POLITECNICO DI TORINO

MASTER PROGRAM
ENERGY AND NUCLEAR ENGINEERING

MASTER DEGREE THESIS

MODELING AND DESIGN OF A TWO-STAGE NH3/H2O ABSORPTION CHILLER

Advisor:
LANZINI Andrea

Supervisor at CEA Grenoble:
PHAN Hai Trieu

Supervisor at the Ecole Centrale de Lyon:
CREYSSELS Mathieu

Candidate:
ASTE Fabio

Academic Year 2019/2020

Acknowledgments

This work has been realized within the Solar and Thermodynamic Systems Laboratory (L2ST) inside the Thermal, Biomass and Hydrogen Department (DTBH) of CEA - Alternative Energies and Atomic Energy Commission. To this last I want address my sincere thanks, for the unique opportunity I received and for the personal and professional growth I experienced.

Right after, I need to thanks the institutions that made possible this mobility, the Ecole Centrale de Lyon, the Politecnico di Torino and the Erasmus+ EU Program: I believe that my formation as person, as future engineer and, above all, as European citizen would never have been as rich as it is now after this adventure abroad. I had the opportunity to meet a different culture of learning, working and living, and each one of the people I met during this mobility left something to me: I want to thank everyone of you for sharing your experience.

In particular, I would express my heartfelt gratitude to my tutors, Hai Trieu Phan for CEA, Matthieu Creyssels for the Ecole Centrale de Lyon and Andrea Lanzini for the Politecnico di Torino. I have never felt abandoned to my own, but followed by distance in case of: each problem or doubt has always been solved with your help, especially in this unhappy period of health crisis.

My work would not have been possible without the support of the absorption team of the L2ST: the precious advice of Hai Trieu has been determinant for the system development and for understanding the workplace, while Hélène patiently guided me during the terminal consultation and sizing phase. Thank you for being so willing and kind.

In addition, I need to address some words to the whole laboratory Puma 3. Since my arrival I found an incredible ambiance and I got the opportunity to know each one of you and integrate in this little lab: my experience and my work would not have been so great without all of you. I want to particularly thanks Valdemar and Noe, my office colleagues, for the technical and emotional support: all the fun moments we had together made easier approaching this new workplace. Finally, a special thank to Simone, it might be taken for granted but sometimes just a few words in your mother language are enough to feel at home again.

During this long journey, from my first class to this experience abroad, I have never been alone: many friends accompanied me, in Italy as well as in France, and each one of them gave me something, a lesson, a smile or the right word when I was in need. Sharing with you this years made them unique and precious, full of unforgettable moments.

A special thought goes to my lifelong friends, in the TO3 and the neighborhood: leaving all of you for such a long period has not been simple. Nevertheless, you kept supporting me and even the situation changed, our link, our friendship did not: thank you guys, it means a lot for me.

Last, but not least, I must gratefully thanks my family for making this happen, my mobility, my internship, my whole degree: without your support I would not have done anything, you really made the difference between failing and succeeding. It is important to know that there is always someone, near or far, ready to listen to you in times of need, to give his sincere advice and to celebrate your successes: I will never say it enough, thank you.

Résumé du rapport:

Le but de cette étude est de réaliser une machine à absorption ammoniac-eau innovante avec une architecture double effet de type GAX. L'objectif est de remplacer l'élément GAX (Generator-Absorber heat eXchanger) par des composants commerciales, en réduisant le coût et la complexité du système. Dans ce contexte une étude bibliographique des principaux systèmes à absorption a été effectuée et une attention particulière a été portée au cycle ammoniac-eau. Finalement, l'utilisation des échangeurs à plaques est retenue comme la meilleure solution, même si cela nécessite de l'ajoute des réservoir de séparation de phase.

Un modèle physique a été construit pour étudier les améliorations possibles de l'architecture, puis des simulations numériques ont été ensuite réalisées afin d'évaluer les performances. Le cycle frigorifique et la configuration en pompe à chaleur ont été également étudiés. Différentes courbes d'inversion du coefficient de Joule-Thomson pour le mélange ammoniac-eau ont été aussi tracées afin d'identifier la condition optimale pour la détente de la solution pauvre.

Les résultats montrent que les systèmes GAX peuvent être réalisés par la technologie des échangeurs à plaques et ils offrent plus de performance par rapport aux systèmes conventionnels (simple effet simple-étage). Les Coefficient de Performance (COP) du cycle frigorifique et de la pompe à chaleur ont été étudiés dans différentes conditions de fonctionnement, en variant les températures des trois sources selon les cas. Dans un premier temps, il est observé que le cycle frigorifique donne des $COP_R > 0.5$ pour une température de froid de -20°C à une température ambiante de 40°C; dans un deuxième temps, il est démontré que la pompe à chaleur peut produire des températures élevées (jusqu'à 125°C en sortie) avec des performances appréciables (COP_{HP}=1.6 à 2); finalement, une comparaison entre les systèmes simple-étage et double-étage a été réalisée. Une faible variation des performances des systèmes double étage est observée: leur plage de fonctionnement est bien plus large que celle des systèmes simple-étage et ce dernier constat est valable aussi bien pour les cycles frigorifiques que pour les pompes à chaleur.

Mots-clés libres: Ammoniac-eau ; NH3/H2O ; GAX ; Cycle frigorifique à absorption ; Pompe à chaleur à absorption ; Échangeur à plaques ; Coefficient de Joule-Thomson ; Simulation numérique.

Abstract:

In this work an innovative ammonia-water double-effect GAX absorption system is investigated. The objective is to replace the complex Generator-Absorber heat eXchanger (GAX) element by commercially-diffused components, decreasing cost and system complexity. A literature review of the most important absorption systems is done: a focus on ammonia-water cycle is conducted as well. As a result, plate heat exchangers are considered the best solution, even if this choice comports the addition of some separation tanks.

A physical model is built to study the possible new architectures and it is detailed in the discussion. Numerical simulations are conducted in order to evaluate the cycle performances for both the chiller and heat pump configurations. Also, the inversion curves of the Joule-Thomson coefficient for ammonia-water mixtures are traced to individuate the best points for the poor solution expansion.

Results show that plate exchanger-based GAX ammonia-water systems are possible and performing with reference to single-stage cycles. The Coefficient of Performance (COP) is investigated in different operational conditions for both chiller and heat pump, varying each time the Ambient Temperature (T_a), the Cooling Temperature (T_e) or the Generation Temperature (T_g) depending on the cases.

The chiller was proved to reach a refrigeration $COP_R > 0.5$ for a T_e=-20°C at T_a=40°C, while the heat pump reached high temperatures (up to 125°C at the hot output) with appreciable performances (heat pump COP_{HP}=1.6 to 2). An increased stability of GAX system performances and a wider operational range with reference to single-stage ones is observed in both chiller and heat pump configurations.

Keywords: Ammonia–water; NH3/H2O; GAX; Absorption refrigeration; Absorption heat pump; Plate heat exchanger; Joule-Thomson coefficient; Numerical simulation.

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Introduction

This internship is part of a wider economic and environmental context where energy consumption, greenhouse gas emissions and waste heat valorisation are strongly interconnected. As reducing the energy need is one of the current global goals, research is really active in this sense: therefore, the development of systems that can enhance low-quality heat fluxes for energy generation, heating and cooling is a growing interest of many energy company and institutions.

CEA, acronym for "Commissariatà l'Energie Atomique et aux Energies Alternatives" (Alternative Energies and Atomic Energy Commission) is one of them: it is a public scientific, technical and industrial research organization and its four main operation areas include low carbon energies (nuclear and renewable energies), defence and security, technological research for industry and fundamental research in physical and life sciences.

The study of waste heat enhancing systems is comprised in the low carbon energies domains, in the view of optimizing the industrial and civil sectors consumption and emission. In fact, the subject of this internship concerns the modeling and design of a two-stage ammonia-water absorption system, a particular thermodynamic machine able to process waste heat to generate different outputs, cooling, intermediate-temperature heating or high-temperature heating. The development of such a system is planned to be carried out during a 5 month period at CEA Grenoble inside the Thermal, Biomass and Hydrogen Department (DTBH).

In this work a first analysis of the technological, environmental and economic context is done to better understand constraints, opportunities and the general interest for this kind of solution. Then, an accurate literature review on the most diffused refrigeration systems is conducted: knowing the functioning of the currently commercialized technologies is essential to individuate the improvement directions. Also, insights on the existing absorption systems are provided, allowing to acquire the necessary basic knowledge for the further development of new architectures. Finally, physical and numerical modeling of the new two-stage ammonia-water absorption cycle is performed, trying to attend the following results:

- prove that alternative GAX systems not equipped with distillation columns are possible and valuable in terms of performance with reference to simple-stage systems;
- reach a cooling Coefficient of Performance $COP_R > 0.5$ for a $T_e = -20°C$ at $T_{amb} = 40°C$;
- reach a heat pump $COP_{HP} > 1.5$ for a $T_{out} = 70°C$ at $T_{amb} = 35°C$;
- size the elements of the systems, especially the Generator-Absorber heat eXchanger (GAX);
- propose a 3D assembly to clarify elements dimensions and space distribution.

The hope for this work is establishing a well-defined starting point for future studies, in a perspective of development and further improvement of two-stage ammonia absorption systems.

1. Study context and objectives

1.1. Environmental and political issues

This study finds his meaning in the contemporary critical environmental situation: as the world energy need is growing at unsustainable rates, with important consequences on air pollution, greenhouse gases emissions and on the environment at global scale, measures to reduce energy waste and to improve generation are needed. Moreover, world political stability is threatened by the limited availability of the actual energy resources and the fight for the remaining reserves is more open than ever. Therefore, the growing energy consumption affects the world in two ways, strategically for the provisioning at country scale, and environmentally as regards climate change. Both of them are key aspects to world survival and cannot be separated, as they are strongly related in causes and effects.

The data in the Figure 1.1 provided by British Petroleum [1] in their annual energy report shows clearly that the magnitude of the world primary energy consumption[1] growth is considerable. In fact, this amount increases annually by 1,6% (10-years average) and struggles to stabilize, threatening to reach 600 EJ per year: Hwang et al. [3] estimate the global energy demand to increase by around 71% from 2003 to 2030, while other researchers consider even possible a doubling or tripling of the consumption as early as 2050 [4].

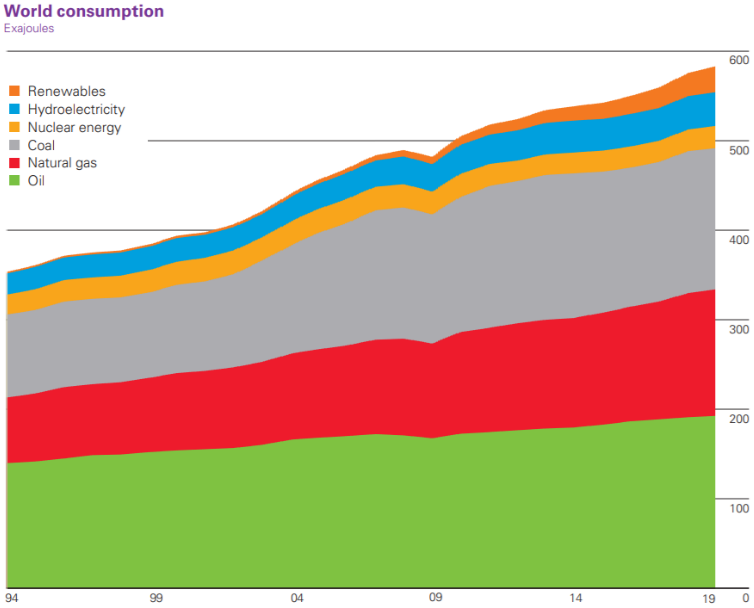

Figure 1.1.: Primary energy world consumption in the period 1994-2019. *Source: BP Statistics, 2020*

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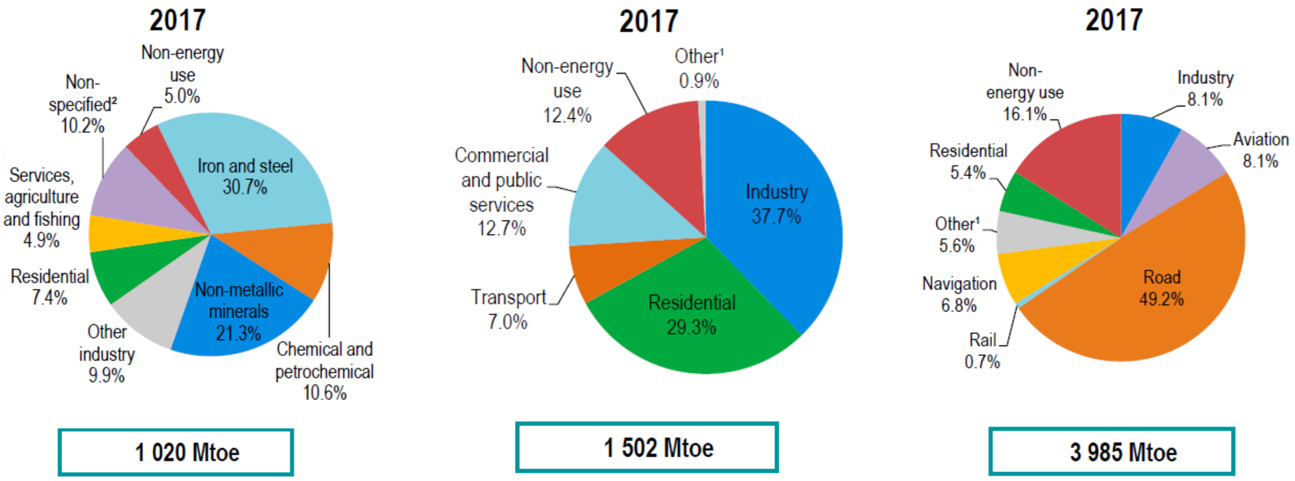
[1] Primary energy consumption refers to the direct use at the source, or supply to users without transformation, of crude energy, that is, energy not yet subjected to any conversion or transformation process. [2]

This huge amount of energy is provided generically by six different sources, but considering the absolute values of each one the accumulated fossil fuels consumption overwhelms the rest: even if this paradigm is changing and other solutions are being developed, for the moment the world is mostly relying on non-renewable energy sources [5].

One of the common points between coal, natural gas and oil is that their final exploitation occurs mainly through combustion, converting their chemical energy into an usable form: as showed in Figure 1.2 for coal and gas the industrial sector (including electricity generation) is the principal one, closely followed by the residential; instead, oil consumption is focused on vehicle propulsion purposes, both road, aviation and navigation. Thus, heat is the most present form of secondary energy in the world and usually its combustion happens at high temperatures: in this conditions its value is great as it can be converted into other kinds of energy with few transformations. However, as known from thermodynamics, the conversion can never be complete and a more or less important part of this heat is rejected to environment as a waste.



(a) World shares of coal final consumption

(b) World shares of natural gas final consumption

(c) World shares of oil final consumption

Figure 1.2.: Fossil fuels world final consumption by sector. *Source: IEA, World Energy Balance, 2019*

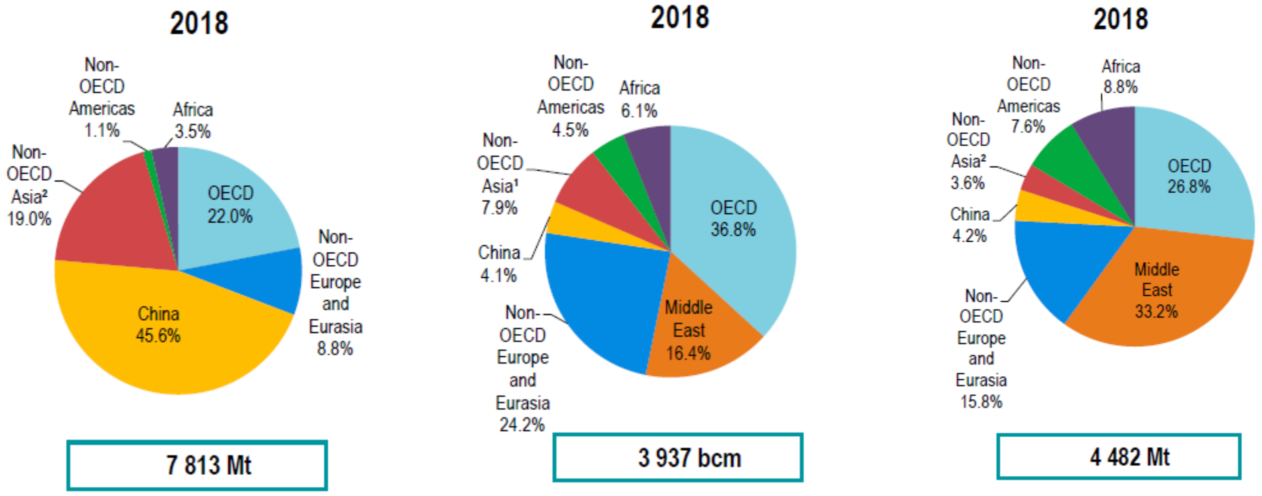
Also known as non-renewable energy sources, fossil fuels are naturally produced by different mechanisms during geological eras: as the name suggests, their quantity will not be regenerated in human timescales and so they are present on Earth in a limited quantity. Moreover, they are not homogeneously distributed and they differ in quality and extraction conditions. Nevertheless, as final consumption energies are mostly derived from them, every country needs to guarantee itself a certain amount of these non-renewable resources: if self production is not possible, the market is the only alternative.

Being well requested goods in a worldwide market makes fossil fuels a strategic opportunity for countries with reserves: for this reason, self-consumption is not absolutely the main driver of the national production.

Instead, it depends from the following factors:

- resource availability;
- technological development of the country;
- energetic needs of the country;
- economical and political interests.

If the first point is obvious, the last three are not. Firstly, even disposing of great reserves, one country might not be able to conveniently extract them and might resort to foreign enterprises reducing the gains and partially losing the direct control on them; secondly, a certain priority can be given to one or another supply chain basing on the market opportunities and the energetic needs of the country; thirdly, production and supply variation can be used as pressure instrument to influence international partners, as the two oil crisis during 70s demonstrate.



(a) Regional shares of coal production

(b) Regional shares of natural gas production

(c) Regional shares of crude oil production

Figure 1.3.: Fossil fuels global production shares. *Source: IEA, World Energy Balance, 2019*

Fossil fuels production among the world is really varied and the Figure 1.3 details the global shares for each category: the most interesting observation is that each nation or group of countries has a predilection in a certain resource, due to the factors cited above.

This unequal distribution explains the complexity of the world energy market: most of the global energy resources are concentrated in few countries that can easily regroup and set up organizations to better manage their market power, increasing it thanks to their coordination. This leads to a tricky situation where economical and political interests are strongly related: for importing countries provisioning might become not trivial to reach. Therefore, these lasts have all the interest in improving efficiency of their energy systems and to develop recuperation technologies to reduce the dependence on third party supplies; vice versa, major producers are the least interested in developing all this, due to the resources abundance onto their soils.

Moving on to the environmental discourse it is interesting to consider the impact of using coal, gas and oil as energy sources: the relation between them and the Greenhouse Gases (GHG) emissions is evident and well known, as fossil fuels require a combustion to release their chemical energy and during this process many pollutants are produced. With the actual technologies, being these three sources the dominant ones in the primary energy consumption, an increase of the global energy need means also an inevitable, more or less important, increase in GHG emissions.

Greenhouse gases are one of the main actors in the context of climate change. They consist in molecules with generally three or more atoms [6] arranged in particular structure that guarantees the fundamental physical property of a greenhouse gas: the absorption of infrared radiation via one or more of the molecule vibrational modes in the infra-red range of 6–25 μm [7]. The absorbed flux is trapped and transferred again to the surface which further warms the Earth: this ability of these gases is called the greenhouse effect [8].

Some of the most important greenhouse gases are CO_2, O_3, CH_4, N_2O, $NF3$, CF_2Cl_2 and in general all the CFCs[2], SF_6[3] and the SF_5CF_3 [7]. However, not all gases behave in the same way and to evaluate the effectiveness of a certain GHG specie many parameters might be taken into account:

- the atmosphere concentration;
- the concentration growth ratio, maily due to human activity production;
- the lifetime in atmosphere;
- the radiative efficiency of the specie.

All of these parameters are correlated to obtain a Global Warming Potential (GWP) with reference to CO_2 that conventionally has a $GWP = 1$: the higher the GWP, the higher the contribution to global warming.

Nowadays, it is proved that some changes in atmospheric composition have occurred and there is a wide agreement on the contribution that they have on climate change.
Citing the Climate Change 2014 Synthesis Report [9]:

> *"Anthropogenic greenhouse gas emissions have increased since the pre-industrial era, driven largely by economic and population growth, and are now higher than ever. This has led to atmospheric concentrations of carbon dioxide, methane and nitrous oxide that are unprecedented in at least the last 800,000 years. Their effects, together with those of other anthropogenic drivers, have been detected throughout the climate system and are extremely likely to have been the dominant cause of the observed warming since the mid-20th century."*

Moreover, the data in Figure 1.4 appears to confirm the previous statement, especially if considered together to those in Figure 1.1: the two trends are similarly shaped and positive and

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[2] Chlorofluorocarbons.

[3] Perfluorocarbons (e.g., CF_4, C_2F_6, SF_5CF_3, SF_6).

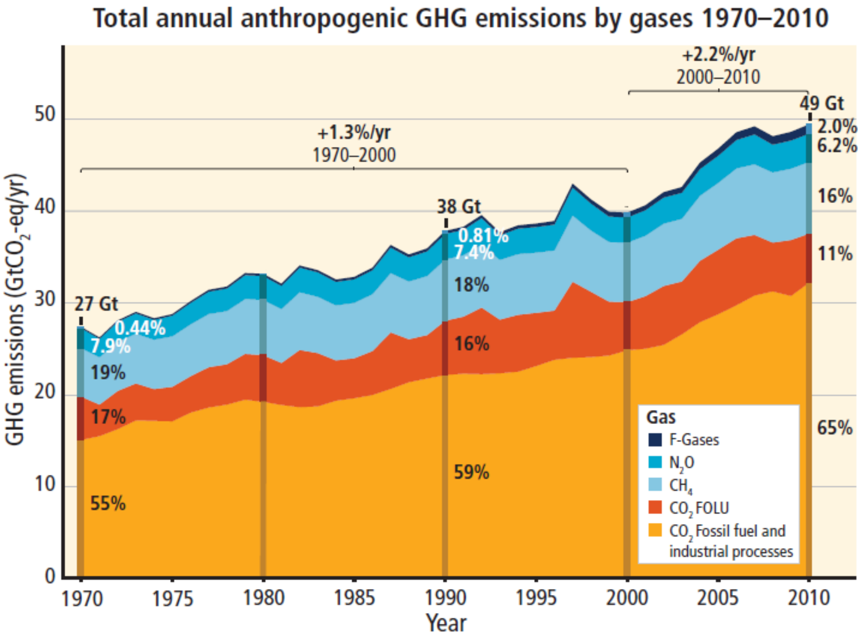

Figure 1.4.: Total annual anthropogenic greenhouse gas (GHG) emissions (gigatonne of CO2-equivalent per year, GtCO2-eq/yr) for the period 1970 to 2010 by gases: CO2 from fossil fuel combustion and industrial processes; CO2 from Forestry and Other Land Use (FOLU); methane (CH4); nitrous oxide(N2O); fluorinated gases covered under the Kyoto Protocol (F-gases). *Source: Climate Change 2014 Synthesis Report*

negative variations are coordinated. In particular, this behavior is well visible in the years 2007-2009, during the Global Financial Crisis: a deep low occurs in both of the diagrams, remarking the connection between emissions and consumption.

The bond that links these two quantities is very strong and depends from the fact that energy production and use (including vehicles fuel) represents the largest source of greenhouse gas emissions worldwide (about 71% of the total in 2010) [10], as detailed in Annexe A.3: therefore, the growing global energetic need implies necessarily an emissions increase.

The previous conclusion is a key point to understand the danger that world is exposing to, a higher consumption will lead to more emissions and so a deeper and less reversible climate change: coordination and cooperation between nations is the only way to avoid the worst scenarios and to equitably manage the world's GHG balance.

As a results of this need, known since the end of 70s, in 1992 most of the world countries reunited in the United Nations Framework Convention on Climate Change (UNFCCC) during the Rio de Janeiro United Nations Conference on Environment and Development (UNCED). The UNFCCC is an International Environmental Treaty that seeks to reduce atmospheric concentrations of greenhouse gases with the aim of preventing dangerous anthropogenic interference with earth's climate system [11]. This institution is supported by many others agencies and organizations, as the Intergovernmental Panel on Climate Change (IPCC) or the World Meteorological Organization (WMO), to provide the policymakers all the information and the data needed to take their decisions.

Since the Rio de Janeiro Conference, many important decisions have been taken and many agreements have been produced and ratified to stop, or at least to limit, climate change: the milestones of this fight against emissions increase are listed later on.

Rio Conference, 1992 This historical convention led to different fundamental results, first of all the creation of the UNFCCC. Also, water usage and supply was discussed during the summit, alternative energy sources to fossil fuels were brought into relief and the ozone layer depletion was introduced as an issue. Some of the document produced were the "Rio Declaration on Environment and Development", "Forest "Principles" and the "Agenda 21". This last one is a schedule for the United Nations organizations and governments, made to help every part to attend its environmental objectives [12].

Kyoto Protocol, 1997 Made some years after the first "Conference of Parties" in Berlin, it is an international treaty that aims to reduce the GHG emissions of the state parties. The key points of the treaty are the recognition of climate change and the role of GHG emission in it, especially human-released CO_2 [13]. This agreement was thought with different commitment periods, the second of whose was agreed in 2012: known as Doha Amendment to the Kyoto Protocol [14], it added some targets to parties and is still waiting for becoming effective, as only 141 parties of 145 needed have ratified the text. Finally, the importance of Kyoto Protocol is due to the economical-political instruments put in operation, like the intergovernmental emissions trading, the clean development mechanism and the joint implementation, that influenced the subsequent agreements.

Rio Earth Summit, 2012 It has been the third international conference on sustainable development and its objectives were to secure renewed political commitment to this subject, to assess the progress and implementation gaps in meeting previous commitments, and to address new and emerging challenges. This conference obtained a major political results as it saw the participation of the most important world leaders to discuss two main themes, how to build a green economy to achieve sustainable development and how to improve international coordination by building an institutional framework: these confrontations finalized in the non-binding document "The Future We Want".

Paris Conference of Parties (COP-21), 2015 The last milestone in term of international environmental conferences is without any doubt the COP-21, focused on limiting global warming through a drastic reduction of greenhouse gases emissions. This ambitious objective was thought to be reached establishing a binding and universal agreement on climate [15], for the first time in 20 years. The main results were the "Paris Agreement" and the establishment of "The 2030 Agenda", a collection of 17 global goals designed to be a "blueprint to achieve a better and more sustainable future for all" [16].

The political effort to contain the emission growth is concrete and the most developed countries are called to play a bigger role in this: as a member of the UNFCCC, European Union has taken challenging engagements for the future, for its member countries and for itself as economical and political entity.

EU 2020 Climate & Energy package The 2020 package is a set of binding legislation defined by the European Union leaders in 2007 and enacted in 2009 to ensure the meeting of EU climate and energy targets for the year 2020. The three key targets set for this period are a 20% cut in greenhouse gas emissions[4], a 20% share of the European energy production from renewable energy sources and a 20% improvement in EU energy efficiency.

As already seen in the Kyoto Protocol, an Emission Trading System (ETS) is internally provided: it is the EU's key tool for cutting greenhouse gas emissions from large-scale facilities in the power and industry sectors and covers around 45% of the EU's greenhouse gas emissions. The remaining 55% is covered by the national emission reduction targets, tailored on each country specific sectors as housing, agriculture, waste, etc.

National targets are set up even for renewable energy production, considering countries' different starting points and their possibility and capability to further increase it.

Finally, the development of low carbon technologies is supported by funding for research and innovation, and energy efficiency is pursued through the EU Energy Efficiency Plan and the Energy Efficiency Directive.

This European effort brought numerous encouraging results: therefore, the legislation has been extended until 2030 and targets have been updated to +30% energy efficiency, 32.5% renewable energy production and -40% GHG emissions.

This concrete engagement by an important geo-political actor as the EU is the signal that world has started moving on the path of climate change fight, as it is a recognized necessity by now: an economical and technological challenge is facing all the world's countries and every nation is expected to answer that call, starting from the most developed ones.

Summarizing, in the last century world energy need knew an extreme growth that continued until the present days, driven by the industry development and the motorized transportation vehicles diffusion.

Non-renewable energy sources have been historically chosen to answer the increasing demand and the scheme has not changed yet: this caused coal, oil and gas to be always more rare resources, with consequent geopolitical tensions in the provided areas and between major importers and exporters.

Moreover, fossil fuels combustion is known to be the first source of GHG emissions, together with other side products as dusts and nitrogen and sulfur oxides. The greenhouse gases are identified as the drivers of the current climate change, increasing Earth's temperature at an alarming rate.

To act against this global trouble, an international cooperation has started: during the last years many meetings and conferences have been organized and numerous agreements have been stipulated between the major countries in the world.

Energy efficiency and waste heat reduction, by mean of low enthalpy energy enhancing, are two of the identified directions to be followed for reducing GHG emission and for containing the temperature increase: being relatively recent concepts, the room for technological improvements is very wide.

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[4] Data is referring to 1990 levels.

1.2. Techno-economical context

In a context of energy efficiency and waste heat reduction, ammonia-water absorption cycles[5] are solutions of particular interest for different reasons.

Essentially, they allow to produce:

- positive cooling (above 0°C)
- negative cooling (0 to -40°C)
- medium temperature heat (15 to 70°C)

Using as sources:

- solar power or waste heat at medium temperatures (60-140°C)
- waste heat at high temperatures (140-200°C)

If solar power is available everywhere, but with differences in intensity and productivity during the year, waste heat can be found mostly next to industrial or energy-intensive process: despite these preliminary remarks, the interest in these sources stays high[6].

As a results of the complexity of the energetic systems, waste heat quantification is a relatively recent subject of discussion and few data is available: some studies have been done at national level in United States [17,18], Norway [19], Sweden [20] and Germany [21], but the International Energy Agency (IEA) is the only institution to provide reliable data about energy flows at global scale involving all the sectors.

In particular, a global waste heat potential evaluation has been done by Forman et al. [22] using IEA data. Starting from global estimations of energy flows and knowing each transformation step, energy balances are calculated: then, the process is repeated until the reach of the final utilization stage and the results are regrouped in the right sector and fuel categories. This approach allows to get the Sankey diagrams reported in the Annexes A.4 and A.5 demonstrating the estimated world energy use.

Taking into account all the sources, it is even more clear the fossil sources contribution anticipated in the Section 1.1. In fact, this quantification shows that the 72% of the global primary energy consumption is lost after conversion and, in further detail, that the 63% of the resulting waste heat arises at a temperature lower than 100°C. These results appear to be coherent with the previous national estimations, especially with the US Department Of Energy (DOE) report in 2008 [23]: there was stated that 20-50% of input energy in industrial manufacturing processes was lost as heat with about 60% being released at a temperature lower than 230°C.

In their evaluation, Forman et al. highlight the sectoral efficiencies differentiating electricity and the four main economic sectors, as detailed in Figure 1.5a. The shares of hot exhaust gas and effluent losses are in all the four categories above 30%, meaning that a big availability of waste heat exists. The most of it is expected to come from electricity power plants and transportation for two reasons. Firstly, a large quantity of plants in the world operates through

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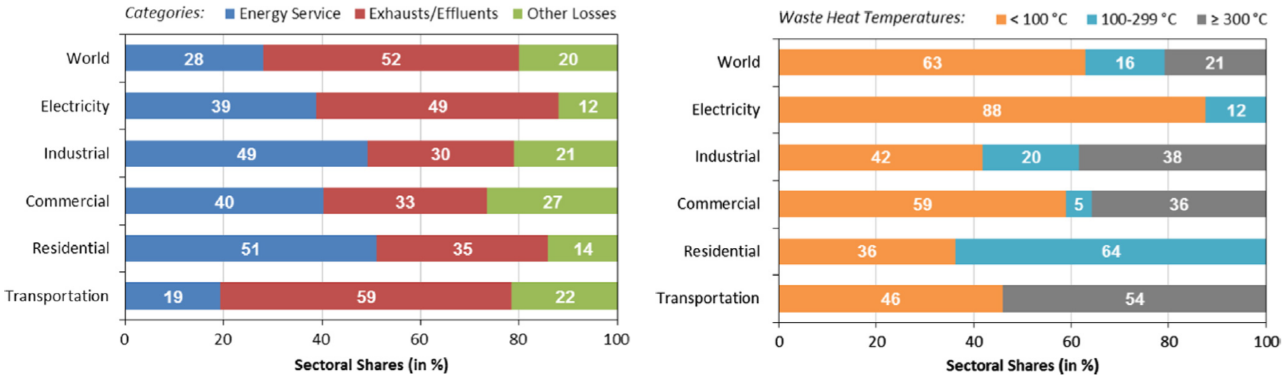
[5] AAHP is the common acronym for Ammonia Absorption Heat Pumps and AARP for Ammonia Absorption Refrigeration Plants (also called Ammonia Absorption Chillers).

[6] The distinction between solar-derived heat and waste heat is made because in the first case a solar concentration system can be specifically deployed to feed the absorption machine, while in the second case an external source is needed.

steam-based thermodynamic cycles, therefore dealing with temperatures in the range of 500-725°C [24] (nowadays reaching 760°C according to [25]): even using high-tech recuperation systems the efficiency does not exceed 50% and so a good part of the input heat is lost. Secondly, being road vehicles the main category of transportation means in the world and being operated through small combustion engines which efficiency is low, the result is a significant energy loss.



(a) Sectoral shares of balance factors.

(b) Sectoral shares of waste heat distribution.

Figure 1.5.: Sectoral waste heat quantification and classification. *Source: Forman et al., 2016*

What is less evident in this discourse is the temperature at which this waste heat arises: this point is also analyzed by Forman et al. and the results are summarized in Figure 1.5b. It emerges that the dominant portion of exhaust gas and effluents has a temperature below 100°C, while just a minor percentage is available at high or extremely high temperatures: this fraction is mostly coming from industry and commercial sector, where processes occur at well-defined conditions and heat recuperation is not always possible.

Temperature, or better the temperature difference between the hot and cold sides of a system, is an indicator of heat quality: the higher the difference, the higher the quality. This means that it is preferable to concentrate on high-temperature waste energy. The last assessment of Forman et al. about energy potential leads to the following conclusion:

> *Amongst all sector the Carnot potential is low. Only waste heat from industry and transportation is available at a comparatively good quality.*

This last statement refers in general to the possibility of transforming the available heat in work[7], but there still exist the possibility to enhance it as a hot source for other applications.

The interest in industry waste heat recuperation is confirmed by different studies, especially the already cited [21]. In their, work Pehnt et al. concentrate on the German industrial sector where they expect about 18% of the annual industrial final energy consumption to be available as waste heat at temperatures above 60°C (12% if considering heat above 140°C).

Industry has in general a considerable need of process heat at different temperatures, for example for drying processes, warm baths in mechanical production, distillation and evaporation

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[7] In fact, in the article the authors calculate this potential through a Carnot efficiency, differentiating between exergy and anergy and neglecting this last one as a potentially useful component.

of fluids. Thus, the sources of waste heat can be single machines or whole systems, whose energy balance is normally not trivial. A diagram about the distribution of the heat demand detailing the temperature levels of the consumption for each industry sector is reported in the Annexe A.6.

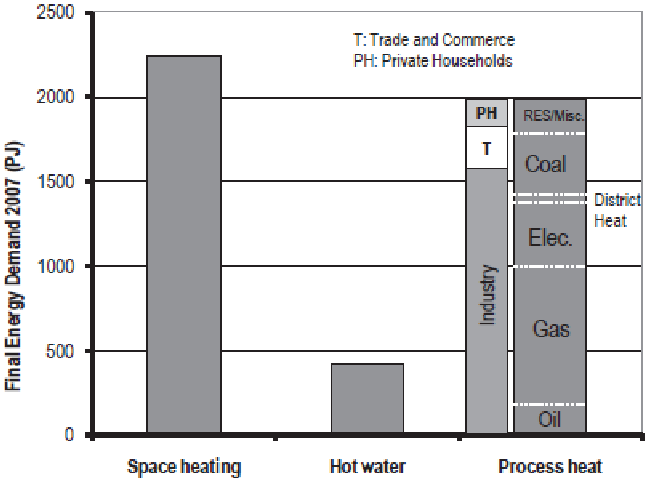


Figure 1.6.: Comparison of the process heat demand to the total heat demand in Germany industry in 2009. *Sources: BMWi, 2010; Pehnt, 2009*

The amount of process heat demand is important with reference to the total heat demand as the Figure 1.6 shows, and moreover the temperature levels are not absolutely the same for the three categories: space heating and domestic hot water production require by far a lower quality heat and are, at the same time, one of the possible application field for waste heat recuperation. In addition, heat rejected by one industry can be utilized by another one nearby, enhancing the global efficiency of the industrial area.

Therefore, industries shall not be closed systems but they should integrate in the surrounding social and economical context: villages, agricultural activities and other industrial facilities are opportunities for sharing waste products, in this case heat, and enhance them.

This may happen in different ways, considering that industrial waste heat can be released at low (<60°C), medium (<140°C) or high (>140°C) temperatures: each outlet condition allows some specific applications.

First of all, high temperature heat can be just transported to other industrial or civil consumption points by latent thermal containers using salts or heat oil to stock the energy, or also by pipelines creating a district heat network: hot effluents and exhausts are normally suitable. As an alternative, high temperature fluxes can be utilized, under certain conditions, to produce electricity by mean of Rankine Cycles, Organic Rankine Cycles (ORC) or Kalina processes using an ammonia-water mixture as working fluid. Lastly, high temperature heat can be utilized to generate cooling or heating through many absorption machines, in particular ammonia absorption refrigeration plants (AARP) or heat pumps (AAHP).

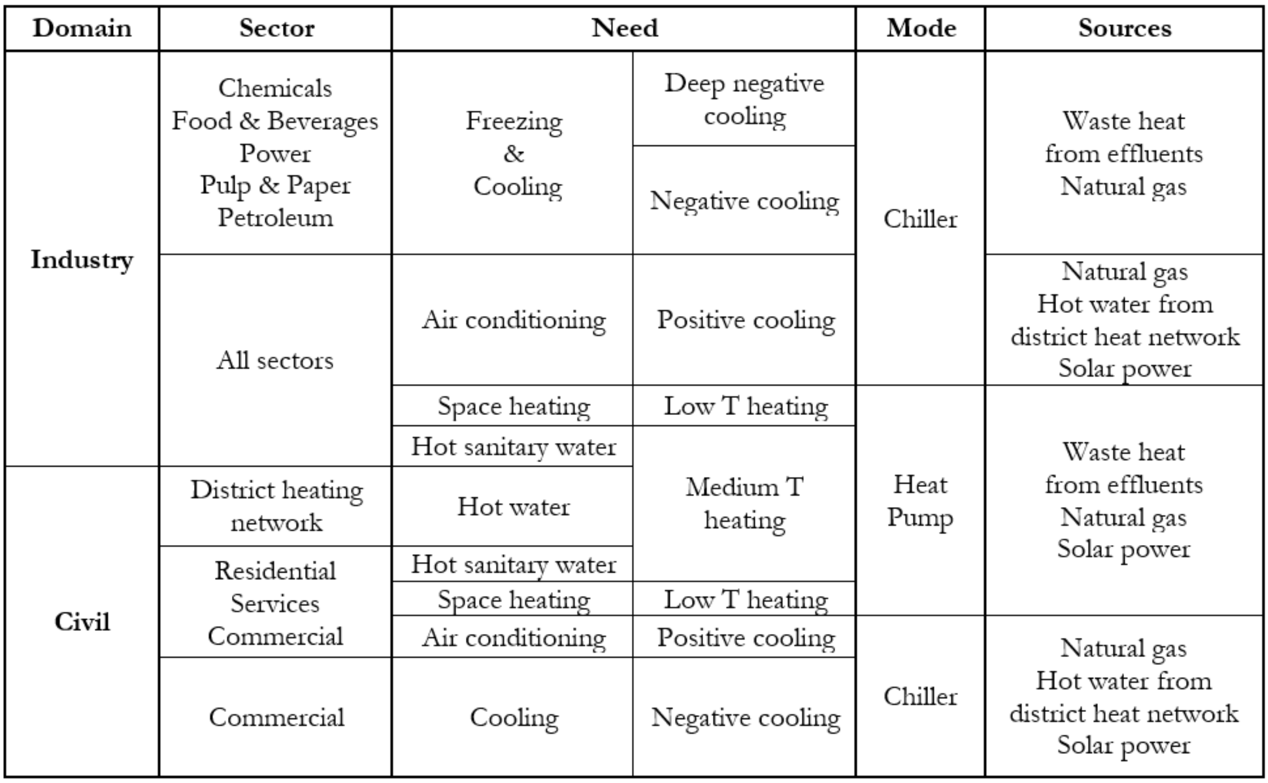
Applications for medium temperature waste fluxes are less as their quality is lower, so normally they can be transferred to the district heating network, to other facilities or used to operate some low-generator-temperature AARP or AAHP.

Finally, waste heat at temperatures below 60°C is difficult to enhance, but through a heat pump it is possible to reach temperatures suitable to district heating and domestic hot water generation[8].

Similar considerations on waste heat fluxes can be done for whatever energy sector because, as showed in the beginning of this section, the industrial field is just one of those concerned by intensive heat losses.

Forman et al. and Pehnt et al. demonstrated providing reliable data that waste heat is available, technically exploitable and that also an economical interest in its recuperation exists. The family of ammonia absorption machines integrates well in this techno-economical context, being able to produce positive and negative cooling and medium temperature heating starting by a medium/high temperature source instead that electricity. Solar powering is also possible, opening an interesting path for residential application development.

The Table 1.1 summarizes the main application domains and the working modes for different configuration of absorption systems.



Domain	**Sector**	**Need**		**Mode**	**Sources**
Industry	Chemicals Food & Beverages Power Pulp & Paper Petroleum	Freezing & Cooling	Deep negative cooling	Chiller	Waste heat from effluents Natural gas
			Negative cooling		
	All sectors	Air conditioning	Positive cooling		Natural gas Hot water from district heat network Solar power
		Space heating	Low T heating	Heat Pump	Waste heat from effluents Natural gas Solar power
		Hot sanitary water	Medium T heating		
Civil	District heating network	Hot water			
	Residential Services Commercial	Hot sanitary water			
		Space heating	Low T heating		
		Air conditioning	Positive cooling	Chiller	Natural gas Hot water from district heat network Solar power
	Commercial	Cooling	Negative cooling		

Table 1.1.: Ammonia absorption systems application fields and configurations.

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[8] A particularly convenient operating condition for Ammonia Absorption Heat Pumps occurs when a low-temperature source is available together with a high-temperature source: both of them can be used in the same absorption machine, greatly increasing the recuperation effect.

Absorption systems technology is relatively new and struggles to impose itself on the market because of the competition with traditional vapor compression systems, both chiller and heat pumps. However, some solutions have been successful as in the case of water-lithium bromide absorption chillers that is currently used and developed for air conditioning purposes, especially coupled with solar panels.

Ammonia-water systems are proposed as alternatives to these systems, thanks to the greater variety of working modes: being able to effectively produce heating and positive and negative cooling, they aim to became a crossover system to be deployed in every situation with minor modifications.

To investigate possible economic opportunities in ammonia absorption chillers several market studies have been done [26–29].

The results of these analysis show that the leading companies in the sector are the following:

- Araymond
- ATF
- Avery Dennison Corporation
- Bossard
- Hitachi Appliances Inc.
- Illinois Tool Worksorporated (ITW)
- Johnson Controls
- LG Air Conditioning Ltd.
- MW Industries
- Nippon Industrial Fasteners Company
- Penn Engineering
- Robur Corporation
- Shanghai Fasteners Company
- Stanley Black & Decker
- Thermax Ltd.
- Yazaki Energy Systems Inc.

Moreover, the key countries where this technology is promising are identified: U.S., Canada, the U.K., Germany, France, China, Japan, India, Australia, Mexico, Brazil and South Africa.

Major drivers on the world market for absorption chillers include different characteristics as low maintenance and operating costs, silent and vibration-free operation and the possibility of using several energy sources to drive the process. Other positive points are the possibility to balance loads, to reduce the dependence from electricity, and the long service life. These machines are also environmentally friendly compared to classic vapor compression systems, thanks to lower pollutant emissions and the use of non-GHG refrigerant fluids.

Increasing demand for energy-efficient cooling solutions is expected to boost the sector development. Furthermore, there is an estimated absence of electricity infrastructure in developing countries, who are so interested in having independent devices. Finally, development of food processing and chemical sector will play a major role in creating market opportunities [28].

North America accounts for the largest share of ammonia absorption refrigeration plants (AARP) market and is expected to lead the global market during the forecast period 2013-2025: this is due to strong adoption from the regions food processing and petroleum industries.

In Europe, the growth of the AARP market is estimated to be limited by the steady demand from the frozen food sector. A better situation is expected for Asia Pacific, Middle East and Africa (MEA) where considerable growth opportunities for absorption chillers manufacturers will occur. This is due to overall economic growth in the region: in fact, steady growth in the local food processing sector is expected to ramp up demand during the forecast period [26]. Finally, Latin America will experience moderate development due to increasing acceptance across different countries. Due to extensive use in the natural gas sector, the Middle East and Africa will probably account a great share in the revenues of absorption chillers.

For the ammonia absorption heat pump (AAHP) side less information is provided in detail as market studies usually treat the whole category of heat pumps: this is due to the classical system really high competitiveness, that dampens interest in this new technology. Despite this, the growth of the construction industry along with increasing implementation of stringent new building regulations by worldwide governments, especially China, Japan, the U.S. and Europe, are expected to be key factors driving the demand for AAHPs for residential applications. Subsidies on the purchase of heat pumps provided by governments and rising use of renewable energy are set to boost the demand for heat pumps.

Also, the possibility to have devices that can be used both for cooling and heating is likely to boost the demand and the investments for R&D in the forecast period. However, the lack of customer awareness and the higher cost of initial set-up are hampering the growth of this market. The lack of technical expertise to install these systems in existing infrastructures is further restraining the growth of this market [30].

To conclude the global market situation assessment, a research of the commercially-ready ammonia absorption machines is done: all the data collected is resumed in the Table A.1 in the Annexes.

This research shows that many little manufacturers produce this kind of systems, while the biggest corporations do not provide open-access data or catalogs, preferring a tailored sizing for each customer. However, what resulted is a good variety in nominal powers (30kW-10MW), a slightly prevalence in chillers on heat pumps, and efficiencies coherent with the state of the art of these machines. Different application are proposed covering all the fields and almost all the possible source types.

For what concerns in the detail this discussion that will further treat two-stage NH3/H2O absorption chillers modeling and design, Robur Corporation is the only firm to clearly declare to be able to construct GAX[9]-based machines, without giving details on their performances though.

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[9] The Generator Abosrber heat eXchanger is a special component designed for ammonia-water absorption systems. It allows the absorption of the refrigerant into the poor solution on one side, while evaporating the refrigerant from the rich solution on the other side. It allows to recover some absorption heat and to increase the global system efficiency.

1.3. Technological challenges

Ammonia absorption refrigeration plants and heat pumps (AARP and AAHP) have many advantages as thermodynamic systems, including the not negligible possibility to operate in reversible mode. These systems normally have high reliability and long life cycle due to the absence of moving parts (except for the solution pump): also, a lack of vibrations and therefore of noise makes these machines interesting for the comfort they can guarantee to customers. Not rarely hospital, schools and upscale hotels choose them for air conditioning purposes.

The choice of ammonia as refrigerant fluid has been necessary to reach very negative (chiller case) and positive (heat pump case) temperatures, that the other absorption systems cannot stand, and to improve the operating range. In fact, lithium bromide absorption chillers are very sensible to external conditions, limiting the suitable application areas and purposes.

Ammonia has also the quality of being a natural fluid with non-greenhouse gas properties (its GWP is 0): this makes the NH3/H2O mixture a great solution for meeting the environmental goals, especially considered that using waste heat instead electricity helps to reduce CO_2 emissions.

In addition to this, AARPs and AAHPs are normally operated with cheap or free heat sources, so the Operating Expenditure (OPEX) stays lower than the standard vapor compression machines. The possibility to feed ammonia absorption systems with different sources allows multiple configurations depending on the available opportunities offered by the surrounding natural and anthropic context: for example, a symbiosis with nearby industries can be set-up, or a stand-alone configuration can be chosen.

Nevertheless, some negative points strongly influence the diffusion of this kind of machines and for a major parts they are related right with the nature of the refrigerant fluid.

To start, as high pressures are required to condensate the ammonia-water mixture, each component is subjected to a considerable mechanical stress and in general it must be airtight to avoid leaks. Vice versa, low pressures can be further necessary to evaporate the mixture, with analog issues.

Secondly, being ammonia and water two fluids with high volatility, the separation of the two vapor phases is a serious issue. Exiting from the generator, as it will be further explained, the purity of the refrigerant fluid is influenced by the presence of water particles: an additional process called rectification is required. This leads to a more complex architecture and a larger overall dimension, which constitutes is one of ammonia-water pair main flaws. In addition, increasing performance requires more components with consequent more difficult setup and maintenance than standard chillers: the lack of expertise in this field, absorption machines not being so diffused in the world, just worsen this point.

Lastly, NH_3 is known to be corrosive and particularly at high temperatures: special metal alloys have to be chosen to produce the pipes, the separation tanks and all the other components to ensure the durability of the system. Unluckily, it also results toxic for humans and special security devices need to be included in the machines to guarantee safety, notably in domestic applications.

For all the reasons listed until now, the production cost of these systems are normally elevated: the Capital Expenditure (CAPEX) for this kind of solution is considerably higher than its standard competitors and just in a long-term view OPEX and CAPEX will balance. A lack of mass production infrastructure worsen the situation.

However, a slightly major cost would be generally accepted in change of better performances: unluckily this is not the case, because absorption machines are not yet capable of reaching the same efficiency of standard vapor compression ones. A more detailed analysis of this point will come further in the discussion.

Some obstacles are present even outside the machine itself, as the adoption of this solution is actually effective with cheap or free sources. Unluckily, waste heat is not available everywhere and solar coupling is mostly a niche application. District hot water feeding would be interesting, but generally is a paying service.

To conclude, a further amelioration of ammonia absorption machines is needed to effectively challenge standard thermodynamic systems.

First moves will probably concern the simplification of the architecture to make everything more manageable, and not just a simple component reduction that would deeply affect efficiency.

Secondly, an increase in the overall performance will make these systems more desirable to investors eyes, in particular an improvement of robustness and a wider operative range.

Finally, the lowering of the costs, maybe realized through governmental subsidies, new materials and a large-scale production, will be determinant for the success of this technology.

1.4. Internship objectives

The internship at CEA Grenoble is positioned in the context of absorption machines research and development, in particular its final goal is the modeling and sizing of a two-stage NH3/H2O absorption chiller equipped with a Generator Absorber heat eXchanger (GAX) section.

To overcome the issues referred to in the previous Section 1.3, the system is expected to take advantage of the contemporary plate exchanger technology, as well to introduce some additional architecture improvements. However, the chosen refrigerant fluid will remain ammonia and only two stages of pressure would be admitted.

The internship goals are the following:

1. Creating a complete cartography about existing GAX-based absorption machines (both chillers and heat pumps);
2. Defining a physical model of the whole GAX system;
3. Conducting a numerical simulation of the performances;
4. Performing a comparison with standard single-stage solution to evaluate the convenience in this technology;
5. Starting the sizing of the key components of the new cycle.

In particular, this study results will be practically applied into some ongoing projects for deep negative cooling and heating purposes.

The applied methodology is mostly based on the classical physical modeling, with an integration of numerical simulation tools thanks to the EES software[10]. The fluids thermodynamic properties are calculated through the software REFPROP[11], while the mechanical design of the components is obtained by directly demanding quotes to specialized manufacturers. The final system assembling is studied in the SolidWorks software environment[12].

Finally, the internship timetable is:

- 1 month devoted to the literature review;
- 1 month dedicated to the physical modeling;
- 1 month for the numerical simulation;
- 1 month dedicated to the component design;
- 1 month, the last, devoted to the writing of the final report of the Final Year Internship.

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[10] Engineering Equation Solver version 10.362, http://fchartsoftware.com/ees/

[11] REFPROP version 9, https://www.nist.gov/srd/refprop1

[12] SolidWorks verdion 2019, https://www.solidworks.com/fr/solutions

1.5. Conclusion

In the last half-century the world has experienced a strong growth of its energy need: coal, oil and natural gas have been largely exploited to satisfy the global demand and despite the technology improvements, as nuclear and renewable energies, fossil fuels still constitute the major share of world primary energy consumption.

Non-renewable energy sources are known to be environmentally hazardous because their combustion, that represents their standard final transformation, releases greenhouse gases, the major contributor to occurring climate change, and commonly other side-products as dusts, NOx and SOx, responsible to local environmental pollution. Another major problem comes from the need to ensure energetic provisioning, a fundamental point for each country. As the world energetic system relies enormously on its limited reserves of fossil fuels, the stability of certain regions of the world might be put at risk by the geo-political interests of other nations.

For the reasons cited before, limiting energy consumption is a global double interest: therefore, in the last decades an international cooperation to reduce emissions and to limit the global energy need growth has started. Many treaties have been set-up at a worldwide level to attends the environmental objectives. The European Union defined its community targets in the 2020 Climate & Energy directive, further updated and extended until 2030.

Ammonia absorption machines play an interesting role in this game, proposing themselves as an alternative to conventional chillers and heat pumps: in fact, they can use heat as driving source instead of electricity and this characteristic is even more interesting when free heat is available, as waste heat or solar heat. Being able to exploit free heat makes this systems both eco-friendly and convenient to operate.

Waste heat is largely available on Earth: almost the half of primary energy input is wasted as hot effluents or exhaust gas, mostly available at low temperatures. The sectors where there is a considerable quantity of waste heat at an appreciable quality are industry and transportation. The focus on the first sector has been done by a German study, where the substantial importance of process heat with reference to total heat demand has been reported.

Despite these application opportunities are well-known, ammonia absorption chillers and heat pumps are still diffusing slowly, with the exceptions of United States and Asia. However, expected trends for the future are positive: for absorption chillers, drivers will be the growing demand of frozen food sector and the possibility to run independent devices where a lack of electricity infrastructure exists; for heat pumps, increasing implementation of stringent building regulations and subsidies for green heating systems will raise the demand.

Ammonia absorption systems are reputed for having a high reliability and a long lifetime, together to a high comfort and a low operational cost. However, a global amelioration of these machines is needed to overcome the historic flaws: fluid material corrosion, high pressures, low performances and high investment cost. To achieve better performances the Generator Absorber heat eXchanger (GAX) technology has been developed in the past years and is nowadays on the market.

The goal of this 5 month internship is to improve this concept, simplifying the architecture, lowering the manufacturing costs and improving the global efficiency. Moreover, an operational condition range increase would be an appreciated result.

2. State of the art

The discover of fire set a fundamental milestone in human history: better living conditions and technological development were possible thanks to the ability of controlling it, warming homes and heating furnaces. Being able to start a heat source wherever needed made man conscious of the power he had onto the environment, that slowly started bending to his willing.

Many thousand years after, someone started wondering something more: as managing heat was simple then, the new challenge for humanity became producing cold.

The origin of refrigerating systems dates back to the first half of the 19th century[1], when inventors experimented the first vapor compression-based machines using ethyl ether as refrigerant: unluckily, the possible success got slowed down as the fluid was toxic and flammable, too dangerous for commercial purposes. A few years later the air-compression cycle appeared, preparing the way for new fluids, notably the CO_2.

Almost at the same time in France, Ferdinand Carré invented and patented (in 1859) the first ammonia absorption machine: designed for an industrial use, this system proved to be capable of producing huge blocks of ice and successively also portable models were manufactured [31].

Its heat-fed functioning astonished the public and the success came very fast: it dominated the market and conquered all the United States. Surfing on the wave, another French engineer, Charles Tellier, invented the first conservation cabinet [32].

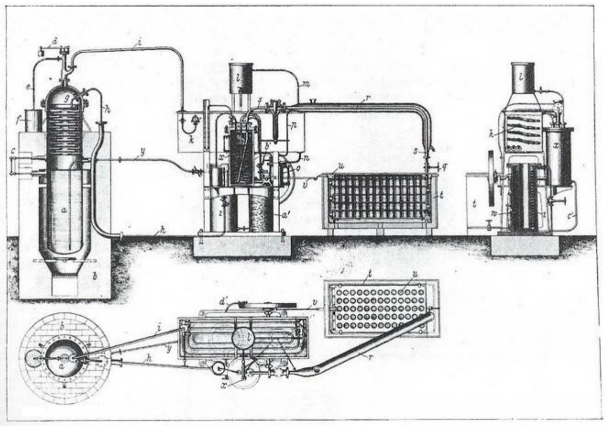

Figure 2.1.: F. Carré ammonia absorption chiller.
Source: http://www.hevac-heritage.org

That was the golden age of absorption chillers: nevertheless, their success was to be ephemeral. Indeed, in the last quarter of the 19th century, the discovery of new fluids definitively decided the development direction in the refrigeration field: the era of the vapor compression systems began, lasting until today.

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[1] A pioneer system was set-up in 1834 by the American Jacob Perkins, followed a few years after by the Scottish James Harrison.

2.1. Refrigerating systems

The term refrigeration, as history can testify, is strongly related to the standard thermodynamic cycle that is normally used to achieve the goal: however, its meaning is a bit wider. In fact, refrigeration is simply defined as human-made cooling through any process [33], as schematized in the Figure 2.2. The cooling process generally involves two sources with the heat being transferred from the colder side to the hotter one. However, there exist some niche technologies that do not exactly fit this concept, as further better explained.

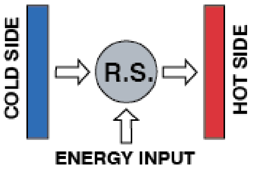

Figure 2.2.: Generic refrigeration system.

This brief introduction is necessary because refrigerating systems have evolved since the start of vapor compression era, and now differ much in physical principles, design and applications. They can be classified in the following principal categories: cyclic, non-cyclic and material property-based. Nevertheless, some others base their functioning on very particular processes or concepts and are mostly being developed at a research stage.

The simplest of the four classes is that of non-cyclic refrigeration systems: actually, they just exploit a phase change or a temperature difference between a substance and the volume to be cooled. Changing his thermophysical state the refrigerant absorbs some heat from the surroundings and so cooling is provided: melting ice or sublimating dry ice are common ways to do so. Once exhausted, the substance has to be recharged with some new one to keep cooling going.

Passing to cyclic refrigeration, cooling occurs through a thermodynamic cycle that transfers heat from a cold source to an exterior hot sink: evidently, the heat flux goes in the opposite direction than the natural one, but this is possible thanks to some proper refrigerant fluid temperature variations. To make the cycle happen the fluid needs some energy, provided by the machine by a compressor or a pump: then, the refrigerant undergoes a double heat exchange with the external fluids alternated by an expansion, before concluding its path returning to its starting state.

Known that, some differences can be done in term of fluid mechanism used: if a phase change is present during the heat exchange a vapor cycle occurs; vice versa, with no phase change the process is called gas cycle. Moreover, the first category can be further classified on the mechanical way used to increase pressure: a vapor-compression refrigeration occurs using a compressor, while an absorption refrigeration occurs using a liquid pump.

Vapor-based The vapor-compression cycle, also called Kelvin cycle, is the most diffused one at worldwide level thanks to his historical use and to the fact that it is simple to realize. The cycle is composed by a refrigerant fluid whose pressure is increased by a compressor: then, it is cooled and condensed by an exterior fluid and after expanded in a throttle valve, where pressure abruptly decreases. This causes flash evaporation and the refrigerant temperature drop. Being very cold, the fluid is evaporated in a thermal exchanger where it absorbs heat from an external source: this cooling constitutes the system useful effect.

Absorption cycles Also known as Carré cycles from their inventor, these thermodynamic systems belong to the family of vapor cycles and rely on the refrigerant condensation and further throttling. Thus, phase change is again a fundamental point: what is different with reference to the vapor-compression case is exactly the way how pressure increase is performed. Indeed, the compressor is replaced by a pump: this allows to use much less energy to step-up pressure, but it forces to have liquid instead of a gaseous phase. Absorption systems solve this obstacle using two or three fluids, one normally liquid, the absorbent, and the other vaporized, the refrigerant. Before the pressure increase the refrigerant vapor is absorbed by the liquid absorbent, so they become a single fluid that can effectively be pumped. After that, they are separated: the refrigerant continues towards the standard vapor-compression components, while the absorbent is recirculated.

Gas-based Gas cycles deeply differentiate from the previous vapor-based ones because of their cooling principle: they do not use latent heat to transfer heat from one source to another. Instead, they exploit the gas different pressures to change temperature along its path inside the machine. Being the fluid a real gas, the ideal gas law $PV = nRT$ is not completely applicable: however, huge temperature differences can still be reached thanks to the Joule–Thomson effect[2].

These systems are therefore used to reach temperatures even below the hundred Kelvin degrees, especially for gas liquefaction or superconductors cooling: notable application examples are the Stirling cycle, the Linde-Hamson Process [34], the Claude Process and the Reverse Brayton Cycle.

The material property-based category takes advantage of some particular physical properties of certain elements or composites to produce cooling. A notable example is that of thermoelectric junctions, which exploit the Peltier effect. Otherwise, magnetic and elastometric refrigeration are also possible, but for minor applications.

Thermoelectrics The Peltier effect is the reverse phenomenon of the Seebeck effect: the electrical current flowing through the junction connecting two thermoelectric materials emits or absorb heat per unit time at the junction to balance the difference in the chemical potential of the two materials [35]. This way a refrigeration cell can be set up, operating between two temperature levels and consuming electrical energy. Despite the efficiency is really low, this technology still has an interest, especially where conventional cooling systems cannot be placed due to space occupancy (microelectronics above all).

Other physical properties Magnetic refrigeration is a cooling technology based on the magnetocaloric effect, an intrinsic property of magnetic materials. This effect is defined as the heating or cooling of a magnetic material due to a variation of the applied magnetic field. The interest in this technology is currently due to the possibility of efficiently cooling at room temperatures [36, 37]. However, many others theoretical applications are possible, as hydrogen liquefaction, large building air conditioning, and vehicle and high-speed computers cooling [38].

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[2] In thermodynamics, the Joule–Thomson process consist in forcing a real gas or liquid through a throttle valve or a porous plug while keeping it insulated from the environment. The resulting effect is a the temperature change of the fluid, positive or negative depending on its Joule-Thomson coefficient.

Elastocaloric refrigeration is a relatively new principle that comes from a special property of super elastic materials. The elastocaloric effect consists in the material temperature variation when subjected to a mechanical stress: in fact, the molecules in the crystalline lattice undergo a structure transformation, absorbing or releasing energy depending on the final phase. However, materials with this properties are mostly alloys and further research is required to properly produce them. Finally, energy losses due to hysteresis constitute another major challenge [39].

As anticipated, there exists some other niche refrigeration methods that find an application in extremely specific fields, as fundamental research and cryogenics.

Laser cryocooling can benefit of the application of ultra-stable lasers and interferometers, which are extremely sensitive to vibration. This technique uses the Doppler Process for cooling down a fluid, even reaching values of about 0K. In particular, lasers are used to force out particles with too much kinetic energy, reducing the vibrations of the fluid atoms and thus its temperature [40]. These systems are utilized from some research institutions for studying the Bose-Einstein condensate at a fraction of Kelvin.

Pulse tubes work by transporting heat against a pressure gradient in a process called surface heat pumping. The piston compresses the working gas and every gas particle moves towards the closed end of the pulse tube. So, the pressure is highest closest to the hot end and decreases to zero at the bottom of the pulse tube: moreover, the pressure gradient directly results in a temperature gradient [41]. Then the piston retracts and the gas undergoes an adiabatic expansion, further cooling it. As the expanding gas enters a component called regenerator it absorbs heat from the surrounding pulse tube walls, cooling them. Record low temperatures achieved with this basic design are 124K with a single stage and 79K using two stages [42].

Thermoacoustic refrigeration is a new cooling concept that offers advantages including high efficiency, reliability and being environmental friendly [43]. The thermoacoustic effect consists the conversion of heat energy to sound energy or vice versa: in fact, appropriately modulated sound waves flowing through a porous solid can generate a temperature gradient inside it. Moreover, as sound waves can replace pistons and cranks in the machine, no moving parts are necessary in the process. Finally, utilized fluids are usually inert gases, with consequent environmental benefit [44].

Lastly, the Vortex Tube is a mechanical device that separates a compressed gas into hot and cold streams. It does not have any moving parts, as pressurized gas is just injected tangentially into a swirl chamber and accelerates to a high rate of rotation. At the end of the tube a conical nozzle is placed, allowing only the outer shell of the compressed air is to escape outside. The inner part of the air flux is forced to return in an inner vortex of reduced diameter within the outer vortex. The temperature difference between the outer shell, hotter, and the inner shell, colder, is explained through vortex physics [45].

Concluding this brief overview about refrigeration systems, many technologies are currently available to accomplish different goals. Conditioning and industrial cooling are the main field of application, followed by gas liquefaction and superconductors cooling: this is sufficient to justify the preponderant diffusion of vapor and gas refrigeration systems, while all the others rest mostly at a research level. As the subject of this discussion is the modeling of a vapor machine, that strongly differs from gas-based one for operational conditions and functioning principle, just vapor-compression and absorption systems will be analyzed in more detail.

2.1.1. Vapor compression systems

The vapor-compression cycle operates cooling through four essential components: a compressor, a condenser, a throttle valve and an evaporator. This system exploits the phase change of its refrigerant fluid to remove heat from the cold source and to further release it into the hot sink.

A little precision about terminology is necessary: the term "cold source" indicates that this external fluid is the heat source (providing low-temperature heat to the evaporator), instead the label "hot sink" indicates that this second external fluid receives some intermediate-temperature heat from the condenser. The adjectives cold and hot are attributed to the external fluids being the temperature of the source lower than the temperature of the sink. So, being $T_2 > T_1$ heat finally flows from a colder entity to a hotter one: for the Second Principle of Thermodynamics this is possible only if an external energy input is provided. The Figure 2.3 schematizes the work and heat flux exchanges.

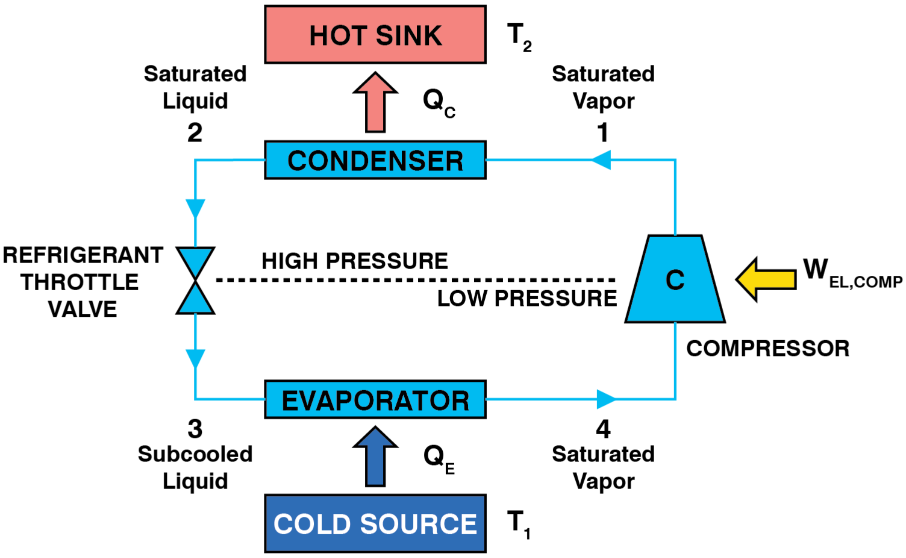

Figure 2.3.: Vapor-compression cycle general scheme.

In fact, to allow fluid circulation and the proper phase changes a pressure difference is present in the cycle: normally it is realized thanks a compressor that compress the inlet refrigerant vapor. As the fluid used behaves normally as a gas, this compression causes also a temperature increase. Now, the refrigerant temperature at the condenser admission is high, greater than the hot sink fluid one: a heat exchange occurs, releasing energy to the external fluid. Cooling down, the refrigerant liquefies and passes through the throttle valve: its pressure drops and, thanks to the Joule-Thomson effect, temperature decrease drastically. Thereafter, entering the evaporator the refrigerant is a cold liquid that interfaces with an external hotter fluid (still cold, but the refrigerant is colder): an heat exchange happens and the external low-temperature heat is transferred from the source to the evaporator. The refrigerant increases its temperature and evaporates, returning to the compressor as a vapor, while the external fluid cools down, generating the useful effect Q_E (in heat pumps the useful effect is Q_C).

Summarizing, these are the temperature levels in the system: $T_C > T_2$; $T_2 > T_1$; $T_1 > T_E$. Pressure levels are just two and they are determined by the condensation and evaporation conditions: at the condenser side the pressure is higher, and lower in the evaporator. So, $P_C > P_E$.

Performances The performances of thermodynamic systems have been studied in detail over the years, and the best results can be obtained through a particular cycle called Carnot cycle. Unfortunately, this is an idealized energy conversion cycle having totally reversible characteristics and therefore no losses: real cycles will always behave worse. Moreover, and that will be clarified in the next paragraph, in a Carnot cycle an infinitesimal temperature difference is sufficient to effectively exchange heat: therefore, condenser and hot sink temperatures, and evaporator and cold source temperatures can be considered equivalent ($T_E = T_1$; $T_C = T_2$). This will not be the case of real cycles.

Observing the work and energy fluxes through the First Principle of Thermodynamics it results:

$$\dot{Q}_C = \dot{Q}_E + \dot{W} \tag{2.1}$$

Chiller Then, the Coefficient Of Performance (COP) for refrigeration is defined as the net cooling power produced at the lowest temperature divided by the rate of the net work [46]:

$$COP_R = \frac{\dot{Q}_E}{\dot{W}} \tag{2.2}$$

Further, the Second Principle of Thermodynamics for a Carnot cycle operating between the same temperatures T_1 and T_2 schematized in Figure 2.3 requires that, for reversible operation, the net entropy production is zero:

$$\frac{\dot{Q}_C}{T_2} - \frac{\dot{Q}_E}{T_1} = 0 \tag{2.3}$$

Substituting temperature values to the net input power in the Eq. (2.2), using Eqs. (2.1) and (2.3), it results:

$$COP_{R,Carnot} = \frac{T_1}{T_2 - T_1} \tag{2.4}$$

Heat pump Vapor compression systems have another notable application over refrigeration: in fact, they can be used for heat pumping, for example in an air conditioning context. The useful effect in this case becomes Q_C, so the heat transferred to the hot sink. The general performance coefficient can be defined:

$$COP_{HP} = \frac{\dot{Q}_C}{\dot{W}} \tag{2.5}$$

Through a similar procedure than before the following Carnot COP can be obtained:

$$COP_{HP,Carnot} = \frac{T_2}{T_2 - T_1} \tag{2.6}$$

and consequently the following relation, valid for both real and ideal cases:

$$COP_{HP} = 1 + COP_R \tag{2.7}$$

Thermofrigopump (TFP) or Simultaneous Heating & Cooling system (HPS) Recently a new kind of thermodynamic machine has been developed and it is now emerging on the market: even if the cycle architecture does not really change from the vapor-compression one, it features the possibility to simultaneously provide both cooling and heating at interesting utilization temperatures. Also, it can adapt to a different demand of each product within a certain operational range and can be operated in different modes depending on the case [47]. Having a double useful effect (both Q_C and Q_E) this solution maximizes both the real and the Carnot COPs:

$$COP_{TFP} = \frac{\dot{Q}_C + \dot{Q}_E}{\dot{W}} \tag{2.8}$$

$$COP_{TFP,Carnot} = COP_{HP,Carnot} + COP_{R,Carnot} = \frac{T_2 + T_1}{T_2 - T_1} \tag{2.9}$$

However, as real systems always involve losses (all transport processes contribute to losses), the Carnot relations provide only an upper bound to cycle performance: in most cases the real performance is much less than the Carnot COP obtained through the temperature-based equations.

The general expressions (2.2), (2.5) and (2.8) are always valid, for both ideal or real cycles.

Vapor compression machines operates with limited real COPs, lower than Carnot COPs, typically in excess of 3.0 for the chillers and of 4.0 for the heat pumps [48]: this performance is enough to withstand the market concurrence and, with reference to the other refrigeration systems, COP is the best point of this machine. Evidently, the thermofrigopumps show even better performances, although remaining a niche application for the moment: in the best conditions they can operate in excess of 7.0[3].

Nevertheless, many disadvantages are present, first of all the kind of refrigerant fluids utilized. If once natural fluids were chosen, as ammonia, sulfur dioxide, methyl chloride and dicholormethane, they soon had to leave the place to CFCs and HCFCs, which had better performances and lower price. Unluckily, they are strong greenhouse gases and they contributed considerably to the Ozone Depletion. In 1997, CFCs and HCFCs were forbidden by the Kyoto Protocol of the United Nations Framework Convention on Climate Change: this opened the way to hydrocarbons, that have a much lower Global Potential Warming power.

The second big disadvantage for vapor-compression machines is the electrical feeding, because this kind of energy is really valuable and its production normally implies a great greenhouse gases emission. For the moment few solutions to these two problem are available: instead, the efforts have concentrated to keep performances above all the concurrency, even in a cascaded configuration with multi-stage vapor compression systems.

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[3] https://www.swegon.com/fr/Assistance/brochures/brochures—production-de-chaud-et-de-froid/thermofrigopompe/ , accessed last 22/11/2020.

2.1.2. Absorption systems

This type of refrigeration systems, although being vapor-based, quite differs from the vapor-compression ones: the pressure increase is meant to be realized through a pump now, and the necessity of pumping the refrigerant instead compressing it forces to have a binary or ternary fluid mixture, adding some complexity. The rest of the system (condenser, throttling valve and evaporator) remains generally the same than in vapor-compression systems.

Therefore, the troublesome process in absorption machines is the refrigerant generation: the compressor is replaced by more components that accept low pressure and temperature refrigerant as input and provide high pressure and temperature refrigerant vapor as output. This process involves some internal heat exchanges and three external fluxes, as shown in Figure 2.4.

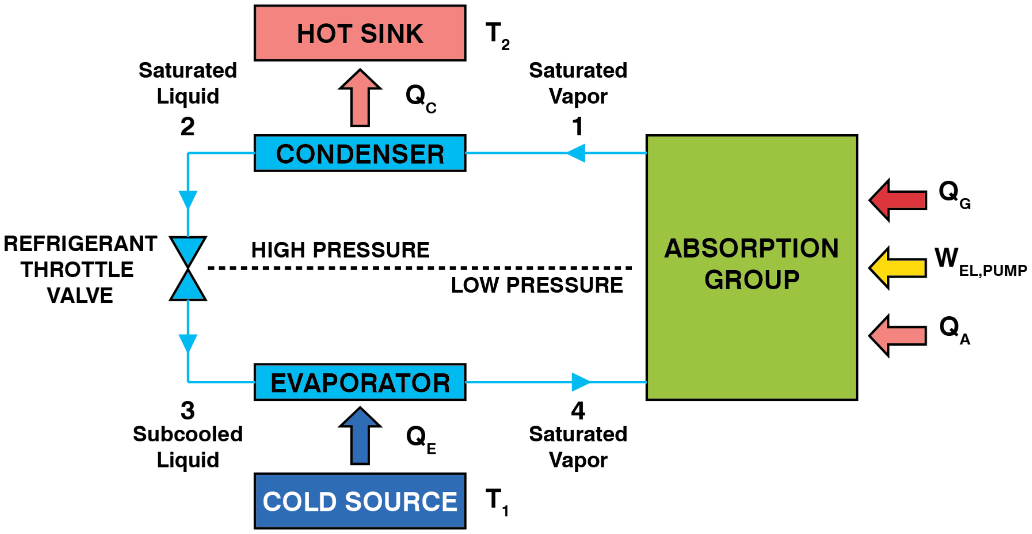

Figure 2.4.: Absorption cycle general scheme.

Instead of an only electrical input, absorption machines require a high temperature source (80-200°C) and just a tiny electrical feeding. Moreover, the absorption process will generate some intermediate temperature waste heat, to be released to the hot sink.

The interest in this technology, that may not appear evident, consist in the difference of electrical energy consumption with reference to standard vapor-compression systems. In fact, this machine makes the most when applied in coupling with a free or low cost heat source, where the only consumption to care about is electrical energy.

Compressor work From the general equation of work:

$$dL = Fdx = PAdx = PdV \tag{2.10}$$

Assuming that the fluid is an ideal gas, with a certain specific heat ratio $\gamma = c_P/c_V$ and remembering also the perfect gas law $pv = RT$ and the isentropic relation $pV^\gamma = cost$, the compression work is obtained:

$$L = \frac{p_2 v_2 - p_1 v_1}{1-\gamma} = c_P T_1 [(\frac{p_2}{p_1})^{\frac{\gamma-1}{\gamma}} - 1] \tag{2.11}$$

Pump work Recalling the First Principle of Thermodynamics $\Delta U = Q - L$ and the definition of enthalpy $h = u + pv$, with few passages is possible to derive the pump ideal work [49]. Writing enthalpy in differential notation:

$$dh = du + pdv + vdp \tag{2.12}$$

it is possible to substitute $dq = du + pdv$ from the First Principle, obtaining $dh = dq + vdp$. Finally, knowing that work con be expressed as a difference of enthalpy $dL = dh$, in the case of a incompressible fluid with isentropic conditions $(dq = 0)$ it results:

$$L = h_2 - h_1 = v(p_2 - p_1) \tag{2.13}$$

That means, for a liquid the work is driven by the pressure change magnitude: however, being the specific volume really little, this value stay also remains low.

A different discourse must be done for gases: in fact, both pressure and volume vary considerably. The work needed for a compression is generally much higher than the case of the pump. For example, as calculated by D. Triché [50] using ammonia, the ratio between the two works is:

$$r = \frac{W_{compr}}{W_{pump}} \simeq 96 \tag{2.14}$$

The electrical energy saving is consistent and even changing the fluids in the absorption process, as it is detailed in the next Section 2.2, the convenience in pumping instead compressing the fluid remains. However, absorption machines have some important flaws that make them complex to build and manage, keeping COPs far from the ideal Carnot ones: for example, an absorption chiller typically has a thermal Coefficient of Performance (COP_{TH}) between 0.5 and 1.5, that is not exceptional [51].

2.2. Absorption cycles

Absorption cycles can be operated with different fluids for reasons that will further described, but whatever mixture is used the absorption pumping method remains the same. The main components needed to realize the pressure increase and the refrigerant generation are highlighted in green in the Figure 2.5: absorber, generator, solution pump and a solution throttle valve constitute the core of the generation section. The rest of the cycle is composed by standard components, already known from the vapor-compression system: in fact, as the cooling principle similarly bases onto the refrigerant phase change, the transformations are the same.

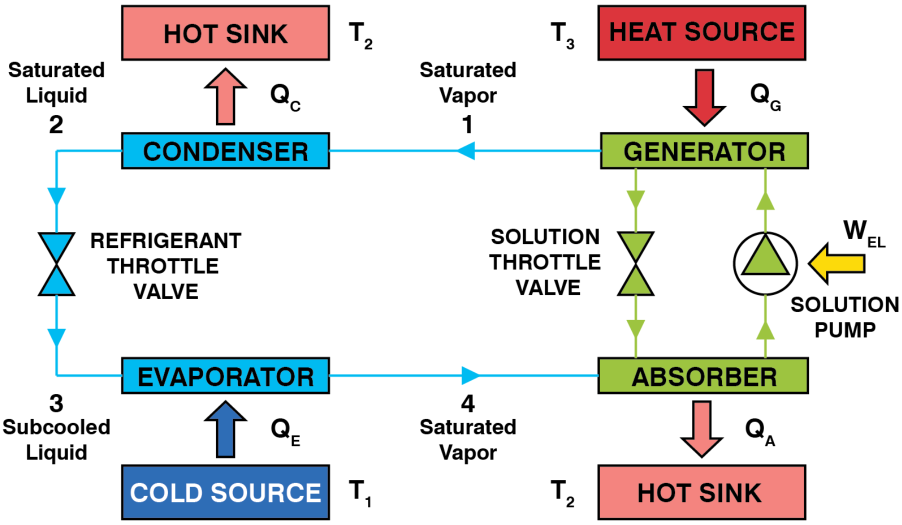

Figure 2.5.: Absorption cycle detailed scheme.

Analyzing in more detail the absorption block, the absorber is the component dedicated to the dissolution of the refrigerant vapor into the solution, a fundamental step for absorption systems: in fact, the pressure increment is realized through a pump and a liquid must be provided. Although, the refrigerant is vaporous: through this smart transformation the vapor is trapped in a liquid, called absorbent, and a liquid solution of absorbent and refrigerant is created. Being, the absorption process exothermic, to maintain a good reaction efficiency it is necessary some cooling: the removed heat is normally released to the environment or, in the case of heat pumps, to an external fluid.

The solution pump has no particular characteristics, unless being compatible with the solution: this point is not to be underestimated because the fluids can be corrosive or dangerous, so a proper system needs to be provided. Moreover, the top and bottom pressures, together with the pressure increase, generally constitute a constraint for the pump choice.

The generator is the other characteristic component: in fact, it is charged of the separation of the refrigerant from the solution coming from the pump. This happens thanks to the evaporation of the refrigerant, realized using an external, high temperature heat source that heats the solution until saturation. In this condition the refrigerant starts to evaporate while the absorbent stay liquid: the former is collected and sent to the conventional refrigeration part of the machine, the latter, now poor in refrigerant and not interesting anymore for the vapor generation, is expanded through the solution throttle valve and sent again to the absorber.

In an ideal absorption cycle, all these transformations happen with unitary efficiency and best output conditions, while it is not absolutely the case in practice: for example, rich solution exiting the absorber normally is not saturated, and the refrigerant Exiting the generator may contain traces of the absorbent. So, other components or processes are required to ensure the good system working, but with a performance loss.

To evaluate and compare absorption the machine performance a Carnot cycle can be taken again as reference: nevertheless, it differs from the one used for vapor-compression systems as now the architecture is different and, more precisely, involves two thermodynamic cycles instead of just one. In fact, as shown in the Figure 2.6, the absorption machine can be presented as a conventional Rankine refrigeration cycle in which the compressor is replaced by a motor cycle.

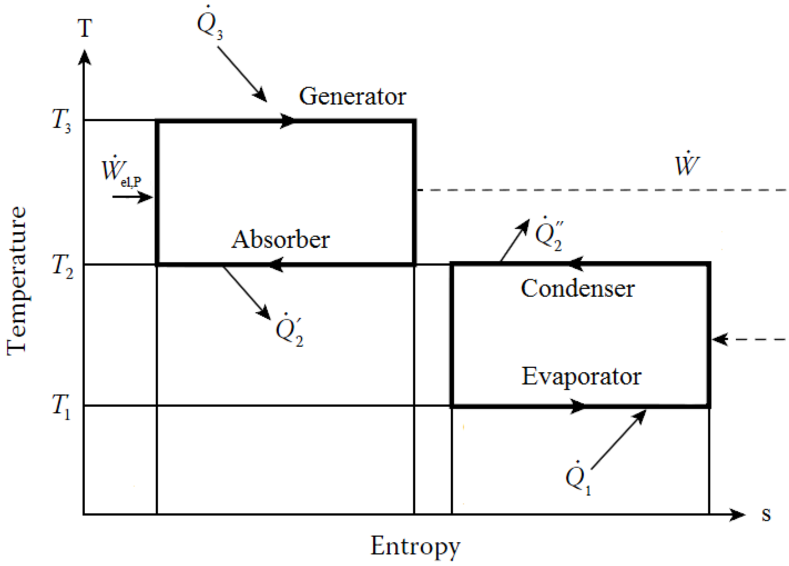

Figure 2.6.: Idealized representation of an absorption machine as the combination of a Carnot heat engine and a Carnot refrigeration cycle. *Source: Radermacher et al., 2016*

In this schematic representation of the Carnot absorption cycle three temperature levels are present: the highest temperature T_3 corresponds to the generator heat source, T_2 is the intermediate heat rejection temperature (or the hot output in heat pump case) and the lowest T_1 is the cooling temperature (or the cold source for heat pumps).

Performances The definition of Coefficient of Performance does not change, it is always the ratio between the useful effect and the input energy: although this time a precision on its calculation is needed.

Electrical energy and heat are two different kind of energy vector, with different associated entropy and therefore they cannot be summed while calculating the performance coefficient. This has even more sense from an economical point of view, the price of energy and heat is very different and in fact absorption machines are usually installed where a free-heat source is present. Therefore, the electric efficacy and the thermal COP need to be distinguished.

Thermal COPs In this case the useful effect is compared with the heat input Q_G:

$$COP_{th,R} = \frac{\dot{Q}_1}{\dot{Q}_3} = \frac{\dot{Q}_E}{\dot{Q}_G} \tag{2.15}$$

$$COP_{th,HP} = \frac{\dot{Q}_2' + \dot{Q}_2''}{\dot{Q}_3} = \frac{\dot{Q}_A + \dot{Q}_C}{\dot{Q}_G} \tag{2.16}$$

By assuming thermodynamic reversibility and applying the First and Second Laws these equations can be converted into expressions that depend only on temperature. The Carnot Thermal COPs result:

$$COP_{th,R,Carnot} = \frac{T_3 - T_2}{T_3}\frac{T_1}{T_2 - T_1} \tag{2.17}$$

$$COP_{th,HP,Carnot} = \frac{T_3 - T_1}{T_3}\frac{T_2}{T_2 - T_1} \tag{2.18}$$

Similarly to vapor-compression cycles, vapor-absorption systems can also be operated to provide simultaneous heating and cooling [52]. In this case the previous results become, remembering the general Eq. (2.8):

$$COP_{th,TFP} = \frac{\dot{Q}_2' + \dot{Q}_2'' + \dot{Q}_1}{\dot{Q}_3} = \frac{\dot{Q}_A + \dot{Q}_C + \dot{Q}_E}{\dot{Q}_G} \tag{2.19}$$

$$COP_{th,TFP,Carnot} = COP_{th,HP,Carnot} + COP_{th,R,Carnot} = \frac{(T_3 - T_1)T_2 + (T_3 - T_2)T_1}{T_3(T_2 - T_1)} \tag{2.20}$$

Relation between compression and absorption Carnot COP The vapor cycles share something more than a part of the architecture, as their Carnot cycles are strongly related. In fact, the absorption Carnot COP can be defined in all cases as the vapor-compression one with a generation penalty due to the presence of the motor cycle.

Recalling the Eq. (2.17), it is possible to write:

$$COP_{abs,R} = \frac{T_3 - T_2}{T_3}\frac{T_1}{T_2 - T_1} = \left(1 - \frac{T_2}{T_3}\right)\frac{T_1}{T_2 - T_1} = \frac{T_1}{T_2 - T_1} - \frac{1}{T_3}\frac{T_1 T_2}{T_2 - T_1} \tag{2.21}$$

Then, remembering the Eqs. (2.4), (2.6) and (2.7) about the vapor-compression COPs, the previous equation can be written in a different form:

$$COP_{abs,R} = COP_R - \frac{T_2}{T_3}COP_R = COP_R\left(1 - \frac{T_2}{T_3}\right) \tag{2.22}$$

The interesting point in this formulation of the absorption refrigeration COP is that knowing the working conditions of a conventional chiller and the temperature level of the available heat source, it is really easy to compare the respective vapor-compression and absorption ideal cycles.

In fact, usually T_2 for the chiller case is the ambient temperature, while for the heat pump it is normally T_1. The absorption heat pump COP can be obtained from the (2.22) using the (2.7):

$$COP_{abs,HP} = 1 + COP_{abs,R} = COP_{HP}\left(1 - \frac{T_1}{T_3}\right) \tag{2.23}$$

These results can also be applied to the termofrigopump. After some algebra, starting from Eq. (2.20) it is possible to obtain:

$$COP_{abs,TFP} = \frac{T_3 - T_2}{T_3}\frac{T_1}{T_2 - T_1} + \frac{T_3 - T_1}{T_3}\frac{T_2}{T_2 - T_1} = \frac{T_3(T_2 + T_1) - 2T_1T_2}{T_3(T_2 - T_1)} \tag{2.24}$$

With a last manipulation and remembering the Eq. (2.9) this equation can be expressed as a function of only vapor-compression COPs and T_3:

$$COP_{abs,TFP} = \frac{T_2 + T_1}{T_2 - T_1} - \frac{2T_1T_2}{T_3(T_2 - T_1)} = COP_{TFP} - 2\left(\frac{T_2}{T_3}\right)COP_R \tag{2.25}$$

What appears quite evident after these reformulations of the absorption Carnot COP is that a general absorption system behaves always worse than a vapor compressor one in the ideal case. Moreover, it is also clarifies the role of the generation temperature T_3 in the COP: the higher it is, the lower the generation penalty. Depending on the cases, this penalty varies from about 80% (T_1=12°C, T_2=25°C and T_3=80°C) to 60% (T_1=12°C, T_2=25°C and T_3=200°C). This leads to a particular interest in using hotter sources for the generation, as in the case of the multi-stage architectures presented in the Sections 2.2.2 and 2.2.3.

Electric efficacy Returning to the analysis of absorption cycle performance, for the electrical side the relations between useful effect and electric energy input can be written [53]:

$$\epsilon_{el,R} = \frac{\dot{Q}_1}{\dot{W}_{el,P}} \tag{2.26}$$

$$\epsilon_{el,HP} = \frac{\dot{Q}_2' + \dot{Q}_2''}{\dot{W}_{el,P}} \tag{2.27}$$

$$\epsilon_{el,TFP} = \frac{\dot{Q}_2' + \dot{Q}_2'' + \dot{Q}_1}{\dot{W}_{el,P}} \tag{2.28}$$

Unluckily, no temperature-related Carnot electrical efficacy can be provided, having electrical energy null associated entropy. Therefore, simulations are necessary to calculate the ideal electric efficacy, applying the previous general equations to a Carnot cycle.

Absorption Heat Transformer Even if the classical configuration of the absorption systems is the one shown in Figure 2.5, which can be operated both as a chiller or heat pump, there still exists another solution. In fact, the cycle can be reversed: the directions of all fluid streams and all energy streams are inverted and this requires just a little modification of the components (pumps and expansions valves must be provided of a bypass line).

This particular configuration called "Heat Transformer" is schematized in the Figure 2.7.

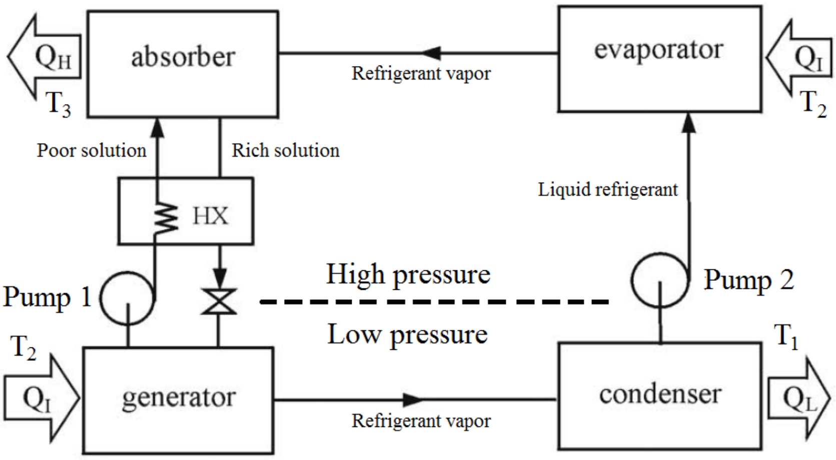

Figure 2.7.: Schematic representation of a heat transformer. *Source: Srikhirin et al., 2001*

In this case the source heat is provided at the intermediate temperature T_2, while the heat rejection occurs at the highest temperature T_3 and at the lowest temperature T_1: this last condition is quite critical because of the low temperatures required by the system, that may be incompatible with the ambient ones. The actual useful effect is thus the heat rejection at T_3.

The name of this cycle comes from the fact that the heat initially at T_2 is transformed in two different fluxes, one hotter and one colder: if comparing with the standard solutions, this cycle behaves like a heat pump, but with the fundamental difference that the output heat flux is hotter that the source one. For this feature this system is also known as "Heat Pump type 2" or "temperature booster" [46]. A thermodynamic analysis of the cycle can be performed observing the ideal Carnot cycle as in the previous standard absorption system case.

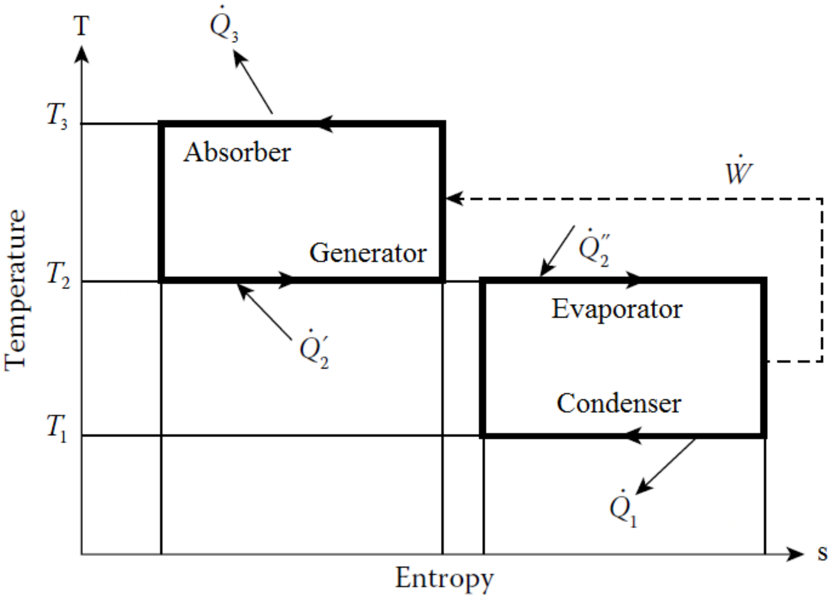

Figure 2.8.: Idealized representation of a Carnot heat transformer. *Source: Radermacher et al., 2016*

As visible in the Figure 2.8, the motor cycle is now represented by the condenser-evaporator circuit, while the absorber-generator one works as the heat pump. Having a such configured system allows waste heat of any temperature to be enhanced at a higher temperature level without any other energy input, except the little work needed to feed the two pumps [51].

The functioning is really similar to the classical absorption cycle, but reversed. The rich solution at low pressure receives some waste heat in the generator, the refrigerant evaporates and it goes towards the condenser; instead, the poor solution is pumped through the solution heat exchanger, reaching the absorber in a second time. The refrigerant vapor is then liquefied in the condenser, it is pumped and it reaches the evaporator: here a second part of waste heat is provided to the fluid, which returns in its vapor phase, but at higher pressure. Finally, the vapor enters the absorber, where it reacts with the poor solution rejecting some high temperature absorption heat to the external fluid. The resulting rich solution is sent again to the generator.

The thermal and electric performances can be calculated in a similar way than in the standard case, but remembering that now the useful effect is $\dot{Q}_3$ and the input energy is constituted by $\dot{Q}_2'$ and $\dot{Q}_2''$:

$$\epsilon_{el,HT} = \frac{\dot{Q}_3}{\dot{W}_{el,P1} + \dot{W}_{el,P2}} \tag{2.29}$$

$$COP_{th,HT} = \frac{\dot{Q}_3}{\dot{Q}_2' + \dot{Q}_2''} = \frac{\dot{Q}_A}{\dot{Q}_G + \dot{Q}_E} \tag{2.30}$$

Adapting the previous COP expression for the respective Carnot cycle, that means properly substituting absolute temperatures to flux variables, it results:

$$COP_{th,HT,Carnot} = \frac{T_2 - T_1}{T_2} \frac{T_3}{T_3 - T_1} \tag{2.31}$$

Finally, this last Carnot COP must be interpreted just as an upper bound on the system performance: in fact, it considerably over-predicts the real COP, even more than with chillers or heat pumps. However, as the driving heat is suitable to be at even lower temperature than in the standard absorption configurations, the interest in this systems remains [46].

What stated before about the differences between the real performance and the ideal one is due to the irreversibilites that occur in the process and sometimes heavily influence the functioning: giving some examples, boundary conditions force to operate between two determined temperature levels, components prevent ideal transformations and the practical necessity of having a reduced exchangers dimension obliges to accept a little temperature difference between the fluids during the thermal transfer, decreasing the performance.

To overcome these flaws two directions that can be followed are the research of better components, always closer to ideal behavior, and the study of new architectures able to internally recover the most energy possible. The third is the study of new fluids with better thermodynamic performances, a subject that is extremely interesting for absorption systems.

2.2.1. Fluids properties

The Carnot cycle performances analyzed previously, idealizing the best solution possible for certain external conditions, are independent from the properties of the working fluid in use. Therefore, the fluid is also idealized as the imaginary substance or mixture that allows each part of the cycle to have the maximum performance. However, reality is not so kind and existing fluids have a strong influence on system performance, determining also realization and operational costs.

In fact, desirable properties in an absorption working fluid are many, but sometimes they are also mutually exclusive. An example is the need for a high affinity between the absorbent and the refrigerant and a low heat of mixing: it is apparently not possible to find a fluid mixture that meets all of the criteria [46]. Thus, a compromise is needed to conciliate good proprieties for both refrigerant, absorbent and mixture.

Refrigerant properties The expected properties for a refrigerant fluid are normally related to the performance in the conventional part of the cycle: the lowest operational temperature and the mass flow rate are the main parameters to be considered.

High latent heat The conventional part of a vapor-based refrigeration cycle is founded on a double change of phase: depending on the configuration, chiller or heat pump, the useful effect is given by the absorbed or released heat during evaporation or condensation. Having a high latent heat allows less fluid to circulate with the same useful effect, as well as allowing lower pressure drops, better compactness and a littler work supplied by the pump.

Low freezing temperature As the refrigerant fluid is expanded to benefit of a temperature decrease, the colder is possible to perform its liquefaction, the wider its operational conditions will be. For this reason, it is not desirable to run into a solidification at low temperatures, otherwise a system jam will occur.

Moderate vapor pressure The vapor pressure or equilibrium vapor pressure is defined as the pressure exercised by a vapor that is in thermodynamic equilibrium with the condensed phase (solid or liquid) at a given temperature [54]. Normally, the condenser is fed with ambient-temperature fluids or, in the case of heat pumps, with an hot fluid. As condenser temperature is fixed, to liquefy the refrigerant the pressure has to be brought to the relative temperature-dependent limit value. If vapor pressure is elevated, a higher pressure will be necessary, with major resistance needed from each high-pressure side mechanical piece.

Low viscosity Viscosity is the fluid resistance to an instantaneous change of shape or arrangements of parts: it causes fluid friction whenever adjacent layers of fluid move with relation to each other. Moreover, as all the transport properties, viscosity is highly affected by temperature. Being the refrigerant normally in vapor phase its value is generally low, but problems can occur in the evaporator flow because after the expansion in the throttle valve the fluid may reach the subcooled liquid condition.

Absorbent properties In a first time, the absorbent is charged to capture the highest quantity possible of refrigerant, while after it has to release it in the most complete and pure way. Therefore, its volatility has the most important role.

Low viscosity Being absorbent a liquid, a different discourse about viscosity is needed with reference to the refrigerant: in fact, liquid viscosity is much higher than for vapor and has a significant impact on the design of solution components such as the pump, the absorber and the generator. The associated pressure head loss for a liquid fluid may be considerable, increasing the electrical consumption and deteriorating the system fluidodynamics.

No solid phase As already said about the freezing point for the refrigerant, also the absorber is desired to stay liquid. Certain elements, mostly metals or salts, can be solid at room temperature and liquid with a little temperature increase. Evidently, solidification would be a problem, jamming the component where it occurs with a consequent blocking of all the system. Therefore, the absorbent must be operated in a condition range where solidification is excluded: the operational range is affected, for example reducing the interest in cold environments.

Low vapor pressure The absorbent volatility has to be the lower possible, or at least low with reference to the refrigerant one: in fact, during the heating in the generator only the refrigerant is desired to evaporate, while the absorbent should stay in liquid phase. If this does not happen, allowing particles of the absorbent to separate and exit the component, a deterioration of the process happens. Avoiding this problem requires another component to realize the refrigerant purification, complicating the architecture and increasing costs.

Mixture properties Mixture properties are mainly related to the absorption process, while some constraints may appear. Also, the environmental and safety aspects are taken into account, preventing an accident to cause major damages.

High affinity between refrigerant & absorbent This propriety allows the refrigerant to be trapped in the absorbent for being further pumped. However, there is a physical limit for gas solubility in a certain liquid, depending on the characteristics of the two fluids in the mixture. When the molecules of a mixture do not interact significantly, that is, when there are not significant attractive or repulsive forces between the dissimilar molecules, then the mixture can approach the ideal behavior: the solubility is maximal and a low pressure is necessary to dissolute the gas. However, for most liquid mixtures the molecules interact significantly and real mixture effects must be considered, first of all the increase of the needed pressure. Moreover, when two miscible species are mixed, the resulting enthalpy is not generally equal to the mass weighted average of the enthalpies of the pure components, and an heat transfer occurs. For the most notable cases, ammonia-water and water-lithium bromide, a large exothermic heat release upon mixing is exhibited.

Low toxicity and environmental impact The hazardousness of a fluid is given by two main factors: the damage it can do to humans in case of exposition and the damages that will affect the environment in case of uncontrolled release. If for the first case safety systems and proper design can effectively limit the risk, for the second point it is more complicated: actually, it is still possible to recover liquids if they are confined in a closed space, but for gases it requires special and expensive equipment. Moreover, in case of leakages the substances will be permanently lost, so this is the true reason for using fluids with non-greenhouse gases properties, in a climate change fight vision.

Thermal conductivity The thermal conductivity is a physical property expressing the ability of a certain material or object to allow heat flowing through it by heat conduction. Therefore, the higher is the conductivity, the easier and more complete is the heat transfer. This property is most relevant when the two exchanging sides are still, while in moving conditions the convective heat transfer coefficient prevails.

Surface tension This property is defined as the force in a liquid surface that causes it to remain continuous by the attraction between the molecules of the liquid [33]. It is particularly important in the absorption process, as it is used to determine the minimum flow rate necessary to obtain an uniform liquid falling film on the exchanger surface.

Ending the presentation of fluid properties, a focus on phases equilibrium is necessary: what is delicate in this discourse is that mixture thermodynamics implies changes in the fluid mass composition, and it happens in the most accentuated way during phase changes. The mass proportion of the equilibrium phases is, in general, not constant and this characteristic is an important property in absorption cycle design: it partially explains the phenomenon of crystallization and the need of a purification step with volatile absorbents.

The bubble-point diagram is unluckily different for every mixture, but a general example as in Figure 2.9 is enough for the detail level of this discussion.

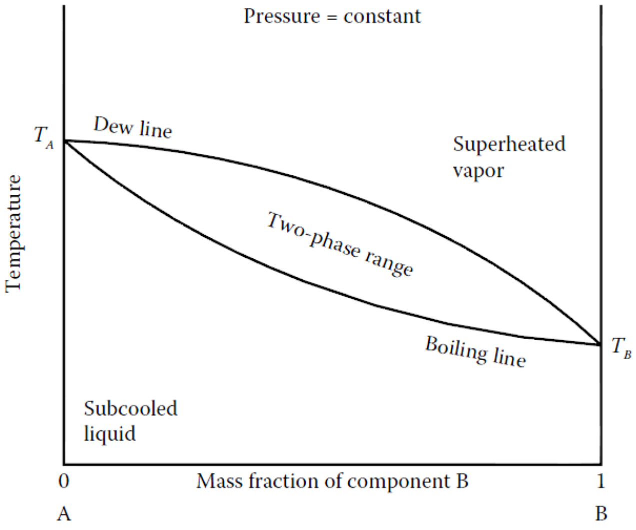

Figure 2.9.: Schematic of temperature concentration diagram (bubble-point diagram). *Source: Radermacher et al., 2016*

Knowing the characteristics that a good fluid pair must present in order to be considered effective in absorption machines, it is comprehensible why ammonia-water and water-lithium bromide have imposed as the conventional absorption working fluids[4].

Firstly, both of them have high latent heat, so a small flow rate is possible, and also they are environmentally friendly, not having greenhouse properties.

Secondly, ammonia has a low boiling point at atmospheric pressure (-33°C at 1 atm) that varies in general from 100°C to -75°C, while water can boil from 0°C to 374°C. Indeed, the biggest flaw of using pure water as refrigerant is the impossibility to perform negative cooling, as it freezes below 0°C, reducing the system operational range.

Finally, theviscosity of the two refrigerants, water and ammonia, is normally low. A little difference is present considering mixtures: at typical solution loop temperatures and concentrations the viscosity of water-lithium bromide is about 10 times larger than the ammonia-water viscosity. The larger viscosity of water-lithium bromide, still having an acceptable value, has a significant impact on the design of all the components in the solution loop. Instead, the thermal conductivity of the two mixtures is about the same.

Analyzing now the mixtures in a global way, H2O/LiBr shows a good combination of the vapor pressures of the two fluids, being the LiBr one almost negligible: the separation process is usually performing. Also, lithium bromide at room temperature and pressure exists in solid phase: this is at the same time an advantage, as it avoid toxicity for humans, and a disadvantage, as it limits operational conditions due to crystallization effects.

Instead, NH3/H2O has the point of allowing a wide operational range, but requiring an additional purification stage of the refrigerant mixture: in fact, vapor pressures of ammonia and water do not differ so much and water particles can easily evaporate during the separation process. Moreover, ammonia is slightly toxic for humans and water is known to be corrosive at hot temperatures and pressures, so an accurate design and material choice is necessary.

The Table 2.1 resumes the most important information about these two major mixtures.

Ammonia-water and water-lithium bromide are not the only fluids ever used for absorption refrigeration: over the years many other pairs have been studied and experimented. The most known are water-sodium hydroxide, water-sulfuric acid, ammonia-sodium thiocyanate, and many ternary mixtures. The results obtained with these different couples of fluids showed that ammonia is difficult to compete with as a refrigerant because of its very good and quite complete proprieties. Therefore, the efforts have been dedicated to the research of new absorbents: however, all the proposed fluids that offered some advantages on one side showed many other negative points.

For example, fluids such as lithium nitrate (LiNO3) and sodium thiocyanate (NaSCN) are interesting absorbents because they eliminate the need for rectification, having a lower vapor pressure than water [55]. Moreover, these two alternative absorbents allow to operate with lower generator temperatures, being higher the vapor pressure difference with the refrigerant, and to have better performances at negative evaporator temperatures. All this has a cost: in fact, viscosity turns to be important, forcing to higher pressure drops, higher circulation rates

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[4] The convention is to report the refrigerant followed by the absorbent.

Property	**Ammonia-Water**	**Water-Lithium Bromide**
Refrigerant		
High latent heat	Good	Excellent
Low freezing temperature	Excellent (-77°C at 6 kPa)	Poor (0°C at 0.6 kPa)
Moderate vapor pressure	Too high	Too low
Low viscosity	Good	Good
Absorbent		
Low vapor pressure	Poor	Excellent
No solid phase	Good	Poor
Low viscosity	Good	Medium
Mixture		
High affinity between fluids	Good	Good
Low toxicity	Poor	Good
Generated vapor purity	Poor	Excellent
Temperature range	-40°C/+20°C	4.5°C/+20°C
Cost [€/tonne]	400	6000

Table 2.1.: Absorption conventional mixtures properties

and a more powerful pump. To overcome this problem, and in general to pursue a further amelioration of the fluid performances, ternary mixtures have been investigated by many researchers, especially coupling two fluids as the absorbent.

Referring to the appreciable properties of lithium nitrate, the ternary mixture NH3-H2O-LiNO3 has been studied in order to reduce the absorbent viscosity with pure LiNO3, resulting in better COP with reference to NH3-H2O [56]. Also, the performance of an absorption heat pump operating with NH3-H2O-LiBr mixtures was investigated, and resulted producing a more pure vapor at the generator, but with a slightly lower COP than the NH3-H2O case [57]. Another fluid studied for the same application has been the NaOH, with a COP increment of 20%.

H2O-LiBr cycles have been the object of many experiments to reduce crystallization risk and to improve absorption efficiency: for this last purpose, H2O-CHO2Na-LiBr and H2O–LiBr–CHO2K were recommend by comparing the mass transfer characteristics of H2O vapor absorption into LiBr and organic salts of sodium and potassium. Also, H2O–LiBr–LiI–LiNO3–LiCl was recommend due to less corrosivity and a crystallization temperature about 35°C lower than that of H2O–LiBr [58].

Another family of fluids that have been investigated is the alcohols: in fact, they offer a high thermal stability, a high output temperature and a satisfying pressure–temperature–concentration diagram. However, most of them have the same toxicity as NH3.

Finally, to exploit low temperatures provided by solar collectors (40–60°C) other exotic mediums have been tested, as acetone–ZnBr2 and halogenated hydrocarbons.

The principal characteristics of the most promising ternary mixtures are listed in Table 2.2.

Table 2.2.: Alternative binary and ternary mixtures physical properties description.

Fluids	Advantages	Disadvantages
NH3 – NaSCN (Sodium Thiocyanate)	No rectification Favorable pressures Good solubility in NH3 Not corrosive Better COP	High viscosity Risk of crystallization
NH3 – LiNO3 (Lithium Nitrate)	No rectification No crystallization Favorable pressures Good solubility in NH3 Not corrosive Lower generator temperatures Better COP	High viscosity
NH3 – H2O – LiNO3 (20-25% of water in the absorbent)	Low vapor pressure Low rectification needed Higher transfer coefficients & less viscosity than binary mixtures	Higher generator temperature than binary mixtures
H2O – CHO2Na – LiBr	Good thermodynamic properties Better absorption efficiency Low toxicity Non-flammability	
H2O – LiBr – LiI – – LiNO3 – LiCl	Higher COP Lower generator temperature	Less corrosivity than LiBr – H2O

The reason why none of these alternative mixtures gained a market foothold is that the property combination exhibited by the conventional pairs, ammonia-water and water-lithium bromide, is hard to compete with. In general, proposed alternatives may address one weakness of the conventional fluids while contributing several additional weaknesses of their own. Therefore, using alternative fluid mixtures is restraint to specialized application, where the granted particular advantages are more important than the related weaknesses.

For the economical and technical current opportunity, meaning waste heat availability and the need in a versatile and performing device, ammonia-water is chosen for the study. Also, this is a quite known mixture whose proprieties have been studied and modelized, so the development of new components and architectures can effectively take advantage of it.

Inversion curve

A quite useful property to know for ammonia-water mixtures is its Joule-Thomson (JT) coefficient. In fact, in a context of performance optimization it is required a more detailed comprehension of throttling thermodynamic effects. The Section 3.3.2 will further discuss this interest, however the main objective is to avoid thermal degradation during the cycle: the fluid expansion is often a cause of temperature decrease, but it is not inevitable. There exists some thermodynamic regions where this effect is less sharp and knowing them is necessary to take advantage of. A chart or diagram about this effect would be really useful to graphically individuate these areas, helping the design.

However, data about Joule-Thomson coefficient of ammonia-water mixture is not abundant, due to the relative interest in this kind of absorption machines and because the expansion in a throttling valve is not usually a critical passage in such systems. Moreover, prediction in ammonia-water behavior during an expansion process is not trivial: mixture thermodynamics implies changes in composition of the system, especially during the phase change as reported in the Figure 2.9. This adds a relevant complexity to the Equations of State: if normally they are relationships between pressure, volume, and temperature, in the mixture context this concept must be generalized to include composition as a variable.

When two miscible species are mixed, the resulting thermodynamic properties is not generally equal to the mass weighted average of the volumes of the pure components. Mixtures where such a simple relationship does hold are termed ideal mixtures: unluckily, ammonia-water behaves like a real mixture. This is caused by the presence of a certain chemical potential, due to the interaction between the mixed fluids, defined as a component of the mixture Gibbs free energy. It causes properties as enthalpy, entropy and volume to vary from the ideal case and, although it is defined in terms of Gibbs free energy, chemical potential is also a key variable in defining phase equilibrium in mixtures. In this context, the chemical potential is found to be as important as the temperature (thermal potential) or pressure (mechanical potential) in understanding mixture thermodynamics [46].

This complexity in determining mixture physical properties makes data about ammonia-water Joule-Thomson coefficient scarce. Therefore, to draw the necessary diagrams for individuating the expansion-favorable regions a numerical approach is employed.

The software EES is chosen for this task. It can rely on a REFPROP set of correlations for determining all the properties for a certain ammonia-water mixture: for a given input condition defined by three parameters, EES is able to calculate all the remaining properties.

The provided thermodynamic properties are: temperature T, pressure P, concentration x, enthalpy h, entropy s, internal energy u, specific volume v and vapor quality q.

First of all, the Joule-Thomson coefficient has been defined:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \rightarrow \mu_{JT} \simeq \left(\frac{\Delta T}{\Delta P}\right)_H = \left(\frac{T_b - T_a}{P_b - P_a}\right)_H \tag{2.32}$$

Then, a model has been set-up to complete the following steps:

1. For a given input concentration x_i, assume a pressure value P_i in the range 0.1 to 100 bar;

2. For the chosen pressure, assume a temperature value T_i in the range -50 to 250°C;
3. Calculate the enthalpy h_i of the considered point;
4. Calculate the temperature T_i' of a point with pressure $P_i' = P_i * 0.95$, same concentration x_i and enthalpy h_i;
5. Calculate the $\mu'_{JT,i}$;
6. Calculate the temperature T_i'' of a point with pressure $P_i'' = P_i / 0.95$, same concentration x_i and enthalpy h_i;
7. Calculate the $\mu''_{JT,i}$;
8. If $\mu'_{JT,i} * \mu''_{JT,i} < 0$ then the considered point at conditions (T_i, P_i, x_i) is an inversion point. Otherwise, T_i must be augmented of a temperature step dT, assumed to be 1°C;
9. Once arrived to the maximum temperature in the range, augment the pressure P_i of a pressure step dP;
10. Finally, once reached maximum pressure it is necessary to update the concentration.

The resulting curves divide the upside region, with positive μ_{JT} and so unfavorable expansion conditions, from the downside one which has a favorable negative μ_{JT}.

The diagram in Figure 2.10 is useful to evaluate the effects of a concentration change in the expanding fluid and to individuate ideal expansion temperature-pressure ranges.

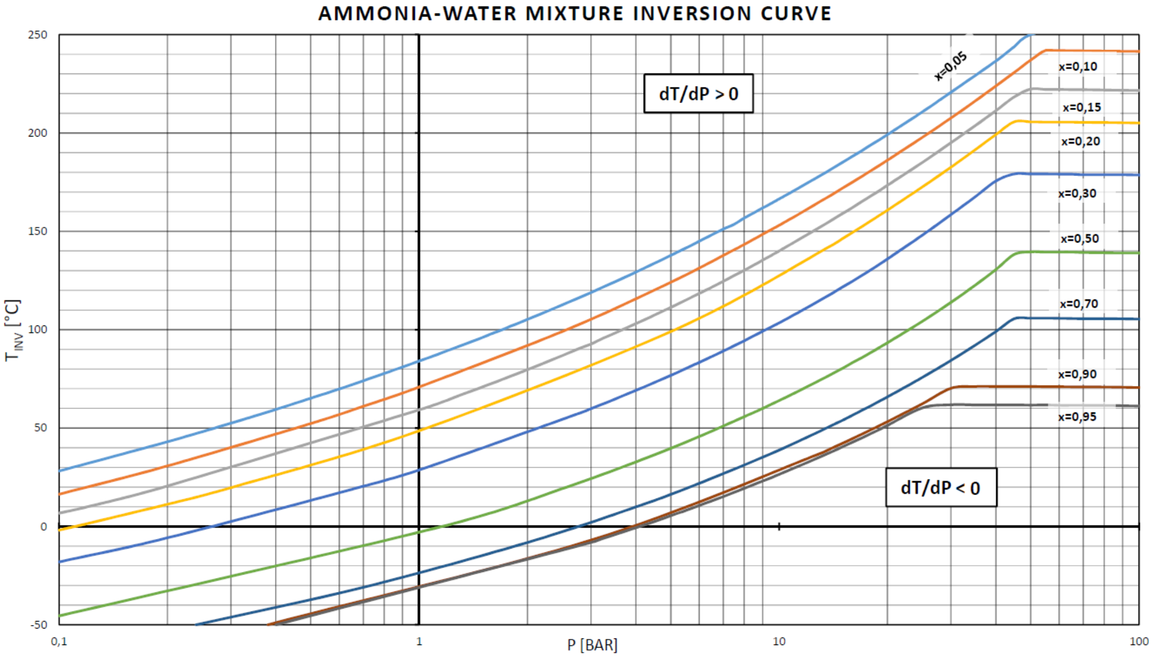

Figure 2.10.: Inversion curve for ammonia-water mixtures in -50/250°C & 0.1/100 bar range).

The position of the inversion curves changes with the concentration: for higher ammonia ratios the limit goes downwards in temperatures, reducing the favorable region for the expansion. However, this criteria gives back a warning that JT coefficient is changing, but without indicating its magnitude.

More information about JT effect intensity is needed, as a trade-off might be a solution for low JT coefficients. Knowing that the expansion is isoenthalpic, a diagram T-p for a certain concentration is drawn. Isoenthalpic lines are drawn, together with saturation vapor and liquid curves. The flatter the line, the more isotherm is the isoenthalpic expansion between two given pressures. Instead, the steeper the line, the higher the JT coefficient. The Figure 2.11 shows a T-p diagram for a $x = 0.20$ ammonia-water mixture.

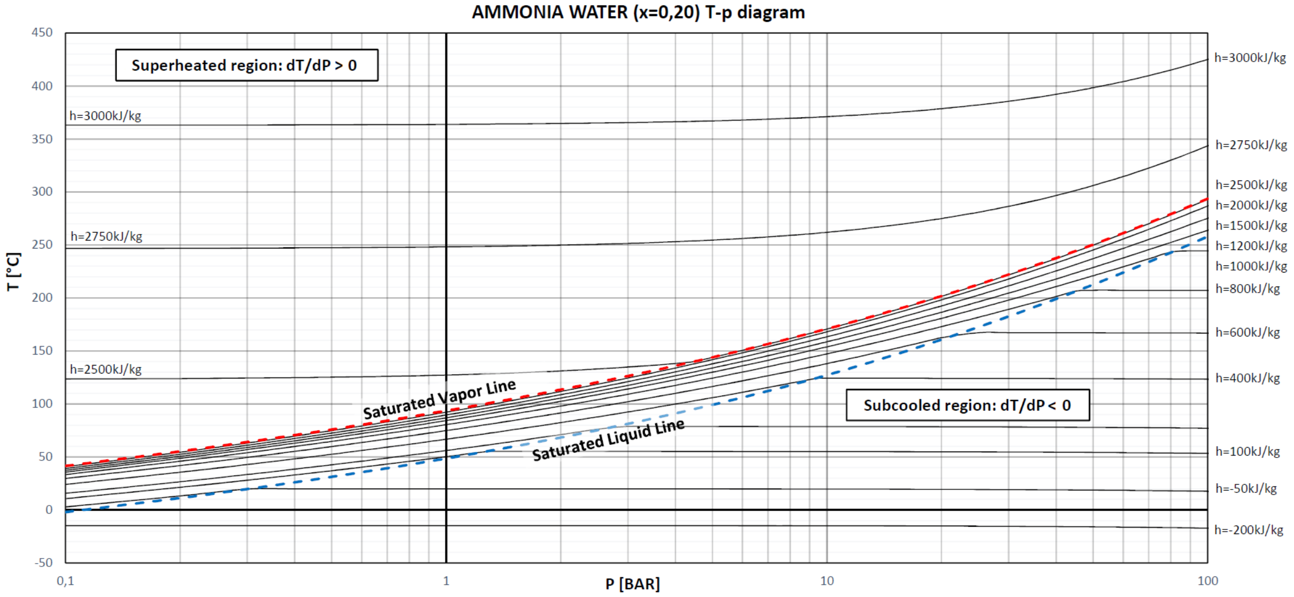

Figure 2.11.: T-p diagram for an ammonia-water mixture (20% ammonia mass concentration).

The final observation about these diagrams is that for an ammonia-water mixture at a certain concentration the inversion curve coincides with the Saturated Liquid Line, so the area with a negative and heating (favorable) Joule-Thomson coefficient is the Subcooled Region. Vice versa, the phase transition area has very positive JT coefficients, producing an intense fluid cooling. The Superheated Region, despite having positive JT coefficients, shows lower slopes of isoenthalpic curves and can be taken into account for the expansion. Higher quality diagrams can be found in the Annexes B.1 and B.2.

2.2.2. H2O/LiBr cycles

Water-lithium bromide absorption cycles are perhaps the simplest absorption systems currently available [46] and also the most diffused ones in the world: therefore, being the main competitors of the ammonia-water systems, they deserve a particular analysis.

The water-lithium bromide cycle dates to the 1950's, when it was introduced as a refrigeration cycle for industrial application. A few years later, a two-stage absorption system was developed for higher performance, becoming soon the industrial standard for heat-operated refrigeration [59]. The interest in the water-lithium bromide cycle has been renewed in these days because of the possible coupling with solar energy [60], as it could be operated with low temperatures at the generator: in fact, even low-cost solar collectors are suitable to be used to power the machine, reducing the overall initial investment. In parallel, multiple-stage technology has progressed increasing COPs, but being able to be utilized only when higher temperature heat sources are available. Triple effect systems can be achieved by adding an extra stage as a topping cycle on the double effect cycle, and four-effect cycles can similarly be obtained. In this way, the heat rejection from the highest temperature level is used in a cascaded way to power the lower temperature stages.

Single-effect H2O/LiBr systems

The single-effect[5] absorption cycle has the simplest architecture in the family of H2O/LiBr systems. Its components are those of a standard absorption machine: absorber, generator, condenser, evaporator, solution pump and two throttle valves, one for the refrigerant and one for the poor solution. As reported in Figure 2.12, just two pressure levels appears, determined by the condensation and evaporation temperatures.

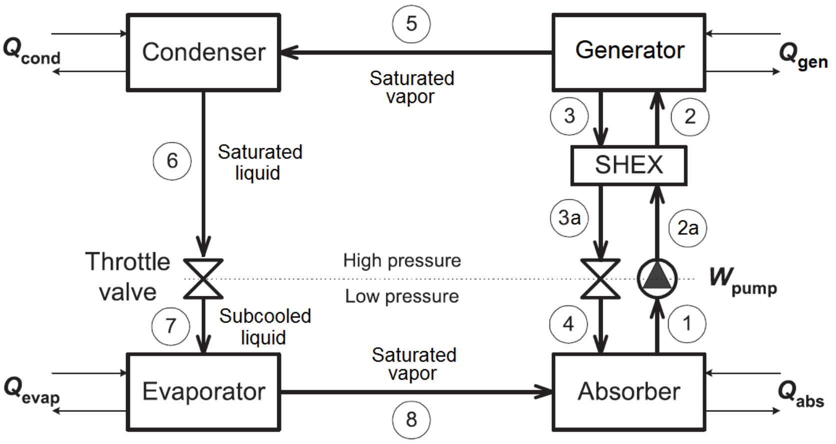

Figure 2.12.: Water-Lithium Bromide single-effect absorption cycle scheme. *Source: Gong S., Boulama K.G., 2014*

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[5] For water-lithium bromide cycles the words stage and effect are commonly used as synonyms when describing the architecture type. That does not apply to the case of ammonia-water cycles.

The solution heat exchanger (SHEX) is the characteristic element of LiBr absorption systems: it is designed to increase the efficiency of the unit. Although not being essential, it allows excess energy to be extracted from the poor solution, coming back to the absorber, and to be transferred to the solution flowing towards the generator, where it will be heated until the evaporating point [61]. The greater the heat exchanger area is, the greater its recuperation effect. However, this is also one of the most vulnerable elements in the systems. Crystallization normally happens here due to air leakage or to a sudden stop of the cycle operation: without a preventive dilution of the rich solution the crystallization point may be reached during the cooling of the fluid, with a consequent jam of the whole unit.

Due to the physical properties of the fluid pair, the H2O/LiBr cycles are typically operated in the following conditions: the low-pressure side is almost in vacuum, kept below 10kPa of pressure to allow water evaporation at low temperatures, while the high pressure side can feature various bars of pressure; high LiBr concentrations are avoided and fluids are forced to stay in a certain range, 45 to 75% LiBr with typical max concentration around 65% LiBr [46]; finally, the generator temperature ranges between 50 and 120°C, with appreciable results already after 75°C. Concluding this overview, the performance of the single effect absorption technology is relatively low, providing a peak cooling coefficient of performance (COP) of approximately 0.7: on the other side the system remains little and simple.

An interesting economical analysis about single-effect water-LiBr absorption system was done by Florides et al. in their work [59]: a 1kW prototype was built, with a total construction cost of 4800 USD[6]. Nevertheless, a large part of this amount was spent for the required auxiliary equipment like vacuum pumps, glass tubes etc., for purchasing flow meters and to conduct experimentation with different types of valves and materials. Neglecting these additional expenses, cost could actually be lowered to about 2500 USD. In addition to this, cost was shown to reduce with the machine size increase: a 10 kW unit, able to cover the needs of a typical insulated house, was estimated to cost 6500 USD. However, the price of a single-effect H2O/LiBr absorption system still showed unable to compete with a similar capacity electric chiller costing only 2500 USD.

Double-effect H2O/LiBr systems

The natural development of the single-effect absorption cycle is the double-effect H2O/LiBr cycle: such a modification of the system was though to take advantage of higher temperature sources, who allowed higher pressures and, in theory, better performances. The first double-effect unit was developed by Southwest Research Institute in 1956-58 with funding from the American Gas Association [60]. This systems proved to be much more competitive and now they are the standard for gas-driven cooling and are produced by a large number of manufacturers worldwide [46].

This configuration features three pressure levels instead of two: in fact, two condenser are contained in the high pressure side, resulting in two different condensation conditions. Also, two generators are set in place to perform twice the desorption of the refrigerant: the name *double effect* refers to the fact that the highest temperature heat input is used twice during

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[6] The real cost was 3000C£ (Cypriot pound) in 2002, when the exchange rate was 1C£ = 1.6 USD.

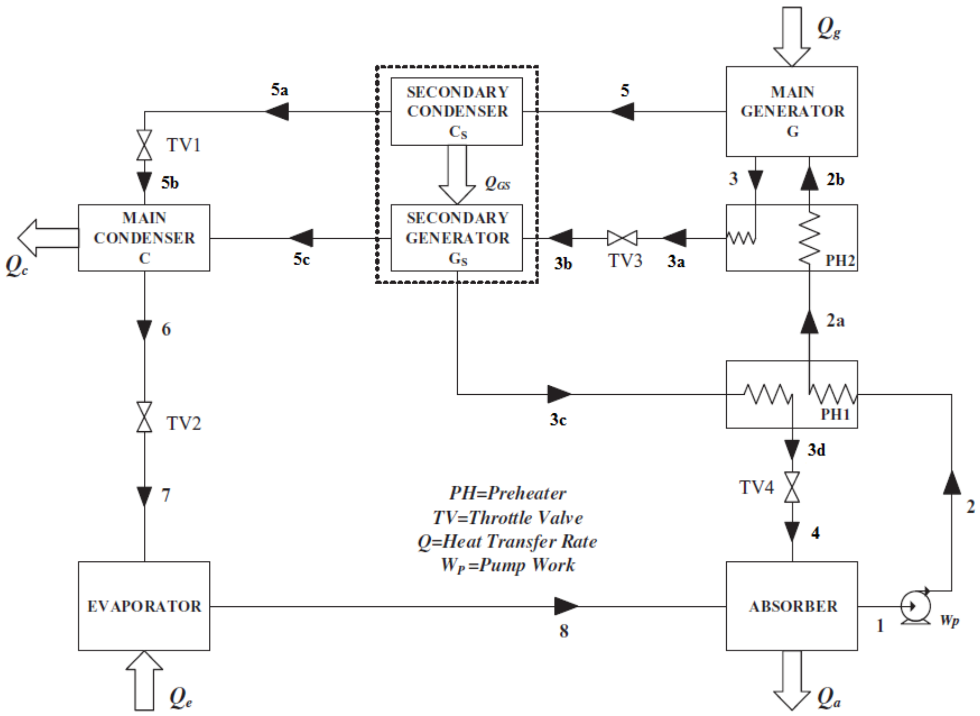

Figure 2.13.: Water-Lithium Bromide double-effect absorption cycle scheme. *Source: Azhar M., Siddiqui M.A., 2016*

the cycle to generate refrigerant vapor. The highest pressure zone includes the following state points: 2-2a-2b-3-3a-5-5a; the intermediate pressure involves instead: 3b-3c-3d-5b-5c-6; the rest lies at the lowest evaporator pressure, almost vacuum.

As Figure 2.13 details, the Main Generator receives a double-preheated rich solution (2b): this is heated at the highest temperature T_G and a part of the refrigerant is evaporated (5). The impoverished liquid fraction (3) is sent to the Secondary Generator, after being passed through an expansion valve reaching the intermediate pressure (3b): this element is fed with the Secondary Condenser condensation heat, operating at higher temperature and pressure. The second refrigerant evaporation is then performed in the Secondary Generator (5c) and the final poor solution (3c) is sent to the absorber. Two additional solution preheaters PH1 and PH2 are placed before the Main Generator, with the same role and problems of the Solution Heat Exchanger in the single-effect cycle.

The high-pressure liquid refrigerant (5a) is then expanded in an expansion valve and joins the intermediate-pressure vapor refrigerant in the Main Condenser (5c): they are both condensed (6) and the resulting fluid enters the conventional refrigeration part of the cycle. It ends with the return of the refrigerant to the absorber.

Working with two high pressure and temperature levels allows to do a fractional separation of the refrigerant, recovering some enthalpy in the Secondary Generator & Condenser: this brings to a better and deeper refrigerant evaporation, increasing the concentration ratio between rich and poor solution. Therefore, decreasing the global flow rates, efficiency increases.

An analytic estimation of double-effect system COP is given by Srihkrin et al. [51], knowing that an absorption machine can always be decomposed into a series of basic stages, which are just single-effect machines in different operational conditions. The useful effect of the main generator is, assuming to be in a single cycle, $1 * COP_{single}$. For any single-effect absorption system, it may be assumed that the heat rejected from the condenser is approximately equal to the cooling capacity obtained. Thus, considering having a secondary generator, the heat supply to this new element is $1 * COP_{single}$.

The cooling effect produced from the second-effect generator now is $(1*COP_{single})*COP_{single}$. Therefore, the COP of the whole double-effect absorption system is the sum of the COP related at the refrigerant produced by the Main Generator, plus the refrigerant produced by the Secondary Generator: $COP_{double} = COP_{single} + (COP_{single})^2$.

According to this analysis, a double effect absorption system has a COP of 0.96 when the corresponding single-effect system has a COP of 0.6: a value that is consistent with Kurosawa and Yoshikawa [62] and Wilkinson [63] estimations, who calculated the double-effect COP in the range of 1.0–1.4. Other theoretical studies of a double-effect absorption system have been provided for various working fluids, showing encouraging coherent results [64, 65].

Finally, to obtain better and more reliable performances in real conditions numerous models have been constructed, exploiting also innovative software and techniques: Azhar and Siddiqui [66] modelized a temperature-and-pressure optimized cycle reaching $COP = 1.7$, while Somers et al. [67] proposed a validated modeling methodology for single and double-effect water-lithium bromide absorption cycles implemented in ASPEN.

The proved convenience in increasing maximum pressure and performing fractional generation stimulated the research in this direction: several types of multi-effect absorption cycles were developed, from *half*-effect to *n*-effect to *1.n*-effect [68]. In particular, triple-effect and four-effect absorption cycles were built and experimented [69]. However, an improvement of COP is not directly linked to the increment of the number of effects. It must be noted that, when the number of effects increases, COP of each effect will not be as high as the one for a single-effect system, adding each time a littler improvement. Moreover, the higher number of effect leads to more system complexity and a bigger cost. Therefore, the double-effect is the only water-LiBr multiple-effect system largely available in the market [70].

2.2.3. NH3/H2O cycles

The ammonia-water cycle is the second major family of absorption systems: originally, the application was just refrigeration because LiBr could not reach negative temperatures, but the reversible characteristic of the NH3/H2O machine made interesting heating and heat transformation also. Ammonia characteristics, roughly presented in the Section 2.2.1, are responsible of the checkered development of this kind of systems, initially promising but soon replaced by more performing cycles: therefore, a brief insight is needed.

Ammonia properties Ammonia is a substance naturally present in the environment, produced and used in large quantities: in agriculture as fertilizer, in industry as a component for explosives, plastic and fibers, but also in food transformation and for cleaning applications. Therefore, it is a commercially diffused product.

At normal conditions, ammonia presents as a colorless gas, lighter than the air with a molecular mass of 17.03 kg/kmol: it can be liquefied with a pressure of about 10 bar (1 MPa) and its critical point is 132.3°C and 113 bar (11.3 MPa). Its boiling point at atmospheric pressure is -33°C, while freezing can occur at about -77°C and 0.06 bar (6 kPa) [46, 71].

Ammonia corrosivity is one important flaw of this element, because it excludes copper as manufacturing material: in fact, NH3 is a very good solvent for copper making problematic the use of any copper-containing alloy. Even chromium-plated brass parts, as well as weldings, are susceptible to ammonia corrosion. Carbon steel is the most common substitute in this case, and nickel-based weldings are needed to resist corrosion. The problem with carbon steel is that water at high temperature and pressure becomes corrosive as well: stainless steel is required and brazing is the standard method to ensure tightness up to 25-30 bar.

Although being suitable to ammonia-water fluid pair, stainless steel has thermal conductivity about one-tenth that of copper. As a result, the heat transfer resistance of the wall material plays a larger role in heat exchangers design: more surface is required and therefore cost increases.

As ammonia and water have high vapor pressures, NH3/H2O cycles are not really susceptible to performance degradation due to the presence of non-condensable gases. These gases can come from the outside (i.e. leakages into the evaporator if operating in vacuum conditions) or from the inside, like the oxygen released during materials corrosion. However, it is good practice to keep all these undesired elements out of the system [46].

The disadvantage of having high vapor pressures is that generator vapor contains a little percentage of water, requiring purification. One way of reducing the H2O content of the refrigerant is to use rectification or dephlegmation, two characteristic processes that constitute the practical difference with water-lithium bromide architectures.

Finally, an interesting property of ammonia is that it has a strong and pungent odor that can be seen as a safety asset since it is self-alarming: even very small leaks in the system are easily noticed thanks to its irritating smell. Being toxic, a more scientific method of leakage detection is to use wet indicator paper that change of color while reacting with ammonia: in this way, even coupling with simple safety systems, users risks can be drastically reduced.

Application areas The difference in utilization domains with reference to H2O/LiBr Absorption Refrigeration Systems (ARS) are due to NH3/H2O ARS ability of providing very low refrigeration temperatures (down to -60°C), compact unit size due to the low specific volume of NH3 operating at high pressures, trouble-free operation with no risk of crystallization and cycle reversibility. Solar applications are investigated as well, being possible to produce cooling and heating thanks to cycle reversibility: during winter, solar panels can be used to generate heat for direct heating or for feeding an absorption heat pump (or even an heat transformer); during summer, when the solar heating is not needed and the solar potential is quite high, the cycle can be used for refrigeration. This will actually justify the huge investments made on solar panels, the system not remaining idle during its peak producing times.

Having a wider operational conditions range makes these systems suitable for refrigeration in trawler chiller fishing vessels, for food engineering processes and also in desalination systems, which are highly energy-intensive [72]. In particular, freshwater demand has gradually increased due to population growth and lifestyle improvement, and refrigeration and air-conditioning demand are expected to raise as well in hot environments, as Spain and the south of Europe. Desalination and refrigeration, two essential products in these areas, can be provided through a single combined system instead of separate, low-efficiency processes.

Improvements Being the COP and the cost the two main obstacles to ammonia-water systems diffusion and being not able to decrease costs, many advanced cycles have been studied to improve performances of single-stage cycles: now they come in different variations and implementations, with optional components or even with additional stages. Ejectors and compressors have for example analyzed as ways to improve absorption increasing pressure in the absorber, while recently an absorption-resorption cycle has been developed by Berdasco-Ruiz using polymeric membranes to increase the heat and mass diffusion efficiency [73].

Two-stage ammonia-water absorption systems have been introduced in the past to offer the potential for increased efficiency (coefficient of performance) or increased temperature lift (difference between lowest temperature and the heat rejection temperature). In general, the term “two-stage” for ammonia absorption systems refers to the inclusion of two solution circuits, so these cycles can be thought of as being composed of two single-stage units. The term “double-effect” refers to a configuration in which a certain quantity of heat is used twice to generate refrigerant vapor, therefore to obtain a better efficiency [46]: this is the typical case for heat pumps or chiller in normal condition. Instead, the term “double-lift” is used to indicate that the goal is increasing the temperature lift[7], therefore this is mostly the case of low-temperature chillers operating in non-favorable external conditions.

A tradeoff between two-stage and single-stage systems was introduced in 1911 by Altenkirch and Tenckhoff [74]. The concept of GAX, acronym for Generator-Absorber heat eXchanger, was created for achieving higher effect performance with a relatively simple cycle configuration: in fact, it appears to be a single-stage configuration while taking advantage of two-stage characteristic. This system is the heart of this work and is better detailed in the Section 2.3.

Finally, Devault and Marsala developed an ammonia-water two-stage, triple-effect cycle [75]. Although showing promising performance, possibly reaching COP over 1.5, the architecture resulted quite complex.

Single-stage NH3/H2O systems

Single-stage ammonia-water systems are really similar to the already discussed water-lithium bromide ones: the main difference is the presence of a refrigerant purification stage after the generator, due to a little percentage of water in the vapor (about 5%) after the generation. This element is shown in the Figure 2.14 just above the generator.

This element operates a partial cooling of the outlet vapor mixture, condensing a fraction of it and therefore reducing the refrigerant flow rate towards the condenser: the global efficiency of the cycle is affected, slightly decreasing. The geometry of the rectifier is also schematized in the Figure 2.14, representing the vertical development of the element: in fact, generator and

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[7] The temperature lift is defined as the difference between the evaporator and the external rejection temperature.

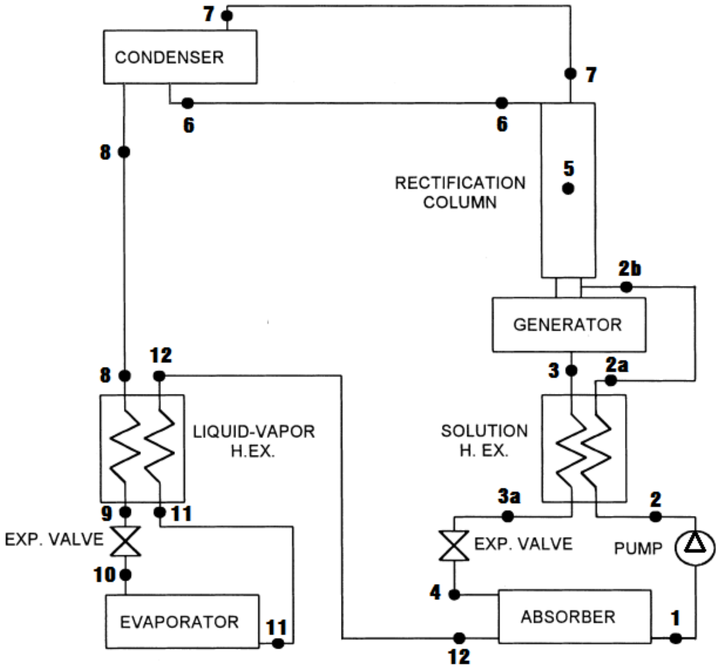

Figure 2.14.: Ammonia-water single stage absorption cycle. *Source: Fernandez-Seara, Vazquez, 2000*

absorber are usually designed as distillation columns to exploit falling film heat and mass exchange and to take advantage of fluid stratification. Therefore, these two components normally results bulky.

The cycle thermodynamic transformations do not differ at all from the LiBr case, except for the rectifier, so what detailed in the Section 2.2.2 can still be applied to this case. Instead, it is interesting to analyze the modeling of the NH3/H2O cycle that constitutes the reference for the design of real systems.

In general, ideal cases are modelized to compare different architectures at a macro-scale, neglecting the majority of the loss factors. However, more detailed models are used to evaluate realistic performances, taking into account a certain number of assumptions: in this way the influence of internal and external parameters can be precisely analyzed, together with the positive or negative interactions between themselves. Parametric analysis are usually conducted to this scope.

The most common assumptions for single-stage ammonia-water absorption cycle models are the following [46, 76, 77]:

- steady state operation;
- no heat loss in components and in pipes;
- no pressure drops;
- no concentration changes in the pipes;
- saturated liquid exiting condenser;
- saturated vapor exiting generator;
- exchangers effectiveness as 0.8;
- absorption efficiency as 0.8;
- pump global efficiency as 0.7.

The typical input parameters are:

- generator inlet temperature;
- evaporator outlet temperature;
- condenser inlet temperature;
- absorber inlet temperature;
- exchanger minimum ΔT;
- evaporator cooling load;
- generator inlet flux;
- rich solution mass flow rate;
- rectification ratio RT.

Therefore, through a parametric analysis the effects of the variation of a single parameter on the system can be observed. As the major challenge for this system is to improve efficiency, the results are usually referred to COP, increasing or decreasing, but other outlet variables or effects can be studied, too.

Effect of exchangers effectiveness The exchanger effectiveness is a parameter that indicates how much of the maximum heat is actually exchanged by the two interfacing fluids: normally it depends from a lot of factors, as fluid properties, component materials, geometry and flow rates. Moreover, exchangers usually require a minimum temperature difference between the two fluids in each part of them: this condition is necessary to contain the components dimensions, otherwise an almost infinite exchange area will be needed. Concluding, improving exchanger effectiveness, by an efficiency increase or lowering the minimum ΔT, improves the COP: in fact, the system will approach a bit more to the Carnot cycle, which features unitary exchanger efficiency and no negligible ΔT required for the heat transfer. However, improving this parameter in reality usually means increasing cost, needing better manufactured, high-performing components.

Effect of Condenser temperature The condensation temperature has two main effects: varying pressure on the high-pressure side and varying inlet temperature of the refrigerant in the precooler. As increasing pressure of the generation side brings some benefits in refrigerant vapor purity, on the other side a hotter fluid entering the evaporator demands a higher flow rate. These effects compensates and the COP experiences minor variations. Instead costs change: lower condensation temperature allows lower pressure, so less constraints on the components and less material to ensure resistance.

Effect of Absorber temperature The absorption process, being exothermic, shows better behavior at lower temperature conditions. The saturation point varies its refrigerant concentration direct proportionally to pressure and inversely to temperature. Therefore, low temperatures and high pressures are preferable. With a deeper and more complete absorption the solution flow rate decreases, strongly improving the COP.

Effect of Evaporator temperature The evaporator temperature has the principal effect of determining the lower pressure value: therefore, in simple-effect cycles, a lower evaporator temperature decreases the COP. Also, if vacuum conditions occur, cost increases due to the necessity of assuring tightness.

Effect of Generator temperature The generator temperature is a very influencing parameter and, perhaps, the most variable one: it can depend from the heat source, and in this case is independent, or it can be specifically adjusted by a control system. Determining the effects of its variations is not evident, but experimental studies and researches showed that all cycles have a temperature that maximizes the COP [77]. This value, called Optimal Generation Temperature (OGT), can be influenced either by design parameters (components efficiencies, distillation column reflux ratio, pressure drops, evaporator temperature difference, etc.), or by the thermal operating conditions (evaporation, absorption and condensation temperatures): therefore it is characteristic for each cycle configuration and external input values, and complex control strategies are developed to maintain the generator temperature as close as possible to the OGT.

Due to real, non-steady conditions of the external sources and the difficulty to predict the OGT, absorption machines usually operate out of their design point: the COP usually sets out of the optimum. As a consequence, an important amelioration point for ammonia absorption systems is increasing cycle robustness, making COP more stable against little parameter variations.

To increase the overall performance of simple-effect ammonia cycles different approaches have been tried. However, all measures that lead to performance improvements have a common feature: they are based on thermodynamic losses minimization, and the simplest way to accomplish this task is reusing waste heat within the cycle. New components, especially economizers, and architecture modifications are required to perform this "internal heat exchange": precooler, solution heat exchanger (SHEX), recirculations and heat integration are well known solutions in this sense. The SHEX has already been analyzed in the H2O/LiBr section, and the condensate precooler has the same function, but on the refrigerant side: a part of the condensate heat is transferred to the evaporated fluid entering the absorber. The vapor having higher enthalpy, this leads to increased absorber heat transfer and theoretically a bigger size. However, a lower evaporator temperature finally requires less flow rate for the same cooling effect, with a net performance benefit. An important difference with vapor compression chillers exists: in fact, in absorption systems an ideal condensate precooler always improves the COP, while in standard systems its benefits are often overwhelmed by performance penalties in the compressor.

A second precooler benefit has to do with the temperature glide in the evaporator: in fact, even a little percentage of water causes a high temperature glide if trying to get a fully saturated vapor at the outlet. The best option for dealing with this phenomena is to accept some liquid at the evaporator exit and then evaporate it in the precooler.

Finally, with reference to LiBr systems, ammonia-water ones are more suitable to a precooler because of the higher pressures: therefore, sensitivity to pressure drops is much lower.

Rectification is another process where heat harvesting is easy: as the fluid exiting from the generator is really hot and that rectification temperatures are generally about 75-95°C, it is possible to perform this transformation using some rich solution exiting from the absorber. The recuperated heat reduces the energy input in the generator. On the same principle, the higher, hotter part of the absorber can be cooled by the rich solution just exiting from its bottom, remembering its distillation-column geometry. A double positive effect is obtained: absorption process is improved thanks to the cooling, and a decrease of generator heat input is achieved raising the rich solution temperature. Therefore, using internal fluids to partially cool some suitable components is an effective and easy-to-implement way to increase COP.

The solution recirculation is the last of the three main internal heat exchange mechanisms: in the generator, the exiting poor solution may be heated again at low temperature to better exchange in the SHEX. In the same way, the absorber can be cooled by its own outlet rich solution, but without needing a specific exchanger: usually these recirculations are done by an internal coil. Even if the recirculation effect depends on the architecture used, a sensible improvement can be obtained: in the case of generator recirculation, COP can be increased of the 12.5%, with a decrease of 30% of the SHEX heat load, and a further 11% reduction of both the absorber heat rejection and the desorber heat requirement [46].

All this results, from the parametric study to the system modifications, contributed to the development of single-stage ammonia-absorption cycle: nevertheless, performance in classical application conditions remains below 0.75. Even not being really performing and quite costly, this system has been practically applied: small-capacity units for residential to small commercial air-conditioning (17 to 105 kW) are manufactured by Robur Co., while larger capacity refrigeration plants are produced by Energy Concepts Co.[8] (280 kW at -30°C and COP of 0.45) and Colibri bv[9] (320kW at -9°C with a hot water source of 93-82°C).

Bigger size applications have been also studied in the literature [78], notably by Kalinowski et al. [79] who showed that 5.2 MW waste heat could be recovered from a 9 MW gas turbine to generate cooling with a COP varying between 0.41 and 0.47: this evaluation seems to be coherent with the previous data, even if performances strongly depend on the cycle design and the refrigeration temperature. Baxter Engineering Ltd. is currently commercializing ammonia-water systems for the same purpose[10].

Single-stage NH3/H2O Heat Transformer Heat transformers have been quickly presented in the Section 2.2, where the principal characteristics have been discussed: above all stands the pure heat upgrade from an intermediate temperature to a higher temperature without requiring any other input energy deeply differentiates these systems to conventional absorption cycles. In fact, normally the heat pump hot output is not the hottest fluid in the cycle, as a higher temperature heat source is required.

However, what has not been told yet is that many fluids are suitable for the goal: almost all the fluid pairs that are suitable for conventional absorption systems can be used quite effectively in heat transformers. In all cases, the advantages and disadvantages listed in the Section 2.2.1 remain valid. For this purpose water-LiBr has been the most investigated couple so far, demonstrating the possibility to achieve COPs in excess of 0.5: despite this, the classical problems of corrosion, viscosity and crystallization limits the operational range and thus the Gross Temperature Lift (GTL) achievable.

Ammonia-water properties appear to be interesting in this sense, being able to work with lower temperatures (no crystallization risk) and to provide higher temperature lifts: the COP is slightly worse, but considering that the input heat is likely to be waste heat (therefore free), this point is not so critical.

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[8] http://www.energy-concepts.com

[9] http://www.colibri-bv.com

[10] http://www.baxterenergy.com/

A new parameter called Gross Temeprature Lift is needed to qualify this system's performances: it is defined as $GTL = T_{w,out,ABS} - T_{w,in,GEN+EVA}$ and it represents the temperature increase between the heat source fluid and the output fluid temperature. Its importance is evident as heat transformers are used to boost waste heat to a higher temperature level, the higher the GTL, the better the effect.

The architecture of an ammonia-water heat transformer is schematized in Figure 2.15.

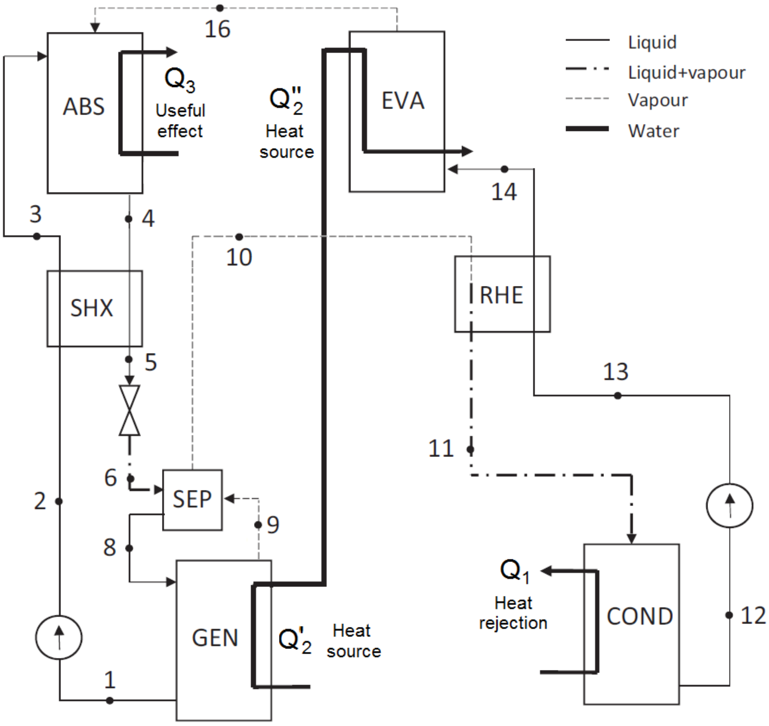

Figure 2.15.: Single-stage ammonia-water heat transformer cycle. *Source: Garone et al., 2017*

The thermodynamic cycle involves the same components of the standard absorption cycle, but reversed in their position and role. The first difference concerns the pressure levels: in fact, the generator and the condenser operate at the lowest pressure, while the absorber and the evaporator at the highest one. This is exactly the opposite than the normal situation.

The cycle starts in the generator, where the liquid rich solution (8) is heated by the intermediate temperature heat source $\dot{Q}'_2$: the refrigerant evaporates (9), while the poor solution (1) is pumped (2) trough the solution heat exchanger (SHX) reaching the high-pressure absorber (3).

The refrigerant vapor (9) undergoes a sort of rectification in the separator tank, then the moves towards the Re-Heater (10), it cools down (11) and it is liquefied in the condenser, rejecting heat to the environment. The liquid refrigerant is now pumped (13), it heats in the Re-Heater and reaches the evaporator (14), when it is heated again by the external source $\dot{Q}''_2$. The resulting high-pressure vapor is sent to the absorber (16), where it reacts with the poor solution coming from the generator.

In the absorber, the reaction of absorption happens at high pressure and temperature: thus, the cooling fluid can be heated considerably, obtaining the useful effect $\dot{Q}_3$.

The saturated rich solution (4) is then sent to the solution heat exchanger (5), it is expanded and sent to the separator tank: the remaining liquid fraction (8) finally flows in the generator, making the cycle start again.

Some prototypes have been constructed during the last years, a notable case is the one realized by Garone et al. in 2017: it reached a COP_{th} of 0.35-0.47 and a ε_{el} of 18-50 with feeding waste heat of 60-64°C and a GTL up to 25°C [80]. Being able to work with condensation temperatures of 8-16°C, it demonstrated being suitable even for winter conditions.

Two-stage NH3/H2O systems

As introduced before, two-stage ammonia-water systems are the direct evolution of single-stage ones: however, staging can be used for two mutually exclusive purposes, efficiency improvement (i.e. COP) or to increase the temperature lift. Therefore, the most important two-stage ammonia-water cycles can be classed in double-effect, double-lift and triple-effect. A particular case of extreme interest is the single-stage, double-effect cycle, also known as GAX cycle.

Two-stage, double-effect system A double-effect system essentially is composed by two solution circuits side-by-side, but operating in slightly different conditions. The refrigerant exiting the precooler is split and sent to the two stages: each one is composed by absorber, desorber[11], solution pump and solution throttle valve. The conventional part of the system (condenser, throttling valve, evaporator) does not change, receiving the two vapor streams in the condenser, producing the cooling effect and feeding again the two absorbers. In general, the stage fed with external heat is enumerated "2" and the other one, fed with internal heat only, is labelled "1".

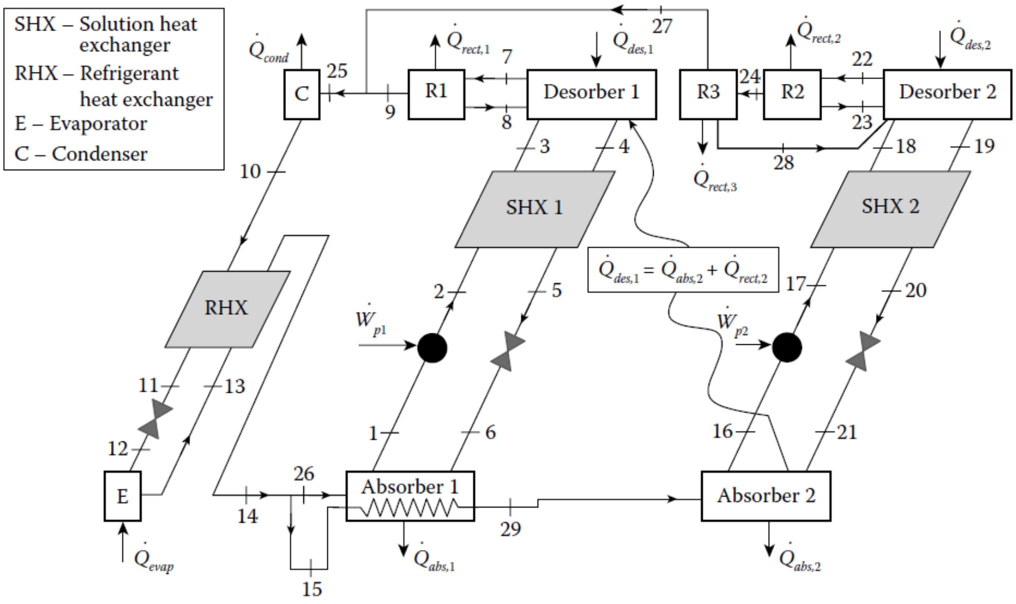

Figure 2.16.: Two-stage, double-effect ammonia-water absorption cycle. *Source: Herold et al., "Absorption Chillers and Heat Pumps", 2016*

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[11] Desorber is another name for the generator, as the desorption is the opposite of the absorption reaction.

Therefore, the Desorber 1 is supplied by the combined heat rejected by the Rectifier 2 and the Absorber 2, recuperating a considerable part of Desorber 2 input energy: the second effect consists exactly in the further utilization of this heat flux (coming from Rectifier 2 and Absorber 2) to perform another desorption, made thermodynamically possible by a higher temperature level in the Desorber 2. Instead, the condensation temperature stays quite low, so it can not be recuperated.

Compared to the double-effect water-lithium bromide system shown in Figure 2.13, that has three pressure levels, the ammonia-water double-effect has only two. However, it can be arranged in a three-pressure configuration in the same manner as the water-lithium bromide system, but the outer circuit would experience extreme pressure conditions due to ammonia high vapor pressure.

An interesting consideration about this systems is that the lower stage works generally well, while the upper stage contributes only a modest increment in performance: a big performance penalty results from the large water content of the vapor leaving the high-temperature Desorber 2, which finally produces only about 30% of the refrigerant vapor flow [46].

The considerable water percentage in vapor exiting the outer desorber causes also control problems during the machine operation, as to reach the steady-state all parameters have to be constant in the two circuits: this is prevented by vapor concentrations that are different and unbalanced. This point is usually solved introducing a bleeding line between the two circuits: the rectification process is simplified and performances result even better.

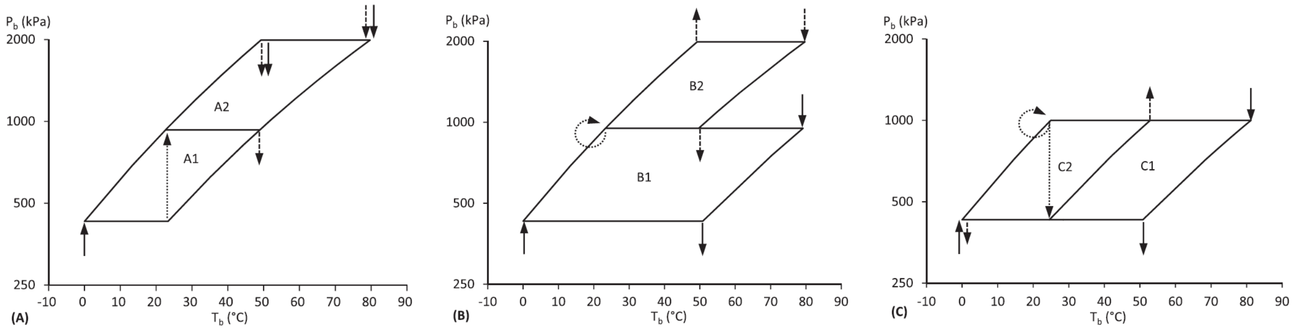
This side-by-side cycle shows only a modest improvement in performance over a single-stage cycle, despite requiring a more complex architecture. However, its theoretical importance is great because it created the basis for the GAX development.

Two-stage, double-lift system In single-stage ammonia-water chillers, air-cooled heat rejection implies the raise of condenser and absorber temperatures with the growth of the ambient one, creating the need for higher driving heat temperatures, usually well above 100°C: the introduction of an outer loop decreases the generator temperature, allowing, for example, solar powering [81]. Problems occur also at low-temperature applications, where it can happen that the solution field is too narrow to accommodate a single-stage ammonia-water cycle at the required heat rejection temperature. In both cases heat rejection to the environment is the problem: lower temperature for the sinks are required. Therefore, double-lift cycles are designed to make the absorption systems suitable for extreme conditions by the introduction of a second solution loop.

Alefeld and Radermacher have described the three conventional double-lift cycles [82].

The pressure-staged cycle (2.17a) can be seen as the cascade of two single-effect refrigeration cycles, A1 and A2, where the evaporator of A2 is thermally coupled to the absorber of A1, who rejects there its excess heat. Also, having a lower temperature, the absorber A1 can produce a more refrigerant-rich solution, increasing the efficiency of the low pressure circuit. The overall thermal COP can be estimated like $COP_{TH,R}/(1-1/COP_{TH,R})$.

In the vapor-exchange cycle (2.17b) the concept is cooling the lower pressure circuit (B1) condenser by releasing heat to the the higher pressure loop (B2) evaporator, at lower temperature: being the environment hotter than the B1 condenser temperature, heat rejection would not be possible otherwise. In this case, the overall thermal COP is $COP_{TH,R}/2$.



(a) Pressure-staged (type A). (b) Vapor-exchange (type B). (c) Resorption (type C).

Figure 2.17.: Two-stage, double-lift conventional cycles. *Source: Aprile et al., 2015*

Both A and B cases operate at three pressure levels, and as shown in the Figure 2.17, the secondary cycle experiences really high pressures.

Finally, an interesting double-lift cycle operating at lower pressures is the resorption cycle (2.17c). It has just two pressure levels and it can be seen as the superposition of a classical absorption refrigeration cycle (C1) and a heat transformer cycle (C2), in which C1 condenser heat is rejected into the C2 desorber: this last is operated at a suitable temperature (lower than the ambient) to be the condenser thermal sink. The overall thermal COP is $COP_{TH,R} * COP_{TH,HT}$. According to this simplified cycle analysis, the vapor-exchange cycle (B) promises to reach the highest thermal COP, but also the highest pressures [83]. Vice versa, the resorption cycle (C) is appreciated for its the relative simplicity, even with worse performances. More detailed examples for the three cases are reported in the Annexes C.1, C.2 and C.3.

Two-stage, triple-effect system As told in the paragraph about double-effect NH3/H2O systems, the realization of a three pressure level cycle like the LiBr one is possible [84]: the wide solution field of ammonia-water mixture can accommodate unusual cycles with high COPs, for example the most famous Kangaroo cycle. Two single-stage absorption cycles are nested, the smaller one inside the larger external circuit. That can remind the double-lift vapor-exchange cycle (B) which operated with 2 low temperature heat sources, but here is the difference: within the triple-effect cycle there is just one high temperature heat source, all the effects base on heat recuperation from other components. In fact, thanks to the highly exergetic input, absorber and condenser of the outer stage operate at sufficiently elevated temperatures so that their heat rejection can be used to drive the the inner cycle desorber. Thus, one unit of input energy is used three times to produce cooling capacity: the first time in the external generator, the second in the condenser feeding the inner generator and the third time in the external absorber, always feeding the internal generator.

A system based on this triple-effect concept was patented by DeVault [85]: it was estimated to have 18% higher cooling efficiency (COP = 1.41 compared to COP = 1.2 for a double-effect) and lower pressure (701 psi instead of 1000 psi)[12]. In addition, pumping power was significantly reduced (less than 50% that of the double-effect cycle) and potentially construction cost was expected to be lower, due to 33% less total heat exchange needed [75].

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[12] Pressure conversion: 100 psi = 6.89 bar

Single-stage, double-effect system

A particular improvement of ammonia-water absorption cycles comes from a further development of the two-stage, double-effect architecture as suggested by Altenkirch at the beginning of the 20th century. Theoretically, for a given mass flow rate in the system the two solution circuits 1 and 2 experience certain inlet and outlet temperatures: now, assuming an arbitrary reduction of the solution pumps flow rates and keeping constant all the external parameters, to keep constant the fluxes in the two circuits the involved temperature glides must increase. The new situation can be idealized as the dashed lines suggest in the Figure 2.18.

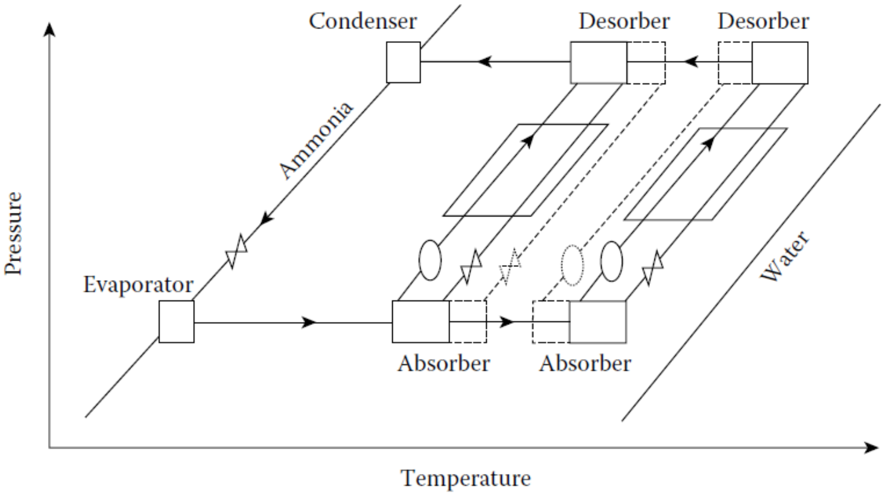

Figure 2.18.: Schematic of a two-stage, double-effect cycle approaching to GAX configuration. *Source: Herold et al., "Absorption Chillers and Heat Pumps", 2016*

Decreasing the rich solution flow rate step by step, the colder, inner cycle temperature 1 and the hotter, outer cycle temperature 2 will eventually coincide: therefore, it can be imagined that the two dotted lines completely disappear, originating the concept of GAX.

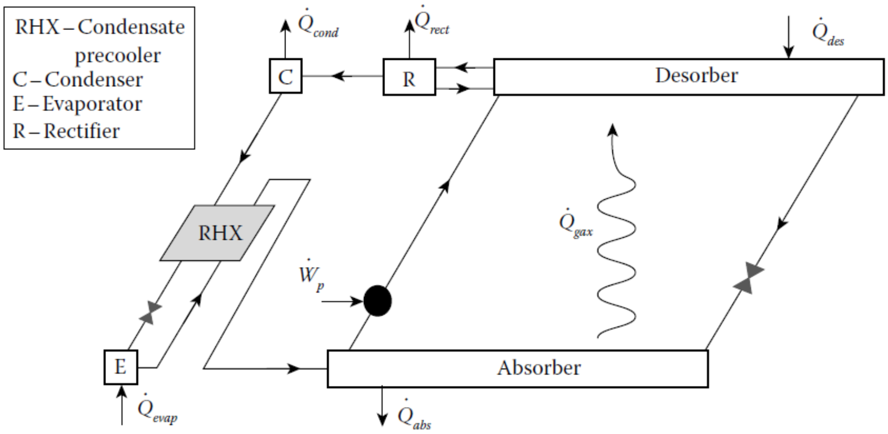

Figure 2.19.: Schematic of the final GAX configuration. *Source: Herold et al., "Absorption Chillers and Heat Pumps", 2016*

The internal heat exchange before done between the Absorber 2 and the Desorber 1 is still present, but in a hidden way: now, the hotter part of the absorber[13] exchanges heat with the colder part of the desorber, similarly reducing the net input energy need. The temperature level of the heat source however rests elevate. Thanks to this concept, a part of the absorber heat is transferred to the generator, hence the name Generator-Absorber heat eXchanger (GAX).

This cycle has different peculiar characteristics, as it exploits twice the input heat, being thus "double-effect", but it performs all that within a single solution loop remaining single-stage. Having a relatively simple heat recovery principle and a higher COP with reference to single-effect, single-stage systems makes this cycle really interesting for high temperature applications. Moreover, the reduced number of components with reference to two-stage, double-effect solutions makes it less costly. For these reasons the GAX is the best tradeoff between a cheaper, less performing single-effect system and an expensive, more efficient two-stage, double-effect cycle.

Advanced architectures for NH3/H2O cycles

The ammonia-water cycles introduced in the previous paragraphs give a wide overview of the current technological advancement, having been studied, and often built and tested during the past years. As a result, the simple increase in the number of stages and effects seems not a viable way to get a further improvement due to costs and complexity, justifying the raise of the GAX cycles as the actual best tradeoff for the NH3/H2O fluid pair.

This means that something in the cycle improvement approach has to change: arranging in a cascaded way many cycles does not work anymore, the solution might be changing the cycle itself. Effectively, a component variation has been already proposed for the GAX cycle, with promising results.

Thinking about the classical single-stage cycle, an improvement direction appears quite evident: if the rich solution was able to carry more refrigerant, the global performance would increase. In fact, the cooling (or heating) is generated by the refrigerant flowing in the conventional part, while the absorbent does not provide an useful effect itself: however, it heats in the generator and this has an energetic cost. Therefore, the less absorbent circulates, the less heat is wasted.

In standard cycles the absorption reaction is limited by three factors: the fluids nature, the cooling temperature and the evaporation pressure. The first parameter cannot change, as it is assumed that ammonia-water is the chosen fluid pair; the second parameter may change, but it depends from external conditions, so it is not really controllable (unless using groundwater); the third parameter is the one to be modified.

Hybrid cycle The simplest way to increase pressure is, of course, using a compressor: the saturated vapor coming from the evaporator can be increased in pressure, decoupling the absorber from the evaporator low pressure. In this way, optimal absorption conditions can be provided, varying the pressure ratio as required: by consequence, an additional electric energy

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[13] Remember that in the P-T-x diagram the higher temperatures are on the right and the oblique lines represent constant concentration processes.

consumption is necessary. Such absorption cycles involving a compressor are normally called hybrid systems, as they use both vapor-refrigeration techniques (compression and absorption) to produce the useful effect. The Figure 2.20 details graphically this solution: to note that the one in the figure is a GAX cycle, as the Hybrid-GAX is the most convenient application for the compressor in ammonia-water cycles (+20% COP with reference to single-stage systems [86]), but the same modification can be applied to a single-stage system.

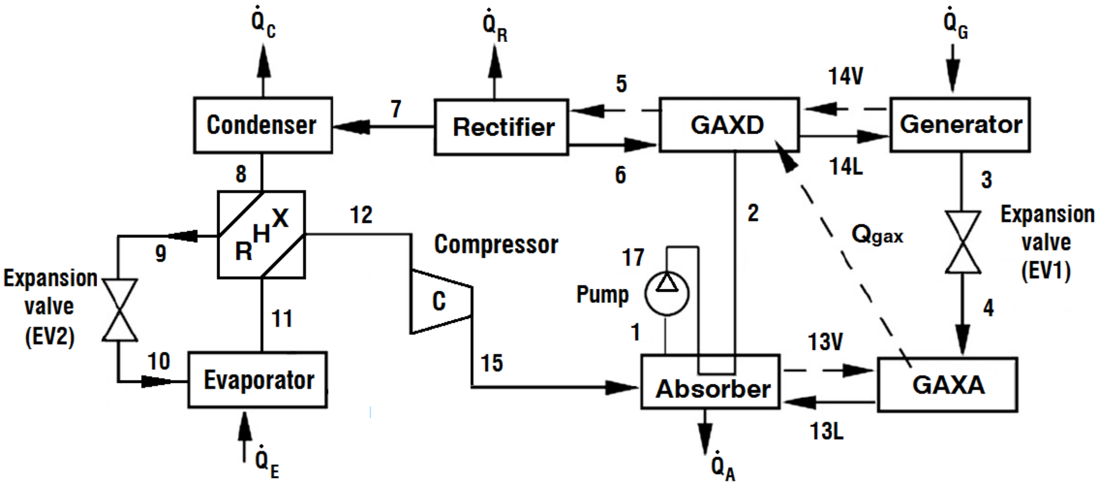


Figure 2.20.: Schematic of the Hybrid-GAX cycle. *Source: Dixit et al., 2015*

Using a compressor right after the evaporator has another advantage besides improving the absorption reaction: in fact, as the evaporation temperatures are pushed to extreme negative values, as -40°C or below, the required pressure for the process to happen begins to be below 1 bar. This means, for the whole low-pressure side of the machine, vacuum operation with all the related problems: the evaporator, one pre-cooler side, the absorber and the GAXA must be airtight, complicating the design.

The compressor avoids all this: the only component to operate in vacuum condition is, in the case, the evaporator. This means three pressure levels, but in an extremely convenient way.

Finally, another point has to be faced and it is the performance calculation. In fact, an additional electric consumption is needed to operate the compressor, so the electric efficacy results:

$$\epsilon_{el} = \frac{Q}{\dot{W}_{el,P} + \dot{W}_{el,C}} \tag{2.33}$$

with Q being the cooling or heat pump useful effect.

As the electrical consumption is directly related to the pressure ratio, as stated in the Eq. (2.11), a tradeoff between increase in COP and decrease in the ε has to be found: relying on a hybrid system allows more refined control strategies depending on the economical constraints and the sources availability.

Ejector cycles The ejector is a mechanical component that uses a high-pressure fluid to drive a low-pressure fluid, mixing them and obtaining an intermediate pressure at the output. This component is interesting because it has no moving parts at its interior: as the pressure increase is reached without mechanical work, this device is also called thermo-compressor.

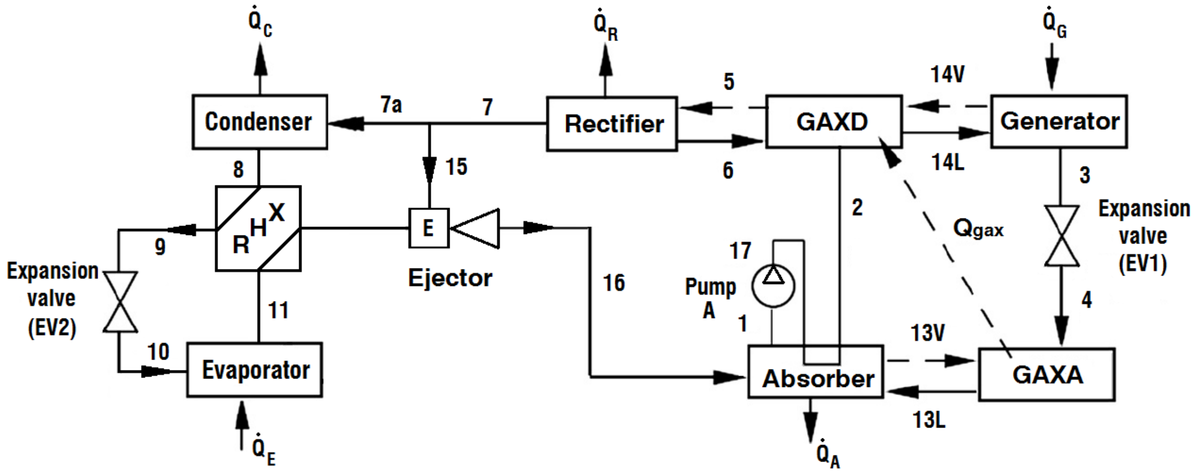


Figure 2.21.: Schematic of the Ejector-GAX cycle type A.

The Figure 2.21 proposes to employ the ejector to increase the absorber pressure, as in the hybrid absorption cycle. This time no additional electrical energy is required, but the heat duty in the generator increases due to the additional recirculation flow. The global COP is expected to increase thanks to the pressure increase in the absorber, but the optimum functioning point is not evident to reach.

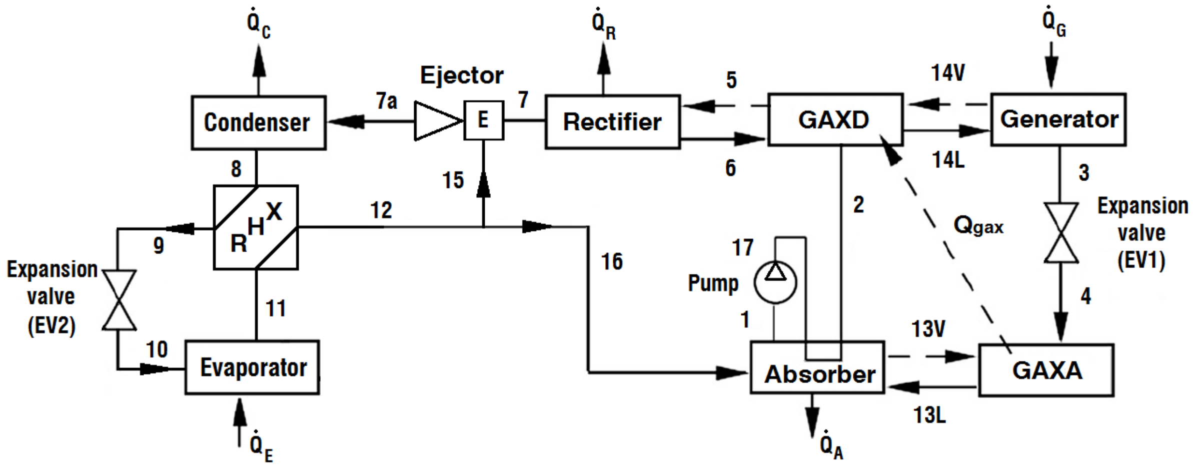


Figure 2.22.: Schematic of the Ejector-GAX cycle type B.

Another way to increase performances through the use of this component is recirculating some vapor coming from the evaporator: the Figure 2.22 shows this solution, that takes advantage of the already available refrigerant before it admission in the absorber.

In this way all the flow exiting the rectifier acts as the driving fluid, being able to drag much low-pressure vapor with just a tiny pressure lost: for a part of the refrigerant the absorption-desorption process is avoided, reducing the flow rate in these components. Globally, it results advantageous to run the high-pressure side at a slightly bigger pressure to save some ready-to-use refrigerant, as the COP increases of about 20% with reference to a standard GAX cycle [87].

The use of the ejector is often associated with the GAX cycle as it offers a great effect while coupled with this architecture, but the same principles can be applied to the standard single-stage cycles. Also, an Ejector-GAX type B version using a compressor instead of the ejector has been tested: it is called Hybrid-GAX model B and shows similar performances.

Branched-GAX cycle If the previous three solutions are more or less suitable to any ammonia-water absorption cycle, the following improvement is not, as it is only applicable to GAX architectures. In fact, there exists another solution to increase the performance while using a GAX cycle: maximizing the internal heat recuperation.

Knowing that the GAXA, the highest temperature part of the absorber, is responsible to the heat transfer to the GAXD, it is desirable to increase its available heat. The more heat is generated by the absorption in this section of the absorber, the more heat can be provided to the generator, with a consequent reduction of the external energy need.

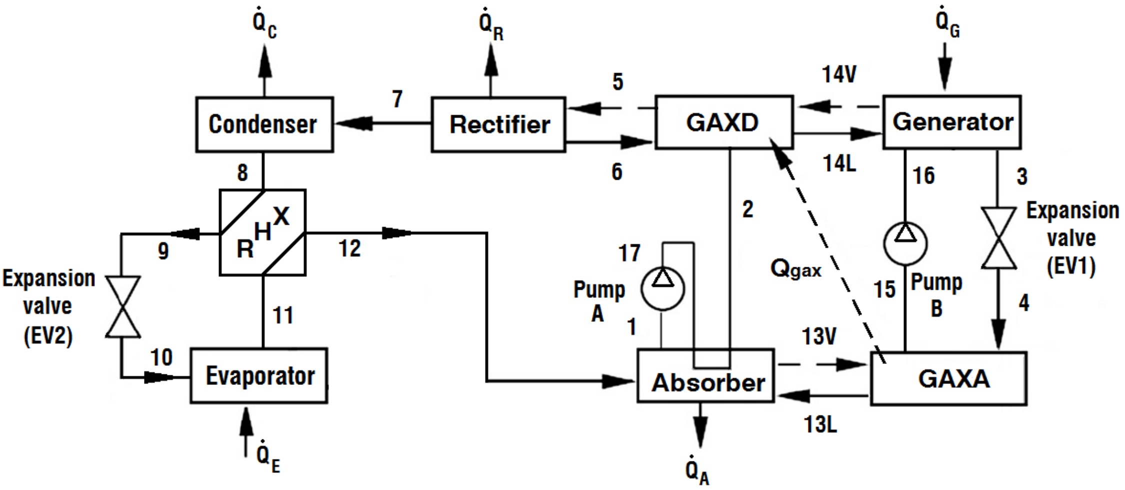


Figure 2.23.: Schematic of the Branched-GAX cycle.

The absorption reaction is exothermic with fixed energy release per unit mass: if more heat is needed, more reacting mass should be provided. Therefore, the solution circulation is boosted between the generator and the GAXA. At the bottom of this last element the solution is slightly enriched in refrigerant, but is still able to perform absorption at a lower temperature: although, in this situation its absorption heat would not be recuperated. Therefore, just a part is sent to the absorber to continue the cycle as in the standard GAX, the rest is directly sent to the generator by the Pump B (detail in Figure 2.23).

Then, the slightly enriched solution is heated at high temperature and the refrigerant is separated as usual: the poor solution returns to the GAXA and the cycle starts again. This sort of bypass allows to have more poor solution circulation in the GAXA, with an increased high-temperature absorption heat release. Nevertheless, an additional electrical consumption is needed to drive the Pump B, so the electric efficacy becomes:

$$\epsilon_{el} = \frac{Q}{\dot{W}_{el,A} + \dot{W}_{el,B}} \tag{2.34}$$

The net effect is however expected to be around the 20% better than the standard GAX [88].

2.3. NH3/H2O GAX absorption chiller

The Generator-Absorber heat eXchanger (GAX) ammonia-water absorption system can be definitely represented as single-stage cycle: there is only one solution pump and all the major components that occur in a single-stage cycle, such as absorber, desorber, evaporator, and condenser, are present just once. Another difference is that the solution heat exchanger is no more envisaged, being replaced by the GAX: the heat transfer is represented by the dashed line, going from the hotter part of the absorber (GAXA) to the colder part of the generator (GAXD). The Figure 2.24 shows the classical representation of the GAX cycle.

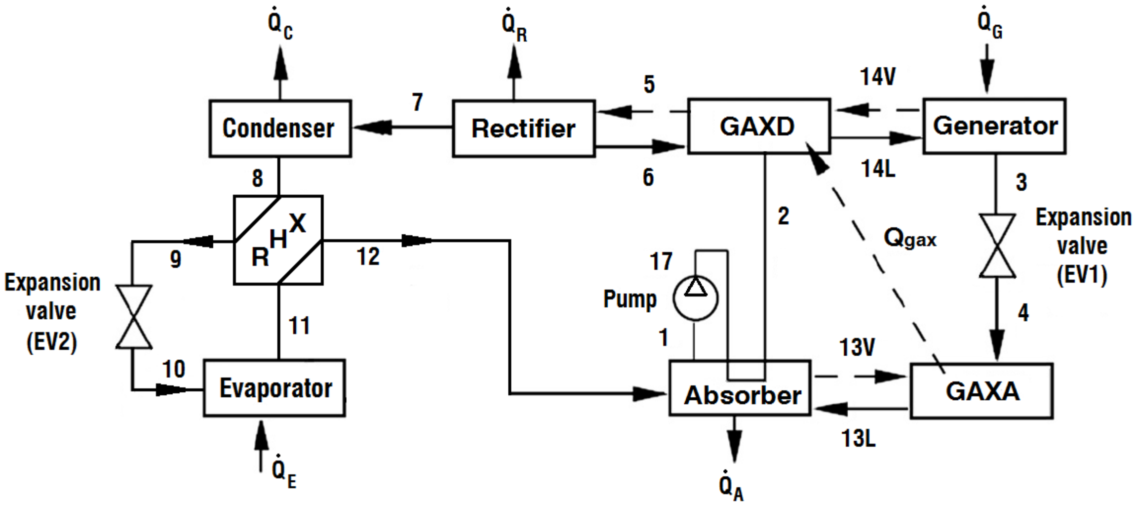


Figure 2.24.: Schematic of ammonia-water GAX absorption cycle main components and heat and mass transfers. *Source: Yari M., Zarin A., Mahmoudi S., 2000*

To allow the heat transfer from GAXA to GAXD a temperature difference between the two must exists: pressure and concentration in the generator and the absorber are the driving parameters of this phenomenon [89]. In fact, they are expressly maintained in such a way to cause a temperature overlap, providing the possibility for some of the absorption heat to be rejected into the generator, thus leading to a higher COP. This temperature overlap is an attractive characteristic of the GAX cycle using ammonia–water and cannot be realized in the water–lithium bromide absorption cooling systems due to the too much narrow solution concentration field [88].

Observing heat transfers that occur between the absorber and the generator, the rich solution performs a passage in the intermediate-temperature part of the absorber, that is hotter than the solution itself: a first rough heat recuperation is done, even improving the absorption process along the distillation column. Despite being a full-fledged heat transfer (via the rich solution) from the absorber to the generator, this is not considered a GAX process. The main difference between these two transformations is conceptual: a GAX heat transfer must lead to a rich solution vapor generation, therefore the heat transfer must occur at a temperature higher or equivalent to the rich solution boiling point [90]; otherwise, it is just a heat recuperation and the relative section is called SCA (Solution-Cooled Absorber), and distinguished from the GAX. Another difference, more practical, consists in the heat transfer method: in the case of the SCA the rich solution usually exchanges with the absorber mixture through a submerged coil, or similar; for the GAX different scenarios appear, as direct and indirect methods to perform this exchange are possible. The most known GAX technology is further detailed.

2.3.1. Functioning generalities

Referring to the schematic cycle in Figure 2.24, the rich solution (1) is pumped to the Solution-Cooled section of the Absorber (SCA) to take advantage of a slightly higher temperature: then, it enters the GAXD where it receives heat from the GAXA. A first desorption takes place, the vapor separates and rises towards the rectifier (5) while the heavier liquid fraction (14L) falls towards the bottom of the generator. Similarly, the rich solution is heated and evaporated (14V) by the heat source: the lower falls the liquid, the higher temperatures it encounters, improving evaporation. The saturated liquid part (3), that can no more be evaporated, is expanded and sent again to the GAXA (4) for the absorption.

The refrigerant is injected from the bottom of the absorption column (12) and rises by density difference (13V), while the enriched solution falls from the top (13L) until saturation at point (1). Being the absorption exothermic, the higher section of the GAXA warms up and a part of this heat is transferred to the GAXD: this exchange is not evident at all and different approaches are possible to realize it, as further detailed.

Returning to the coolant circuit, the steam from the GAXD enters the rectifier, which uses an external source for cooling. The purified water vapor (7) is then condensed (8), pre-cooled (9) and expanded to the correct evaporating pressure (10). In the evaporator the refrigerant is evaporated (11) with the heat provided by an external fluid, whose cooling is the final useful effect of the cycle.

As in all the representations of the absorption cycles on the T-p-x diagram, the righter one component is, the higher is its temperature: in this diagram further simplifications occur, neglecting for example the concentration variations, and the graphic choices may be a bit misleading. In fact, the transfers 13V/13L and 14V/14L happen inside two distillation columns driven by natural convection (density difference): they are carried on vertically and not horizontally, as the standard diagram may let imagine.

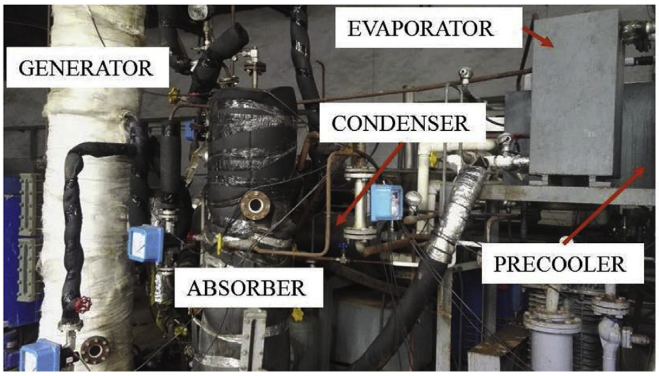


Figure 2.25.: GAX absorption system prototype. *Source: Wang et al., 2019*

The Figure 2.25 gives an idea of an real disposition of the components in a GAX absorption system.

Finally, a particular solution that often occurs in the architecture is the integration of the rectifier in the generator column: if on one side its length increases, the condensate never exits, remaining inside the column and contributing to further rectification while falling again towards the generator. Thus, the only outlet is steam ready for use. Moreover, the choice to use the rich solution exiting the absorber as the cooling-side fluid for the rectification allows to recover this heat. In general, the generator has a very important height to allow a good dynamics of all the processes detailed so far: desorption, steam separation and rectification with condensate heat and mass recovery.

2.3.2. Generator-Absorber heat eXchanger

In 1996, Fuesting et al. patented a redesigned Generator Absorber heat eXchanger component for an NH3/H2O absorption refrigeration system that claimed to be able to perform the GAX heat exchange in a direct way, without using an intermediate fluid, but the cycle fluid itself. In addition, the absence of a secondary fluid simplified the architecture (i.e. no secondary fluid pump and no relative electrical consumption), reducing costs. The inventors claimed finally better efficiency thanks to direct heat transfer [90].

The proposed component essentially is a pressurized cylinder with fluid distributors (46, 47) and coil exchangers (43, 44) at the interior. The free space in the cylinder is used for the absorption process, both in the upper and bottom parts, while the coils are used to circulate and heat the rich solution. Therefore, the bottom section of the absorber is configured as the Solution-Cooled Absorber, while the upper section constitutes the absorber-generator heat exchanger, replacing the separate heat transfer loop reported in many prior art GAX cycles [90]. As the thermodynamic cycle proposed by Fuesting et al. does not change from the one schematized in Figure 2.24, just the passages involving the GAX are described.

The poor solution enters the top of the cylinder (46) while the refrigerant is injected into the lower part of the GAX column (between 43 and 47) and reacts with the poor solution falling by gravity: being ammonia a gas, the hotter part rises in the upper section (36), guaranteeing the refrigerant feeding to both absorber sections. Instead, the rich solution enters the coil (43) in the lower absorber heat exchanger (35): here the latter increases its temperature until point (45), where a splitting occurs.

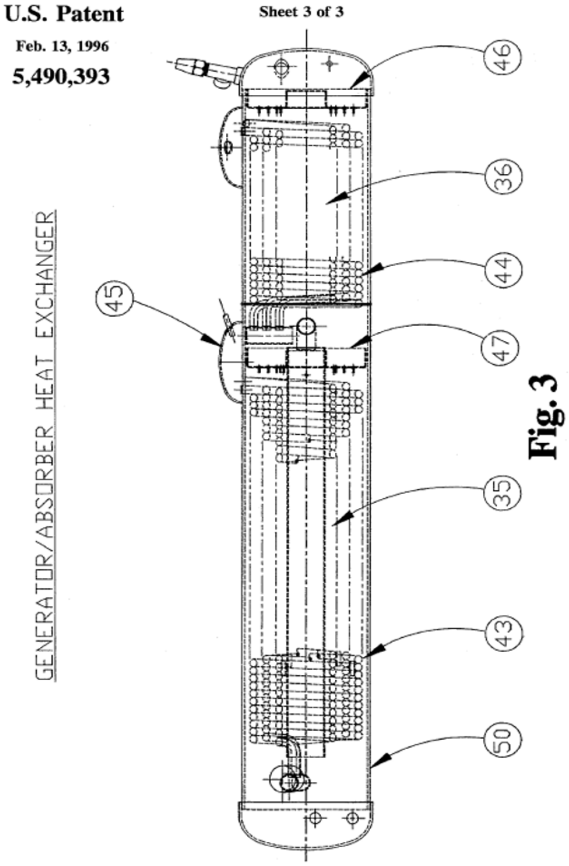


Figure 2.26.: GAX section prototype.
Source: Fuesting et al., 1996

The necessary heat is provided by the poor solution-refrigerant mixture that continues the exothermic absorption process, already started in the upper part: when the absorption is concluded and the poor solution is saturated, it exits at the very bottom of the absorber (50). The lower absorber heat exchanger (35) is sized to raise all the coil-flowing rich solution to the saturation temperature corresponding to the generator pressure. Then, at point (45) the flow is split in two, with a first portion being routed directly to the upper part of the analyzer (21, not in figure, but detailed in the Annexe C.4), and the second portion passing through the GAX coil (44) in the upper absorber-generator heat exchanger (36).

While in the coil (44) the rich solution is heated by the hot poor solution which surrounds it (36). This portion of the rich solution becomes two-phased as its temperature rises and the liquid fraction concentration changes. The splitting point (45) is conceived to improve rich solution evaporation: decreasing its flow rate the outlet temperature increases, generating a larger vapor fraction. After passing through the upper absorber-generator heat exchanger (36), the second portion of rich solution is returned to the bottom of the analyzer.

Considering the generator column, included in the cycle detail in the Annexe C.4, the not-yet-evaporated rich solution starts to fall down from the analyzer to the generator, where high temperature heat is provided. Approaching the hot source, the rich solution warms up and the refrigerant starts desorption, rising towards the top after evaporating. Instead, the poor solution is sent to the top of the GAX (46) to start the loop again.

For completeness, the analyzer is a part of the distillation column located at the top of the generator: it consists of a variable number of plates positioned horizontally. In this section the vapor coming from the generator is cooled, also thanks to the first portion of fluid split in point (45) which falls from the top: being this one at saturation temperature, it is cooler than the vapor coming from generator. Since water has lower saturation temperature, water vapor gets condensed on the plates sides, falling down again into the generator: vice versa, the vapor heat contributes to the partial evaporation of the refrigerant in the rich solution. This double benefit explicates the need for different height inlets in the analyzer.

Finally, once reached the top of the column the gaseous ammonia refrigerant moves to the rectifier, terminating the generation process.

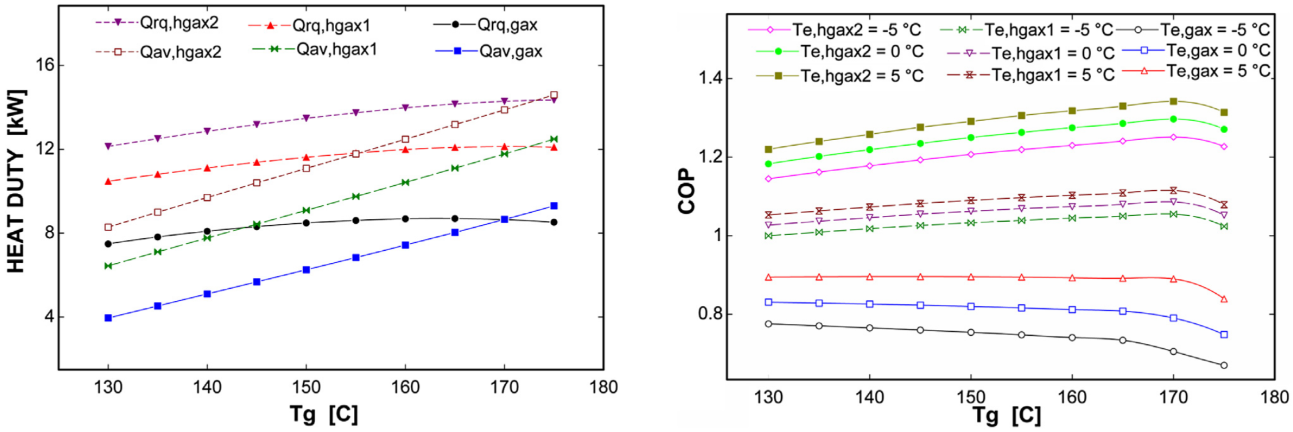
With this arrangement and the adjustment of the absorbent flow through the GAX section, the claimed efficiency improvement stays around of approximately 30%.

2.3.3. Performances

As seen before, the GAX process effectiveness depends on various factors, above all the chosen design, the geometry and the other constructive parameters of the GAX. Nevertheless, the thermodynamic conditions of the involved fluids are extremely important to perform a good recuperation: many studies have been conducted through First and Second Law analysis to evaluate COP, exergetic efficiency and heat duty variation in different operating conditions [86, 91]. GAX effectiveness showed to depend mostly on three parameters: generation temperature, condensation temperature, and degassing range. The degassing range Dx is defined as the difference in the rich and the poor solution concentrations [86].

Effects of generator temperature Considering a fixed operational condition, it is observed that as the generator temperature increases the poor solution concentration x_3 decreases. Assuming that degassing range stays constant (variable Dx case is discussed further), this implies a proportional reduction in strong solution concentration x_1, resulting in the increase of the strong solution mass flow rate. Therefore, a positive variation of the GAXD required heat Q_{RQ} occurs. However, as the absorber temperature rises due to the increased poor solution temperature exiting the generator, even the GAXA available heat Q_{AV} increases.

As the Figure 2.27a shows, there is a temperature for which $Q_{RQ} = Q_{AV}$: this is the Optimal Generator Temperature for the generator-absorber heat exchanger process, leading to the best recuperation for that operational condition.



(a) Heat duty vs. T_g at T_c=45°C and T_e=5°C.

(b) COP variation with T_g at T_c=45°C.

Figure 2.27.: Temperature influence on GAX heat duty and COP. *Source: Dixit et al., 2015*

The study also analyzes the effects of an increase in condenser temperature: Dixit et al. observe a general increase of generator and absorber thermal loads, but of negligible magnitude.

For the evaluation of the effects of the generator temperature on the COP, also the evaporator temperature influence is taken into account: the Figure 2.27b indicates that there is a particular value of the generator temperature at which the maximum value of COP is obtained, for each fixed value of evaporator, absorber and condenser temperatures. The last observation about generation temperature derives from the comparison of the two diagrams in Figure 2.27: the OGT for the GAX heat transfer and the OGT for the whole cycle COP appear to coincide. Thus, it is possible to affirm that generator energy need Q_G reduction is more significant than the increment in the evaporator heat load (and useful effect Q_E), remembering the definition $COP_R = Q_E/Q_G$.

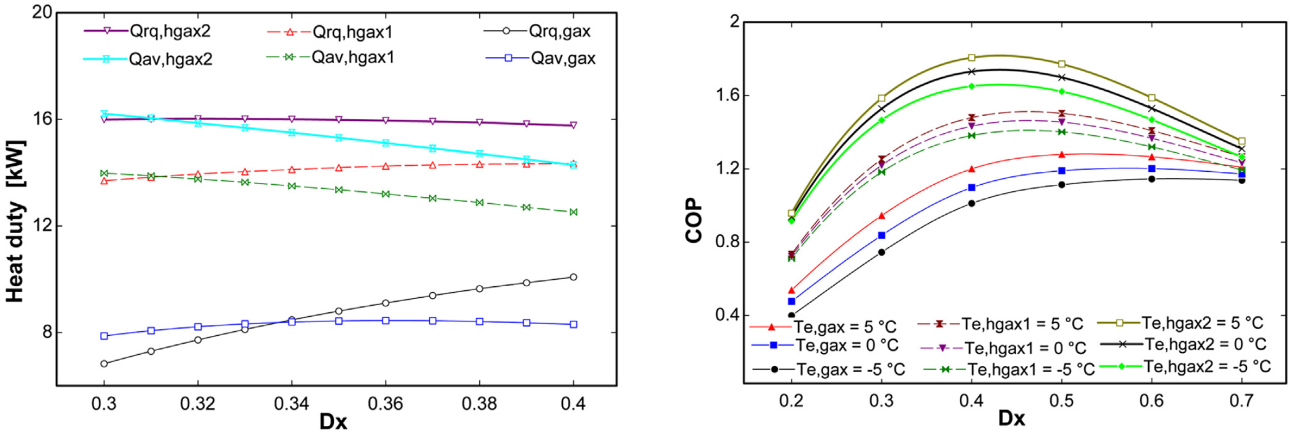
Some additional data about exergetic efficiency is provided: for a GAX cycle exergetic efficiency lies in between 21% and 75% and the temperature optimum does not coincide with the OGT. Finally, it is observed that the influence of generator temperature on exergetic efficiency is more prominent than on COP [91].

Effects of degassing range The concentration variation of the solution in the GAX cycle is another major parameter influencing the performances: heat duty and COP vary considerably in function of Dx.

Keeping constant operational conditions, required heat Q_{RQ} and available heat Q_{AV} converge to an equal value really fast, more than in the generator temperature case: the values of degassing range should be between 0.30 and 0.34 for better internal heat recovery, as shown by Figure 2.28a. Above 0.34 the GAXD missing heat would be provided by the generator itself, increasing its heat duty.

However, Figure 2.28b shows that an increase of Q_{RQ} does not implies a COP decrease: for the GAX cycle, the higher the degassing range (and so the GAXD required heat), the higher the COP. This is not true for the Hybrid-GAX, that has in fact different characteristics.

Therefore, there exists a degassing range value at which COP attains the maximum for a fixed generator, condenser and evaporator temperatures: this is called the Optimum Degassing



(a) Heat duty versus degassing range at T_g=170°C, T_c=40°C and T_e=-5°C.

(b) COP versus degassing range with T_g=170°C and T_c=40°C.

Figure 2.28.: Degassing range influence on GAX heat duty and COP. *Source: Dixit et al., 2015*

Range (ODR). For the standard GAX it lies in the interval of 0.55-0.65, about the half of the value that guarantees the best internal heat recovery. In fact, an increased concentration difference on one side increases the heat load needed for the desorption, but on the other increases the refrigerant vapor production, decreasing the rich solution flow rate. As data demonstrates, for GAX cycles the rate of decrease of mass flow rate at higher degassing range is much higher than the Q_{AV} one, making the former effect the dominant one [86].

To resume, the GAX cycle provides the highest COP of any single-effect absorption cycle due to the possibility of a considerable internal heat recovery: however, further improvement is possible, as the advanced-GAX cycle numerical simulations demonstrate.

The interest in this systems is growing, mostly in the key of solar coupling: many studies have been conducted for both cooling and heating purposes with promising results. Parabolic solar collectors and fresnel concentrators have been proved suitable as generators with thermal COPs of 0.3-0.85 and electrical efficacies between 5.1 and 10, for sizes about some kilowatts at the evaporator [89, 92].

In addition to solar purposes, novel applications for the ammonia GAX absorption cycle have been developed: one notable case is the system studied by Park et al. [52] in order to supply both chilled and hot water simultaneously, but using a single hardware.

Finally, conventional applications were studied. Absorption heat pumps have been investigated [93,94] as well as the chillers [95] to improve their performances and internal heat recovery: in the latter study, for example, an internal heat recovery of approximately 55% of the total heat supplied in the generator was obtained with a generation temperature of 192°C, even with a relatively high COP of 0.58.

2.4. Conclusion

Artificial cooling is a quite recent concept, born in the first half of the 19th century and concretized by F. Carré who patented the first refrigerating machine: driven by heat, as electricity was really precious and not reliable, that was the first absorption refrigeration system ever built. However, operating fluids were dangerous and the performance was not exceptional: to overcome these flaws new refrigerants were studied and new architectures appeared. The vapor compression systems took the lead since the beginning of 20th century and still are the more efficient option for this purpose.

Nevertheless, the increased environmental concern and the increasing cost of electricity created a suitable situation for the comeback of the absorption systems: waste-heat feeding, non-GHG fluids and high reliability of these machines are the most appreciated features of this renewed technology. Nevertheless, high initial costs due to complexity, fluid corrosion and relative constraints on materials choice slow down the commercial diffusion.

Vapor absorption refrigeration systems perform their useful effect as the vapor compression ones: through a double phase change, a high-pressure liquefaction and a low-pressure evaporation, heating and/or cooling are provided. The flow is assured by an absorption-desorption mechanism to take advantage of a pumping instead of a compression: this way, a consistent electrical energy saving is possible.

The main fluid pairs used for this process are water-lithium bromide and ammonia-water: however, different applications are envisaged for the two, depending on the physical properties of the mixtures. In particular, absorbent properties appear to be the most limiting.

H2O/LiBr systems are widely used for climatization, and double, triple and multi-effect cycles have been designed to increase efficiency and operational condition range.

Instead, NH3/H2O cycles allow different configurations, thanks to the larger operational field of the fluids: deep cooling, climatization, heat pumping and heat transforming are all available applications of this reversible cycle. Single-stage machines are currently commercialized, while two-stage double-effect, double-lift or triple-effect cycles have been recently investigated.

A particular and well known single-stage NH3/H2O cycle is the Generator-Absorber heat eXchanger (GAX): this concept bases on the possibility, for a certain pressure and solution concentration, of creating a temperature overlap between the upper part of the absorber and the lower part of the generator. Thus, a heat transfer is possible to recover this available internal heat, increasing the global system performance.

Further improvements of this architecture have been developed, in particular through an absorber pressure increase that is demonstrated to be advantageous for efficiency: the Hybrid-GAX realizes it through a compressor, with an additional electrical consumption, while the Ejector-GAX perform this pressure increase in an ejector, with an additional heat consumption [87]. Both of them exists almost on paper.

3. New architecture study

GAX absorption systems are thermodynamically promising technologies, as proven by the numerous numerical studies that have been carried on them. Different usages can be considered, as both chiller, heat pump and heat transformer configurations are functional and performing. Moreover, the operational field is wide with reference to the one of water-lithium bromide.

The diffusion of this technology is essentially hindered by its cost that can not even come close to those of vapor compression systems, making the game absolutely unfair. The manufacturing of the GAX component as designed in the literature, a long metallic cylinder with two separated sections, numerous shell penetrations and pressurized coil exchangers in the inner volume, is complicated and expensive.

Firstly, the only actually usable material is stainless steel because of the corrosion problems presented in the Section 2.2.3. As mechanical resistance can be easily achieved increasing the elements thickness, the weak spots are the geometrical discontinuities that concentrate the mechanical efforts: there, a larger material quantity is required to avoid ruptures.

Secondly, the realization of the penetrations and the connections of the different internal and external parts raises another problem: in fact, if classical weldings can be realized with particular anti-corrosion alloys, tightness at high pressures would not be guaranteed. To overcome these problems the brazing technique is the most practical solution at the moment, but it is not evident to perform, especially with little components.

Lastly, only prototypes have been realized and often with different characteristic related to the particular test being performed. Thus, designers and manufacturers can not efficaciously take advantage of the previous results as the few data present in the literature refers mostly to different models. GAX standardization is not yet reached, so costs remains those of tailored components, hence very high.

As manufacturers of current Generator-Absorber heat eXchangers are hard to find, and even in the case they are able to realize this component they remain expensive, it might be interesting to adapt some already existing technology to the GAX purpose.

The two transformations occurring in the GAX are the poor solution absorption of the refrigerant and the rich solution desorption: a preliminary assessment showed that for each one of these processes many studies had already analyzed the possibility of using plates exchangers. The falling film distribution of the liquid solution was thought to be advantageous in terms of absorption heat and mass transfer, increasing convection and diffusion coefficients. Physical models for plate exchanger-based absorption [50] and desorption [96, 97] were proposed and compared to experimental data: results showed a good accuracy of model predictions and interesting performances in experimental exchangers, arousing interest in this sense.

Summarizing, as plate exchangers revealed to be suitable for absorption and desorption, even if at research stage, it is reasonably to go further thinking about their implementation in absorption cycles.

Plate exchangers appear currently as one of the best opportunities to lower the price of absorption systems, as they are a well-known technology that proved itself during the past years and that is actually diffused all over the world. Series production is possible with standardized characteristics, but also prototyping is easier than conventional systems: in fact, the experience in this field allows the manufacturers to better predict and improve effectiveness, being able to calculate or simulate heat and mass transfers inside the component. Costs are therefore lower than classical absorbers or generators.

In addition, with a plate exchanger-based GAX maintenance is facilitated and the operational costs reduced: having separated pieces allows to easily perform inspections, simplifies problem detection and also allows to effectuate more accurately the measurements needed to the system control. The possibility to rapidly disassemble the broken parts to replace them is another great advantage, impossible with a huge, complex block: the total producible time is increased, reducing technical stops.

If the absorber and the generator alone fit plate exchangers, the GAX theoretically should fit them too: the absorption and the desorption can effectively be conducted inside the different channels, while heat transfer occurs through the plates themselves.

An overall dimension diminution of the solution circuit would be possible with this new configuration, no more vertical stacks of big elements would be needed. However, the removal of the distillation columns would require a separate stage of rectification, that can actually be solved with another plate exchanger, and also the insertion of a vapor separation tank because density stratification would not be an option anymore.

Concluding, at the current state of the art, absorption systems can be redesigned to eliminate the bulky and complex distillation columns for absorber, generator and GAX: nevertheless, a slightly higher number of relatively simpler elements is necessary to carry out the same transformations. Advantages in systems configuration, operation, maintenance and dimension, as well as a strong decrease of its cost due to the larger component availability, are foreseen. Therefore, a plate exchangers-based GAX NH3/H2O absorption cycle is decided to be further studied.

3.1. Methodology

The key points of the study of a new GAX configuration implementing plate exchangers are many, and for satisfying all of them a precise approach is followed. The main goal is to design a refrigeration system, possibly operating at certain nominal conditions further detailed. In addition, the study of the heat pump configuration is considered interesting. All the heat transfers are required to happen inside plate exchangers, so the distillation columns must disappear. Then, performances and COP in particular must be higher than in the single effect case.

To reach these goals the following procedure is used:

1. A literature study is performed to understand the basic principles of absorption systems, the relations between dependent and independent parameters, and the best improvement paths;

2. A single-stage chiller is then modeled to calculate performances in steady-state through the software EES. The choice is to replicate the cycle of Boudehen et al. [98] because the main results are reported in their article, so a verification of the model accuracy is possible. It will constitute the reference for the improvement evaluation;

3. An ideal GAX chiller is also modeled, basing on the design of Wang et al. [93] for different reasons. Firstly, this is meant to constitute an upper theoretical limit for GAX performances; secondly, this model would help to individuate the transformations that usually are included in standard GAX cycles; lastly, a heat duty analysis is done to define which components are the most important in the standard GAX architecture;

4. As the plate exchanger-based GAX can not do the required transformations through the same components of the standard GAX (distillation columns are no more allowed), new elements are introduced in the architecture to overcome this point. A physical model is defined for each one of them, preparing the further implementation in a EES numerical model;

5. Once the new architecture is set up, tests are carried on to verify opportunities of COP improvements, better internal heat recovery and overall system simplification. One alteration at the time is allowed to clearly evaluate the effects. Each positive modification is kept, the other are discarded and this process is repeated iteratively;

6. When the the obtained configuration shows no more major improvements directions, meaning that each further performance increase is negligible or would require too many additional elements, the process is stopped and results are compared with the initial goals. If the conditions are fulfilled, the last architecture is adopted as the final one and minor adjustments basing on the desired operational conditions are done, taking into account also the economic aspects;

7. Finished the new GAX chiller architecture design, a similar procedure is done for the heat pump configuration. However, results from the previous steps are taken into account to advance more rapidly.

3.2. Physical model

As the procedures for modeling the single-stage and ideal GAX cycle are already detailed in the two related publications, this section just deepens the new architecture (plate exchanger-based) physical modeling aspects.

In the standard GAX, the distillation columns host two principal transformations: a heat transfer and a phase separation. If the first can efficaciously be replaced by the plate exchanges, for the second it is necessary to introduce a new component: the separation tank. In this element a biphase fluid enters the volume and the vapor and liquid parts separate by gravity. Arranging the Wang et al. architecture it is possible to obtain the configuration in Figure 3.1.

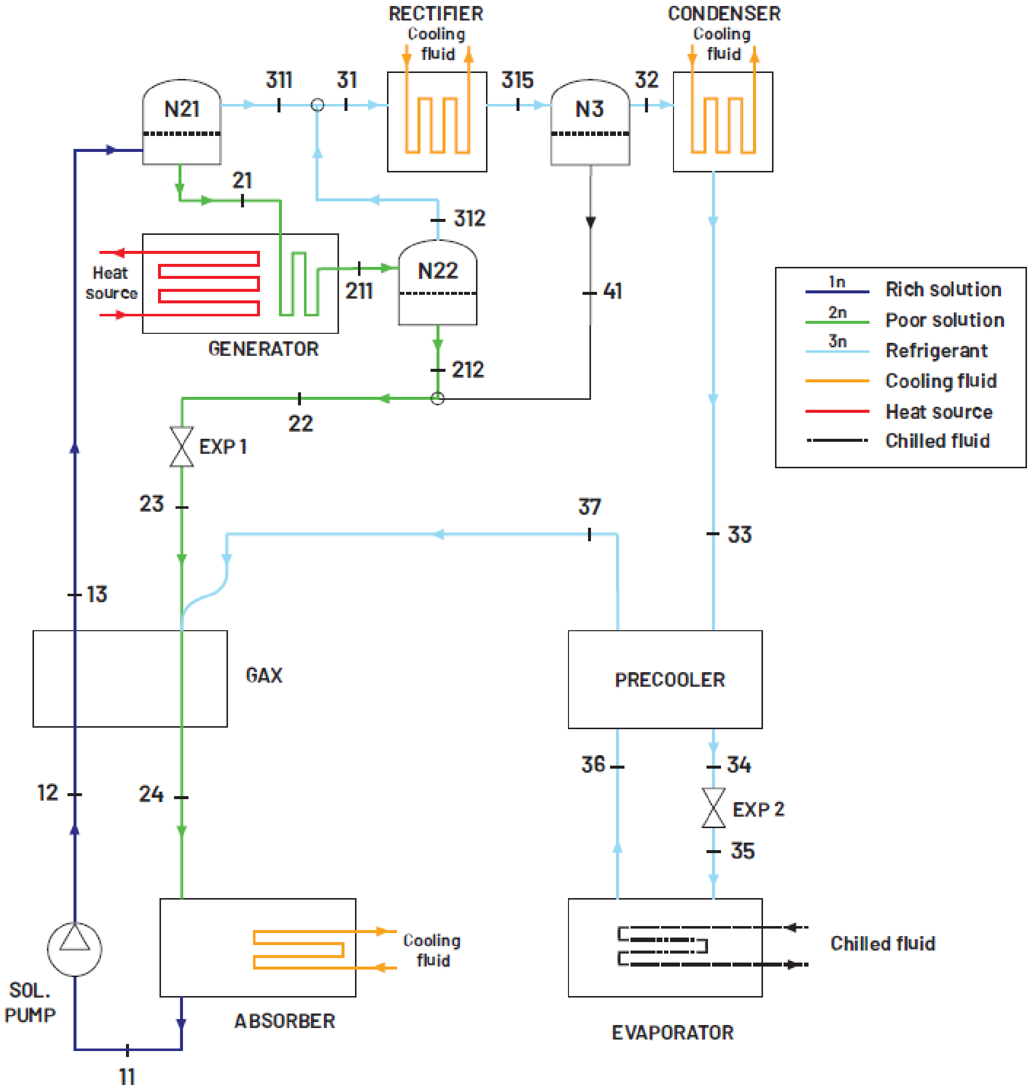


Figure 3.1.: Schematic of plate exchanger-based GAX system: configuration A0.

The represented system has the classical functioning of an absorption cycle, with the feature of a GAX component to perform internal heat recovery. The state points are labeled depending on the flowing fluid in the point: for the rich solution, the first digit is 1; for the poor solution it is 2; for the refrigerant, 3; for the condensate, 4. The other digits differentiate the points. However, the details of this architecture are discussed in the next Section 3.3.

Each one of the elements of the system (pump, separation tanks, exchangers, etc.) is thought as a volume control with the proper inputs and outputs. Thus, the conservation of energy and mass is imposed: for the latter, both water and ammonia must conserve.

$$\text{Total mass conservation} \rightarrow \sum_{i=1}^{n} \dot{m}_i = 0 \tag{3.1}$$

$$\text{Refrigerant mass conservation} \rightarrow \sum_{i=1}^{n} \dot{m}_i x_i = 0 \tag{3.2}$$

$$\text{Energy conservation} \rightarrow \sum_{i=1}^{n} \dot{m}_i (h_{i,out} - h_{i,in}) - Q + W = 0 \tag{3.3}$$

However, in the last equation the term Q is positive as it refers to the entering thermal flux in the system; instead, the term W results negative due to the classical fluid convention, but it is a minor issue as it is present only in the pump balance.

The property calculation is a point of relevant importance when dealing with mixtures because correlations are needed to approximate the real behavior of the fluids: the software EES provides NH3/H2O thermodynamic values basing on the REFPROP correlations and allows to calculate the principal parameters. They are:

- temperature T $[K]$;
- pressure P $[bar]$;
- refrigerant concentration x $[-]$;
- enthalpy h $[kJ/kg]$;
- entropy s $[kJ/kg]$;
- internal energy u $[kJ/kg]$;
- specific volume v $[m^3/kg]$;
- quality vapor ratio q $[-]$;

Differently from monophase fluids three inputs are needed to define a state point: when two fluids are mixed together properties depend also on the mass fraction of each one (i.e. $h = f(T, P, x)$). Moreover, the final value usually is not just the mass weighted average of the single phase properties due to their chemical interaction, as detailed by Herold et al. [46].

Heat carrier fluid The external heat carrier fluid has been studied, as it has be adapted to the climatic conditions imposed in the design requirements. Therefore, it must remain liquid at outside temperatures down to -30°C and must not be denatured when heated over 180°C. The other selection criteria have been heat capacity (ρc_p), viscosity, heat exchange capacities in the exchangers, but also corrosion, flammability and toxicity. In addition, the choice is made to use the same one in all the four exchangers (absorber, condenser, evaporator and second rectification stage).

The chosen fluid matches the characteristics of propylene glycol, but with better temperature stability. However, as the producer provided just a discretized table with the main properties (specific heat, conductivity, viscosity and density) instead than some correlations, and considered that the heat carrier fluid behavior is real, a polynomial interpolation is developed for each property data set. In this way, for each thermodynamic condition all property values are calculable.

Modeling requires a certain grade of approximation for adapting reality to a mathematical set of equations, more or less articulated. For relatively little systems as the one in discussion some simplifications are legit because the precision required is not high and because the phenomena involved are relatively predictable. Thus, the following assumptions are made for the whole thermodynamic cycle:

- steady-state operation of each component;
- no pressure drops in components and pipes;
- adiabatic components and pipes;
- heat exchangers always guarantee the needed contact area;
- ideal thermal sources and sinks;
- real external fluids.

Even under these conditions, the model represents quite well the real functioning of the system as the committed errors are negligible as order of magnitude: for designing a new architecture it is considered accurate enough, instead for the study of its control system a dynamic, more complete model should be preferred.

After this brief insight on the global system conditions, a detailed analysis of all the components is done.

Pump The solution pump is a component relatively easy to modelize, as there is just one fluid interacting with the mechanical part of the element. All the imperfections are included in two parameters, the electrical conversion efficiency η_{el} and the mechanical efficiency η_m: the former is defined as the mechanical work produced on the input electrical energy, while the latter takes into account the transmission of this mechanical work to the fluid. The assumed values are $\eta_{el} = 0.9$ and $\eta_m = 0.8$.

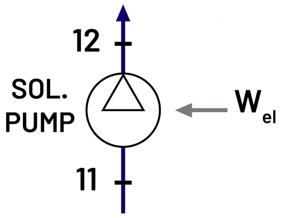


Figure 3.2.: Solution pump scheme.

The electrical power consumption is calculated with the following formula:

$$P_{el} = \frac{\rho \dot{G} g H}{\eta_{el}\eta_m} = \frac{\dot{m} g H}{\eta_{el}\eta_m} \tag{3.4}$$

where H is the total pump pressure head and $\dot{m}$ is the solution mass flow rate. The total pressure head is calculated:

$$H_T = H_Z + H_P + H_K + H_V = (z_b - z_a) + \left(\frac{p_b - p_a}{\rho g}\right) + \left(\frac{v_b^2 - v_a^2}{2g}\right) + \left(\sum H_{yc} + \sum H_{loc}\right) \tag{3.5}$$

where $H_{yc} = f(v, \varepsilon, L, D)$ is a pipe distributed pressure drop and $H_{loc} = f(v, K_{loc})$ is a localized pressure drop. However, due to system compactness and simplicity, height differences are supposed negligible and the kinetic term is neglected as well. Pressure drops are already neglected for the whole system, so the only important term is H_P.

Generator The generator is constituted by a plate exchanger where the external high-temperature fluid heats the rich solution to evaporate the refrigerant, thus obtaining a biphase mixture at the outlet. As all the exchangers, a certain part of the total exchangeable heat can not be transferred due to its finite dimension and to the element imperfections: normally, an effectiveness coefficient is included in the calculations to take into account this point. However, the thermal source is supposed to be ideal, so it can provide fluids at whatever temperature and flow rate: the imperfections in the thermal exchange can be compensated slightly increasing the inlet temperature of the source. Despite the representation in the Figure 3.3 the two fluids exchange in counter-flow, allowing the solution to reach higher temperatures. The generator heat duty is calculated as: $Q_G = \dot{m}_{21}(h_{211} - h_{21})$.

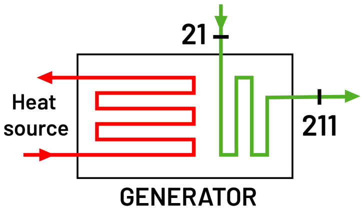


Figure 3.3.: Vapor generator schematic.

The mass flow rate of the external fluid is calculated similarly, assuming $dT = 5°C$ between the inlet and outlet temperatures: $Q_G = \dot{m}_f c_{p,f}(T_{in,f} - T_{out,f})$.

Absorber This elements is needed for the refrigerant dissolution in the absorbent fluid, water in this case. It consists in a plate exchanger where the biphase mixture of poor solution and refrigerant vapor, only partially absorbed in the GAX, finishes the absorption process until saturation. The other side of the absorber is filled with the intermediate-temperature cooling fluid, removing the reaction heat. Usually, a certain degree of subcooling is needed to ensure the liquid saturation at the solution pump inlet: in fact, the presence of any ammonia vapor will seriously damage the pump due to cavitation. Being the absorber an ideal component, thus imperfect, an absorption effectiveness coefficient is used to make more realistic its performances:

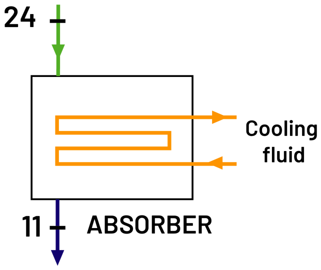


Figure 3.4.: Absorber scheme.

$$\varepsilon_{abs} = \frac{\Delta x_{real}}{\Delta x_{ideal}} = \frac{x_{T11} - x_{liq,T26}}{x_{liq,T11} - x_{liq,T26}} \tag{3.6}$$

where the concentration difference in the real case and in the ideal one are compared. Its value is assumed to be 0.8 and the absorber heat duty is calculated as: $Q_A = \dot{m}_{11}(h_{24} - h_{11})$.

The mass flow rate of the external fluid is calculated as in the generator case, assuming $dT = 5°C$ between the inlet and outlet temperatures: $Q_A = \dot{m}_f c_{p,f}(T_{in,f} - T_{out,f})$.

GAX The Generator-Absorber heat eXchanger gathers the features of the two previous components, the generator and the absorber: therefore, this element is the most difficult to predict the performance of.

Its sizing will require a lot of effort and will be based onto experimental evidences and empirical correlation, so while building the physical model, firstly an ideal GAX is used with both sides operating with unitary effectiveness. After, for system performances calculation their values would be adjusted to 0.8 that is a reasonable value for both generator and absorber.

The internal heat recuperation is calculated as the exchanged flux between rich solution and poor solution-refrigerant mixture. Having assumed no heat losses the two values must coincide: $Q_{GAX} = \dot{m}_{13}(h_{13} - h_{12}) = \dot{m}_{24}h_{24} - (\dot{m}_{23}h_{23} + \dot{m}_{37}h_{37})$.

On this last point, the mixture has to be treated carefully: the two fluids are mixed just before the admission in the GAX, so a fictitious point (23') is effectively used in the numerical model.

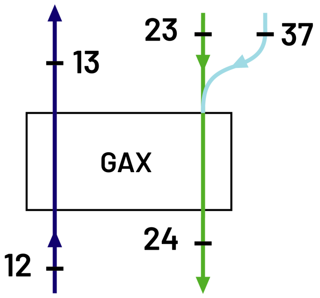


Figure 3.5.: GAX schematic.

Rectifier This element is used to condensate a little fraction of the vaporous mixture before entering the conventional refrigeration section: as water is less volatile than ammonia, the liquid fraction is poorer in refrigerant, increasing the vapor concentration. The separation between the two phases is further done in the separation tank N3.

The outlet temperature T_{rect} is a fundamental parameter for the system, as it determines the purity (the ammonia concentration) of the refrigerant fluid reaching the condenser and the evaporator. The phase change conditions are strongly influenced by the water content in the vapor, so both the high pressure and low pressure values in the cycle are related with the rectification temperature. However, the generation temperature T_{gen} and the ambient temperature T_{amb} influence the refrigerant maximum concentration as well: in the first case the T_{gen} allows more or less refrigerant in the rectifier, while the T_{abs} sets the saturation concentration in the absorber. A new parameter is introduced to take into account the relationships between these parameters, all influencing the refrigerant production. The Rectification Ratio (RT_{rect}) is defined as:

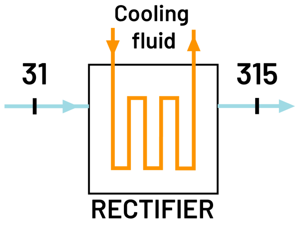


Figure 3.6.: Rectification section schematic.

$$RT_{rect} = \frac{T_{gen} - T_{rect}}{T_{gen} - T_{abs}} \text{ with T in [°C]} \tag{3.7}$$

Condenser The condenser has no particular function other than liquefying the refrigerant and it is assumed to do so at constant external fluid temperature: high flow rates are required on the external side to keep low the inlet-outlet temperature increase, but the absorption cycle is not actually influenced by this assumption. Vice versa, the temperature of the cooling fluid determines the pressure needed for condensating the vapor at a certain refrigerant concentration: a dT_{ech} is still to be provided, as the condenser is a real exchanger. Complete vapor saturation is assumed at the outlet.

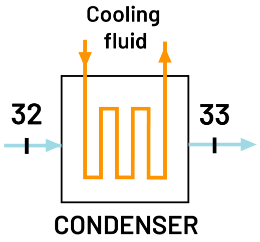


Figure 3.7.: Condenser scheme.

Finally, the pressure is calculated $P_{cond} = P_H = f(T, x, q)$: this value is the minimum pressure value to be guaranteed in the high-pressure side of the system.

Evaporator The physical functioning of the evaporator is quite similar to the condenser one, unless the transformation is the opposite: in this case an external fluid has to be cooled, providing low-temperature heat to the almost liquid refrigerant.

However, in this case the exiting vapor is not assumed at saturation: as detailed in the Subsection 2.2.3, it is more convenient to complete the evaporation in the precooler, thus maintaining a lower evaporator temperature. In fact, it is to keep in mind that phase changes for real mixtures do not generally happen at constant temperature and concentration.

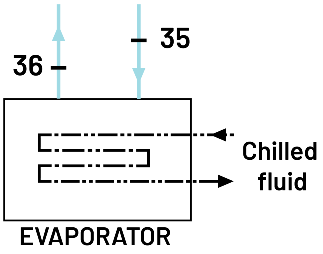


Figure 3.8.: Evapor. scheme.

Nevertheless, the evaporation pressure is calculated as the condensation one, depending on the external fluid temperature, the refrigerant concentration and the vapor quality (assumed to be 96%) at the outlet: $P_{eva} = P_L = f(T, x, q)$.

This pressure value remains the same in the absorber setting a limit for the absorption: the lower is the refrigerant pressure, the less of it can be dissolved in the water. Advanced GAX architectures try to fix this problem introducing an intermediate pressure level after the precooler.

Precooler The role of the precooler has been widely discussed in the H2O/LiBr and NH3/H2O single-stage systems state of the art, and its functioning remains unchanged in this application. The liquid refrigerant exchanges its excess heat before the expansion: reducing its temperature improves the cooling effect, and heating the low-pressure side refrigerant completes its evaporation. The main obstacle is the pressure difference between the two sides because at deep negative evaporation temperatures the low-pressure side can experience vacuum conditions.

This exchanger works with a liquid fluid on one side and with a vapor on the other: the heat transfer is possible with reasonable exchange areas, but the effectiveness is function of many geometrical and construction parameters.

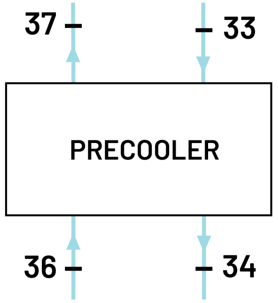


Figure 3.9.: Refrigerant precooler schematic.

A correction coefficient is required because assuming an ideal behavior would lead to an overestimation of the performances: the $\varepsilon - NTU$ method is chosen for this purpose.

e-NTU method The Number of Transfer Units Method is an approach to quantify the heat transfer when the inlet and outlet temperatures can not be determined by a simple energy balance: in fact, a part of the theoretically exchangeable heat is not transferred due to the exchanger imperfections.

As first point, the heat capacity rates have to be calculated ($C = \dot{m} * c_p$) for both the hot and cold fluids: the smaller of them indicates which fluids limits the exchange.

$$C_{min} = min(C_h, C_c) = min(\dot{m}_h c_{p,h}, \dot{m}_c c_{p,c}) \tag{3.8}$$

Thus, the ideal transferable heat is quantified as: $q_{max} = C_{min}(T_{h,in} - T_{c,in})$, where the temperature difference correspond to the maximum gradient possible between the two fluids inlets.

However, this represents the ideal case: in the real case, the transferable heat is multiplied by a coefficient between 0 and 1 that reduces its value. In fact, the effectiveness of an exchanger is the ratio between the real exchanged heat and the ideal exchangeable heat:

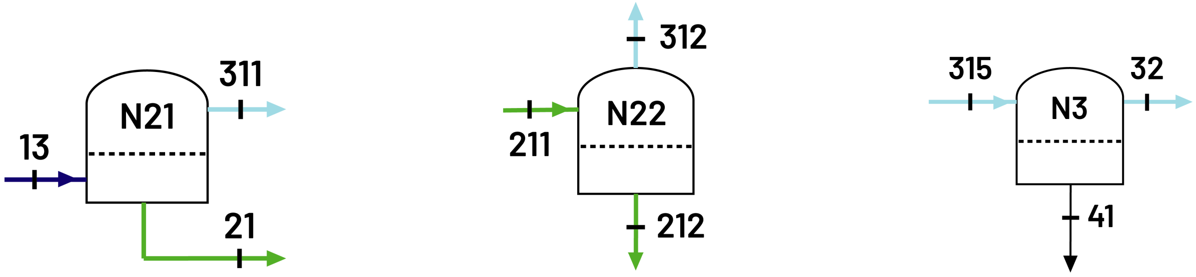
$$\varepsilon = \frac{q_{re}}{q_{max}} \tag{3.9}$$

From this expression it is possible to obtain the real outlet temperatures:
$q_{re} = C_h(T_{h,in} - T_{h,out}) = C_c(T_{c,out} - T_{c,in})$. Also: $q_{re} = \varepsilon C_{min}(T_{h,in} - T_{c,in})$.

Finally, the effectiveness of whatever exchanger can be estimated with empirical correlations extrapolated from experimental data and basing on the element geometry: $\varepsilon = f(NTU, C_{min}/C_{max})$. In this case, as the geometry is not known, the moderate value $\varepsilon = 0.8$ has been chosen to be conservative.

Separation Tanks N21, N22 and N3 The separation tanks are a big novelty with reference to classic absorption systems. Using distillation columns for the processes of generation and absorption, the different phases stratify by density and no further separation is needed. Despite this, the required height to ensure a good performance is elevated: that was one of the interests in eliminating these bulky parts.

The separation tanks do not require to be in a particular position, they can be placed at the side of the other elements as their functioning is really basic: the biphase fluid enters the tank at intermediate height, then the liquid part falls by gravity and the vaporous fractions rises. Even if being absolutely necessary to the good functioning of the cycle, they allow a more rational distribution of all the elements, facilitating the set up and the maintenance.



(a) Rich solution tank. (b) Poor solution tank. (c) Refrigerant tank.

Figure 3.10.: Separation tanks schematic.

The sizing of this elements is not evident, as precise inlet velocity conditions have to be satisfied and the geometrical dimensions have to respect certain proportions to guarantee a good system fluid-dynamic: moreover, they act also as ammonia or water reservoirs, giving some inertia to the cycle and allowing a range of operational conditions.

Nevertheless, having assumed that the systems operates in steady-state conditions, strong simplifications are done. First of all, the outlet fluids are perfectly saturated; secondly, the phases separation is ideal; lastly, heat and mass transfer happens ideally.

This point will be really important further on the discussion of new architectures, as the separation tank N21 in Figure 3.10 will be designed as a mixing chamber besides being also a separator: this to recover more heat from the generator vapor to the rich solution.

Expansion Valves - Poor solution and Refrigerant This components are the interface between the high-pressure and the low-pressure side: flowing through them the fluid loses its pressure level and varies its temperature according to the Joule-Thomson effect. Throttling valves are usually assumed isenthalpic ($h_b = h_a$), so the same hypothesis is done in this work. The first expansion valve, named EXP 1, is traveled by the poor solution, instead the EXP 2 is placed after the precooler and it expands the refrigerant vapor.

(a) Solution throttling valve.

(b) Refrigerant throttling valve.

Figure 3.11.: Expansion valves schematic.

As visible in the Figure 3.11 the modeling is really simple, so, after having calculated the mass and energy balances, the remaining properties can be found as functions of enthalpy, concentration and pressure: $(T, u, s, v, q) = f(P, x, h)$. Although, a more detailed analysis of the thermodynamic effects of an expansion through a throttle valve is presented in the Section 3.3 during the chiller study.

Summarizing, the main aspects of the physical model have been presented so far:

- the assumptions for the whole system and for each component have been highlighted;
- the principal physical principles and laws utilized have been described;
- the thermodynamic properties of interest in the transformations have been introduced;
- finally, the set of parameters useful to characterize the elements behavior (i.e. RT, exchanger effectiveness, etc.) has been defined.

During the improvement study many components have been temporarily implemented to evaluate the effects on the system parameters and on the performances: their modeling is carried with the same procedure previously presented.

3.3. Chiller case

Recalling the methodology in the Section 3.1, the new architecture study places after the literature review where some basic knowledge is acquired: therefore, the standard characteristics and dynamics of ammonia-water absorption systems are no more the object of the discussion. The interest moves on their adaptation to plate exchangers and further optimization.

As declared in the points 2 and 3 of the methodology two precursor models are built, one for the single-stage NH3/H2O cycle and the other for the ideal GAX: their results in terms of COP and fluids performance will be compared to the new proposed systems.

The goals for the new architecture are essentially four:

- realize a working cycle, demonstrating that distillation columns are not essential;
- overcome the single-stage chiller COP in positive cooling ($T_e = 5°C$);
- obtain $COP > 0.5$ at $T_e = -20°C$ and $T_{amb} = 40°C$;
- increase operational conditions with reference to the single-stage chiller.

3.3.1. Architectures

The first plate exchanger-based architecture to be analyzed is the one whose elements have been discussed in the physical model Section 3.2: the Figure 3.1 represents the system schematic. This architecture comes from the adaptation of standard GAX transformations to plate exchangers and separation tanks in the most accurate way possible: thus, no optimization is done yet.

GAX A0 cycle The following brief summary of all the transformations that are provided in the new cycle details the three main fluid paths, rich solution, poor solution and refrigerant.

Starting from the rich solution path, this fluid exits the absorber (11) in liquid phase, then it is pumped (12) and it crossed the GAX (13), ideally starting the desoprtion. The biphase rich solution reaches the separation tank N21: the vapor fraction exits at the top (311) going towards the rectifier, while the slightly poorer liquid phase exits from the bottom (21), towards the generator.

The liquid rich solution is then heated (211) by the external hot source and exits generator in biphase state. A second separation occurs in the tank N22: the vapor (312) is sent to the rectifier, the poor solution (212) goes to the expansion valve EXP1. After the expansion (23), the poor solution rejoins the refrigerant (37) in the GAX starting the absorption (24): the final passage in the external-fluid cooled absorber completes the solution circuit.

Coming back to the refrigerant, the two vapor flows are mixed together (31) before the admission in the rectification section: the biphase mixture (315) is separated in N3. The condensate (41) is sent to the poor solution exiting the separation tank N22. Instead, the almost pure refrigerant vapor starts then its conventional refrigeration cycle, with condensation (33), precooling (34), expansion (35) and evaporation (36), before coming back to the GAX.

This architecture presents three separation tanks, while just two are strictly necessary for the system operation: the separation tank N22 and N3. The tank N21 is required to better simulate the standard GAX functioning, as it does a preliminary phase separation that allows to have pure liquid at the generator inlet. In fact, further heating the vapor already generated in the GAX would be useless, and having a biphase fluid inside the generator would even worsen its performance.

Results Many simulations are executed to explore the system response to different operational conditions, with particular care to the pressure change effects. The following relations are observed:

- an increase in the ambient temperature T_{amb} causes an increase in the high pressure P_H. Therefore, the separation tank N22 decreases consistently its vapor production rate, even if the purity slightly increases. The heat input to generate the same amount of refrigerant increases;
- a decrease in the evaporation temperature T_e causes a decrease of the low pressure P_L. This causes a lower concentration of the rich solution, with consequent increase in its flow rate and generator heat consumption;
- at constant pressures, varying the temperature at the generator can be both advantageous and disadvantageous: an Optimum Generation Temperature exists for most operational conditions.

Globally, performances are worse than the expectations, COP remains too close to the single-stage one. In fact, the rich solution does not perform a consistent desorption in the GAX, exiting mostly in liquid phase: this negative behavior is even stronger at low evaporator temperatures, when absorber pressure is lower and the rich solution is not much concentrated.

In addition, the GAX recuperation effect is limited by the low temperature of the absorption side: the point (37) at the precooler outlet is normally colder than the point (12), so the transferable heat comes entirely from the hot poor solution (23). After the mixing, the temperature of fictitious point (23') is not elevated: the higher it is, the larger the recuperation effect.

The problem consist exactly in the fact that during the isenthalpic expansion in the solution throttling valve (EXP1) a huge temperature loss is experienced by the fluid (about 5°C/bar): therefore, the GAX potential effect is reduced. This important thermal degradation due to a fluid expansion suggests that the poor solution Joule-Thomson coefficient is not favorable with this temperature and pressure conditions. Thus, further insights on ammonia-water mixture Joule-Thomson coefficient are done, obtaining the diagrams illustrated in the Section 2.2.1.

The results of this analysis show that the expansion occurs at a too much high temperature, at too low final pressure and at a too high concentration: as P_L is assumed to be dependent to the evaporation conditions[1], temperature and concentration are the parameters suitable to be varied.

One interesting fact is that the concentration in point (22) results from the mixing of the saturated poor solution (212) and the condensate fraction of the refrigerant vapor (41): this

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[1] This point is one of the differences with the advanced-GAX systems that often dissociate evaporator and absorber pressures.

last is really concentrated in refrigerant and, even if its flow rate is small, the contribution to the poor solution concentration increase is noticeable. Instead, its temperature is lower so a little positive effect on this side happens. However, the first effect dominates.

The other consideration that can be made is the following: being the condensate rich in refrigerant and relatively hot (in certain conditions it can be hotter than the fluid in tank N21), a recuperation in the the generator is interesting to be studied.

Finally, it is observed that point (13) has a temperature between (31) and (315): therefore, as the rectifier has a relevant heat duty, a partial internal recuperation can be done. Moreover, using the rich solution as cooling fluid would increase the vapor fraction in it, improving the separation tank N21 efficacy.

Resuming, the GAX A0 architecture offers four improvement paths:

1. Decreasing poor solution admission temperature in the Expansion Valve 1;
2. Decreasing poor solution concentration in the Expansion Valve 1;
3. Enhancing the condensate value in terms of refrigerant and heat recuperation;
4. Introducing a preliminary rectification stage cooled by the rich solution exiting from the GAX.

GAX A1 cycle This architecture takes advantage of the previous results and tries to accomplish all the improvements proposed: the implementation of each one of them is described.

The principal modification of the cycle A0 is the introduction of a Solution Heat Exchanger (named Economizer in the Figure 3.12) completely operating in the high-pressure side: this results to be a great idea for many reasons. The first is that this exchange is of reasonably simple realization: the temperatures of the fluids are suitable to do this exchange in whatever operational condition, the pressure level is the same on both sides and no particular transformation occurs besides heat transfer. Thus, a plate exchanger is perfectly adapted to perform this task. The only note is that the rich solution side slightly increases its vapor quality, but that point constitutes exactly the second advantage: an important saving in term of energy occurs and the vapor fraction entering the tank N21 becomes larger. Third and last, the main goal of decreasing the poor solution temperature in the solution throttling valve is reached, limiting the temperature degradation during the expansion.

The second architecture variation consists in the insertion of a rich-solution cooled rectification stage before the standard one: thus, another plate exchanger is added, improving the internal recuperation. The rectifier generally features a really hot vapor inlet, due to the high temperature required in the generator to separate the refrigerant from the absorbent: this arrangement allows to use this excess heat to increase the rich solution desoprtion, enchanching the role of the tank N21 and reducing the generator flow rate.

Finally, remaining in the view of the generation optimization, an adjustment in condensate recirculation is done. Being hot and really rich in refrigerant, mixing just before tank N21 admission would be advantageous: unluckily, combining a biphase fluid with a pure liquid could be complicated, even if simulations showed a larger COP increment. The choice of mixing just after the separation tank, therefore unifying (21) and (41), is preferred being both pure liquids: the refrigerant concentration inside the generator increases and also a little rectification heat recovery is done. The overall effect is positive, increasing the COP and further decreasing temperature and concentration at the solution throttling valve inlet: suggested improvement paths 2 and 3 are then implemented, resulting in the architecture shown in Figure 3.12.

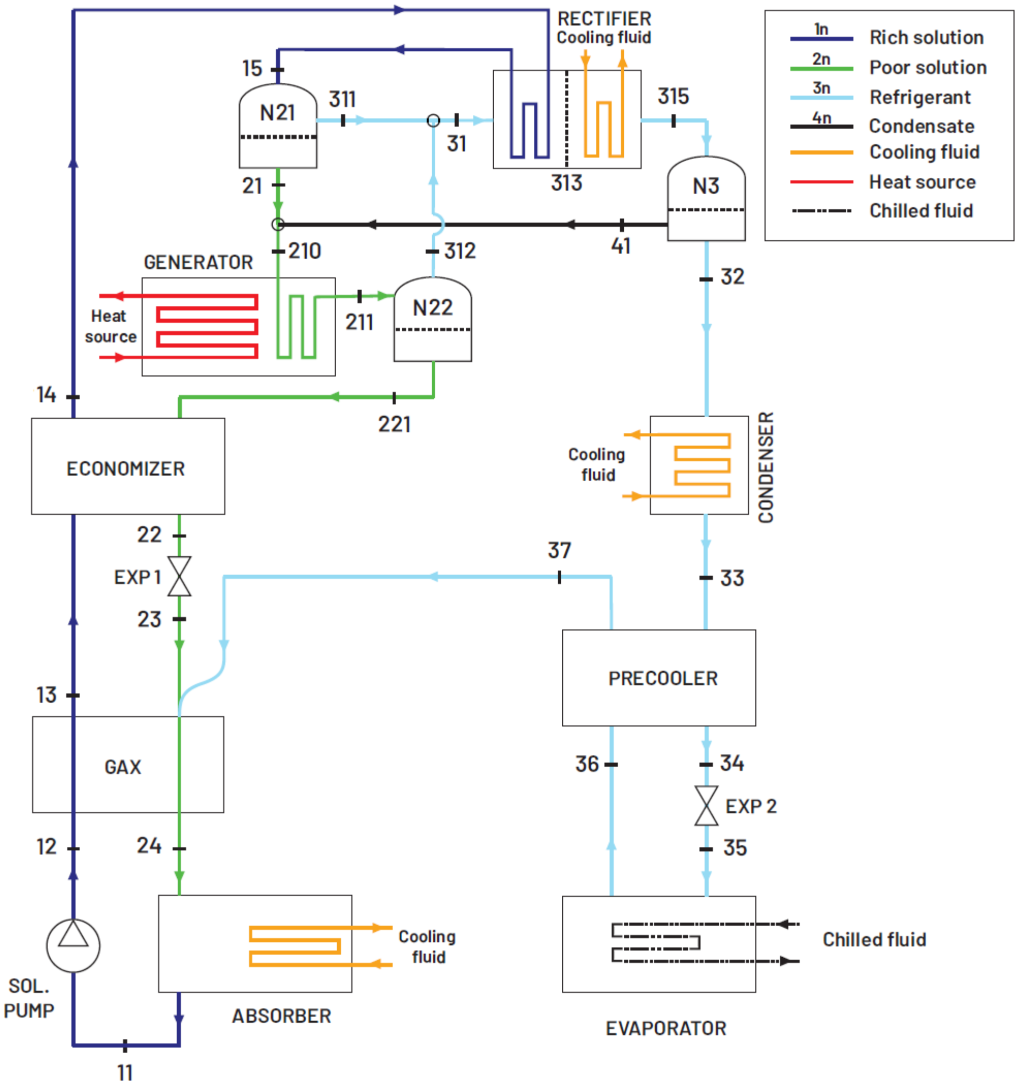


Figure 3.12.: GAX architecture improvement: configuration A1.

Results The cycle performance is way better than the previous case, but still needs to increase in order to be competitive with single-stage ammonia-water systems: results are however encouraging in this sense.

After an accurate analysis of the temperatures and of the elements heat duties it emerges that all the modifications implemented brought positive effects on the system: however, it is possible to go further.

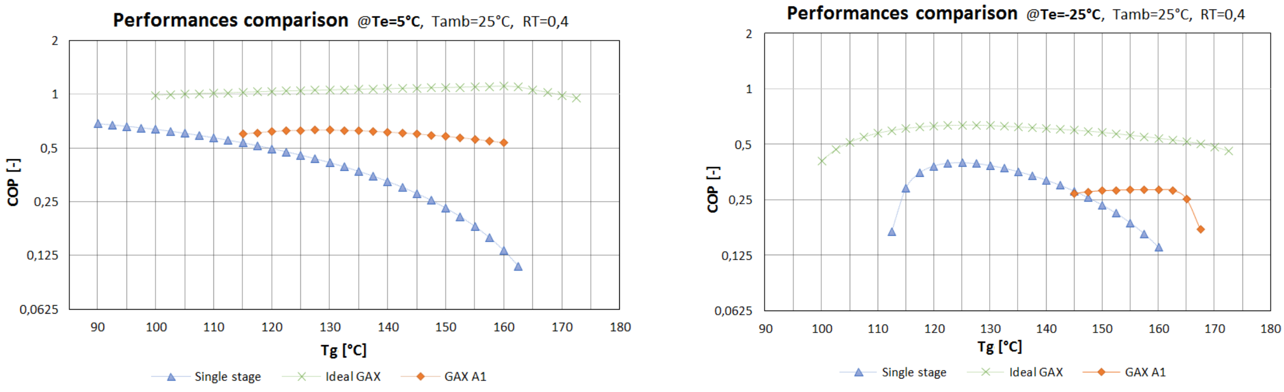
Observing both the economizer and the solution-cooled rectifier, it emerges that the rich solution heating is not optimized with the available internal sources: in fact, the poor solution at tank N22 outlet is hotter than the vapor at the rectifier inlet, and it has even a bigger heat capacity. Therefore, a better configuration would use the solution just exiting the GAX to perform the rectification. The rich solution entering the separation tank N21 would be more vapor-rich, decreasing heat duty in the generator.

Even if decreasing point (22) temperature and concentration brings some benefits to the system, thermal degradation is still present: at low evaporation pressures it appears to be inevitable and thus the only way to increase GAX internal recuperation is raising the inlet refrigerant temperature (37).

Finally, an issue with the parameter RT emerged: this indicator is useful to qualify the relation between generator, rectification and ambient temperature, but not to objectively characterize a determined configuration. In fact, two operational conditions can return the same RT, but having all different temperatures: to efficaciously characterize the rectification process it would be better to use the rectification temperature T_{rect} that is a measurable and well-defined parameter.

Also, T_{rect} is a direct indicator of the refrigerant concentration x_{ref} in the conventional part of the system: x_{ref} strongly influences the condenser and the evaporator pressures, therefore it is relevant when comparing two systems.

Despite all these flaws in the simulation, performance diagrams show some good points, as visible in Figure 3.13.



(a) COP vs. T_g at T_e=5°C and T_{amb}=25°C.

(b) COP vs. T_g at T_e=-25°C and T_{amb}=25°C.

Figure 3.13.: Generator and evaporator temperatures influence on GAX A1 architecture performance.

Globally, the two diagrams report an ideal GAX efficiency that is more or less the 30% better than the single-stage one in its best working condition: it is important to highlight this point because the robustness of single-stage systems is one of their principal flaws. In fact, operational conditions deeply influence their useful effect, as shown by the really variable dark blue curve in the graphs.

The proposed GAX A1 has a more constant trend, but still stays below the single-stage performance: however, working well even with high temperature sources opens a set of possibilities for the recuperation, as higher quality internal heat fluxes are available. Thus, further optimization is thermodynamically possible and envisaged by the not-yet-satisfactory performances.

Concluding, the GAX A1 architecture greatly increase GAX A0 performances, but still has to be improved. Some directions have to be investigated:

1. the solution-cooled rectification stage should be fed with GAX outlet rich solution;
2. the refrigerant temperature at GAX admission might be increased, internally exploiting waste heat fluxes or with an independent preheat;
3. as the generation block composed by the generator and the two separation tank N21 and N22 is traveled by numerous fluids at high temperature, a particular attention to its configuration can bring some benefits.

GAX A2 cycle The final proposed architecture for the plate exchanger-based double-stage NH3/H2O absorption chiller is the one schematized in Figure 3.14.

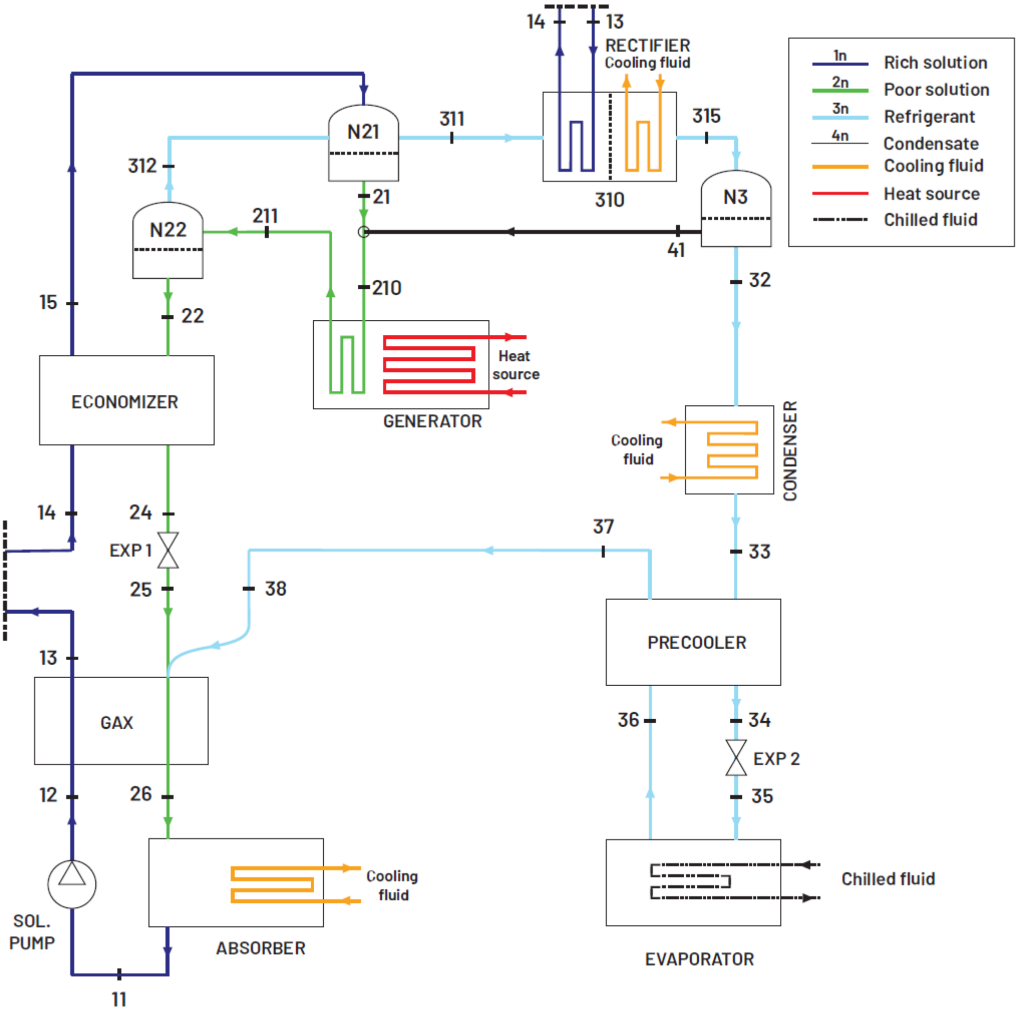


Figure 3.14.: GAX architecture improvement: final configuration A2.

The modification in the rich solution path is the most easy variation and, having been already discussed before, it does not deserve a particular insight. The proof of the utility of this solution can be demonstrated analytically through an exergetic analysis between the two configurations, or more rapidly through a numerical simulation.

Vice versa, the hypothesis of preheating the refrigerant (37) entering the GAX is more complex to be evaluated: there are many ways to realize this idea, but the real efficacy is not easy to predict. In fact, the available internal sources able to heat the refrigerant and contextually needing to be cooled are the following:

- the refrigerant vapor at condenser inlet;
- the vapor mixture entering the rectifier;
- the vapor mixture exiting the tank N22;
- the poor solution exiting the tank N22;
- the condensate exiting from the tank N3;
- the poor solution exiting the GAX;
- the poor solution entering the solution throttling valve.

Not all of these possibilities are investigated: a first screening is done to reduce the cases to be studied. In fact, heat transfer between gaseous fluids requires big exchangers and usually is not really performing due to the low heat transfer coefficients. Therefore, a simple pinch analysis diagram is done to compare the heat capacities rates ($C = \dot{m} * c_p$) of the fluids: the final decision is made to exclude the three first gas-gas exchanges, keeping the liquid-gas ones. This because hot vapor sources in this cycle normally have both lower mass flow rates and specific heat capacity than hot liquids, resulting in really tiny heat capacity rates.

The remaining cases are studied introducing an additional plate exchanger between points (37) and (38), traveled by both the refrigerant and the hot internal fluid. Also, the possibility of feeding this heat exchanger with an hot external source is considered. However, no one of these configurations shows relevant improvement, most of them generate negative effects, indeed: the idea of preheating the refrigerant to raise GAX absorption side temperature is discarded.

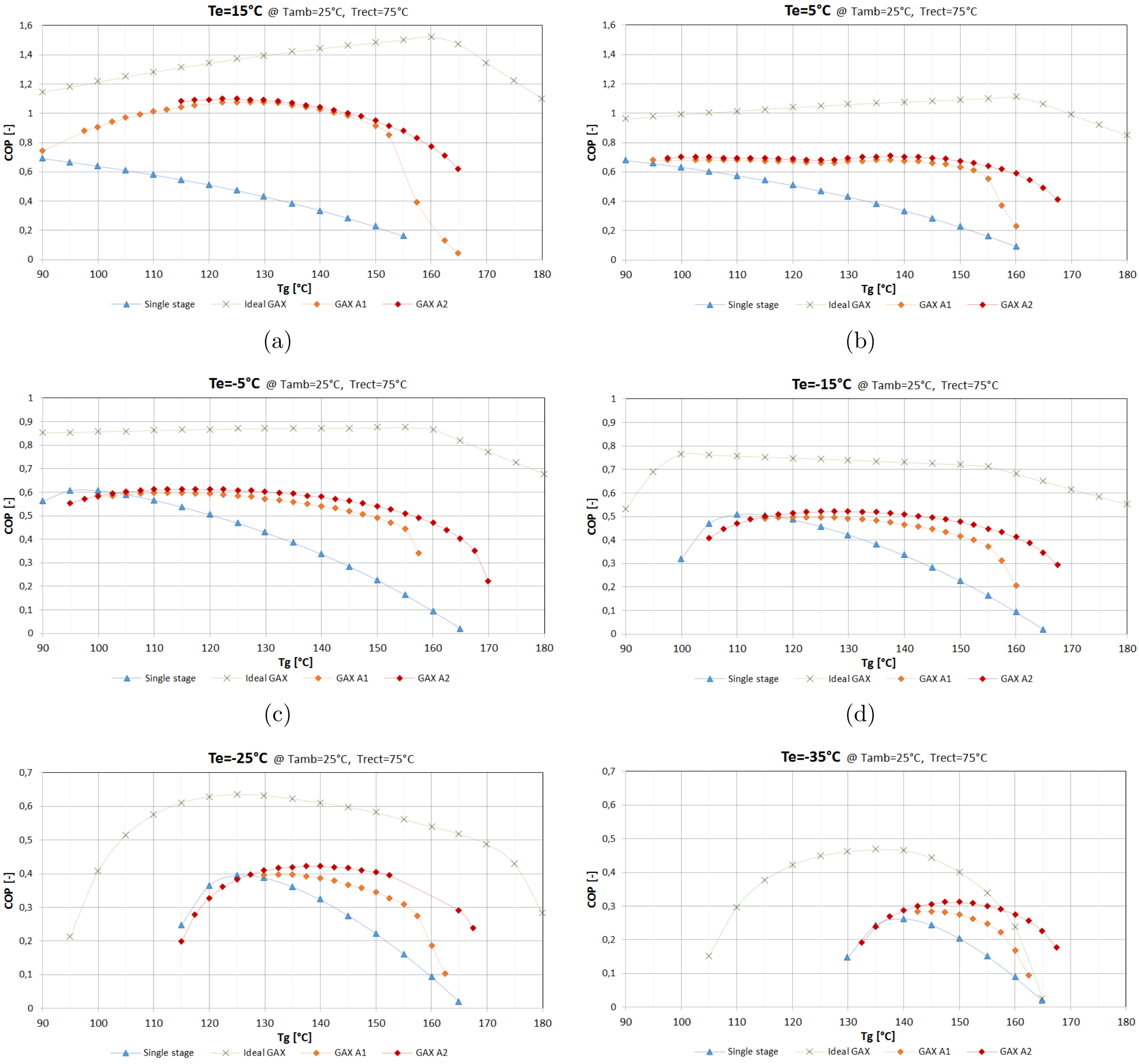
Finally, a particular insight has to be done on the second modification introduced in the GAX A2 architecture: the connection between the two separation tanks N22 and N21. This might seem a bizarre idea, but a huge difference exists in mixing the two vapor flows before and after the tank N21. The vapor exiting from the separation tank N22 exits at temperature generator, therefore really hot: if mixed after the tank N21 the resulting vapor would experience a temperature increase, but its caloric content would be wasted in the rectifier. Therefore, it is better to use this hot vapor to perform a last generation inside the separation tank N21: the vapor (312) can be forced to exchange with the colder rich liquid fraction at the bottom of the tank N21, evaporating a part of it.

Exploiting this heat recuperation opportunity allows to have, with same external conditions, a larger, colder and more concentrated vapor flow rate at rectifier admission, decreasing both generator and rectifier heat duties.

The feasibility of this solution has been proved asking some separation tank manufacturers, but the real effectiveness depends from many factors: for the calculation it has been assumed like the previous, $\varepsilon = 0.8$.

3.3.2. Simulation results

As the GAX A2 architecture is assumed as the final configuration, many simulations are effectuated to explore performances and sensitivity to the main parameters.



(a) (b)

(c) (d)

(e) (f)

Figure 3.15.: Generator and evaporator temperature influence on COP for different cycles.

The various diagrams in Figure 3.15 provide interesting information about the new architecture GAX A2. The first diagram (a) shows with great evidence the COP difference between single-stage cycle and the GAX ones: however, the cooling temperature is not so cold, just 15°C at the evaporator. The generator temperature influences quite effectively the performance and its optimum temperature lays at low temperatures, differently to the ideal GAX that shows it OGT at about 160°C.

The COP drops decreasing the evaporator temperature, making almost negligible the gain in the cases of -5°C (c) and -15°C (d) at the evaporator. The interesting fact is that the shapes of single-stage and GAX cycle are totally different: the former operates at his best for a small set of low temperatures, strongly worsening otherwise; the latter shows good and stable performances for a wide range of generation temperatures, describing well-defined parables.

Last but not least, the differences between GAX A1 and GAX A2 performances justify the improvement: if under positive cooling conditions (a-b) they behave more or less alike, that is not the case for negative cooling. The gain is even more evident at -25°C or -35°C at the evaporator (e-f).

A note that is really important to keep in mind is that the rectification temperature $T_{rect} = 75°C$ is imposed instead of the parameter RT_{rect} to compare the four cycles: this causes a little bias in the interpretation of the results. This is also relied to the ambient temperature chosen, $T_{amb} = 25°C$: these two conditions are particularly favorable for the single-stage cycle that operates at his best. Different situations, as it is shown before, would cause the GAX A2 coefficient of performance to overwhelm the single-stage one. A more accurate comparison should consider for each cycle the best COP possible for certain a T_e and T_{amb}.

The demonstration of the COP dependence on rectification temperature is proved by the following Figure 3.16. The range of evaporation temperatures between $T_e = 15°C$ and $T_e = -25°C$ has been studied and it results that decreasing the evaporator temperature the best COP requires higher rectification temperatures: in fact, it passes from 65°C to 80°C with $T_{amb} = 25°C$.

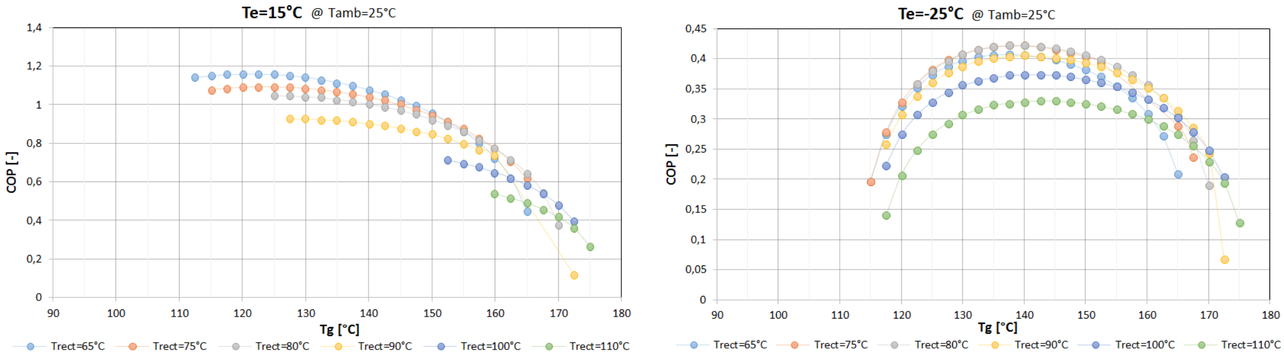
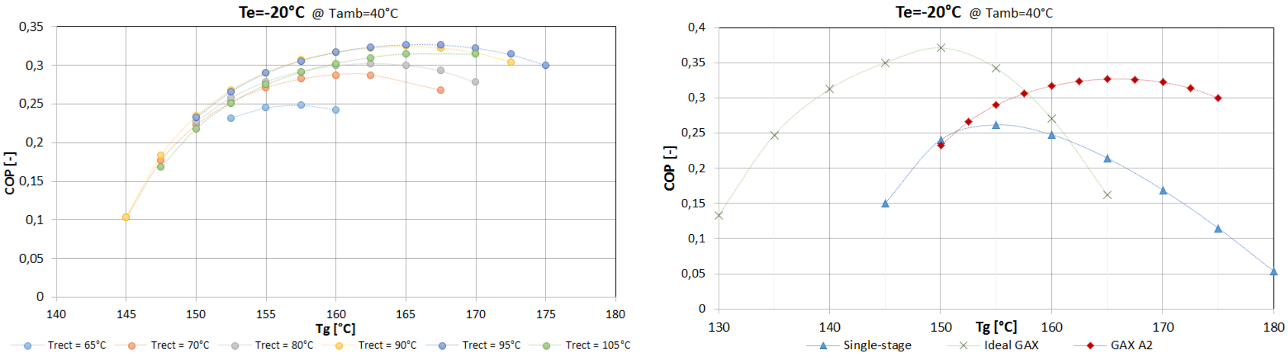


Figure 3.16.: Rectification temperature effect on COP for different external conditions.

Nominal conditions As the GAX A2 architecture showed to operate well in normal conditions, the interest exists to observe it behavior in nominal conditions of $T_{amb} = 40°C$ and $T_e = -20°C$.

The influence of the rectification temperature is investigated again and the results are reported in Figure 3.17a: the incidence of this parameter decreases, as the minimum and maximum COPs differ of just a little (0.325-0.25). However, performances are way worse than the previous case in Figure 3.16: almost 0.15 is lost just increasing the ambient temperature of 15°C. Thus, a considerable dependence between T_{amb} and the optimum rectification temperature emerges, indicating a relative complexity in predicting the best operational condition in the GAX cycle.

In this situation, the external temperature is assumed higher than the standards, simulating an application in hot environments or during peak periods in summer. An increase of the ambient temperature means a higher pressure to condensate the refrigerant and a worsening of the absorption process: coupled with a low evaporation temperature really challenging operational conditions are realized.



(a) T_{rect} effects on COP.

(b) COP change due to T_g variation.

Figure 3.17.: Nominal conditions ($T_{amb} = 40°C$, $T_e = -20°C$) GAX A2 performances.

The GAX system, thanks to the many internal heat recovery solutions, shows to be robust against changes in external constraints: its operational range remains wide differently from the single-stage that rapidly loses its efficiency, as shown in the Figure 3.17b. Moreover, at low evaporation temperatures the plate exchanger-based GAX remains quite close to the performance of the almost ideal model proposed by Wang et al. (labeled "Ideal GAX") based onto distillation columns: the trend of the GAX A2, even if lower of about 0.07 in COP, indicates a sturdier behavior facing extreme conditions. This characteristic of plate exchanger-based two-stage absorption systems was one of the key point to be demonstrated for justifying their further development: an easier control combined with a wider operational range might be a really interesting feature for commercial purposes.

3.4. Heat Pump case

In the chapter dedicated to the state of the art the functioning of absorption cycles was detailed: in particular, it was highlighted the relation between chillers and heat pumps, which differ in the useful output and operational conditions, but essentially not in the architecture. Therefore, the interest arises in developing a plate exchanger-based GAX heat pump to similarly take advantage of the internal recuperation.

Recalling Eq. (2.7) the heat pump COP is expected to be higher than the chiller one, but this relation between COPs is true only when the cycles work in the same external conditions: usually this is not the case.

Starting for the most similar parameter, the generation temperature range is alike, with just some little differences in the optimum position: the variation of the working point causes quite the same effects that in chillers.

Instead, evaporation temperatures are usually higher, above 15°C, because cooling is not the goal: further, the chiller study showed that operating with high evaporator temperatures caused the COP_R to increase consistently, so the same is expected for heat pump performances. However, a good feature for an absorption heat pump would be operating with decent COP_{HP} at nearby-negative temperatures, allowing application in cold environments.

The fundamental difference that totally opposes the two cases is the intermediate fluid condition: in fact, absorber and condenser in chillers are separately cooled by two ambient-temperature fluids while in the heat pump configuration they are traveled in series by a fluid that gets heated twice. Thus, their operational temperature rises in order to generate a sufficiently hot output at T_{out}, the useful one.

This heat carrier fluid is normally expected to reach 65-70°C for room heating or hot domestic water production: evidently, the higher its temperature, the higher its value. The main challenges are two: increasing the heat carrier fluid temperature increases the pressure in the generation block, with problem in tightness and component resistance; also, a higher cooling fluid temperature decreases the maximum concentration of the rich solution. The consequence of these effects is generally a COP decrease.

The objectives for the heat pump new architecture are the following:

- realize a working cycle that provides internal heat recuperation, demonstrating the effectiveness of plate exchanger-based GAX in heat pump systems;
- generate an outlet fluid of at least 70°C with a $COP_{HP} > 1.5$ and $T_{amb} = 35°C$;
- increase the operational range with reference to single-stage cycle.

3.4.1. Architectures

As the proposed chiller architectures were acceptable, the main achievements have been kept to speed up the development of new cycles. The connection between the two separation tanks is preserved, differently from the solution-cooled rectification stage that is removed. The Figure 3.18 details the starting heat pump configuration.

GAX HP1 cycle This proposed cycle utilizes the literature approach for heating the heat carrier fluid, admitting it at the a condenser and exiting after the absorber. Hence, the condensation happens at relatively low temperature and pressure, while the absorption reaction is cooled by an already quite hot fluid: the rich solution concentration is limited by the high temperature, although manufacturing costs can be reduced thanks to the lower pressure in the generation side. Despite this tradeoff between absorption performances and system highest pressure value, results are encouraging: the cycle already overcomes $COP = 1.5$ and the heat carrier fluid output temperature reaches 70°C.

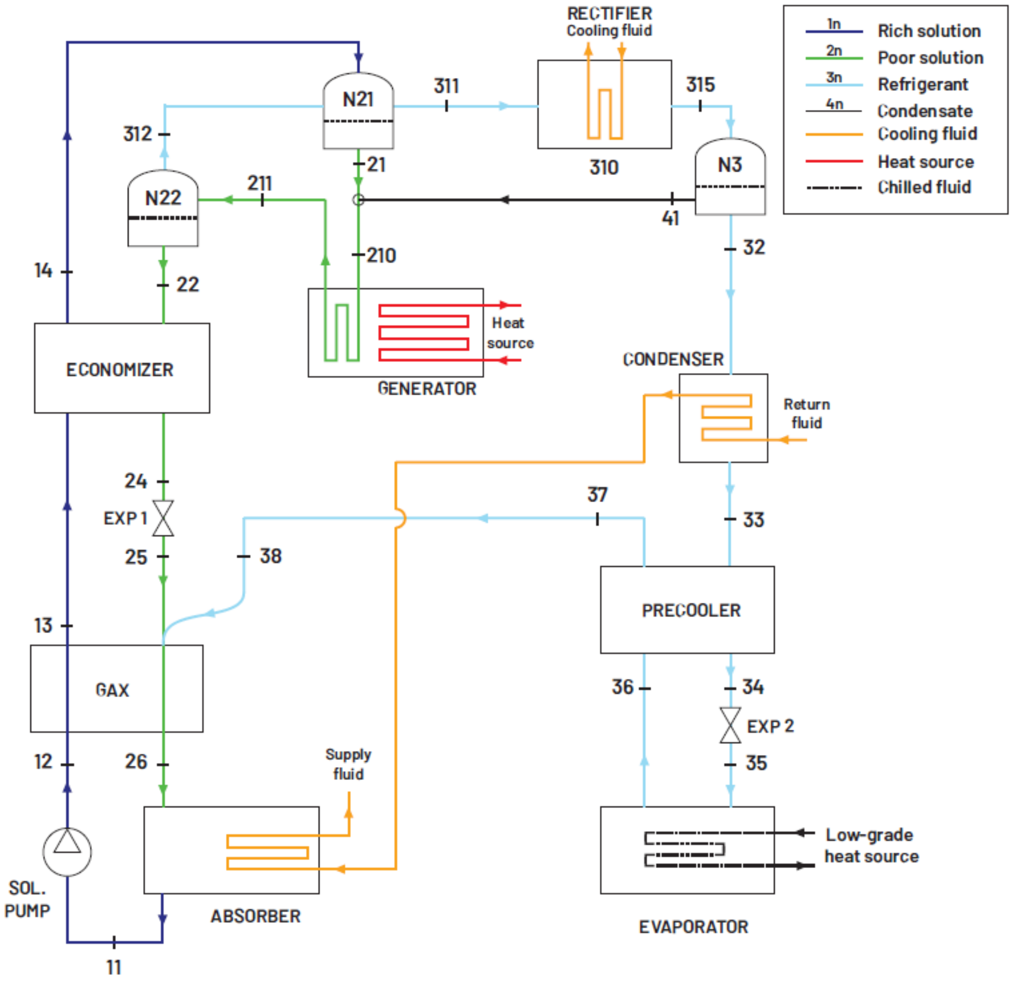


Figure 3.18.: GAX Heat Pump architecture: configuration B1.

Some further improvements can still be done: as the rectifier operates at high temperatures, a preliminary rectification stage appears to be sensed. However, the best position to perform it is not evident, as the rich solution exiting the pump or the GAX is suitable: both cases are evaluated numerically.

Among an overall good behavior, the only parameter that is slightly disappointing is the rich solution maximum concentration, as predicted before: it is, in fact, not really high. To improve the absorption process, a further cooling of the absorber and a pressure increase in the evaporator should be provided. These points can be satisfied totally or partially in three ways:

- an additional absorption stage is provided, cooled by the evaporating fluid;
- an additional absorption stage is provided, cooled by the low-grade heat source that firstly heats up in the absorber, decreasing rich solution saturation temperature, and that after gets cooled in the evaporator, increasing its pressure;
- the cold heat carrier fluid inlet is placed in the absorber and the outlet is moved to the condenser, without adding new elements.

All the previous solutions are realizable, but the first two imply the addition of an extra plate exchanger: even if the second solution theoretically offers the best gain, the third one is privileged because it does not require additional components.

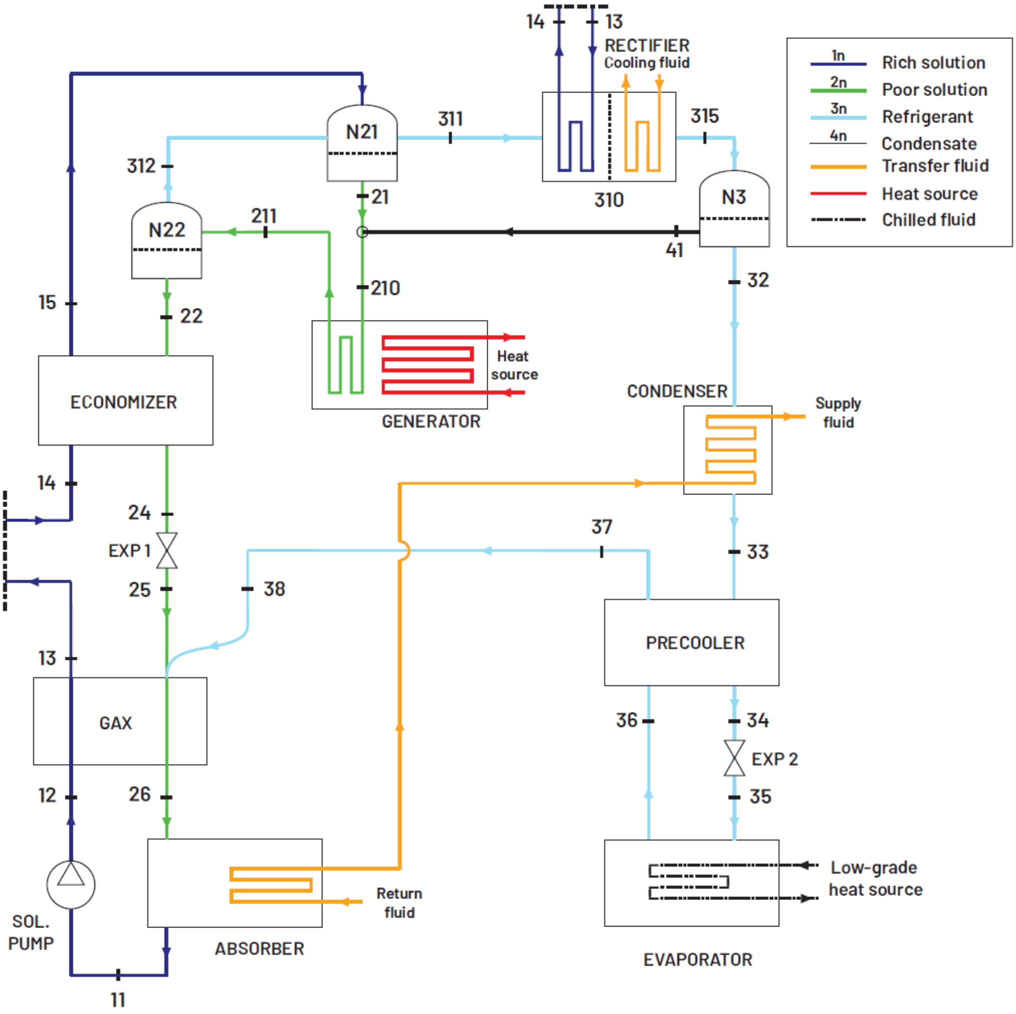


Figure 3.19.: GAX Heat Pump improvement: final architecture B2.

GAX HP2 cycle The discussed improvements in rectification and absorption are tested: the solution-cooled rectification is found to be significant, with the retained best position after the GAX on rich solution side. However, the difference in COP increase is not really big.

On the side of absorption and condenser cooling, the inversion of the heat carrier fluid path is also simulated: a higher pressure in the generator block is observed, while a contextual performance coefficient raise is driven by the rich solution concentration increase. This last one alone contributes to a COP improvement of about 0.2 points (from 1.6 to about 1.8), making legitimate to wonder if the increased cost for high pressure-resistant components are effectively worthwhile.

Considering the results of the simulations, the final retained cycle is represented in Figure 3.19. However, further testing is necessary to better understand the limits of these kind of systems, as high pressures and temperatures in the components expose at new risks and challenges: a focus is needed on the operational range of the proposed cycle and also on its stability, in term of maintain of high performances independently of the external conditions.

3.4.2. Simulation results

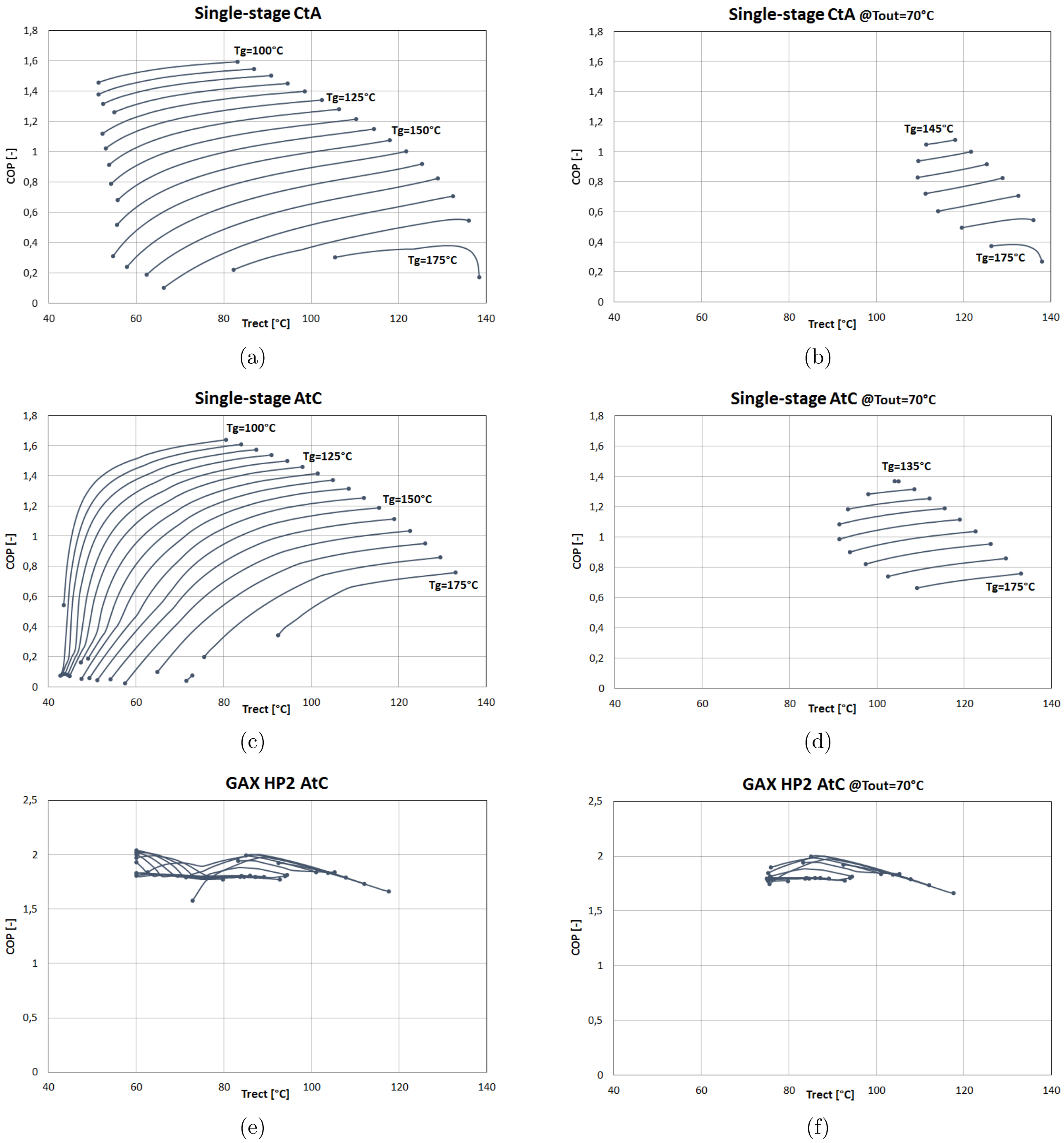
As the GAX interest is first of all increasing the performance with reference to single-stage systems, therefore a dedicate model for the standard NH3/H2O absorption heat pump is created. This is further modified to include the two possible paths of the heat carrier fluid, Absorber-to-Condenser (AtC) and Condenser-to-Absorber (CtA).

During the simulations some interesting features emerged for both the single-stage and the GAX models: in particular, the relations between COP, rectification and generation temperatures change with reference to the chiller case. Before, really little combinations of T_{rect} and T_g had good COPs and thus cycle functioning was limited to a small operational range. Vice versa, heat pumps can be run more or less efficiently in a really wide condition range.

Another important aspect has to be considered, though: for single-stage cycles, the heat carried fluid temperature at the output (called T_{out} in the discussion) is not constant and strongly varies with the other parameters. Therefore, even if the cycle shows to have many possible numerical solutions with acceptable COP values, it might not respond to the expectations in term of output temperature level.

In the Figure 3.20 it is possible to observe the difference in the wideness of the single-stage cycle ranges: the operational conditions that allow having an output fluid at minimum 70°C (b-d) are way less than the possible ones (a-c). This fact can be easily explained for the case of Absorber-to-Condenser configuration. The refrigerant exiting from the rectifier and separated in the tank N3 is the heat source for the transfer fluid: the hotter it is, the higher is the possible T_{out}. So, the first criteria to attend an hot output is having an higher T_{rect}. However, the generation temperature plays also a role, influencing the absorber temperature that is responsible for the first heating stage of the carrying fluid: if it is not enough, the condenser heating would not be able to reach the expected temperature. Something similar happens for the Condenser-to-Absorber configuration, although the rectification temperature is less incident than the generation one.

Knowing that AtC mode is the better one in term of COP, the rectification temperature assumes a more relevant role in representing the performances of the cycle, being the limiting factor of the output fluid temperature: in the Figure 3.20 the COP is represented as a function of T_{rect}, while the T_g is kept constant for each data series. Thus, this situation is opposite to the chiller classical performance diagrams just to ease diagrams interpretation.



(a) (b)

(c) (d)

(e) (f)

Figure 3.20.: T_g and T_{rect} influence on the COP for different heat pump cycles (at $T_{amb} = 35°C$).

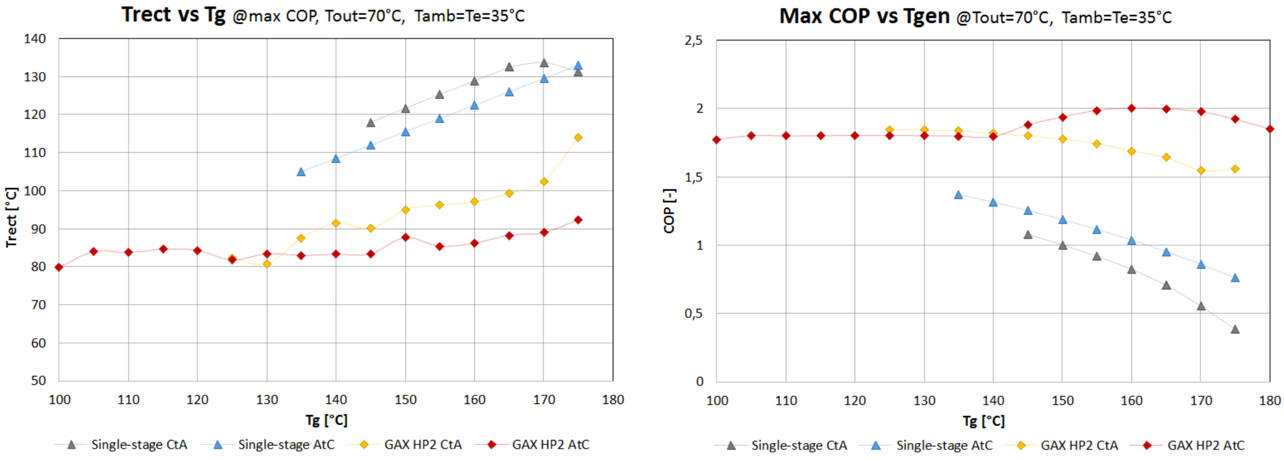
As already said, single-stage cycles show a really little area of suitable conditions for producing more than 70°C at the hot outlet: in both cases this region is situated at elevated T_{rect} and also high T_g. Differences in performances are also evident: the (d) region features higher COPs, more suitable generation temperatures and it covers more rectification temperatures, demonstrating the convenience of the Absorber-to-Condenser configuration.

In the generic output temperature diagrams (a-c) the same difference can be observed: moreover, the CtA curve shows a stark end near $T_{rect} = 50°C$ while the AtC diagram converges gradually to its limit point.

Observing now the two GAX figures (e) and (f) it is clear that the system behavior is revolutionized. Firstly, COPs are generally higher, mostly included between 1.6 and 2.1: really promising values. Secondly, the different T_g series are more or less superposed, indicating that the importance of this parameter exists, but it is lower than in the single-stage cycles: operating outside design conditions, that is normally the real case, would not be terrible for the system performance. Finally, all the range of T_{rect} generates elevated COPs, therefore the rectification temperature can be effectively varied to research the cycle optimum point. This last feature is not trivial, as usually the generator temperature is imposed by the source: being able to regulate on the rectification temperature would be practically interesting.

For all these reasons, the diagram (f) with $T_{out} > 70°C$ does not differ much from the generic one: as the T_{rect} is the most limiting factor for T_{out}, all the operational conditions before a certain value of T_{rect} are excluded. The lost area is not as big as in the previous case.

Before proceeding over, a note on the GAX heat pump system with the Condenser-to-Absorber configuration: it has not been included in the Figure 3.15 as its contribution would have been minimal. The same results of the GAX AtC are obtained, just a bit worse: COPs are generally 0.2 points lower and the above-70°C T_{out} region is slightly smaller.



(a) Best T_{rect} depending on T_g.

(b) COP change due to T_g variation.

Figure 3.21.: Best functioning point comparisons for single-stage and GAX architectures.

Describing the serviceability features of the various configurations does not clarify unequivocally if GAX systems are also the most performing for a given T_{out} and T_{amb}: a different approach is then utilized. Through the software EES, the best functioning point is researched for each T_{out}, T_{amb} and T_g varying the T_{rect}, then T_g is updated. A factor that has to be kept into consideration is that all the simulations of this section refer to $T_{amb} = 35°C$, that coincides also with the inlet heat carrier fluid temperature. Evidently, a more accurate study should involve different ambient temperatures to validate these trends with larger certainty.

However, the results are reported in Figure 3.21: as expected, the GAX-based cycles perform better and, under a certain T_g, the difference between Absorber-to-Condenser and Condenser-to-Absorber scheme is negligible. Vice versa, with hotter generation temperatures the AtC configuration behaves better.

Single-stage cycles are both overwhelmed by the two-stage ones and in general they confirm the convenience in feeding first the absorber with the heat carrier fluid.

An empirical relation that emerges from the two diagrams is that a higher rectification temperatures leads to lower performances: this trend is confirmed both for single-stage and for GAX cycles.

The GAX configured in Absorber-to-Condenser mode has proved better than what literature suggested, now the question should concern how far performances can be pushed: therefore, the thermodynamic and mechanical limits of the system are explored.

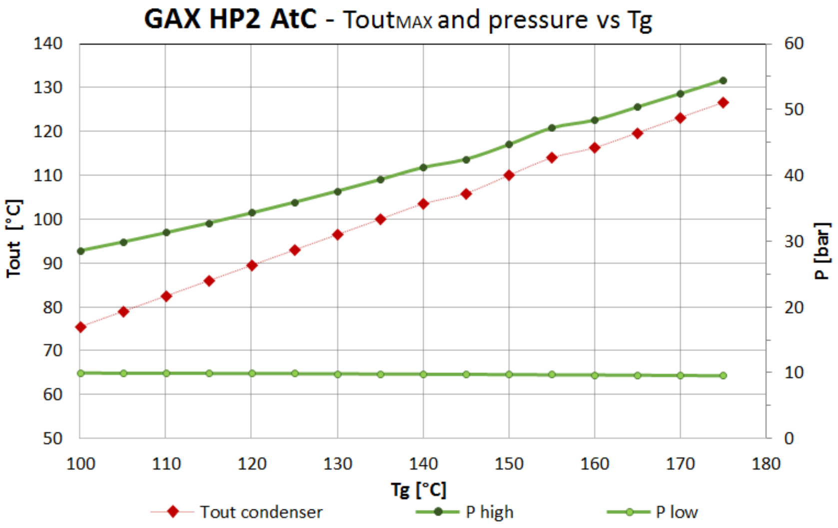


Figure 3.22.: Maximum heat carrier fluid output temperature and pressures relation with T_g.

A heat pump has the goal of producing as output an hot fluid: the higher is its temperature, the most appreciable is the system. Through the simulations it is observed that for increasing generator temperatures the maximum T_{out} also increases: this happens in an almost linear manner, so no limitations seem to be present on this side, as the Figure 3.22 shows. What constitutes a considerable flaw for the system is the pressure: in fact, the condensation pressure, that is the highest in the cycle, proportionally follows the temperature growth reaching the enormous value of $P_{high} = 54bar$ at $T_{out} = 125°C$ and $T_g = 175°C$. Vice versa, the lowest pressure of the cycle remains constant, not depending from the generator temperature, but from the evaporator one: in this simulations this last is fixed at $T_e = T_{amb} = 35°C$, so results confirm the expectations.

The last point to be cleared is the thermodynamic convenience of producing hot fluids at high pressures, because being possible does not imply being worthwhile: nevertheless, proving that high COPs are maintained in extreme conditions would open a series of interesting application paths. The COP at the maximum T_{out} condition is represented in Figure 3.23 together with the maximum T_{out}, for both the GAX AtC and the single-sage AtC cycles.

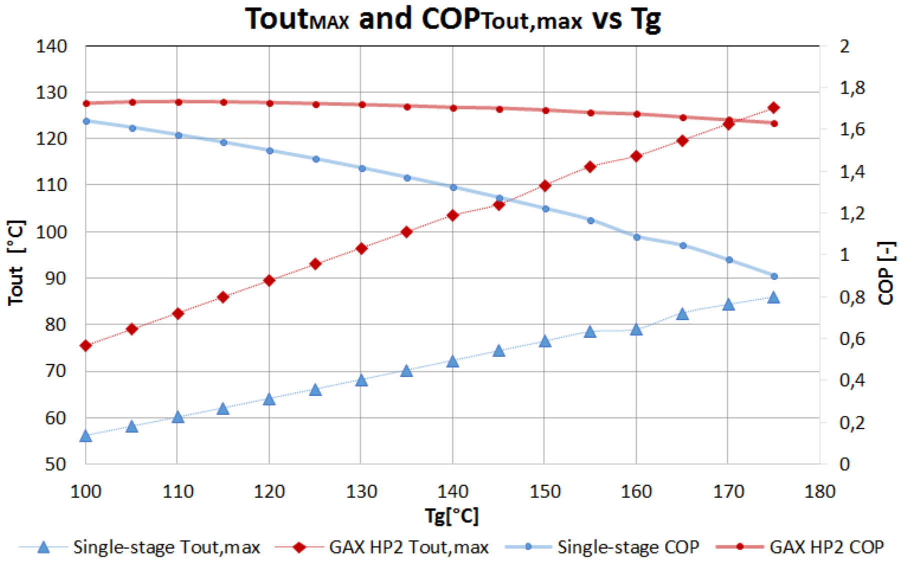


Figure 3.23.: Maximum heat carrier fluid T_{out} and COP for single-stage and GAX heat pumps.

The diagram brings to evidence a great number of important elements. First of all, the COPs of the GAX cycle show an extreme stability against the heat carrier fluid output temperature and the generation temperature: in less of 0.2 COP points are included all the generation temperatures in a range of 75°C. Moreover, these values remain high, always above $COP = 1.6$.

Nevertheless, previous simulations showed that approaching $COP = 2$ was possible: in fact, the maximum T_{out} condition is not usually the best one, as the fluxes in the absorber and the condenser should be perfectly balanced to partially heat the heat carrier fluid in the most complementary way possible. As heat transfers depends on available temperatures, lot of variables are involved and the max T_{out} and max COP conditions usually do not meet: further improvements in this sense could be really useful for GAX heat pump development.

The Figure 3.23 exalts the GAX, but at the same times shows how poorly the single-stage cycle behaves: the COP literally crumbles at high T_g, while maximum T_{out} stays rather low. This poor performance is due to the lack of an internal heat recuperation system that does not allow to take advantage of high temperatures at the generator: the valuable heat is just partially used and then wasted, not even being able to properly heat the carrying fluid. The GAX effectiveness with reference to standard systems is clearly proved.

Concluding, it is thermodynamically possible and relatively advantageous to run a GAX heat pump with a really high T_{out}, but realization costs would be enormous: also, regulatory problems would arise due to the risks connected to the operation in extreme conditions. Therefore, as it stands the technology for pressurized elements, the commercially-interesting operational limit is set to about $P_{high} = 30bar$, for a theoretical $COP = 1.8$ and almost $T_{out,max} = 80°C$.

3.5. Conclusion

The interest in NH3/H2O two-stage absorption systems comes from the wider operational range they have with reference to LiBr/H2O cycles. Performances are either good thanks to the internal heat recuperation, so GAX systems are a valid solution. Nevertheless, the cost for a standard GAX is high and price must decrease in order to be commercialized: thus, a simplification in the assembly is necessary to ease manufacturing and a standardization of the GAX component would also be really helpful for cost decrease.

Instead using a single tailored, bulky and complex element, the innovative idea is to perform the same transformations through commercially available components. Studies have been already carried on absorption and desorption processes inside plate heat exchangers, so they are proposed for implementation in the cycle. Although, new additional components are required to complete the GAX transformations, as separation tanks to divide liquid and vapor phases inside the system. Further insights are necessary to optimize the new architectures and to understand the role of the new elements.

Single-stage and standard GAX numerical models are firstly required for determining the main relations between the parameters, and then for comparing the global performances of the new cycles. Thus, models of the plate exchanger-based GAX cycle have to be built to test the different possible configurations: each new arrangement is simulated, the good features are kept and some evaluations are done to further improve the system. This process is repeated until no consistent improvement is still realizable.

Before numerical simulations are performed, a physical model needs to be established: each component is considered as a control volume where mass and energy balances must be satisfied, then the First and Second Principles of Thermodynamics are imposed all over the system. Fluids are considered to be real, so properties are obtained through software functions or analytic correlations. The elements performances are generally considered real and thus corrected by the mean of efficiency (η_{el}, η_m) or effectiveness $(\varepsilon_{ech}, \varepsilon_{abs})$ coefficients: for the latter, the $\varepsilon - NTUmethod$ is put in evidence.

The chiller GAX case is studied with different goals: demonstrate the independence from distillation columns; overcome single-stage systems performances; prove the capability of working at low temperature with good efficiency. To do so, three main steps have been necessary. Firstly, the GAX A0 architecture is configured: no optimization is done yet, but all the standard GAX transformations are recreated with commercially available components, as plate exchangers and separation tanks. The second GAX A1 arrangement introduces a solution-cooled rectification stage and the condensate recuperation, achieving a little COP increase. Finally, the last GAX A2 architecture totally changes the approach to vapor separation in the generation block: the two tanks are connected in series, allowing a further heat recuperation and an even better COP.

The influence of the generation temperature T_g is then studied: generally a value that maximizes the Coefficient of Performance (COP) exists and it is called Optimum Generation Temperature (OGT). Similarly, even an Optimum Rectification Temperature (ORT) exists as well.

Also, the relations between the evaporator temperature T_e, the ambient temperature T_{amb} and the COP are investigated: temperatures are usually the externally imposed variables of the systems, as they usually are independent and uncontrollable. Performances showed being strongly affected by their variation: a decrease of T_e and an increase of T_{amb} cause a noticeable drop in COP, and vice versa.

However, the comparison of the GAX A2 architecture with the single-stage cycle shows a really positive behavior, improving the standard performances: the COP is generally 20-30% higher and more constant against operational condition changes, especially in extreme conditions (low T_e and high T_{amb}).

Most of the results of the chiller architecture study are utilized to develop the respective heat pump plate exchanger-based GAX cycle. As the operating conditions are mostly the same the GAX A2 is used as the starting base, with the important difference of the intermediate-temperature fluid path: now it flows from the condenser to the absorber in series, as the useful effect is given by its temperature increase.

The new architecture GAX HP1 keeps almost all the features of the GAX A2, except the preliminary rectification stage. Results are quite good, but little improvements are still possible: the GAX HP2 restores the solution-cooled rectifier, as its utility is proven also in this system.

The main point of discussion is the direction of the heat carrier fluid: quite important differences in COP and pressure are observed between the Condenser-to-Absorber (CtA) and the Absorber-to-Condenser (AtC) flow. The latter behaves better, even if higher mechanical resistance is demanded to elements in the high pressure side of the system.

Due to the different arrangement with reference to the chiller case, parameters importance slightly changes: T_{rect} reveals to deeper influence the performance of the cycle, both in term of COP and of maximum outlet temperature T_{out} of the carrying fluid. The generator temperature continues to be a determinant factor, as an Optimum Generation Temperature (OGT) still can be found for most working points.

Simulations of single-stage heat pumps show a wide difference in operational conditions with reference to GAX systems: the latter appears to be sturdier, being able to maintain high COPs for a large number of T_{rect} and T_g combinations. Also, the maximum output temperature possible with the two kind of cycles is observed: as before, the GAX provides the better results overwhelming the single-stage ones.

Limitations to the heat pumps operational conditions for both single-stage and two-stage cycles are determined by the pressure level in the high pressure side: as more material and more complex manufacturing is required to withstand extreme conditions, costs increase significantly with the cycle maximum pressure. Also, taking into account the risks and the regulatory aspects due to pressurized system operation, commercial interests limit the system highest pressure to about $P_{high} = 30bar$, with consequent $T_{out,max} = 80°C$.

Conclusion

This work concerned the modeling and design of a GAX ammonia-absorption system, in both chiller and heat pump configurations. After a first geopolitical, environmental and techno-economic contextualization, the principles of refrigeration have been introduced: a focus on absorption systems has been done, with a particular attention to the fluids properties. Then, the acquired knowledge allowed the development of new architectures for two-stage NH3/H2O absorption cycles.

The initial goals for this study were: proving that GAX systems could be effective also without the classic distillation columns; developing a cooling cycle with a Coefficient of Performance $COP_R > 0.5$ for an evaporator temperature T_e=-20°C at an ambient temperature T_{amb}=40°C; developing an heating cycle with $COP_R > 0.5$ for a T_e=-20°C at T_{amb}=40°C; sizing all the components; modeling a 3D assembly of the machine.

During the discussion of the work many results have been presented. The main achievements have been: the realization of a performing chiller cycle, capable to operate in a wide range of external conditions (T_{amb}=5°C to 40°C) with variable evaporator temperatures (T_a= +15°C to -40°C); the realization of a heat pump architecture able to reach really high temperatures (up to 125°C at the output temperature T_{out}) with appreciable performances (COP_{HP}=1.6 to 2); the creation of a diagram detailing the Joule-Thompson coefficient variation for ammonia-water mixtures, useful for further exergetic optimization; finally, the realization of a brief, but complete overview of two-stage ammonia-water absorption systems could also be included in the achievements, as further studies might take advantage of.

The first three initial objectives have been completely reached, even with large margin in the case of the heat pump configuration. Vice versa, the sizing of the system elements has not been completed and thus also the 3D model has not been built. This two last goals have been strongly influenced by the retards in the simulations and, in minor part, by the difficulties found in the design of the main components of the system, GAX and economizer above all.

However, in this work a few other imprecision have been committed: in the chiller architecture study the comparison between the best functioning points for single-stage and GAX cycle has not been done; in the heat pump case the effects of T_{amb} variation have not been investigated; finally, in any case an exergetic analysis has been done, neither on the single components nor on the whole system.

There are numerous upgrade perspectives for two-stage NH3/H2O absorption systems, in particular for what concerns the elements configuration: advanced architectures, provided of a pressure-increasing device between the conventional and the absorption sides of the machine, have already been studied for the GAX cycle showing good results. Also, more robust numerical models could be coded as simulation problems often occurred in the EES environment. Finally, better data post-treatment can be done: for example, conducting a parametric analysis and performing an exergetic analysis on the components, a deeper optimization would be possible.

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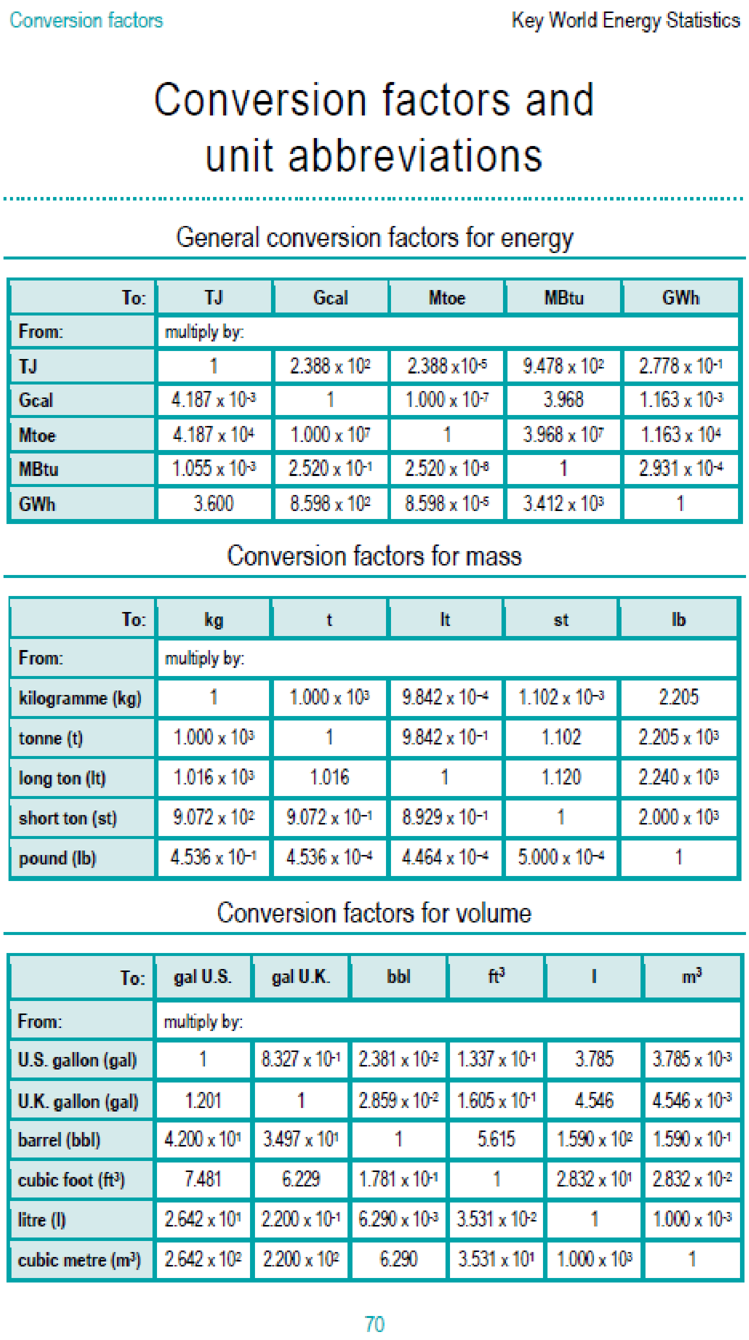
A. Study context data and diagrams



Conversion factors

Key World Energy Statistics

Conversion factors and unit abbreviations

General conversion factors for energy

To:	TJ	Gcal	Mtoe	MBtu	GWh
From:	multiply by:				
TJ	1	2.388×10^{2}	2.388×10^{-5}	9.478×10^{2}	2.778×10^{-1}
Gcal	4.187×10^{-3}	1	1.000×10^{-7}	3.968	1.163×10^{-3}
Mtoe	4.187×10^{4}	1.000×10^{7}	1	3.968×10^{7}	1.163×10^{4}
MBtu	1.055×10^{-3}	2.520×10^{-1}	2.520×10^{-8}	1	2.931×10^{-4}
GWh	3.600	8.598×10^{2}	8.598×10^{-5}	3.412×10^{3}	1

Conversion factors for mass

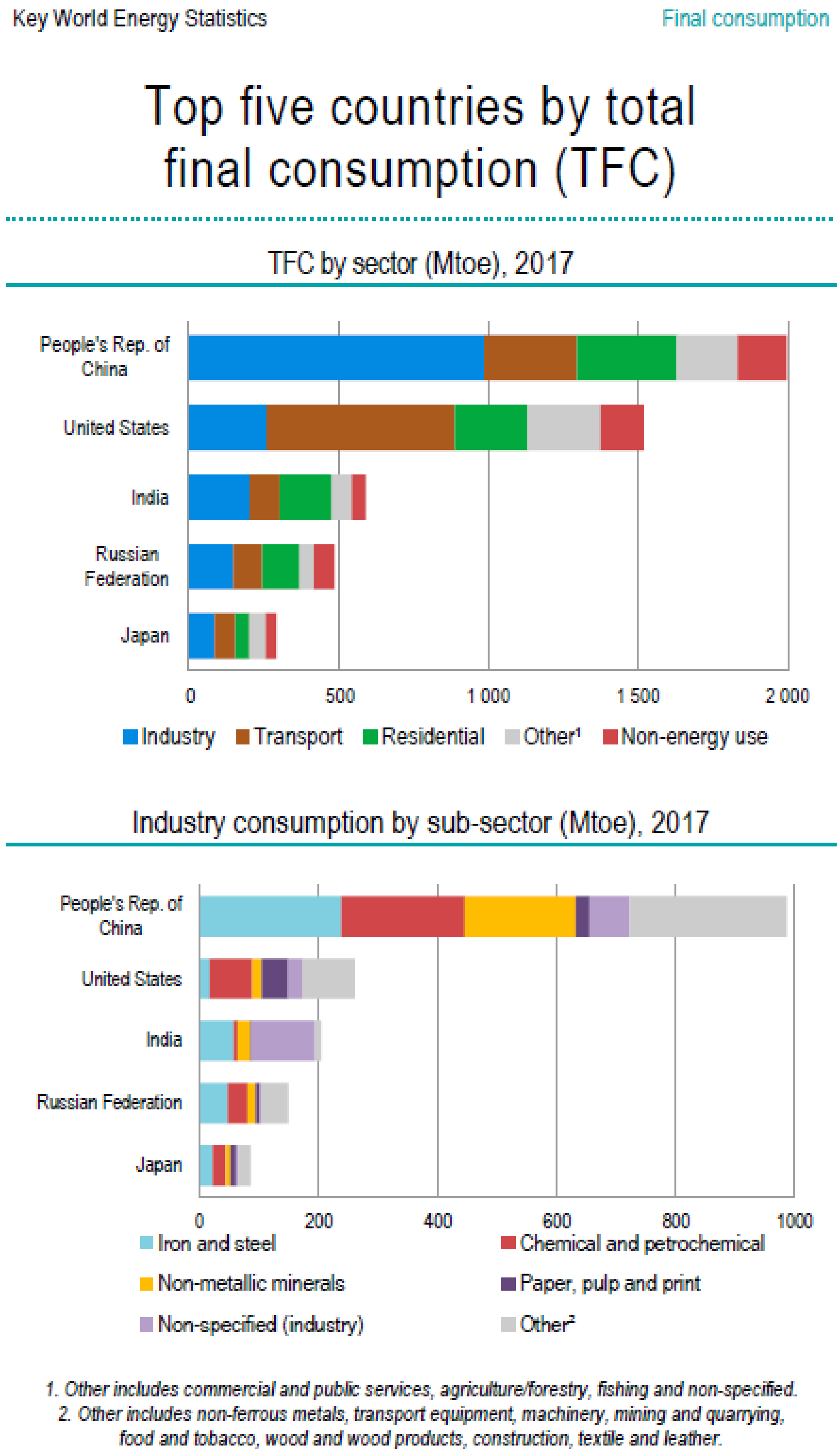
To:	kg	t	lt	st	lb
From:	multiply by:				
kilogramme (kg)	1	1.000×10^{3}	9.842×10^{-4}	1.102×10^{-3}	2.205
tonne (t)	1.000×10^{3}	1	9.842×10^{-1}	1.102	2.205×10^{3}
long ton (lt)	1.016×10^{3}	1.016	1	1.120	2.240×10^{3}
short ton (st)	9.072×10^{2}	9.072×10^{-1}	8.929×10^{-1}	1	2.000×10^{3}
pound (lb)	4.536×10^{-1}	4.536×10^{-4}	4.464×10^{-4}	5.000×10^{-4}	1

Conversion factors for volume

To:	gal U.S.	gal U.K.	bbl	ft^3	l	m^3
From:	multiply by:					
U.S. gallon (gal)	1	8.327×10^{-1}	2.381×10^{-2}	1.337×10^{-1}	3.785	3.785×10^{-3}
U.K. gallon (gal)	1.201	1	2.859×10^{-2}	1.605×10^{-1}	4.546	4.546×10^{-3}
barrel (bbl)	4.200×10^{1}	3.497×10^{1}	1	5.615	1.590×10^{2}	1.590×10^{-1}
cubic foot (ft^3)	7.481	6.229	1.781×10^{-1}	1	2.832×10^{1}	2.832×10^{-2}
litre (l)	2.642×10^{1}	2.200×10^{-1}	6.290×10^{-3}	3.531×10^{-2}	1	1.000×10^{-3}
cubic metre (m^3)	2.642×10^{2}	2.200×10^{2}	6.290	3.531×10^{1}	1.000×10^{3}	1

70

Figure A.1.: Conversion factors and unit abbreviations. *Source: Key World Energy Statistics 2019*



Key World Energy Statistics

Final consumption

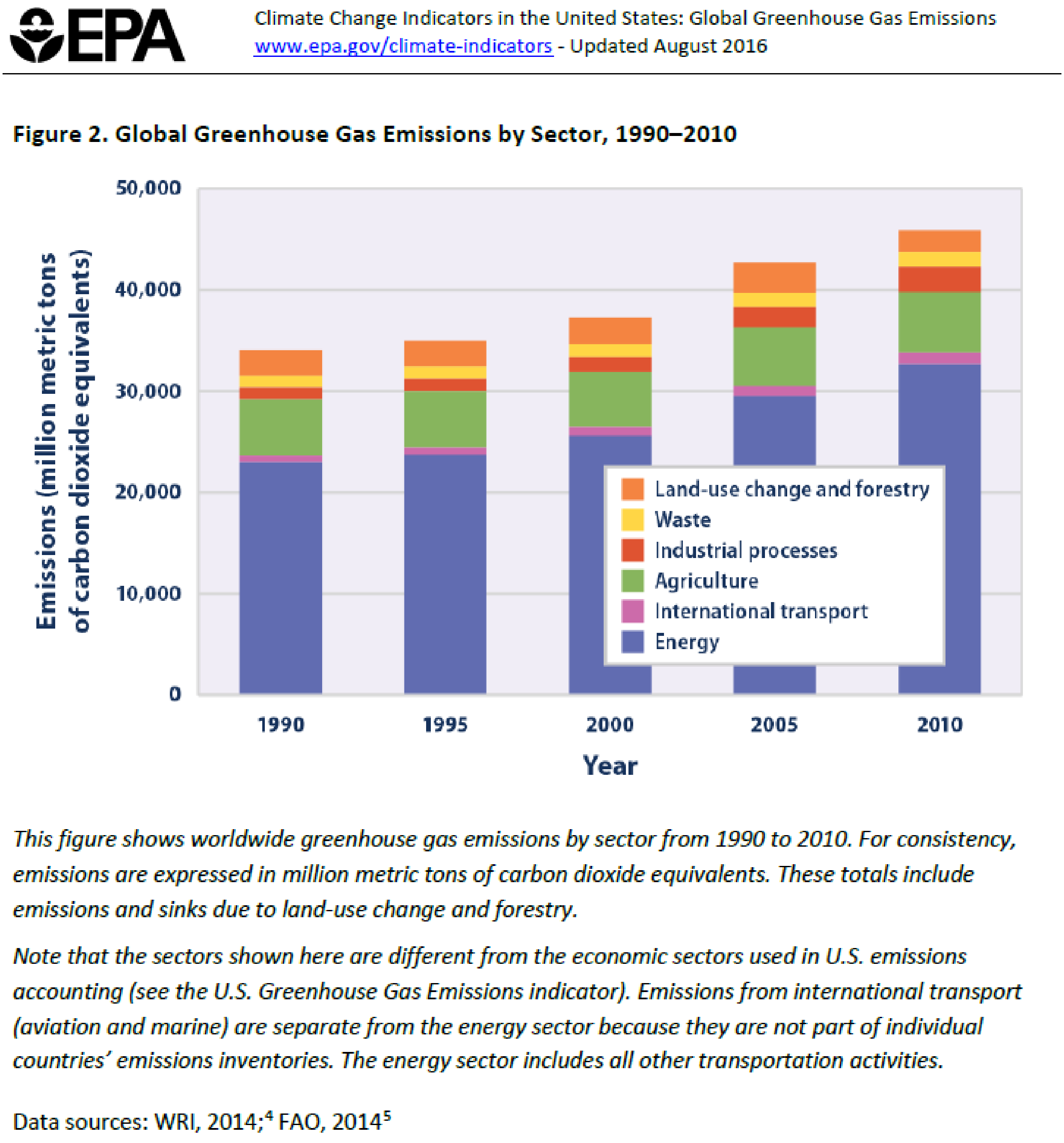
Top five countries by total final consumption (TFC)

TFC by sector (Mtoe), 2017

Industry consumption by sub-sector (Mtoe), 2017

1. Other includes commercial and public services, agriculture/forestry, fishing and non-specified.
2. Other includes non-ferrous metals, transport equipment, machinery, mining and quarrying, food and tobacco, wood and wood products, construction, textile and leather.

Figure A.2.: Top five countries by total final consumption (TFC) and detail on industry consumption sub-sector (Mtoe). *Source: Key World Energy Statistics 2019*



Climate Change Indicators in the United States: Global Greenhouse Gas Emissions
www.epa.gov/climate-indicators - Updated August 2016

Figure 2. Global Greenhouse Gas Emissions by Sector, 1990–2010

This figure shows worldwide greenhouse gas emissions by sector from 1990 to 2010. For consistency, emissions are expressed in million metric tons of carbon dioxide equivalents. These totals include emissions and sinks due to land-use change and forestry.

Note that the sectors shown here are different from the economic sectors used in U.S. emissions accounting (see the U.S. Greenhouse Gas Emissions indicator). Emissions from international transport (aviation and marine) are separate from the energy sector because they are not part of individual countries' emissions inventories. The energy sector includes all other transportation activities.

Data sources: WRI, 2014;[4] FAO, 2014[5]

Figure A.3.: Global Greenhouse Gas Emissions by Sector, 1990-2010. *Source: United States Environmental Protection Agency, 2016*

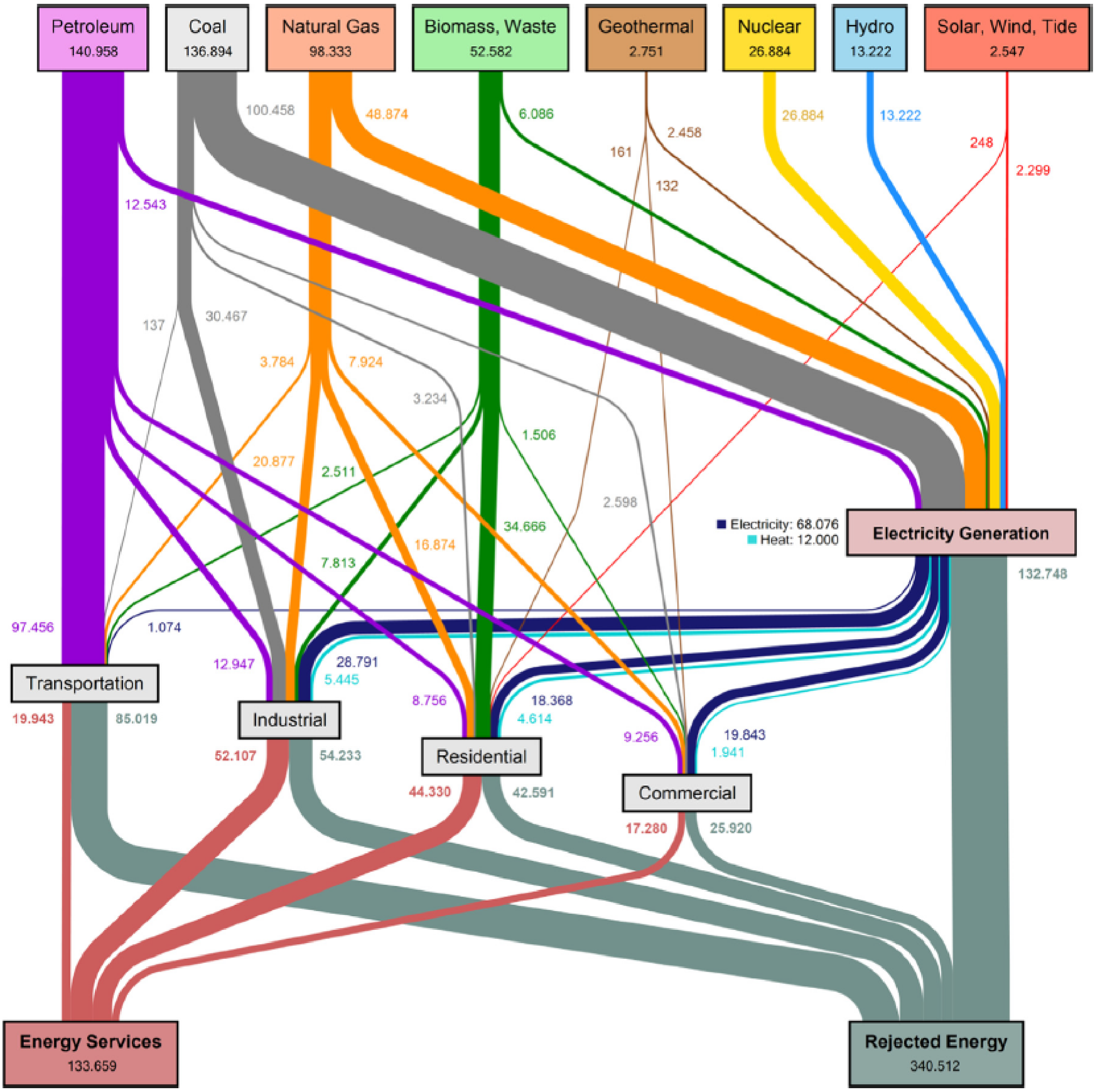


Figure A.4.: Sankey diagram about the estimated world energy use of 2012 in PJ, excluding fuel processing and non-energy use (total consumption of primary energy carriers: 474.171 PJ). *Source: Forman et al., 2016*

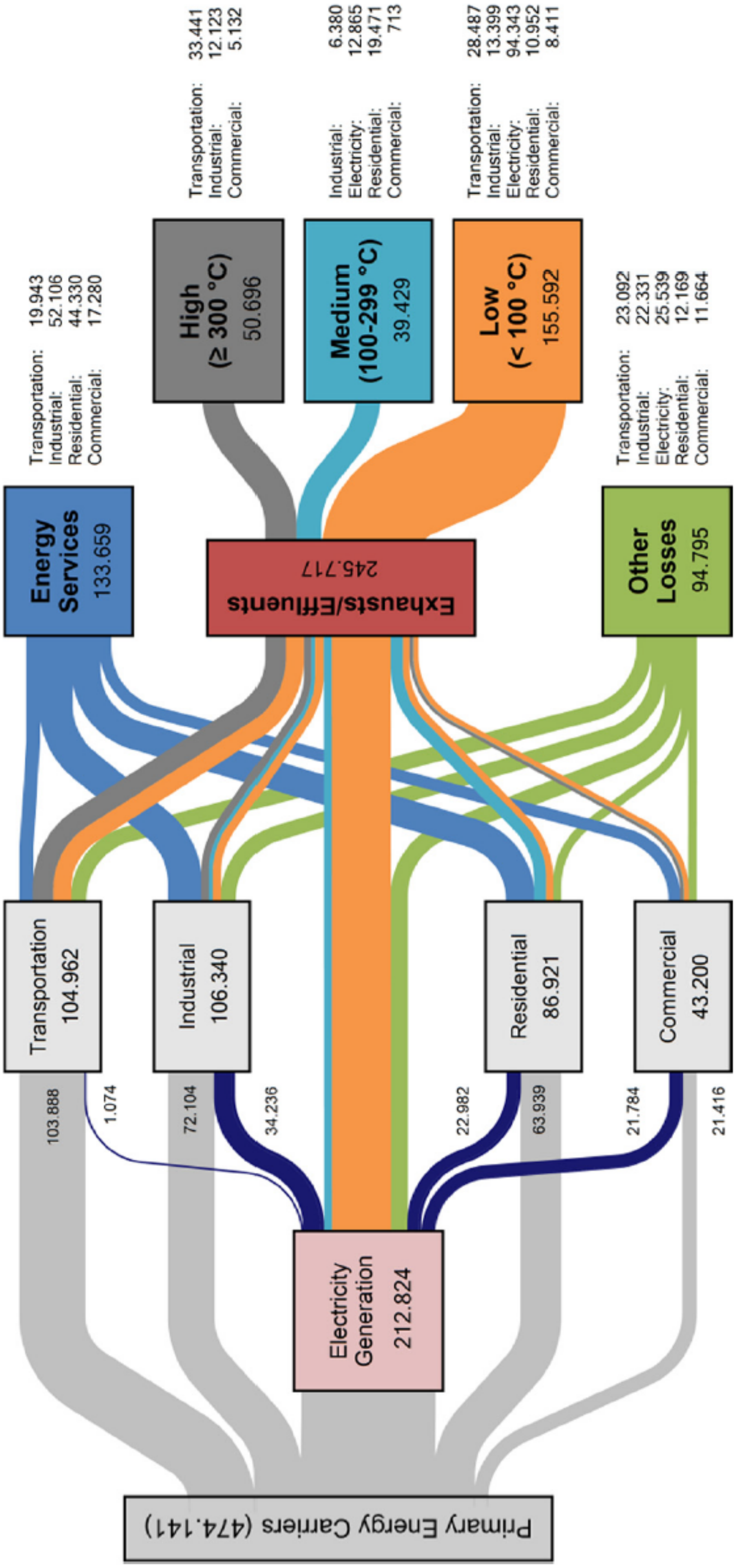


Figure A.5.: Sankey diagram about the estimated global waste heat distribution of 2012 in PJ (according to theoretical approach). *Source: Forman et al., 2016*

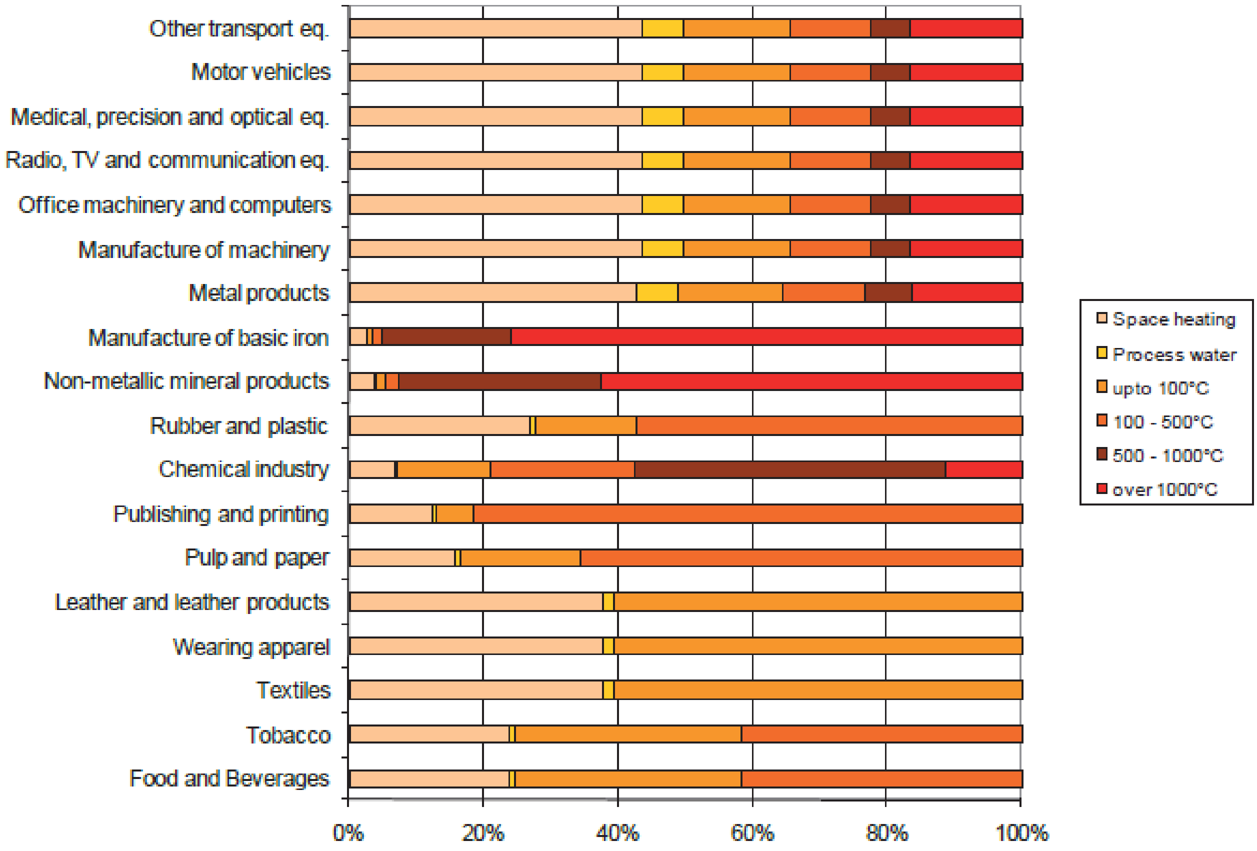


Figure A.6.: Distribution of heat demand according to temperature levels and industries. *Source: Wagner, 2002*

Manufacturer	**Nation**	**Mode**	**Industrial status**	**Nominal Input Power**	**COP_R**	**COP_{HP}**	**T_{GEN}**	**T_{COLD}**	**T_{HOT}**	**Source**	**Generator type**
				[kW]			[°C]	[°C]	[°C]		
AGO	Netherlands	Chiller	Commercial	100-3000	0.5-0.6	-	90-160	-5 to -40	25-30	Multi source	-
		Heat pump	Commercial	1000-3000	-	0.5	40-70	65-55	70-90		
Baxter	Italy	Trigeneration	Commercial	50-10000	-	-	110-250	-60	-	Hot vapor	Thermal exchanger
Colibris	Netherlands	Chiller	Commercial	180-250	0.8	-	70-170	-60	-	Multi source	Thermal exchanger
ENEA	Italy	Reversible	Prototype	29	0.62	1.46	100-95	12-7	31-35	Hot water	Solar vacuum collector
RoburCorp	USA	Chiller	Commercial	27	0.65	-	-	3		Gas	Burner
		Heat pump	Commercial	27	-	1.4	-	-	65	Gas	Burner
Seppro	USA	Chiller	Commercial	80-8000	0.4		110-180	-		-	
SolarNext	Germany	Chiller	Commercial	40-100	0.5	-	70-98	-10 to 5	-	Hot Water	Thermal exchanger

Table A.1.: Manufacturers and technical parameters of current ammonia absorption systems.

B. Joule-Thomson diagrams for NH3/H2O mixtures

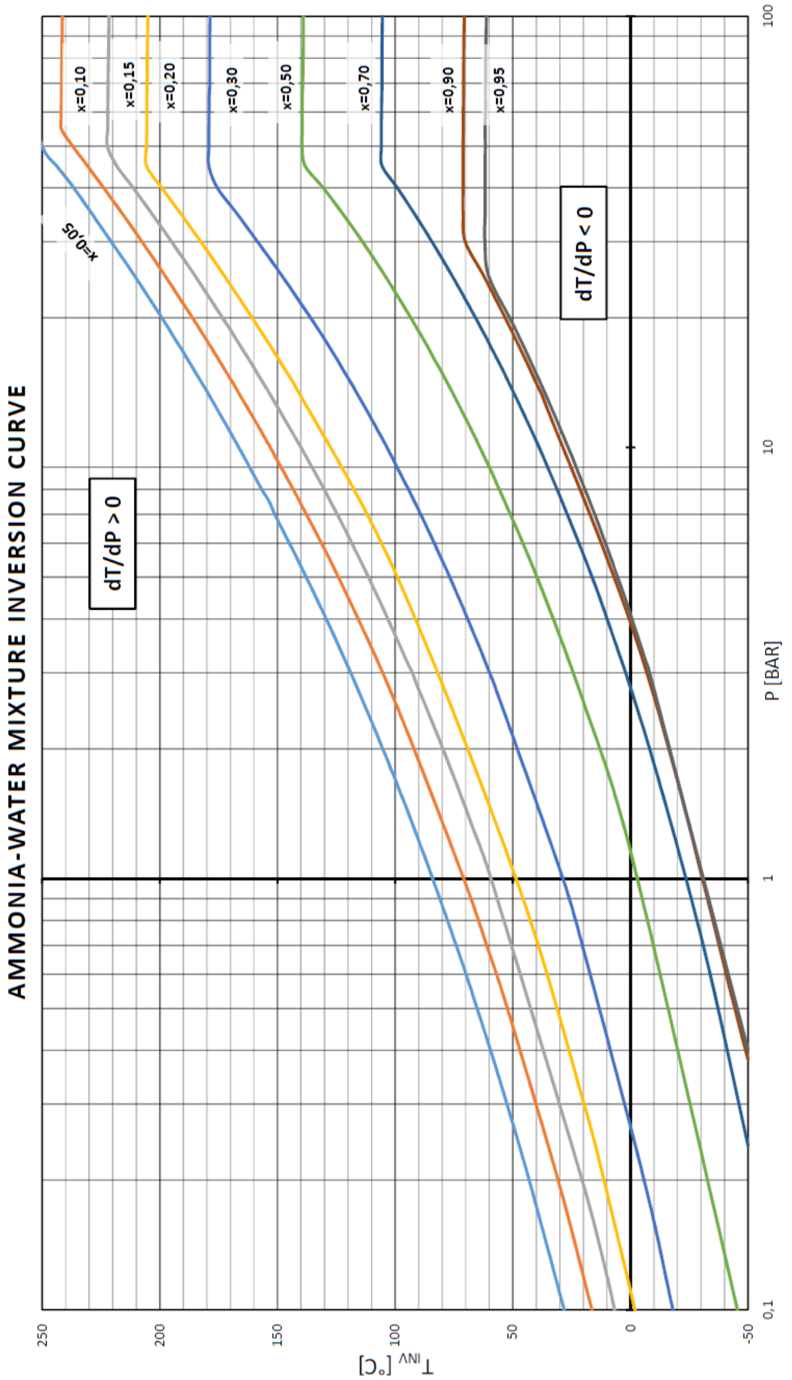


Figure B.1.: Inversion curve for ammonia-water mixtures in -50/250°C & 0.1/100 bar range).

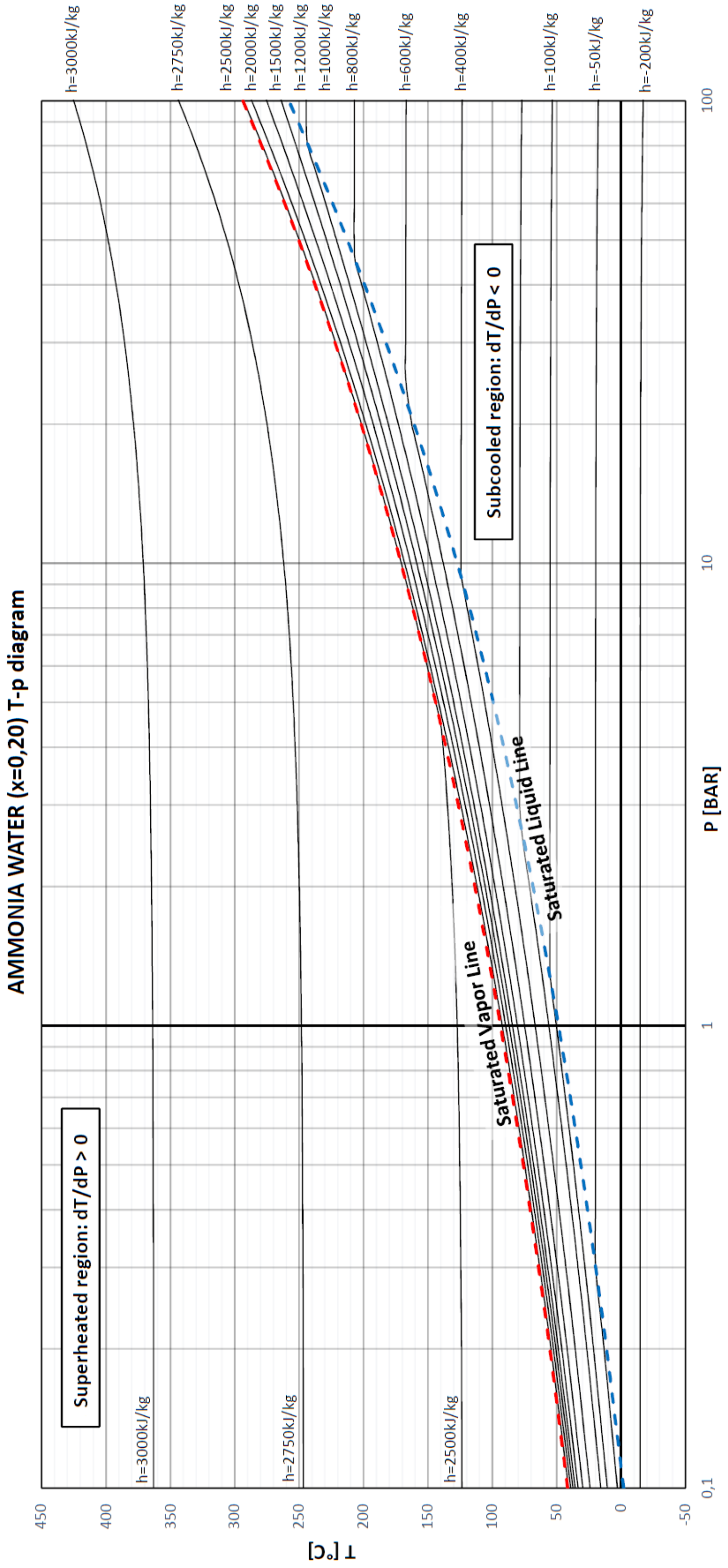


Figure B.2.: T-p diagram for an ammonia-water mixture (20% ammonia mass concentration).

C. Schemes of NH3/H2O absorption cycles

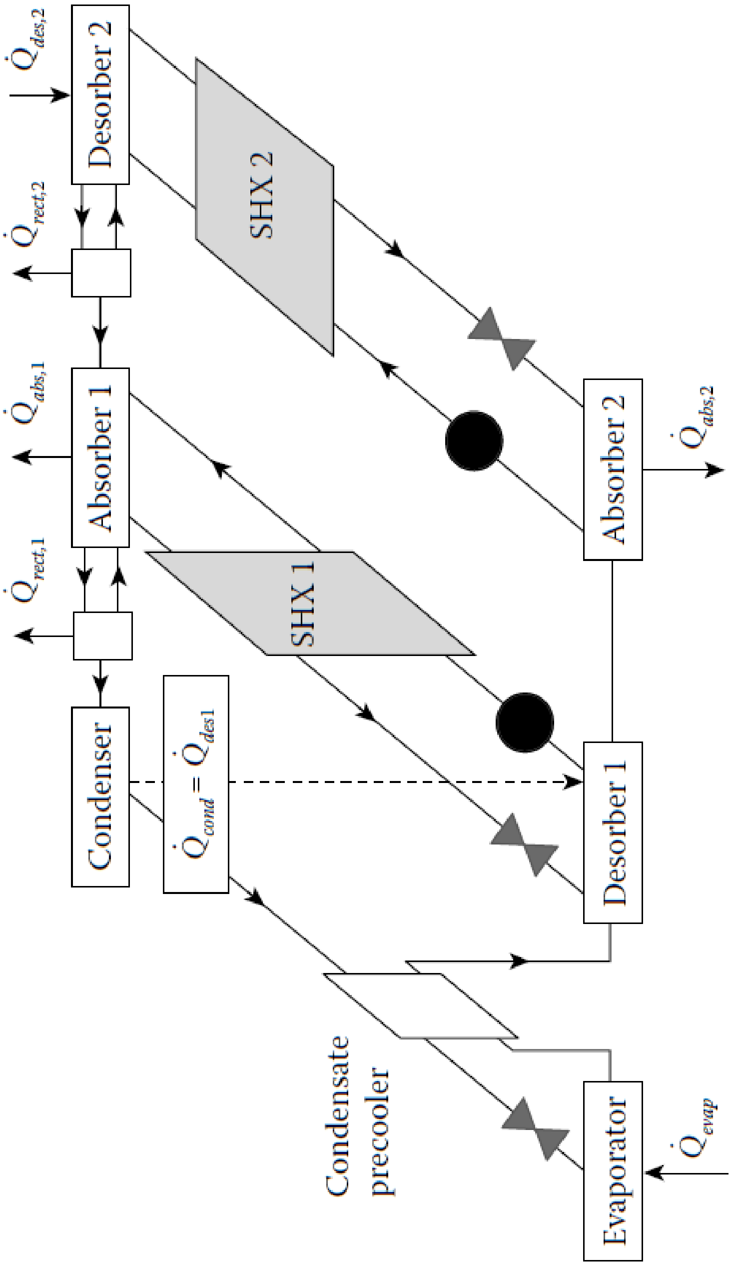


Figure C.1.: Two-stage, double-lift resorption absorption ammonia-water cycle (type C). *Source: Herold et al., "Absorption Chillers and Heat Pumps", 2016*

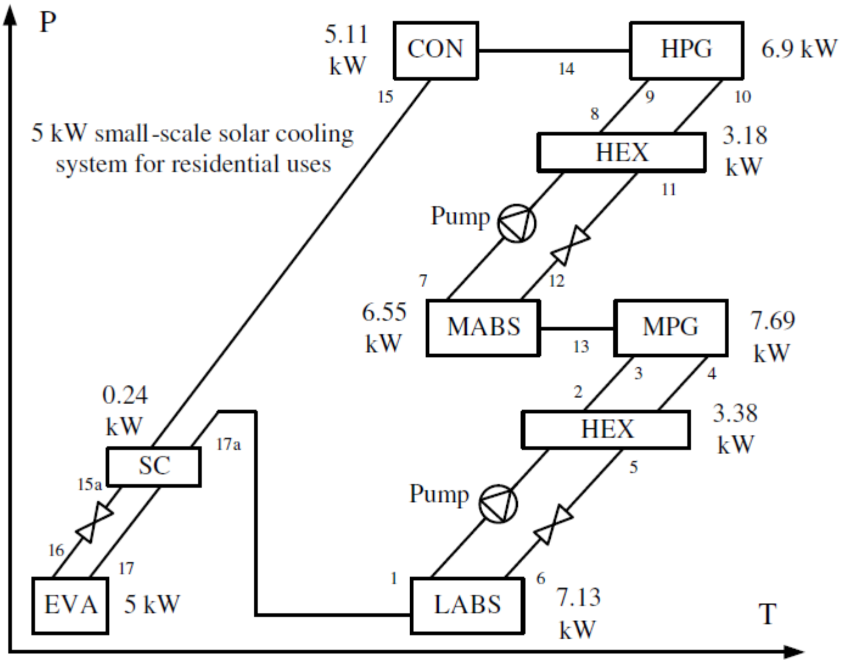


Figure C.2.: Two-stage, double-lift vapor-exchange absorption ammonia-water cycle (type B). *Source: Wang, Lin, Xia, 2011*

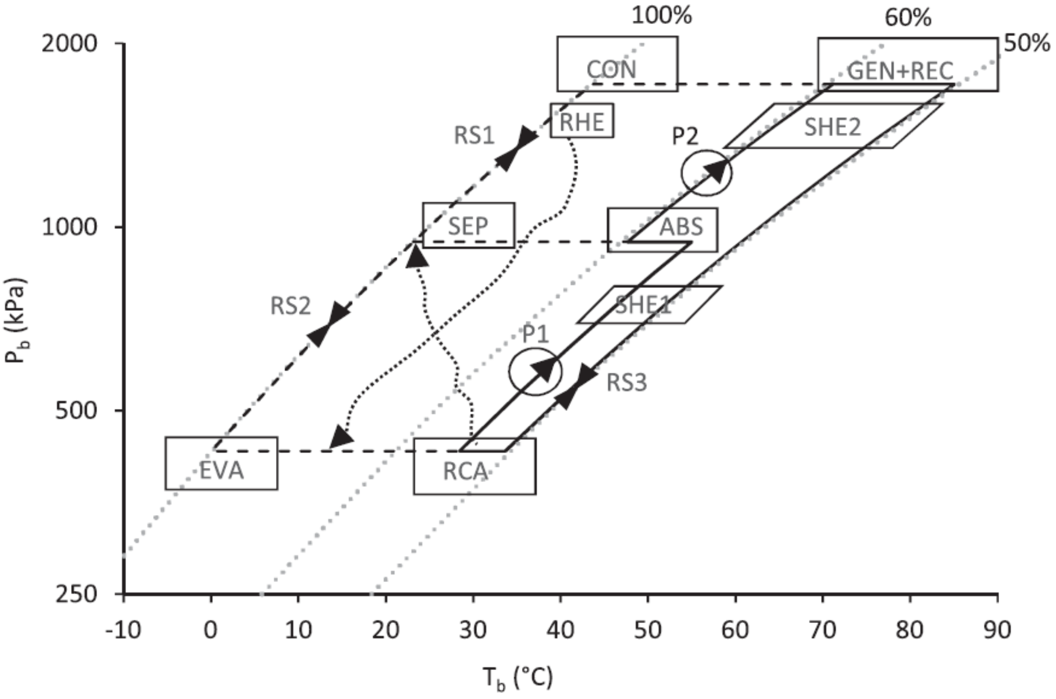


Figure C.3.: Two-stage, double-lift pressure-staged ammonia-water cycle (type A). *Source: Aprile et al., 2015*

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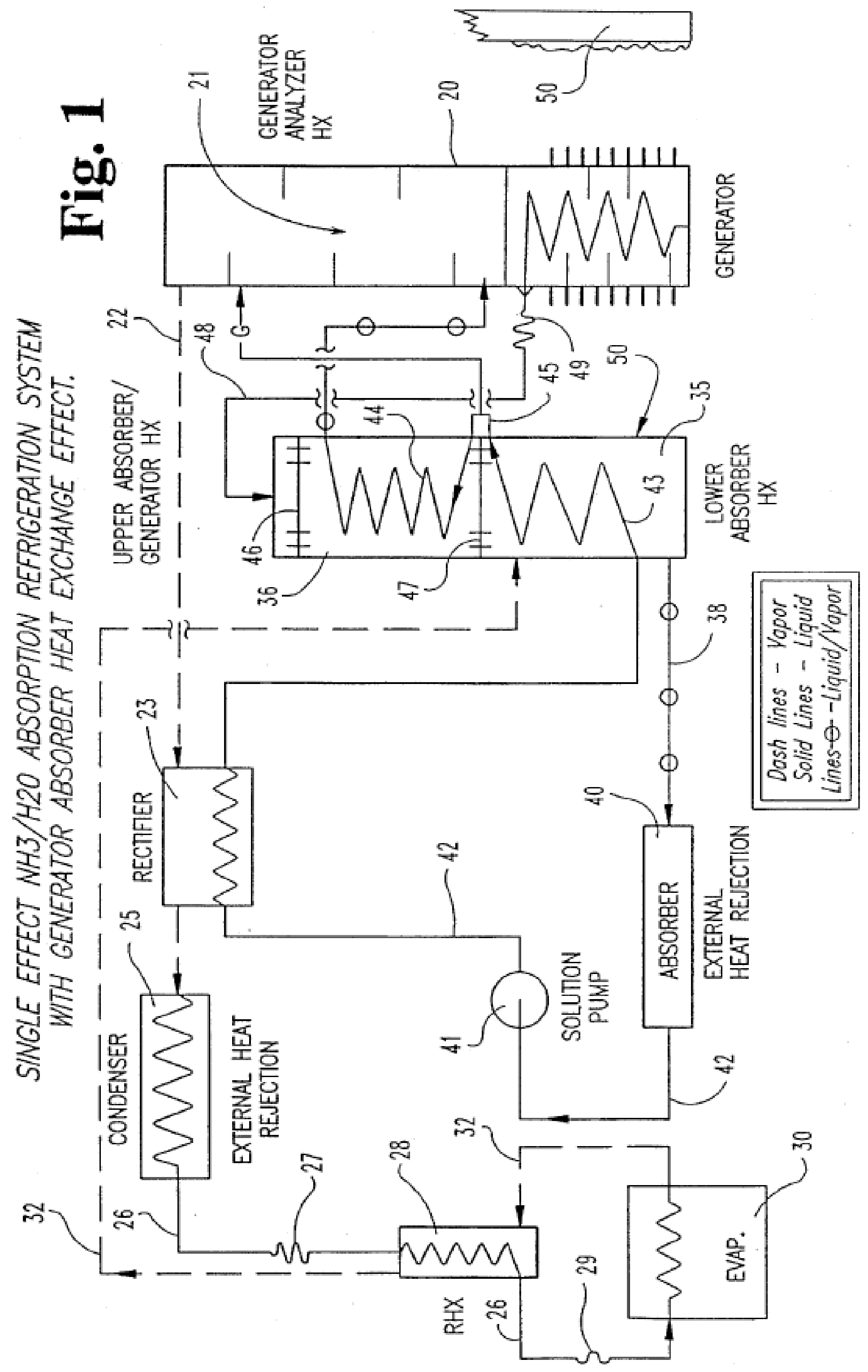

Figure C.4.: Detail of the Generator-Absorber heat eXchange (GAX) thermodynamic cycle proposed by Fuesting et al. *Source: Fuesting et al., 1996*