).

$$h_3 = m_{v2} h_{3v} + m_{l2} h_{3l} \quad (= m_{v2} h_{3v} + m_{l2} h_{3l}) \quad \text{(B.3)}$$

$$T_3 = thho(x_0, p_2, h_3) \quad \text{(B.4)}$$

Internal heat exchanger: The input data are $T_4$, $T_{3p}$, $p_2$, $\dot{m}_a$, $m_{l2}$, $x_p$, $x_s$ and $\Delta T_{\text{min},e}$. The output variables are $T_{4e}$, $T_{3e}$ and $Q_{\text{ex}}$. Heat exchange is possible only if $T_4 > T_{3p} + \Delta T_{\text{min},e}$. A first estimate of $T_{3e}$ is made by using Equation (B.5). $Q_{\text{ex}}$, $h_{3e}$, $h_{4e}$ and $T_{4e}$ are calculated by using Equations (B.6), (B.7), (B.8) and (B.9) respectively.

$$T_{3e} = T_4 - \Delta T_{\text{min},e} \quad \text{(B.5)}$$
\[ h_{3e} = h(x_2, p_2, T_{3e}) \]  \hspace{1cm} (B.6)

\[ Q_{ex} = \dot{m}_o m_{12} (h_{3e} - h_{3p}) \]  \hspace{1cm} (B.7)

\[ h_{4e} = h_4 - \frac{Q_{ex}}{\dot{m}_o} \]  \hspace{1cm} (B.8)

\[ T_{4e} = thho(x_o, p_2, h_{4e}) \]  \hspace{1cm} (B.9)

If \( T_{4e} < T_{3p} + \Delta T_{min,e} \), \( T_{4e} \) is recalculated using Equation (B.10), as well as \( h_{4e}, Q_{ex}, \) and \( h_{3e} \) using Equations (B.11), (B.12) and (B.13) respectively. Finally, Equation (B.14) is used to calculate \( T_{3e} \).

\[ T_{4e} = T_{3p} + \Delta T_{min,e} \]  \hspace{1cm} (B.10)

\[ h_{4e} = h(x_o, p_2, T_{4e}) \]  \hspace{1cm} (B.11)

\[ Q_{ex} = \dot{m}_o (h_4 - h_{4e}) \]  \hspace{1cm} (B.12)

\[ h_{3e} = h_{3p} + \frac{Q_{ex}}{\dot{m}_o m_{12}} \]  \hspace{1cm} (B.13)

\[ T_{3e} = thho(x_2, p_2, h_{3e}) \]  \hspace{1cm} (B.14)

**Desuperheater**: The input data are \( T_{3e}, T_{3v1}, \dot{m}_o, m_{12}, m_{22}, p_2 \). The output data are \( T_{3p}, T_{3v} \) and \( Q_{desup} \). A first estimate of \( T_{3v} \) is made using Equations (B.15) to (B.19).

\[ T_{3v} = tsat(x_2, p_2, 1) \]  \hspace{1cm} (B.15)

\[ h_{3v} = h(x_2, p_2, T_{3v}) \]  \hspace{1cm} (B.16)

\[ Q_{desup} = \dot{m}_o m_{12} (h_{3v} - h_{3e}) \]  \hspace{1cm} (B.17)
\[ h_{3v} = h_{3v1} - \frac{Q_{\text{desup}}}{\dot{m}_w m_{v2}} \]  
\[ T_{3v} = \text{thho}(y_2, p_2, h_{3v}) \]

If \( T_{3v} \) is lower than \( T_{31} + \Delta T_{\text{min,sup}} \), a new estimate of \( T_{3v} \) is chosen and \( T_{31} \) is recalculated using Equations (B.20) to (B.23). These calculations are repeated until \( T_{3v} \geq T_{31} + \Delta T_{\text{min,sup}} \).

\[ h_{3v} = h(y_2, p_2, T_{3v}) \]  
\[ Q_{\text{desup}} = \dot{m}_w m_{v2} (h_{3v1} - h_{3v}) \]  
\[ h_{31} = h_{3e} + \frac{Q_{\text{desup}}}{\dot{m}_w m_{l2}} \]  
\[ T_{31} = \text{thho}(x_2, p_2, h_{31}) \]

**Set-up of the model:** a set-up similar to the one used for the wet compression cycle is used. A succinct flow chart is given in Figure B.2.

### B.2 Comparison with the wet compression cycle

In this section a brief comparison of the COP behaviour in relation to the overall concentration for both the cycles will be given for examples 1.3, 2.2 and 3.1. The COP curves are given in Figures B.3 to B.6.

The concentration range over which solution recirculation cycle calculations can be achieved is larger than for the wet compression cycle. At the low concentration side the constraint of point 3 not being in the subcooled region, is verified at lower concentrations because of the application of dry compression (see Section 4.5.1). At the high concentration side the limitation that point 3 should not be in the superheated region does not apply, thus the highest concentration is only limited by the maximum pressure allowed in the cycle.

In all cases, the COP curve for the wet compression cycle follows the same variations as the COP curve for the solution recirculation cycle. The concentrations corresponding to the maximum COP are also very close to each other. On the largest part of the curve the
Figure B.2: Succinct flow chart of the solution recirculation cycle calculation program.

The wet compression cycle appears to perform better than the solution recirculation cycle, but this advantage can be very slight (Figure B.5). At the limits of the curve, the advantage of the wet compression cycle is generally reduced to nil.

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Figure B.3: COP comparison for example 1.3.

Tw2 = 25 °C, Tw4 = 15 °C, Tw3 = 85 °C  
\( \dot{n}_{reux} = 3.42 \text{ kg/h}, \dot{n}_{ixes} = 9.21 \text{ kg/h}, \text{ COP}_{ix} = 9.09 \)
\( n_{we} = 0.67, \Delta T_{min} = 5 \text{ K}, p_1 = 2 \text{ bar} \)

Figure B.4: COP comparison for example 2.2.

Tw2 = 60 °C, Tw4 = 70 °C, Tw3 = 90 °C  
\( \dot{n}_{reux} = 12.96 \text{ kg/h}, \dot{n}_{ixes} = 12.96 \text{ kg/h}, \text{ COP}_{ix} = 12.10 \)
\( n_{we} = 0.85, \Delta T_{min} = 5 \text{ K}, p_1 = 2 \text{ bar} \)

Figure B.5: COP comparison for example 3.1.

Tw2 = 31 °C, Tw4 = 52 °C, Tw3 = 60 °C  
\( \dot{n}_{reux} = 14.00 \text{ kg/h}, \dot{n}_{ixes} = 40.00 \text{ kg/h}, \text{ COP}_{ix} = 12.49 \)
\( n_{we} = 0.70, \Delta T_{min} = 5 \text{ K}, p_1 = 6 \text{ bar} \)
Appendix C

Choice of an equation of state

C.1 Introduction

The development of equations of state has followed three main paths. The first two, the Van der Waals's family of cubic equations of state and the Beattie-Bridgeman family of equations of state, are empirical or semi-empirical. The third path is that of theoretical equations of state derived from the statistical mechanics theory. In the following sections, a brief overview of these three categories is given. Some other equations, not belonging to these series, like the Martin-Hou equation, are not treated here because, despite their accuracy, they have not gain widespread use owing to their complexity and the lack of information on mixture applications. More information on the different equations of state can be found, for instance, in Edmister [1983], Kyle [1984], Reid [1987] and Wark [1995].

C.2 The family of cubic equations of state

The first cubic equation of state (Equation (C.1)) is given by Van der Waals in 1873. The term b is a corrective factor representing the volume occupied by the molecules themselves, and the second term accounts for the attractive forces between molecules. The parameters a and b must be fitted to experimental critical temperature and pressure values.

In 1949, Redlich Kwong introduced a modified expression to take into account the temperature dependence of the second term (Equation (C.2)). The RK equation of state
\[ p = \frac{RT}{V-b} - \frac{a}{V^2} \]  \hspace{1cm} (C.1)

has proved to be a useful equation of state and is considerably more accurate than the Van der Waals equation, although the accuracy is less at the phase boundary.

\[ p = \frac{RT}{V-b} - \frac{a T^{-0.5}}{V(V+b)} \]  \hspace{1cm} (C.2)

In 1964, Wilson modified the temperature dependence of the second term by using the acentric factor \( \omega \) and the reduced temperature \( T_r \):

\[ p = \frac{RT}{V-b} - \frac{a \alpha}{V(V+b)} \]  \hspace{1cm} (C.3)

with

\[ \alpha = T_r (1 + (1.57 + 1.62 \omega)(\frac{1}{T_r} - 1)) \]  \hspace{1cm} (C.4)

In 1972, Soave used the same equation (Equation (C.3)) with a modified \( \alpha \) parameter in the so-called Soave-Redlich Kwong equation:

\[ \alpha = (1 + S(1 - T_r^{0.5}))^2 \]  \hspace{1cm} (C.5)

with

\[ S = 0.480 + 1.574 \omega - 0.176 \omega^2 \]  \hspace{1cm} (C.6)

This equation is more accurate than the Wilson equation for vapour-liquid phase equilibrium predictions at moderate and high pressures (above 1 bar), for light hydrocarbons and for non-polar fluids. However, its accuracy is low for superheated vapour, because the liquid density predictions are poor and, furthermore, the use of this equation leads to an unrealistic universal compressibility factor of 1/3. To alleviate these shortcomings, Peng and Robinson modified in 1976 Equation (C.3) in the following way:

\[ p = \frac{RT}{V-b} - \frac{a \alpha}{V(V+b) + b(V-b)} \]  \hspace{1cm} (C.7)

where \( \alpha \) is defined by Equation (C.5) and \( S \) by Equation (C.8):

\[ S = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \]  \hspace{1cm} (C.8)

The Peng-Robinson equation gives very accurate vapour predictions for hydrocarbons and is therefore used in many calculations for refinery plants.
C.3 The Beattie-Bridgeman family of equations of state

The five constants Beattie-Bridgeman equation of state (Equation (C.9)) was introduced in 1927 and owing to its acceptable accuracy in the gaseous region was widely used until 1940.

\[ Z = 1 + \frac{B_o - \frac{A_o}{RT} - \frac{C}{T^3}}{V} - \frac{bB_o - \frac{aA_o}{RT} + \frac{CB_o}{T^3}}{V^2} + \frac{bCB_o}{T^3V^3} \]  

(C.9)

In 1940 the Benedict-Webb-Rubbin (BWR) equation of state (Equation C.10) was proposed and fitted with methane, ethane, propane, n-butane and mixtures.

\[ Z = 1 + \frac{B_o - \frac{A_o}{RT} - \frac{C}{RT^3}}{V} + \frac{b - \frac{a}{RT}}{V^2} + \frac{\alpha a}{RTV^3} + \frac{C}{RT^3V^2} \left(1 + \frac{\gamma}{V^2}\right) e^{-\frac{\gamma}{V^2}} \]  

(C.10)

Despite deficiencies at high densities, in the critical region and with mixtures, the BWR equation is one of the most accurate equations of state that is applicable to vapour and liquid phases. Several modifications have been proposed to increase its validity range and to alleviate its main disadvantage, which is a great sensitivity to uncertainty in experimental data that leads to different sets of constants for different sets of experimental data. One of the most successful generalisations of the BWR equation is the Starling-Han [1972] equation (Equation (C.11)) based on the Starling modified BWR equation, where the 11 constants are a linear or an exponential function of \( \omega \).

\[ p = \rho RT + (B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}) \rho^2 + (bRT - a - \frac{d}{T}) \rho^3 \]  

\[ + \alpha(a + \frac{d}{T}) \rho^6 + \frac{c \rho^3}{T^2} (1 + \gamma \rho^2) e^{-\gamma \rho^2} \]  

(C.11)

In 1975, Nishuimi and Saito add four temperature dependent terms to obtain improved accuracy for heavier hydrocarbons and in 1980 they extended the equation to polar fluids by adding polarity parameters. Since that time, many modifications have been made with higher numbers of constants (up to 52).

C.4 Theoretical equations of state

Theoretical equations are based on statistical mechanics and on the calculation of the Helmoltz free energy. In 1885 Thiesen presented the first virial equation (Equation
(C.12)), which gives an expression of the compressibility factor as an infinite power series of the specific volume, deduced by the examination of the molecular behaviour. The virial coefficients are temperature dependent only, and reflect the interaction between the molecules. The Thiesen compressibility factor, as defined in Equation (C.12), is valid only for vapours at low pressure which are not close to the vapour-liquid transition curve.

\[
Z = \frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots = 1 + B'p + C'p^2 + D'p^3 + \ldots \tag{C.12}
\]

Although this equation is not convenient for practical use, it is of interest because of its general formulation; all close-form equations reviewed in Sections C.2 and C.3 can be put in a virial form when expanded to an infinite series.

Another development in the theoretical equations of state has been the use of the hard sphere and of the hard chain theories. In 1963 Thiele presented a solution of the equation for hard sphere gas under the form:

\[
Z = \frac{1 + \gamma + \gamma^2}{(1 - \gamma)^3} \tag{C.13}
\]

where \( \gamma = b/(4V) \) and \( b \) is the second virial coefficient. In 1972, by means of mathematical manipulation Carnahan and Starling obtained the more accurate Equation (C.14), essentially valid for light hydrocarbons.

\[
Z = \frac{1 + \gamma + \gamma^2 - \gamma^3}{(1 - \gamma)^3} \tag{C.14}
\]

In this equation, the molecules are assumed to be rigid and non-interacting. Carnahan-Starling-DeSantis introduced a second term accounting for long-range attractive forces between molecules in the so-called CSD equation (Equation (C.15)), where \( a \) and \( b \) are defined by the Equation set (C.16).

\[
Z = \frac{1 + \gamma + \gamma^2 - \gamma^3}{(1 - \gamma)^3} - \frac{a}{RT(\nu + \beta)} \tag{C.15}
\]

\[
a = a_0 e^{\alpha T + \beta T^2} \tag{C.16}
\]

\[
b = b_0 + b_1 T + b_2 T^2
\]

The relative simplicity of this equation permits fitting with a minimum of experimental data. However for polar fluids its accuracy may be not very good.

In 1975, Beret and Prausnitz produced a more successful equation by applying the perturbed hard chain theory:
\[ Z = Z_{\text{hard chain}} - \frac{a}{RTv} \]

\[ 4(\frac{\tau}{v_r}) - 2(\frac{\tau}{v_r})^2 \]

\[ (1 - \frac{\tau}{v_r})^3 \]

\[ \text{(C.17)} \]

where \( c \) is an adjustable parameter, \( \tau \) a constant, \( v_r \) the reduced volume and where \( a \) depends on two adjustable parameters, these being the temperature and the molecules involved. The Beret-Prausnitz equation (Equation (C.17)) and its modification by Donahue-Prausnitz in 1978 are applicable to fluids ranging from simple molecules to large molecules and over a very large pressure range. However, without further simplifications, this equation is not believed to be as applicable as the conventional equations, except for systems where few experimental data are available. For non-spherical molecules, the theory of the chain of rotators (COR) has been applied by Chien and Lin [1983] and Kim [1986].

### C.5 Mixtures

Generally, equations of state are first developed for pure substances and then extended to mixtures by the use of mixing rules for combining the pure component parameters. Except for those for virial coefficients, the mixing rules are more or less arbitrary.

**Cubic equations of state:**

The mixing rules for the Van der Waals equation of state are derived from the second virial coefficient mixing rule given in Equation (C.18).

\[ B = \sum \sum x_i x_j B_{ij} \]

\[ \text{(C.18)} \]

For the Van der Waals equation, the parameter \( b \) is assumed to be the arithmetic average of \( b_i \) and \( b_j \), thus the above equation reduces to

\[ b = \sum x_i b_i \]

\[ \text{(C.19)} \]

The parameter \( a \) is assumed to be the geometric average of \( a_i \) and \( a_j \), thus Equation (C.18) reduces to

\[ a = (\sum x_i \sqrt{a_i})^2 \]

\[ \text{(C.20)} \]

The mixing rule for \( b \), as given in Equation (C.19), is also valid for the Redlich-Kwong, Wilson, Soave-RK and Peng-Robinson equations. For the Redlich-Kwong equation, \( a \) may be given by Equation (C.20) or by the Vidal-Huron [1979] mixing rule (Equation (C.21)).
This mixing rule has been successfully used for refrigerant mixtures by Morrison [1994] and Barolo [1994].

\[
\frac{A}{B} = \sum x_i \left( \frac{A_i}{B_i} - \frac{\ln \gamma_i}{\ln 2} \right)
\]  
(C.21)

For the Wilson Equation, \(a\) is given by Equation (C.22):

\[
a = 4.934 RT b \sum x_i g_i \quad \text{with} \quad g_i = 1 + (1.57 + 1.62 \omega_i) (T_i^{-1} - 1)
\]  
(C.22)

For the Soave-RK and the Peng-Robinson equations, the mixing rule is:

\[
a = \sum \sum x_i x_j \sqrt{a_i a_j} (1 - k_{ij})
\]  
(C.23)

where the binary interaction parameters \(k_{ij}\) can be obtained by fitting the equation to experimental VLE data or by using second virial coefficients of binary mixtures.

**Beattie-Bridgeman family of equations of state:**

In 1942 Benedict developed the original mixing rules for the BWR equation described in the Equations set (C.24), which are satisfactory for light hydrocarbon mixtures only.

\[
\begin{align*}
B_o &= \sum x_i B_{oi} \\
A_o &= [\sum x_i A_{oi}^{0.5}]^2 \\
C_o &= [\sum x_i C_{oi}^{0.5}]^2 \\
\gamma &= [\sum x_i \gamma_i^{0.5}]^2 \\
a &= [\sum x_i a_i^{1/3}]^3 \\
b &= [\sum x_i b_i^{1/3}]^3 \\
c &= [\sum x_i c_i^{1/3}]^3 \\
\alpha &= [\sum x_i \alpha_i^{1/3}]^3
\end{align*}
\]  
(C.24)

Since these mixing rules depend entirely on the pure component parameters, it was necessary to modify them with additional parameters specific to the mixture. This was done by Starling, who uses the fugacity to calculate the mixture parameters. The parameters of the Starling-Han equation \(a, b, c, \alpha, \gamma\) and \(B_o\) are defined as in Equation set (C.24), but \(A_o, C_o, D_o, d\) and \(E_o\) are defined by Equation set (C.25), where the \(k_{ij}\) are the binary interaction parameters.

\[
\begin{align*}
A_{oi} &= \sum x_i x_j A_{oi}^{0.5} A_{oj}^{0.5} (1 - k_{ij}) \\
C_{oi} &= \sum x_i x_j C_{oi}^{0.5} C_{oj}^{0.5} (1 - k_{ij})^3 \\
D_{oi} &= \sum x_i x_j D_{oi}^{0.5} D_{oj}^{0.5} (1 - k_{ij})^4 \\
E_{oi} &= \sum x_i x_j E_{oi}^{0.5} E_{oj}^{0.5} (1 - k_{ij})^5 \\
d &= [\sum x_i d_i^{1/3}]^3
\end{align*}
\]  
(C.25)
Theoretical equations of state:

It is possible to apply the above mentioned mixing rules, but a lot of modifications have been presented in recent years. For example, mixing rules can be obtained by combining an equation of state with an excess Gibbs-free energy model (like the Vidal-Hurton mixing rules). This can also be combined with the UNIFAC group contribution method to make predictions in the absence of experimental data.

C.6 Comparison of the equations of state

The main differences between the equations of state presented in the previous sections occurs with respect to the computational time and to the accuracy of the results at high pressures, for polar molecules, and for the liquid phase, since historically, equations of state have been developed to represent the vapour phase behaviour. Furthermore, the equations used should be easily extendable to mixtures, with a reasonable accuracy. The truncated virial equation (**Equation (C.13)**) is simple, but it can be used only for the vapour phase and only for moderate deviations from the ideal-gas behaviour. Cubic equations of state are capable of representing liquid phase behaviour and are effective for curve fitting PVT data, but should not be extrapolated outside the temperature and pressure ranges for which they have been tested. The modified BWR equations also should not be extrapolated outside the regions of fitted data, but they do very well within these ranges and have the advantage of having been tested extensively for many hydrocarbons with respect to almost all thermodynamic properties. The family of theoretical equations is generally interesting for mixtures for which little experimental data is available, but are at present often less accurate than the semi-empirical equations. Generally, it is recommended that the Peng-Robinson equation of state should be used for nonpolar molecules near saturation conditions and a that modified BWR equation like the Starling-Han equation should be used for more extended ranges of temperature and pressure. The better accuracy obtained with the SH equation requires a greater use of computational time because of its more complicated multi-parameter form. However, in many papers about the evaluation of refrigerants in thermodynamic cycles, the theoretical Carnahan-Starling-DeSantis equation (**Equation (C.16)**) has been used (see McLinden [1988], Low [1988], Domansky [1992]). Indeed, this equation can also be recommended for binary mixtures when sufficient data is available to ensure a sufficient degree of accuracy. When few data are available, for example when the use of new refrigerants is to be tested, the use of the Cubic Chain Of Rotators equation should be preferred, since only the critical data are needed, although the results are not very accurate. Since the aim of this work was not to investigate new refrigerants, but to compare the performances of several refrigerant mixtures in several thermodynamic cycles, the choice of an equation of state is reduced to two options: the Starling-Han equation (SH) (**Equation (C.12)**) or the Carnahan-Starling-DeSantis equation (CSD) (**Equation (C.16)**).

In Fedotov [1994], a comparison of the performances of both these equations for several fluorocarbon pairs has been made (this was not necessary for hydrocarbons pairs, since the Starling-Han equation was originally fitted with these components). The results for the CSD equation were obtained by using the program REFPREP from the NIST. The
calculations for the Starling-Han equation are described in Fedotov [1994]. Briefly, the eleven parameters of the Starling-Han equation are simple functions of the critical data $T_c$ and $p_c$, of the acentric factor $\omega$ and of two sets of constants $A_i, A_i$, and $B_i, B_i$. Both these sets of constants were originally fitted by Starling on the thermodynamic data of normal paraffins and their mixtures, so fluorocarbons not included. Using the Starling-Han equation with this set of parameters to calculate the properties of fluorocarbons could therefore lead to unacceptable inaccuracy. The logical way to improve the accuracy is to recalculate the constants $A_i$ and $B_i$ also to fit the data for fluorocarbons. However this would demand quite extensive work and furthermore it would be likely that it will result in a decrease of the accuracy for normal paraffins. Preference was therefore given to the retention of the constants $A_i$ and $B_i$ as they were calculated by Starling, and to work with pseudo-values of $T_c$, $p_c$ and $\omega$. These pseudo-values have no physical meaning, although they are very close to the real values and have been obtained by fitting the results of the SH equation for the saturation pressure and for the saturated liquid and vapour densities to the tabulated data for pure fluorocarbons (ASHRAE [1993]). It was not possible to determine the values of the binary interaction parameters $k_{ij}$ from experimental data on the chosen mixtures, since at that time these data were not available. The interaction parameters for the SH equation where therefore calculated by fitting the SH equation to the more theoretical CSD equation used with theoretical $k_{ij}$ values. However, as soon as experimental data on the tested mixtures are available, better $k_{ij}$ values may be calculated.

In Table C.1 an overview of the main results is given. The errors were calculated with reference to the tabulated properties of fluorocarbons (ASHRAE [1993]) over the temperature ranges indicated in the first column.

For all these refrigerants, the mean error of the saturation pressure is less than 1.6 % for the SH equation, versus less than 0.8 % for the CSD equation; for the vapour density the mean error is less than 1.5 % versus less than 3.6 % respectively and for the liquid density the mean error is less than 2.1 % versus less than 0.6 % respectively. Except for the vapour density predictions, the CSD equation gives better results than the SH equation. However, the error generated by the SH equation remains acceptable. The maximum error in calculating the saturation pressure is less than 3.5 % for the SH equation, versus less than 8.4 % for the CSD equation, for the vapour density it is less than 2.3 % versus less than 10 % respectively and for the liquid density less than 3.5 % versus less than 1.7 % respectively. Therefore it can be seen that the CSD equation sometimes lead to unexpectedly high errors (up to 10 %), which can be avoided when using the SH equation, because of its more appropriate mathematical form. Owing to these considerations, it was decided to use the Starling-Han equation of state. In Table C.2, the mean and maximum absolute deviation between the properties of several mixtures calculated with the SH and CSD equations are given. The exact calculations for the entire temperature and concentration range can be found in Fedotov [1994]. The Starling-Han equation was therefore chosen and implemented in the calculation codes for the wet compression cycle, the solution recirculation cycle and the vapour compression cycle (see Itard [1996]).

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<table>
<thead>
<tr>
<th></th>
<th>satur.</th>
<th>press.</th>
<th>vap.</th>
<th>density</th>
<th>liquid</th>
<th>dens.</th>
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<td>SH %</td>
<td>CSD %</td>
<td>SH %</td>
<td>CSD %</td>
<td>SH %</td>
<td>CSD %</td>
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<td>2.4</td>
<td>1.5</td>
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<td>-70°C</td>
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<td>2.5</td>
<td>1.9</td>
<td>2.4</td>
<td>1.2</td>
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<td>0.9</td>
<td>2.1</td>
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<tr>
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<td>max error</td>
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<td>3.3</td>
<td>1.5</td>
<td>6.9</td>
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<td>1.8</td>
<td>5.2</td>
<td>1.5</td>
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Table C.1: Minimum and maximum errors of calculation using the SH and the CSD equations with reference to the tabulated properties of ASHRAE [1993].

<table>
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<tr>
<th></th>
<th>R23</th>
<th>R123</th>
<th>R125</th>
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<th>R134a</th>
<th>-R123</th>
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<tr>
<td></td>
<td>mean %</td>
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<td>max %</td>
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<td>2.3</td>
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<td>4.4</td>
<td>2.6</td>
<td>6.7</td>
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Table C.2: Mean and maximal deviations between the SH and the CSD equations of state.
References

ASHRAE, 1993 "Handbook of Fundamentals".


Fedotov V., 1994 "Non-azeotropic mixtures in the wet compression heat pump cycle: thermodynamic efficiency", Internal report K-200, Laboratory for Refrigerating Engineering and Indoor Climate Technology, Delft University of Technology, the Netherlands.

Itard L., 1996 "The calculation of the thermodynamic properties of mixtures of halogenated components and of hydrocarbons, and their use in the wet compression-resorption cycle, in the solution recirculation cycle and in the vapour compression cycle", Internal report K-245, Laboratory for Refrigerating Engineering and Indoor Climate Technology, Delft University of Technology, the Netherlands.


Appendix D

T-h and T-s diagrams for several mixtures
Figure D.1: Temperature-enthalpy diagrams of the mixture NH$_3$/H$_2$O for several overall mass concentrations.
**Figure D.2:** Temperature-entropy diagrams of the mixture NH₃/H₂O for several overall mass concentrations.
Figure D.3: Temperature-enthalpy diagrams of the mixture R23/R123 for several overall mass concentrations.
**Figure D.4:** Temperature-entropy diagrams of the mixture R23/R123 for several overall mass concentrations.
Figure D.5: Temperature-enthalpy diagrams of the mixture R125/R123 for several overall mass concentrations.
Figure D.6: Temperature-entropy diagrams of the mixture R125/R123 for several overall mass concentrations.
**Figure D.7:** Temperature-enthalpy diagrams of the mixture R134a/R123 for several overall mass concentrations.
Figure D.8: Temperature-entropy diagrams of the mixture R134a/R123 for several overall mass concentrations.
Figure D.9: Temperature-enthalpy diagrams of the mixture R152a/R123 for several overall mass concentrations.
**Figure D.10:** Temperature-entropy diagrams of the mixture R152a/R123 for several overall mass concentrations.
Figure D.11: Temperature-enthalpy diagrams of the mixture propane/n-pentane for several overall mass concentrations.
Figure D.12: Temperature-entropy diagrams of the mixture propane/n-pentane for several overall mass concentrations.
Figure D.13: Temperature-enthalpy diagrams of the mixture propane/n-butane for several overall mass concentrations.
Figure D.14: Temperature-entropy diagrams of the mixture propane/n-butane for several overall mass concentrations.
Appendix E

Complete results of the case study

A star * on the diagrams indicates that the suction pressure is lower than or equal to 1 bar and a double star ** indicates that the discharge pressure is higher than or equal to 25 bar.
Figure E.1: Optimum COP and corresponding SCD and UA-values with several mixtures and cycles for example 1.1 ($T_{w1} = 10\, ^\circ C$, $T_{w2} = 15\, ^\circ C$, $T_{w3} = 12\, ^\circ C$).
Figure E.2: Optimum COP and corresponding SCD and UA-values with several mixtures and cycles for example 1.2 ($T_{w4} = 46{^{\circ}}C$, $T_{w1} = 65{^{\circ}}C$, $T_{w2} = 49{^{\circ}}C$).
Figure E.3: Optimum COP and corresponding SCD and UA-values with several mixtures and cycles for example 1.3 ($T_{u4} = 15 \, ^{\circ}\text{C}$, $T_{u1} = 85 \, ^{\circ}\text{C}$, $T_{w2} = 25 \, ^{\circ}\text{C}$).
Figure E.4: Optimum COP and corresponding SCD and UA-values with several mixtures and cycles for example 2.1 ($T_{w4} = 60$ °C, $T_{w5} = 70$ °C, $T_{w2} = 55$ °C).
Figure E.5: Optimum COP and corresponding SCD and UA-values with several mixtures and cycles for example 2.2 ($T_{w4} = 70\,^\circ C$, $T_{w3} = 90\,^\circ C$, $T_{w2} = 60\,^\circ C$).
Figure E.6: Optimum COP and corresponding SCD and UA-values with several mixtures and cycles for example 2.3 (T_{in1} = 100 °C, T_{in2} = 140 °C, T_{in3} = 80 °C).
Figure E.7: Optimum COP and corresponding SCD and UA-values with several mixtures and cycles for example 3.1 ($T_{w4} = 52 \, ^\circ C$, $T_{w3} = 60 \, ^\circ C$, $T_{w2} = 31 \, ^\circ C$).
Figure E.8: Optimum COP and corresponding SCD and UA-values with several mixtures and cycles for example 3.2 (T_w2 = 110 °C, T_w3 = 130 °C, T_w4 = 70 °C).
Figure E.9: Optimum COP and corresponding SCD and UA-values with several mixtures and cycles for example 3.3 ($T_{w,i} = 100$ °C, $T_{w,l} = 140$ °C, $T_{s,2} = 50$ °C).
Appendix F

Lay-out of the test-plant
Figure F.1: Lay-out of the test-plant at the NH$_3$/H$_2$O side.
Figure F.2: Lay-out of the test-plant at the water side.
Appendix G

Results of the measurements
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<th>Separator outlet</th>
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Table G.1: Compressor measurements and calculations for Series 2 (*: calculated value;)

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<td>$v_{s}$ m$^3$/m$^3$</td>
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<td>$dev_{s}$ %</td>
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Dev: % of liquid less than or (K) temperature difference with the CLMF model.

Appendix G - 277
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Note: Calculated values.
### Discharge side

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<th>T&lt;sub&gt;r&lt;/sub&gt; [°C]</th>
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<th>m&lt;sub&gt;g&lt;/sub&gt; [kg/s]</th>
<th>P&lt;sub&gt;3&lt;/sub&gt; [bar]</th>
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### Compressor

- W<sub>c</sub> [kW]
- Q<sub>c</sub> [W]
- W<sub>c</sub> [W]
- W<sub>c</sub> [kW]
- W<sub>c</sub> [W]
- W<sub>c</sub> [W]
- SCF [m³/h]
- T<sub>c</sub> [°C]
- P<sub>c</sub> [bar]

### Dev

- Dev: % of liquid less than or (K) temperature difference with the CLMF model.

Appendix G - 279
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Appendix G - 287
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Table G.8: Desorber measurements and calculations for Series 3 (°: calculated value).
<p>| ( P_{in} ) bar | ( T_{in} ) °C | ( T_{out} ) °C | ( \eta_{in} )% | ( \Delta T_{in} ) | ( \Delta T_{out} ) | ( \eta_{ex} )% | ( \dot{Q}<em>{in} ) kW | ( \dot{m}</em>{in} ) kWK | ( \alpha ) kJ/K | ( \beta ) mW/K | ( \Delta T_{in} ) K | ( \Delta T_{out} ) K | ( \eta_{ex} )% | ( \dot{Q}<em>{in} ) kW | ( \dot{m}</em>{in} ) kWK | ( \Delta T_{in} ) K | ( \Delta T_{out} ) K | ( \eta_{ex} )% | ( \dot{Q}<em>{in} ) kW | ( \dot{m}</em>{in} ) kWK |
| 0.61 | 41.7 | 40.1 | 100.00 | 5.73 | 49.9 | 79.01 | 0.1 | 2.4 | 4.3 | 22.2 | 0.2 | 100 | 0.27 | 4.6 | 0.179 |
| 0.36 | 41.9 | 40.1 | 100.00 | 5.41 | 49.9 | 78.79 | 0.2 | 4.3 | 5.5 | 43.3 | 0.2 | 100 | 0.21 | 6.9 | 0.180 |
| 0.41 | 40.9 | 40.1 | 100.00 | 5.22 | 49.4 | 77.89 | 0.2 | 1.7 | 4.0 | 12.2 | 0.2 | 150 | 0.27 | 4.5 | 0.183 |
| 0.39 | 40.4 | 40.1 | 100.00 | 5.21 | 49.2 | 77.22 | 0.1 | 1.7 | 3.7 | 6.8 | 0.3 | 150 | 0.28 | 4.8 | 0.186 |
| 0.59 | 41.0 | 40.0 | 100.00 | 5.25 | 49.5 | 78.31 | 0.2 | 2.7 | 4.6 | 18.2 | 0.2 | 100 | 0.24 | 4.1 | 0.197 |
| 0.61 | 41.8 | 40.1 | 100.00 | 5.43 | 49.4 | 77.63 | 0.4 | 2.8 | 4.8 | 0.4 | 0.2 | 100 | 0.22 | 3.3 | 0.199 |
| 0.74 | 43.6 | 40.1 | 100.00 | 5.44 | 42.8 | 66.79 | 0.8 | 2.8 | 5.0 | 18.2 | 0.2 | 100 | 0.19 | 3.2 | 0.202 |
| 0.84 | 44.9 | 40.0 | 100.00 | 5.33 | 44.0 | 10.30 | 1.0 | 3.2 | 5.7 | 8.1 | 0.2 | 100 | 0.15 | 2.6 | 0.195 |
| 0.61 | 41.3 | 40.1 | 100.00 | 5.22 | 40.1 | 81.97 | 0.1 | 2.4 | 4.1 | 0.8 | 0.3 | 100 | 0.12 | 5.4 | 0.208 |
| 0.54 | 41.1 | 40.9 | 100.00 | 5.16 | 40.1 | 81.63 | 0.2 | 2.3 | 4.6 | 1.1 | 0.2 | 100 | 0.30 | 5.1 | 0.210 |
| 0.29 | 39.7 | 39.7 | 100.00 | 4.96 | 37.91 | 82.74 | 0.2 | 2.7 | 5.0 | 7.2 | 0.1 | 50 | 0.33 | 5.6 | 0.213 |
| 0.64 | 41.8 | 40.9 | 100.00 | 5.29 | 41.2 | 39.73 | 0.4 | 1.7 | 5.0 | 0.2 | 0.2 | 150 | 0.30 | 5.0 | 0.216 |
| 0.64 | 42.2 | 42.2 | 100.00 | 4.88 | 41.8 | 32.30 | 0.3 | 1.5 | 4.8 | 0.1 | 0.1 | 150 | 0.15 | 2.6 | 0.219 |
| 0.07 | 42.3 | 42.2 | 100.00 | 4.78 | 41.5 | 37.71 | 0.0 | 3.2 | 5.0 | 0.2 | 0.2 | 150 | 0.12 | 2.1 | 0.234 |
| 0.52 | 41.5 | 41.0 | 100.00 | 4.74 | 40.7 | 33.92 | 0.1 | 2.9 | 5.4 | 0.1 | 0.2 | 150 | 0.16 | 2.6 | 0.235 |
| 0.79 | 41.9 | 41.5 | 100.00 | 4.75 | 41.1 | 32.51 | 0.1 | 3.1 | 5.7 | 0.1 | 0.2 | 150 | 0.14 | 2.3 | 0.237 |
| 0.24 | 41.1 | 40.2 | 100.00 | 4.69 | 40.3 | 75.59 | 0.2 | 2.8 | 5.2 | 1.2 | 0.2 | 150 | 0.16 | 2.6 | 0.250 |
| 0.03 | 40.9 | 40.4 | 100.00 | 4.73 | 40.1 | 75.99 | 0.3 | 2.4 | 4.7 | 3.4 | 0.2 | 150 | 0.20 | 3.5 | 0.243 |
| 0.76 | 42.3 | 40.3 | 100.00 | 4.92 | 41.5 | 24.66 | 0.4 | 3.1 | 5.5 | -1.3 | 0.2 | 150 | 0.15 | 2.6 | 0.246 |
| 0.50 | 41.6 | 40.2 | 100.00 | 4.69 | 40.6 | 74.26 | 0.0 | 3.0 | 5.5 | 0.7 | 0.2 | 150 | 0.15 | 2.5 | 0.247 |
| 0.66 | 42.0 | 40.8 | 100.00 | 4.84 | 41.0 | 74.08 | 0.1 | 3.0 | 5.5 | -1.2 | 0.2 | 150 | 0.15 | 2.5 | 0.249 |
| 0.35 | 40.9 | 40.9 | 100.00 | 4.56 | 40.2 | 73.63 | 0.0 | 2.8 | 5.4 | -0.2 | 0.2 | 150 | 0.16 | 2.6 | 0.252 |
| 0.28 | 40.6 | 41.2 | 99.33 | 4.48 | 49.8 | 33.53 | 0.5 | 1.4 | 5.8 | -1.8 | 0.2 | 100 | 0.15 | 2.5 | 0.255 |
| 0.52 | 43.3 | 41.0 | 100.00 | 4.72 | 40.4 | 71.02 | 0.1 | 3.0 | 5.4 | 0.2 | 0.2 | 150 | 0.16 | 2.6 | 0.256 |
| 0.19 | 41.4 | 41.5 | 100.00 | 5.22 | 42.4 | 71.86 | 0.0 | 1.3 | 5.6 | 1.2 | 0.2 | 150 | 0.14 | 2.3 | 0.258 |
| 0.98 | 42.7 | 41.7 | 100.00 | 5.96 | 41.8 | 73.13 | 0.3 | 1.5 | 5.7 | -1.0 | 0.2 | 150 | 0.14 | 2.4 | 0.261 |
| 0.55 | 41.6 | 41.0 | 100.00 | 4.73 | 40.6 | 34.35 | 0.0 | 3.0 | 5.4 | 0.5 | 0.2 | 150 | 0.16 | 2.6 | 0.262 |
| 0.54 | 40.8 | 40.9 | 100.00 | 4.73 | 41.0 | 31.05 | 0.0 | 2.7 | 5.3 | 2.0 | 0.2 | 150 | 0.16 | 2.7 | 0.264 |</p>
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**Table G.9:** Temperature profiles in the desorber and in the internal heat exchanger for

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**Table B.10:** Temperature profiles in the desorber and in the internal heat exchanger for

294 - Appendix G
Samenvatting

Dit proefschrift behandelt de thermodynamische analyse en het ontwerp van compressie-resorptie warmtepomp cycli. Compressie-resorptie warmtepompen zijn compressiesystemen die met een niet-azeotropisch mengsel werken. De verdamping in de desorber is onvolledig, zo dat of droge compressie (oplossingskringloop) of natte compressie mogelijk is. Het voordeel van deze cycli is een beter rendement dan met conventionele zuivere koudmedium cycli, vanwege de betere aanpassing van het temperatuurverloop van de warmtebron en de warmteput aan die van het mengsel. Door het gebruik van een mengsel is het ook mogelijk hogere temperaturen te bereiken op lagere drukniveaus, en capaciteitsregeling toe te passen door controle van de concentratie van het mengsel.

In het eerste deel van dit proefschrift wordt een thermodynamische analyse van compressie-resorptie cycli en van natte compressie gemaakt. Voor zuivere koudmedia worden natte en droge compressiesystemen theoretisch beschouwd. Voor mengsels wordt het oplossingskringloopsysteem theoretisch bestudeerd. De natte compressie systemen zijn zowel theoretisch als experimenteel onderzocht.

Uit de studie naar de effecten van natte compressie op verschillende interne warmtepomp cycli kan geconcludeerd worden dat voor zuivere koudmedia die een verzadigde damplijn met een positieve helling in het T-s diagram hebben, zoals bijvoorbeeld R123, natte compressie altijd nadelig is wat de COP betreft. Voor zuivere koudmedia die een verzadigde damplijn met een negatieve helling hebben, is het met natte compressie alleen mogelijk een geringe COP toename te bereiken. Water, waarvoor de COP toename hoger kan zijn, is een uitzondering. Dit neemt niet weg dat natte compressie toch zeer interessant kan zijn voor hoge temperatuur-warmtepompen, omdat het de oververhitting van de damp beperkt en dus de risico's van compressorstoringen en chemische decompositie van het koudmedium en de olie beperkt. Met zeeotropische mengsels is het zeer belangrijk dat de compressor een verzadigde of twee-fasen fluidum kan comprimeren, wil men gebruik maken van het gehele potentieel van deze mengsels om de irreversibiliteiten die zich voordoen tijdens de warmtewisseling met de warmtebron en de warmteput te beperken. De thermodynamische studie van de effecten van gemengd en gescheiden compressie van vloeistof en damp toont aan dat geen van beide wijzen van compressie absoluut de beste is, zodat simulatie van cycli altijd noodzakelijk is om voor iedere toepassing vast te stellen of natte compressie dan wel droge compressie (oplossingskringloop) te prefereren is.

De temperatuur-enthalpie diagrammen, gebaseerd op bekende thermodynamische eigenschappen van niet-azeotropische mengsels, worden gebruikt om de cycli die gebruik maken van deze mengsels te analyseren. Uit de niet-lineariteit van de temperatuurprofielen in de resorber en in de desorber kan geconcludeerd worden, dat een vergelijkende studie van verschillende cycli niet gemaakt kan worden door eenvoudig het interne gedrag van de cyclus te bestuderen. Dit omdat kneeppunten aanwezig kunnen zijn op een willekeurige plaats in de resorber of in de desorber, met als consequentie dat de gewenste externe condities niet bereikt kunnen worden. In het meest simpele simulatiemodel moeten de temperatuurprofielen berekend worden, om te voorkomen dat het voorgeschreven minimale temperatuurverschil wordt onderschreven. De tweede conclusie is dat het gebruik van de logarithmische gemiddelde temperatuur en van het logarithmische gemiddelde temperatuur-
verschil better vermeden kan worden, tenzij een mengsel met een lineair temperatuurprofiel gebruikt wordt, het temperatuurverloop klein genoeg is om gelinealiseerd te worden, of het temperatuurverschil tussen de interne en externe media heel groot is. Met NH₃/H₂O kan het gebruik van het logaritmische gemiddelde temperatuurverschil leiden tot een overschatting van de gemiddelde temperatuur van meer dan 50%. In alle gevallen wordt het gebruik van het isentropisch gemiddelde temperatuurverschil aanbevolen om de temperatuurniveaus waarop de warmtepomp moet werken te berekenen. Het is echter wel zo dat het gebruik van de logaritmische gemiddelde temperatuur om COP’s te berekenen, een fout veroorzaakt die onder 5% blijft.

Benadrukt moet worden dat de definitie van een ideale cyclus, waarop reëlle cycli beoordeeld kunnen worden gebaseerd moet zijn op de externe condities en niet op geidealiseerde eigenschappen van het mengsel. De verwarring tussen interne en externe cycli heeft geen consequenties voor ideale cycli met een constante temperatuurbron en -put, wanneer een zuiver koudemedium gebruikt wordt, omdat beide interne en externe cycli zich als Carnot cycli gedragen. Wanneer de warmtebron en de warmteput een temperatuurverloop vertonen, dan is de ideale externe cyclus die perfect past bij de externe condities, de Lorenz cyclus. Er is geen interne cyclus die perfect bij de Lorenz cyclus past. Voor een gegeven toepassing, is het niet wenselijk de vergelijking tussen de COP’s van een zuivere koudemediumcyclus en van een mengselcyclus te maken met gelijke interne temperatuur niveaus. Een oppervlakteanalyse in het T-s diagram laat zien dat geen cyclus in principe de beste is en dat de relatieve COP’s van zuiver koudemedium- en mengselcyclus sterk gerelateerd zijn aan de externe condities. Niettemin wordt het duidelijk dat hoe kleiner de verhouding tussen de temperatuursprong van de cyclus (het verschil tussen de hoogste temperaturen van de bron en van de put) en het temperatuurverloop van de warmteput, hoe beter de prestatie van de mengselcyclus in verhouding tot die van de zuivere koudemediumcyclus. Dit maakt compressie-resorsatie cycli bijzonder geschikt voor industriële toepassingen. Het gebruik van interne warmtewisseling tussen het koude einde van de resorber en het warme einde van de desorber hoeft in principe niet altijd voordeelig te zijn, maar blijkt in het algemeen toch een positief effect te hebben op de COP. Het gebruik van absorptieve-evaporatieve warmtevisseling vergelijkbaar met die van de GAX cyclus wordt niet aanbevolen, omdat het de verwarmingscapaciteit en de COP reduceert. Rectificatie moet ook vermeden worden.

Voor NH₃/H₂O zijn negen toepassingen gekozen voor een parametrische studie die een breed spectrum van de mogelijke toepassingen van warmtepompen omvat. Alle resultaten betreffende deze toepassingen zijn te vinden in dit proefschrift. Omdat een groot aantal simulaties nodig is om de cycli te optimaliseren, is er gekozen voor het eenvoudigste black-box model dat compatibel is met de voorafgaande thermodynamische analyse. Omdat geen veronderstellingen zijn gedaan over de warmteoverdrachtsoppervlakten of over de warmteoverdrachtscoëfficiënt, is het mogelijk de optimale verdeling van de UA- waarden tussen de resorber en de desorber te berekenen. Voor iedere toepassing worden de prestaties van de natte compressiecyclus, de oplossingskringloop-cyclus en de dampcompressiecyclus met zuivere koudemedium vergeleken voor verschillende mengsels en beoordeeld ten opzichte van de Lorenz cyclus; de COP en de specifieke compressor- verplaatsing (=SCD: volume flow-rate aan de compressor zuigzijde per kW nuttige warmte in de resorber). Met een constante minimale temperatuur benadering en een constant isentropisch rendement, blijkt de COP zeer gevoelig te zijn voor de kwaliteit van de aanpassing van het temperatuurverloop tussen de externe en interne media en dus voor de
totale concentratie. De maximale COP wordt bereikt voor de totale concentratie waarvoor de som van het gemiddelde temperatuurverschil in de resorber en in de desorber minimaal is. Ondanks het feit dat het niet mogelijk is de hoogste COP te bereiken samen met de laagste specifieke compressoroverplaatsing, liggen de SCD-waarden corresponderend met de hoogste COP niet zo ver van de laagste SCD-waarden.

Een entropieanalyse van de natte compressie cyclus wordt ook gemaakt. Die toont aan dat voor de optimale totale concentratie, de belangrijkste verliezen zich in de compressor voordoen, waardoor de compressor de eerste te optimaliseren component moet zijn. Er wordt aangetoond dat een natte compressor met een isentropisch rendement van tenminste 0.75 gebruikt moet worden om de verliezen tot een aanvaardbaar niveau te beperken.

Hoewel de resultaten afhankelijk blijven van de toepassingen, kan een algemeen beeld geschetst worden wat betreft het relatieve rendement van de verschillende cycli. Er wordt aangetoond dat, ook voor kleine warmtebron- en warmteputtemperatuurverloopen, de compressie-resorptie cycli met NH\textsubscript{3}/H\textsubscript{2}O beter zijn dan zuiver koudmedium cycli met 10 tot 30 %, mits de verhouding \( \Delta T_{\text{verloop}}/\Delta T_{\text{verloop,put}} \) kleiner is dan 2. Voor NH\textsubscript{3}/H\textsubscript{2}O geldt deze beperking niet meer voor een groot warmteputtemperatuurverloop (≥30 °C). Als directe consequentie van de betere temperatuurverloop aanpassing in de compressie-resorptie cyclus is de optimale gemiddelde UA-waarde (warmteoverdrachtscoefficient maal warmteoverdracht oppervlakte) in de desorber en in de resorber veel groter (tot 4 keer) dan voor een zuiver koudmediumcyclus. Dit legt de nadruk op de noodzaak van het ontwerpen van hoog rendement compacte warmtewisselaars. Een vergelijking tussen de natte compressiecyclus en de oplossingskringloop cyclus laat zien dat natte compressie met NH\textsubscript{3}/H\textsubscript{2}O altijd tot hogere COP's (met 2 tot 13 %) leidt.

De prestaties van verschillende binaire en ternaire mengsels van fluorkoolstoffen en koolwaterstoffen worden bestudeerd. Een analyse van het T-h diagram laat zien dat voor mengsels van dezelfde chemische groep geldt hoe hoger het verschil tussen de kritische temperaturen van de componenten van het mengsel, hoe groter de niet-lineariteit van de isobaren in het T-h diagram. Dit betekent dat het moeilijk wordt een mengsel voor hoog temperatuurverloop toepassingen te vinden dat goed bij het externe verloop past. Van dezelfde parametrische studie als voor NH\textsubscript{3}/H\textsubscript{2}O kan geconcludeerd worden dat het gedrag van de mengsels het best geschat kan worden door het gebruik van twee parameters \( \Delta T_{\text{verloop,meng}} \) en \( \Delta T_{\text{verloop,meng}}/\Delta h_{\text{verd}} \) waar \( \Delta T_{\text{verloop,meng}} \) en \( \Delta h_{\text{verd}} \) het temperatuurverschil en het enthalpieverschil tussen de verzadigde vloeistof- en damplijnen, voor een druk van 1 bar en een totale concentratie van 0.5 kg/kg. \( \Delta T_{\text{verloop,meng}} \) moet goed passen bij het temperatuurverloop van de warmteput, of, op zijn minst, geen beperkende factor zijn. \( \Delta T_{\text{verloop,meng}}/\Delta h_{\text{verd}} \) moet zo klein mogelijk zijn. Overeenkomstig zal propaan/n-butanaan in het algemeen goed presteren in toepassingen met een kleine warmteputtemperatuurverloop (≤ 15 K) voor een gemiddelde warmteputtemperatuur tot aan 90 °C. Propaan/n-pentane zal redelijk presteren in alle toepassingen voor een gemiddelde warmteputtemperatuur tot 110 °C, behalve voor toepassingen met een groot warmteputtemperatuurverloop (≥ 44 K). R152a/R123 en R134a/R123 presteren redelijk voor toepassingen met een matig warmteputtemperatuurverloop (≤25 K) voor een gemiddelde warmteputtemperatuur tot 110 °C. R125/R123 en R23/R123 zullen in het algemeen niet goed presteren, behalve in sommige gevallen bij toepassingen met een zeer groot warmteputtemperatuurverloop (≈ 80 K), waar R23/R123 wel goed presteert. NH\textsubscript{3}/H\textsubscript{2}O presteert heel goed in alle toepassingen, tot ongeveer 150 °C. Hoe dan ook kan deze classificatie beter gebruikt worden om mengsels
te elimineren dan om er een te kiezen, omdat vanwege de complexiteit van de optimalisatieprocedure, de selectie van een efficiënt mengsel voor een gegeven toepassing het gebruik van simulaties vraagt. Uit de case-studie kan geconcludeerd worden, dat het binaire mengsel NH$_3$/H$_2$O en de ternaire mengsels propaan/n-butaan/n-pentaan en R125/R152a/R123 het minst gevoelig zijn voor de externe condities. Voor NH$_3$/H$_2$O is de COP nooit lager dan 12 % van de maximale COP. De resultaten betreffende de SCD zijn meer verspreid, maar NH$_3$/H$_2$O presteert nooit echt slecht. Het grootste deel van NH$_3$/H$_2$O is de hoge UA-waarde, in het bijzonder voor grote temperatuurverloop toepassingen. Er wordt bevestigd dat voor kleine warmtepump temperatuurverloop toepassingen, de dampcompressie cyclus met zuiver koudmedium het voordeligst kan zijn, vooral voor grote $\Delta T_{\text{prop}}/\Delta T_{\text{verloop,p}}$ verhoudingen. Niettemin zijn zijn SCD en zijn persdruk vaak veel hoger dan die van de andere cycli. In het algemeen blijkt de natte compressie cyclus de beste cyclus te zijn, met een COP verbetering ten opzichte van de oplossingskringloop cyclus, die 50 % kan bedragen. De gemiddelde COP verbetering vanwege natte compressie is, over de negen voorbeelden en negen bestudeerde mengsels, 14 %. Overigens kan bij sommige combinaties externe condities/mengsel de COP van de oplossingskringloop cyclus beter zijn dan die van de natte compressie cyclus.

In het tweede deel van dit proefschrift wordt het ontwerp van een natte compressie-resorptie warmtepomp test-opstelling behandeld, alsmede de analyse van de metingen. De opstelling is ontworpen om een put te verwarmen van 38 °C tot 68 °C, met een capaciteit van 32 kW, door middel van een bron van 40 °C. De technologische opties zijn gekozen overeenkomstig de huidige stand van de techniek van de benodigde componenten, met de beperking dat die commercieel beschikbaar moesten zijn. De resorber is van het plate-finto type, met versprongen corrugaties. De oplossing en de damp stromen in neerwaartse meestroom en het koelwater in tegenstroom daarmee. De desorber is van dezelfde type als de resorber, en verticaal neerwaartse meestroom van de twee-fasen mengsel is gekozen om de drukverliezen zo veel mogelijk te beperken. Het water stroomt in tegenstroom. Roterende compressoren zijn minder gevoelig voor vloeistofinjectie dan zuiger-compressoren, en van de roterende compressoren, vormen schroefcompressoren de beste oplossing omdat hun capaciteit, vermogen en drukverhouding geschikt zijn voor een groot scala aan industriële toepassingen. Echter het bleef niet mogelijk een schroefcompressor te vinden, geschikt voor NH$_3$/H$_2$O, natte compressie en de kleine capaciteit van de opstelling. Uiteindelijk, en ondanks zijn zeer laag rendement is een vloeistofring-compressor gebruikt om de andere componenten van de opstelling te kunnen testen.

Vanwege het gebruik van de vloeistofringcompressor konden de ontwerpwadaart niet bereikt worden. De warmtebron kon alleen tot 53 °C verwarmd worden, met een capaciteit van 9 tot 20 kW. De vloeistof in de perszijde van de vloeistofring compressor is onderkoeld en er werden zeer lage isentropische rendementen bereikt, met als consequentie dat COP’s lager dan 1 werden gevonden. Niettemin kon de externe COP gebaseerd op de verwarming- en koelcapaciteit aan de waterzijde een waarde van 5 bereiken. De analyse van de metingen aan de resorber liet zien dat de vloeistof aan de ingang veel meer onderkoeld was dan verwacht. De totale warmteoverdrachtscoëfficiënt in de resorber varieerde tussen 200 en 1200 W/m²K, en was zeer gevoelig voor de dampnelheid, die hoog gehouden moest worden. De desorber had een zeer matige warmteoverdrachtscoëfficiënt van ongeveer 100-150 W/m²K, waarschijnlijk omdat er miststroming voorkwam, vanwege de hoge damp volumeflow rate bij de ingang en het slechte distributie-systeem. In zowel de resorber als de desorber werden gemiddelde temperatuur-
verschillen van minder dan 8 K waargenomen met minimale temperatuurverschillen tot 1 K. Redelijke overeenstemming werd gevonden tussen de metingen en de resultaten van het parametrische model.

Tot slot worden aanbevelingen gedaan voor verder onderzoek. De warmtepomp moet verbeterd worden, inclusief het gebruik van een betere compressor met een lagere injectie-volumeflowrate. Fundamenteel onderzoek naar het ontwerp van natte compressoren moet geïnitieerd worden en onderzoek naar het ontwerp van hoog rendement compacte warmtewisselaars voor mengselcondensatie en -verdamping moet doorgezet worden.
Laure Itard was born in 1964 in Le Mans, France. She received her primary and secondary education at the public schools of her hometown, Château-du-Loir. Being one of the first girls attending the boys school she feels that this has probably had a permanent effect on her subconscious. She enjoyed a happy, quiet and studious life in her hometown, where she successfully completed her secondary education in 1982 (Baccalauréat C, Mathematics and Physics). From 1982 to 1987, she studied Physics at the university of Le Mans, working part time as a teacher in several secondary schools. After obtaining her MSc degree in 1987, she specialized in Energetics at the university of Reims, obtaining a further degree (DESS) in 1988. She then worked for almost a year at the Research Institute of Electricité de France on infra-red ovens. In 1989 she moved to the Netherlands to be with her future husband. She was appointed as a research assistant (AIO) at the Laboratory of Refrigerating Engineering and Indoor Climate Technology of the TU Delft, where she worked on the present thesis. During this period she started her family, her sons being born in 1991 and 1993. From June 1995 to December 1996, although her thesis was still incomplete, she was given the opportunity to make a preliminary study on adsorption heat pumps. She now works one day a week at the Delft Interfaculty Research Centre "The Ecological City" (DIOC DGO) and three days a week at the Department Study and Development of Deems Consulting Engineers.
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