REVIEW

Thermodynamic and heat transfer implications of working fluid mixtures in Rankine cycles

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The theme of this article is to demonstrate the mutual influence of working fluid properties on the performance of Rankine cycles, heat transfer, and cycle variations. The limitations imposed on the traditional Rankine cycle inherent to the thermodynamics of pure fluids are described. Then, based on Gibbs' phase rule, the additional degree of freedom that is provided by a two-component working fluid mixture is introduced and its advantages and implications are discussed. The potential for efficiency improvement and capacity adjustment are detailed based on experimental results obtained with heat pumps. Further flexibility can be gained when the cycle is modified to allow for liquid subcooling and the introduction of a so-called solution circuit. With this component a large variety of vapor compression, absorption, and combined compression/absorption cycles becomes available, offering new solutions to old and new energy conversion applications such as heat pumping, heat transformation and power generation. New challenges arise from the fact that advanced cycles require very efficient heat and mass transfer surfaces and new heat transfer concepts. The situation is complicated by the nonlinear relationship between the amount of heat released per degree (during the phase change of the working fluid mixture) and the temperature change.

Keywords: Rankine cycle; thermodynamic properties; heat pumps; two-component mixtures

Introduction

The Rankine cycle in its many versions is used as an example for how fluid properties, heat transfer characteristics, and applications influence each other, providing great opportunities or difficulties for efficient energy conversion. This situation represents a worthwhile challenge for research, development, and design.

The characteristic feature of the Rankine cycle is that the working fluid undergoes phase changes between a vapor phase and a condensed phase. In Figure 1a, a process scheme of the conventional Rankine cycle is shown. While the production of work is achieved by the expansion of vapor in a turbine, the recompression of the working fluid, necessary to complete the cycle, occurs in the condensed phase, which can in good approximation be considered to be incompressible. Thus the required work input to the boiler feed pump is very small compared to the work produced. In this way the Rankine cycle overcomes one of the major shortcomings of gas cycles in which a major fraction of the work produced during the expansion process has to be employed to recompress the working fluid.

When the Rankine cycle is reversed, a vapor compression heat pump is obtained (Figure 1b). All directions of energy and fluid flow are reversed compared to Figure 1a. The turbine becomes a compressor, and the pump a turbine or expansion valve. The incompressibility of the condensed phase is of advantage once more. Now an expansion valve can be used instead of a turbine to reduce the pressure of the condensed working fluid. The resulting loss in availability is small compared to the work input to the compressor.

Shortcomings of the Rankine cycle

Especially when heat pump applications are considered (the term heat pump stands here for refrigeration systems as well, since the thermodynamic principle is the same, just the application has changed), some inherent shortcomings of the Rankine cycle manifest themselves. The first is the fact that, in the majority of applications, the temperatures of the heat sink and source fluids vary during the heat transfer process. The temperature of the evaporating and condensing working fluid remains constant. As a consequence, a pinch point is encountered in the evaporator and condenser. Figure 2 shows this situation in a plot of temperature versus the amount of heat exchanged for a heat pump evaporator. The resulting large temperature difference at one end of the heat exchanger leads to irreversibilities that in turn reduce the efficiency of the heat pump or, in other terms, increase the work required by the compressor. This situation has been discussed in a previous review paper.[1] A similar situation is encountered in the condenser as well.

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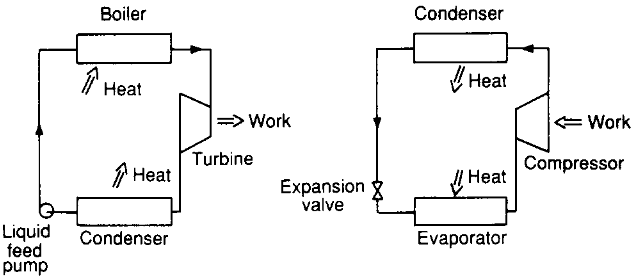

Figure 1 Process scheme of Rankine cycles for power generation (1a) and heat pumping (1b). The one originates from the other, when all directions of energy and fluid flow are reversed

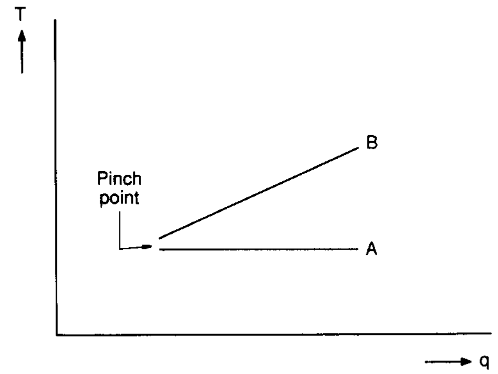

Figure 2 Amount of heat released vs. temperature change of the fluids in an evaporator. Curve A represents the evaporating refrigerant, curve B the water

A second shortcoming of the Rankine cycle is the fact that for a given application a certain working fluid may be the optimum choice. As soon as the operating conditions change, another working fluid would be desirable. This happens, for example, in typical heat pump and air-conditioning applications when the outdoor temperature changes. In heat pumping, when the outdoor temperature is moderate the heat demand of a building is small. Accordingly, the heat pump delivers the required small capacity. In order to do this in a continuous, steady state operation, which is always more efficient than the customary cycling of equipment, a low capacity refrigerant is required. When the outdoor temperature decreases, a higher heating capacity is demanded in order to meet the building load. However, the capacity delivered by a given working fluid decreases with the outdoor temperature for the following reason. As the temperature decreases, the vapor pressure decreases as described by the vapor pressure curves of Figure 3. With the reduced pressure the specific vapor volume increases. Thus the mass flow rate established by the compressor (which is a pump of constant displacement) becomes smaller and the amount of refrigerant that evaporates is diminished, producing less cold. This is just the opposite behavior one wants to see. A possible solution would be to exchange the working fluid as the outdoor temperature changes. However, this is not very practical.

Lastly, a third shortcoming results from the fact that with increasing temperature lift (that is the temperature difference between condenser and evaporator) the pressure ratio across the compressor increases. This results in larger compression losses. The increase in pressure ratio is roughly the same for all fluids likely to be used. Figure 3 shows the vapor pressure curves for a number of fluids in a pressure-temperature diagram. The coordinates are chosen such that the curves are approximately linear. It can be seen from Figure 3 that the vapor

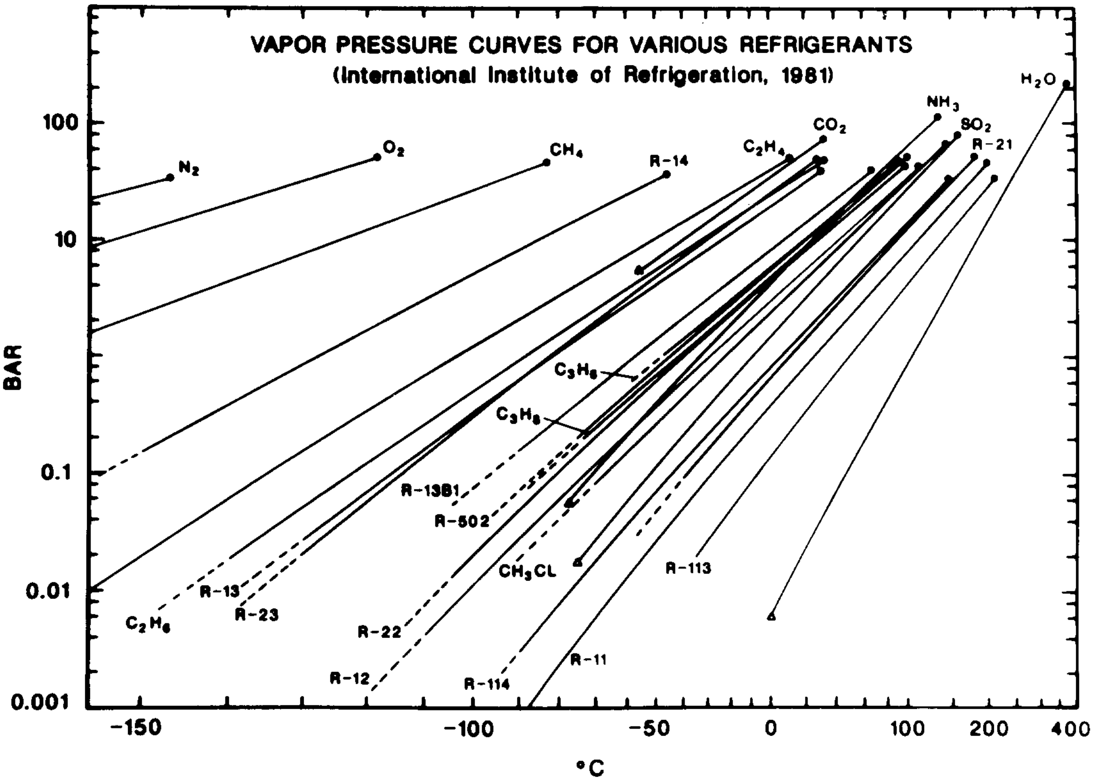

Figure 3 Vapor pressure curves of a variety of fluids. The slopes of the curves for fluids of technical interest are not very different

pressure lines of all fluids have a similar slope (Trouton's Rule). Thus the pressure ratio is similar for all fluids. The pressure ratio for a given application cannot be significantly influenced by merely exchanging the working fluid.

The shortcomings just discussed are caused by the fact that the thermodynamic properties of pure working fluids, the requirements imposed by the Rankine cycle, and the particular application do not match very well. But when working fluid mixtures are used, improvements can be obtained in two ways, through the inherent properties of the mixture itself, or through cycle variations which become available with mixtures. In fact, the introduction of mixtures in the Rankine cycle leads to a wide variety of cycle options that are only now beginning to be explored.

Rankine cycles with mixtures

Gibbs' phase rule states that one obtains a higher variance in a thermodynamic system when more components, i.e., a mixture of fluids instead of a pure fluid, are employed. When a working fluid, B, is added to another one, A, already present in a Rankine cycle, the additional variance manifests itself within the cycle. For the sake of argument a mixture of two fluids is chosen. Multi-component mixtures would have similar effects, but the principal idea can be best explained with the simplest case, a mixture of two components. The most obvious impact is that the temperature during the phase change of the working fluid mixture does not remain constant. One encounters a so-called temperature glide, because the concentration of the mixture changes during evaporation.

Figure 4 shows the evaporation process of a mixture of two fluids of the concentration x_0 in a temperature–concentration diagram that is plotted for a given pressure. The process begins at point 1 with subcooled liquid. While heat is added the temperature rises to the saturation temperature, point 2, on the bubble point line. As additional heat is supplied the liquid begins to evaporate. The concentration of the first vapor bubble is $x_{2'}$, as described by point 2′ on the dew point line. This vapor is in equilibrium with the liquid but has a different concentration, $x_{2'}$. The concentration of the remaining liquid changes along the bubble point line as the evaporation proceeds. At point 3′ the evaporation is complete. Point 3 indicates the saturation temperature of the last droplet that evaporated. Its composition is x_3. The vapor concentration at 3′ is the same as the concentration of the subcooled liquid in the beginning of the process.

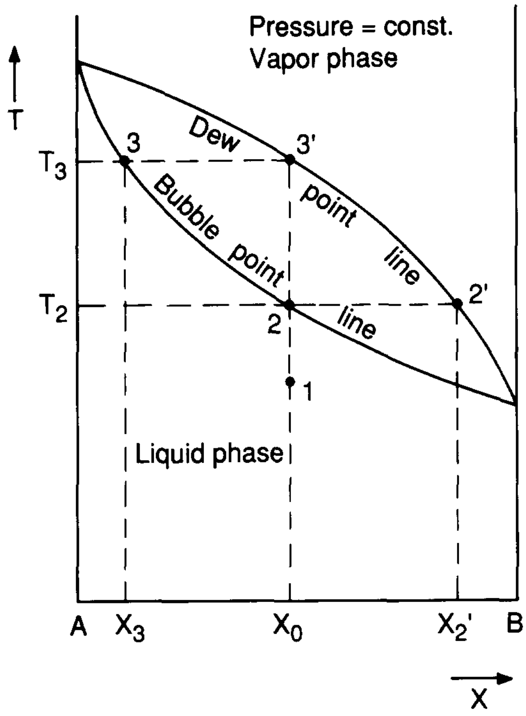

Figure 4 Evaporation process of a mixture in a Temperature–Concentration Diagram. The process starts at point 1 with subcooled liquid and ends with saturated vapor at point 3′

During the evaporation, the saturation temperature changed from temperature T_2 to T_3. The temperature difference $T_3 - T_2$ is called the temperature glide. The size of this temperature glide is primarily determined by the difference of the boiling points of the pure components of the mixture, the temperatures for $x = 0$ and $x = 1$ in Figure 4. A mixture that follows the described evaporation process is called a "non-azeotropic mixture." In the refrigeration field the term NARM was introduced, standing for "non-azeotropic refrigerant mixture."

Efficiency and the gliding temperature interval

The gliding temperature can be used to reduce the mismatch of the temperature profiles (i.e., the amount of heat released per degree temperature change) between the heat transfer fluid and the evaporating or condensing working fluid mixture. A counterflow heat exchanger must be employed. Theoretically the temperature glide can be chosen by selecting a suitable mixture and proper concentration so that the temperature difference at any point throughout a heat exchanger is constant. The result is a more efficient cycle. The earliest suggestion of using a working fluid mixture in vapor compression systems was most likely made in 1888 by Pictet.[2] In 1895 the Lorenz cycle was introduced. It is a reversible thermodynamic cycle that, in contrast to the Carnot cycle, is based on gliding temperatures for the supply and rejection of heat while the expansion and compression are assumed to be isentropic processes.[3] In 1911 this idea was again published in context with absorption heat pumps.[4] The use of mixtures was discussed up and on,[5–14] and experimental work demonstrating improvements began in the 1950's.[6–11,13–15] Research in this field is now conducted in several groups worldwide.

Theory predicts usually significant power savings when mixtures are used as described above. Reality, however, shows that the experimental results seldom lived up to the theoretical expectations. The main reason for the less than expected performance is based on two aspects: the first is related to the thermodynamic properties of the mixture and the second to heat transfer. First, the temperature profile (the amount of heat released per temperature interval) is rarely linear. One usually encounters a curvature that depends on the particular mixture being used and varies with concentration and temperature levels. One or, in some cases, even two pinch points are introduced. Figure 5 shows the three curvatures that actual temperature profiles can exhibit. Figure 6 shows a pressure–enthalpy diagram for the working fluid mixture R22/R11 with a concentration of 60% R22 in the mixture. The major difference between a pure fluid and a mixture is the shape of the isotherm in the two-phase region. While for the pure fluid the isotherm is horizontal, representing constant temperature during a constant pressure evaporation, the isotherm for a mixture is curved and slanted toward lower pressures with increasing enthalpy, representing a temperature glide for constant pressure evaporation. One desires the isotherm to be a straight line for a best match of temperature profiles in the heat exchangers, but this usually does not occur (see Figure 6).

Nevertheless, by using a suitable mixture the average temperature difference for heat transfer is closer to the approach temperature, reducing the irreversibilities compared to a pure fluid. One expects to find an increase in performance, but not to the extent the assumption of linear temperature profiles would suggest. In general, the following rule applies: the smaller the temperature lift and the larger the temperature glide, the better the performance improvement with mixtures compared to pure fluids in vapor compression heat pump cycles.

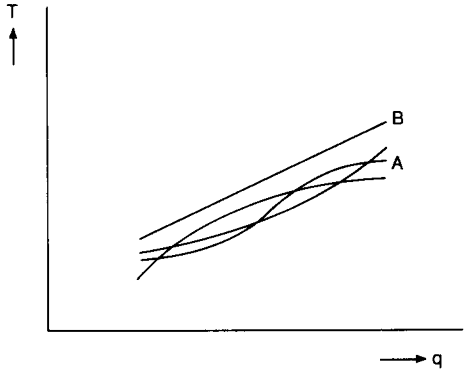

Figure 5 Amount of heat released vs. temperature change of the fluids in an evaporator. Curve A represents three examples for temperature profiles found for evaporating refrigerant mixtures; curve B represents the water

The second aspect that leads to reduced mixture performance is the degradation of the heat transfer coefficient compared to a pure fluid. This is caused by increased viscosity and decreased thermal conductivity and, possibly, by a diffusion-controlled phase change process. Since the more volatile component is enriched in the vapor phase, more of the liquid phase component has to diffuse toward a vapor bubble to enable the production of more vapor. Heat transfer experiments with mixtures have been conducted, and the observed degradation was explained with the phase change process being diffusion-controlled.[16–18] However, recent work seems to indicate, at least for flow boiling of chlorofluorocarbons, that the diffusion process is not a major resistance. The reduction in the heat transfer coefficient is a consequence of degraded transport properties.[19]

The gliding temperature interval has another important implication. For a pure working fluid, the potential for improvement in efficiency by increasing the heat exchange area is quite limited. The pinch point of Figure 2 does not allow the average temperature difference across a heat exchanger to be reduced beyond a given minimum. With a mixture, however (to the extent that the temperature profile is linear), the average temperature difference can be always reduced by increasing the heat exchange area. Thus, while increasing the heat exchange area beyond a certain value does not improve the performance for pure fluids, a sizeable increase in performance can still be achieved for mixtures.

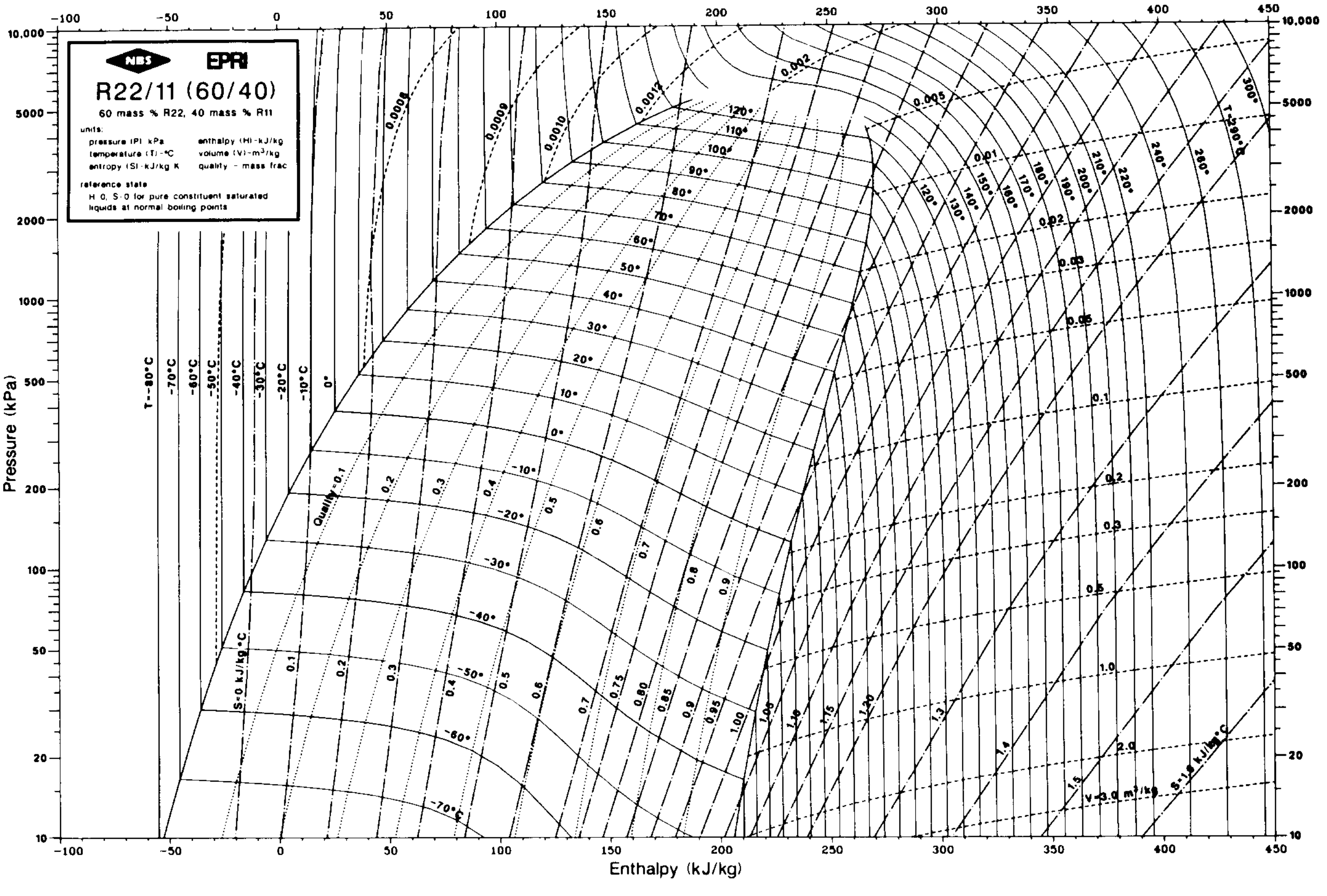

Figure 6 Pressure–enthalpy diagram for a mixture of R22/R11 with 60 weight % of R22. The isotherms in the two-phase region are curved (they would be horizontal for a pure fluid)

Capacity control

Working fluid mixtures have another advantage that is well suited to overcome the second shortcoming of Rankine cycles with pure fluids in heat pump applications. Since a heat pump is charged with two fluids, the vapor density and therefore the capacity can be changed by adjusting the concentration of the circulating mixture. Various methods have been discussed in the literature. The most common approach is by means of distillation techniques. The simplest is to employ only one separation stage. In this case the evaporator itself is used as the distillation plate in the following way. When, for example, the outdoor temperature is decreasing, not all the fluid will evaporate. The more volatile component continues to circulate through the cycle, while the remaining liquid, containing mostly less volatile component, is collected in an accumulator at the evaporator outlet. Thus the overall concentration of the circulating mixture has been shifted to the more volatile component. When the process is reversed the collected liquid will be admitted to the circulating fluid again.[20,21] This method is the simplest, but not the most effective. A more complete separation of the fluids is achieved with an additional accumulator at the condenser outlet. This represents a two-plate distillation. For even better results, a complete distillation column will achieve the most far-reaching composition shift.[7]

Despite the fact that the use of mixtures has its challenges and difficulties, it has been demonstrated in experiments that mixtures improve the performance of heat pumps in both efficiency and capacity control.[6–10,13,15,22]

Vapor compression heat pump with solution circuit

However, there is one conflict of interest. For capacity control, one wants the boiling points of the constituents of the mixture as far apart as possible in order to obtain a wide range of composition shift. A large difference in boiling points implies also that the gliding temperature interval becomes large, too, considerably exceeding the applicable range. The ranges of capacity shift and temperature glide cannot be chosen independently from each other. In order to decouple the capacity control from the temperature glide, the following cycle modification is introduced. For the sake of a wide range in capacity control, the mixture is chosen with a large difference in boiling points, such as ammonia/water, for example. To limit the gliding temperature interval, the evaporation process is not completed. A two-phase mixture leaves the evaporator. While the vapor is separated from the liquid portion, compressed, and delivered to the condenser, the remaining liquid is pumped into the condenser via a separate liquid pump (Figure 7). In this figure the heat exchangers that contain condensing or evaporating working fluid are superimposed on a pressure–temperature diagram similar to Figure 3. Thus the respective locations of the heat exchangers with phase change indicate the pressure and temperature level of the working fluid. The slope of the connecting liquid line represents the slope of the vapor pressure curve. This representation is helpful later on when multi-stage cycles are discussed.

In Figure 7 there is cold liquid coming from the evaporator admitted to the condenser, and at the same time hot liquid is leaving the condenser and entering the expansion valve. It is advisable to introduce heat exchange in between the two streams, the so-called liquid/liquid heat exchanger or recuperator (Figure 7). There are two liquid lines connecting the evaporator and the condenser. One is fitted with an expansion valve, the other with a feed pump. This configuration is termed "solution circuit."

The concept of a vapor compression heat pump with solution circuit was proposed in 1895, as indicated in Ref. 23. It was mentioned again in Refs. 4 and 24. New interest and experimental work started in the late 1970's.[25–30] The project in Refs. 28,28a focused on proving the concept and demonstrating the feasibility of composition shift for capacity control. For the vapor compression cycle with solution circuit, the composition change is simpler to accomplish than in the previously discussed cycle, because the vapor is almost pure ammonia due to the large difference in boiling points.

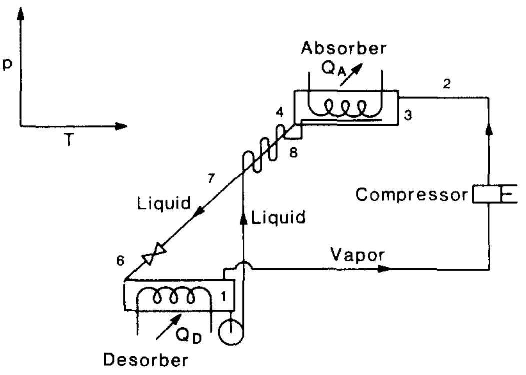

Figure 7 Vapor compression heat pump with solution circuit. The heat exchangers which accommodate a phase change are arranged in a pressure–temperature diagram such that the prevailing pressure and temperature are obvious from their respective locations. The slope of the liquid lines is indicative of the slope of the vapor pressure curve

Other projects focused on the use of the gliding temperature range.[26,30] An advantage is that a given heat pump can be matched to different applications by merely charging it with a mixture of suitable concentration. Also, the pressure level can be adjusted continuously in a wide range by selecting a certain mixture concentration. Thus a heat pump with solution circuit can be matched to applications where single working fluids of suitable properties are not available.[30]

By introducing a working fluid mixture and incomplete evaporation two degrees of freedom are obtained. A certain mixture can be selected for a wide range in capacity control, and the gliding temperature interval can be adjusted as required by controlling the flow rate through the liquid pump. The latter is an opportunity to employ the thermodynamic variable "vapor quality" in a technical application in a range between 0 and 1.0. For pure working fluids a vapor quality between 0 and 1.0 at the evaporator outlet is usually considered a liability.

Internal heat transfer

It is well known that the performance of a thermodynamic cycle can be improved upon by introducing internal heat transfer. An example is the feed water preheating with partially expanded steam in conventional steam power plants. Another example is the liquid/liquid heat exchanger in the heat pump with solution circuit. In the following an additional case is presented.

Under certain conditions the efficiency of a reversed Rankine cycle can be improved when the liquid entering the expansion valve is subcooled. The conventional method in the case of pure fluids is to use a "suction side heat exchanger" which precools the liquid with the cold vapor leaving the evaporator as shown in Figure 8. Due to the particular properties of a given working fluid, this measure can be of advantage or disadvantage, depending on which of the following two com-

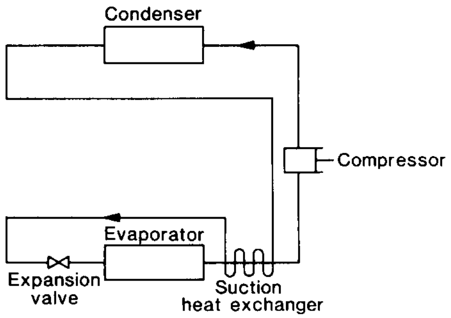

Figure 8 Rankine cycle for heat pumping with suction side heat exchanger for the precooling of the condensed fluid

peting effects is more dominant. First, the subcooled liquid provides a larger cooling capacity in the evaporator, since less fluid has to evaporate for cooling the liquid to evaporator temperature. Second, the superheated vapor entering the compressor requires more work. Only a detailed evaluation of each case will show whether the subcooling in a suction side heat exchanger is beneficial.

In the case of a refrigerant mixture with temperature glide, another option of subcooling becomes available. The liquid is subcooled in a separate duct within the evaporator, which becomes now a three-pass heat exchanger. This concept was proposed for absorption heat pump generators in 1911 and in the early 1980's for NARMs.[4,31] The temperature glide ensures that the heat transfer process is less irreversible for a mixture than for a pure fluid without glide. It has been shown in experiments that this measure can lead to significant performance improvements of 5–10%.[22]

This design improves the efficiency only when there is a temperature glide in the evaporator because only then is the average temperature difference for heat transfer reduced compared to pure fluids. The evaporator capacity is not changed per se, but a lower temperature is achieved at which the evaporation process begins. If the temperature levels are fixed by the application, this measure allows the evaporator to operate at a somewhat higher pressure level instead.

Building blocks for Rankine cycles

The Rankine cycle with solution circuit is a more general version of the basic Rankine cycle of Figures 1a and 1b. Any Rankine cycle can be considered to be composed of at least two building blocks. The first is a compressor or turbine, the second a pair of heat exchangers, such as the evaporator and the condenser. In case of the solution circuit a third heat exchanger is included, namely the liquid/liquid heat exchanger. Figure 9 shows the two building blocks. It is important to realize that the tasks of the building blocks are interchangeable to a certain degree. For example, a turbine accepts high pressure vapor and releases low pressure vapor. A heat exchanger pair of condenser and evaporator (as it is used in a heat pump) does just the same. While the turbine produces work, the heat exchanger pair lifts heat from the evaporator temperature to the condenser temperature. The reverse case is possible as well. A boiler together with a condenser in a power plant produces high pressure vapor from low pressure vapor by acting as a heat driven compressor. In the following we consider examples of how building blocks can be combined with energy conversion cycles. Some of them will be familiar, others may have surprising features. All have in common the fact that they serve as additional examples for the interaction between the cycle, fluid properties, and heat transfer.

Absorption heat pump

Two building blocks in the form of heat exchanger pairs can be connected to an absorption heat pump when, in at least one pair, a fluid mixture is employed (Figure 10). The first pair of heat exchangers, A and B, represents the condenser and evaporator of a heat pump, while the second pair are the boiler (now termed generator) and condenser (now termed absorber) that are operating with a working fluid mixture. The one possible constituent of this mixture is ammonia, the component that predominantly evaporates and condenses, while the second is water, the absorbent, which has the mere purpose of altering the temperature level on which the ammonia undergoes its phase change. The thermodynamic phenomenon employed here is the "boiling point elevation," i.e., the absorbent increases the boiling temperature of the refrigerant such that the refrigerant "condenses" (is absorbed) at a higher temperature than the one at which it evaporates.

The purpose of the absorption heat pump is to use high temperature heat (in the generator to generate refrigerant vapor) to produce a cooling effect (at the evaporator), while waste heat (from condenser and absorber) is rejected. The waste heat may be used for heating purposes, when temperature levels are chosen for that application. The absorption heat pump has

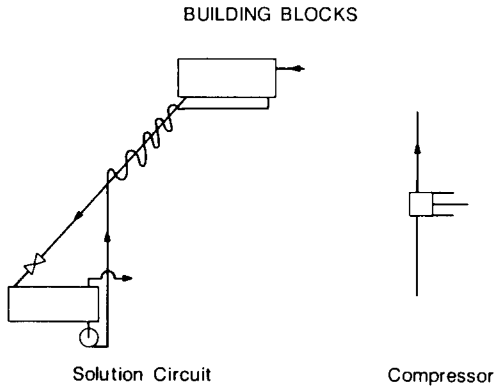

Figure 9 The two building blocks for Rankine cycles. The compressor may be a turbine and the heat exchanger pair may be connected with a single liquid line (as a special case of a solution circuit) which is either fitted with a pump or an expansion valve

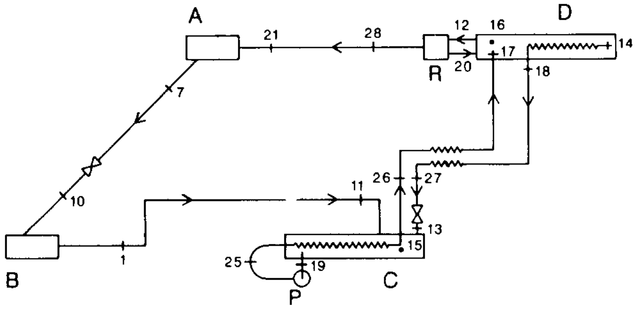

Figure 10 Process scheme of a single stage absorption heat pump. The representation is the same as described in Figure 7

been used for ice production for over two hundred years. A careful review given by Stephan[32] reveals that the first experiments were done in 1777 with the working fluid water/sulphuric acid. The initial machines operated in a discontinuous mode, where two containers were connected, alternating their functions between an evaporator and absorber and a condenser and generator pair. According to the above reference, the first continuously working units were built in the 1860's by Carre, using ammonia/water. The original application was the production of ice. Later, low temperature refrigeration to −60°C was added. The latest research and development projects focus on heating applications.[32–41]

The functions of the two building blocks can be reversed. When all directions of energy and fluid flow are reversed, and accordingly the expansion valves are replaced with pumps and vice versa, one obtains the absorption heat transformer. This device uses heat on an intermediate temperature level to produce heat on a high temperature level, while heat is rejected at the lowest temperature level. A typical application is the upgrading of waste heat to high temperature heat in industrial and chemical processes.[4,42–45]

Until recently the high temperature limit in absorption systems was about 200°C. This is imposed by the thermal stability of the working fluids and especially by the corrosivity of the fluids. New research efforts are directed toward the extension of that constraint to higher temperature levels. New corrosion inhibitors and a selection of other fluids shifted the high temperature limit beyond 250°C.[46]

Two-stage and multi-stage absorption systems

One area where absorption systems gained importance is commercial air-conditioning. In this application the working fluid mixture is water (as the refrigerant) and a solution of lithiumbromide in water (the absorbent). The generator temperature in the system described in Figure 10 would reach about 100°C. This is much lower than the temperature of any common heat source such as process steam or combustion gases. In order to take better advantage of the higher temperature level of the heat source, a so-called double-effect unit has been introduced, which is widely used. The thermodynamic idea is to use the availability of the high temperature heat to the maximum possible extent by introducing internal heat exchange. In this case a condenser provides heat to a second generator within the same system. The scheme is shown in Figure 11. Here the generator, F, operates at such a high temperature level (about 140°C) that the heat of condensation in E of the generated water vapor is at a temperature level sufficiently high to operate a second generator, D, which produces additional refrigerant. Thus the evaporator A is supplied with refrigerant from two sources (double effect), although heat from an external source is supplied to only one generator. While the "single-effect" unit shown in Figure 10 achieves a coefficient of performance of about 0.7, the double-effect unit reaches 1.2. It should be noted that the double-effect cycle in Figure 11 is a combination of four building blocks, all heat exchanger pairs. From another point of view, two single-effect absorption cycles of Figure 10 are combined into the double-effect unit. Therefore this unit is termed a two-stage, double-effect unit.

The idea of better internal heat exchange leads to more efficient equipment. It is important to note that the difference in temperatures between the driving heat and the waste heat was increased. Thus the improvement in efficiency is accompanied by the requirement of heat input of higher availability.

The concept of internal heat exchange in an absorption system can be extended further. For example, two-stage, triple-effect units have been proposed. The concept was described in Ref. 47 and a laboratory unit operated. A patent for a particular unit was obtained.[48] The most efficient triple-effect unit is the following (Figure 12): starting with the double-effect design, in the triple-effect system the heat of the absorber is also used to generate additional refrigerant vapor. Thus one unit of heat of a sufficiently high temperature level is utilized threefold to generate refrigerant. A triple-effect unit has the potential to achieve a cooling coefficient of performance of about 2.0. A prerequisite is that the absorber temperature level is sufficiently high. This can not be achieved with lithiumbromide/water since the salt solution would have to be so concentrated that the crystallization limit is exceeded. Other fluids have to be found.

According to the systematic in Refs. 44, 49 the absorption units of Figures 11 and 12 are two-stage systems. They are composed of a combination of two basic absorption cycles of

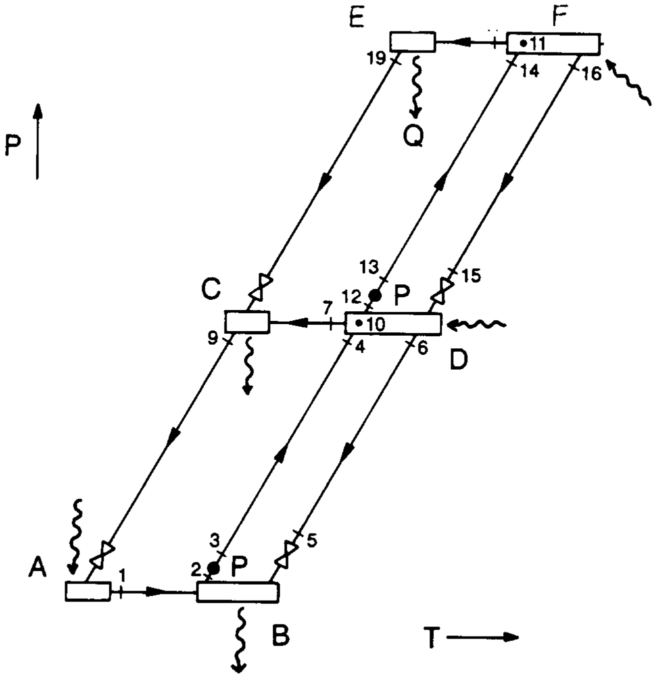

Figure 11 Process scheme of a two-stage, double-effect absorption heat pump. This configuration is commonly employed in water chilling applications. The heat released in condenser E is entirely used in generator D to produce additional refrigerant vapor

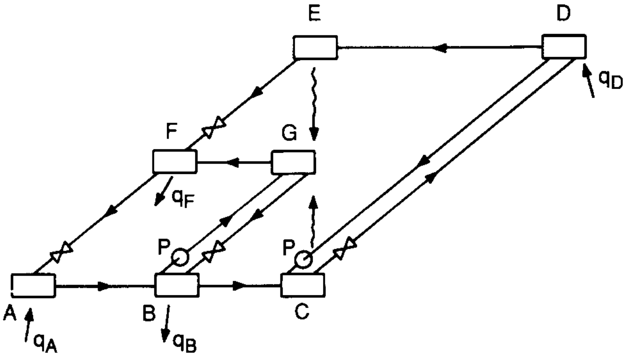

Figure 12 Process scheme of a two-stage, triple-effect absorption heat pump. Generator G is now supplied with heat from two internal sources, condenser E and absorber C

Figure 10. In general, the building blocks for Rankine cycles can be combined into basic cycles which, in turn, can be combined into multi-stage systems. Examples are two-stage heat transformers[44,45] and combinations such as heat-pump–transformers.[50] There is a multitude of multi-stage systems that can be thought of. Many of those have never been studied in any detail. Two publications summarize design rules that allow us to find and study all possible cycle combinations.[44,49]

One important general characteristic of multi-stage systems is that heat, which could be rejected to an external sink, is used within the cycle to generate additional refrigerant vapor, i.e., an absorber and/or condenser provides heat to another generator. This process can be repeated as long as temperature levels permit. Staging can also be employed to increase the temperature lift of an absorption system. This has been done in low temperature refrigeration or when the temperature of the driving heat was low,[37] for example, in solar applications. The following rule is applicable. Building blocks can be combined into multi-stage systems or either increase the efficiency by reducing the temperature lift, or to increase the temperature lift by decreasing the efficiency.

There are additional opportunities to improve the efficiency of an absorption cycle which rely on the same principle as discussed above, but it is less obvious. In Figure 10 the horizontal length of the absorber and generator represents the gliding temperature. This range is now chosen to become so large that the lowest temperature of the generator and the highest temperature of the absorber overlap (Figure 13). Thus a portion of the heat of absorption can be supplied to the generator. A cycle is obtained which incorporates the feature of a two-stage system by using internal heat exchange. Unlike other two-stage or double-effect designs, this design requires only one solution pump and no liquid/liquid heat exchangers at all. This cycle was first proposed in 1911.[4] Only recently has the implementation been undertaken.[37] The project focuses on an absorption heat pump for commercial heating and cooling. In experiments it was shown that a cooling COP of about 1.0 and a heating COP approaching 2.0 is feasible. A complication of this design represents the fact that the performance improvement is limited by the nonlinearity of the temperature glide.[51]

Use of nonmiscible auxiliary fluids, improvement of efficiency

In the systems considered so far it was always essential to the operation of the unit that the working fluid and the absorbent be miscible fluids. The following configuration of an absorption heat pump employs an additional auxiliary fluid, which does not mix with the original working pair. The goal is improved efficiency.[52]

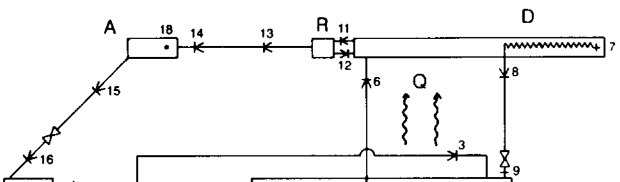

Figure 13 Process scheme of an absorption heat pump with absorber/desorber heat exchange. The gliding temperature range in absorber and desorber are so large that they overlap. Thus the absorber can supply heat to the generator, which is a two-stage feature of this cycle (but only one solution pump and no liquid/liquid heat exchanger is required)

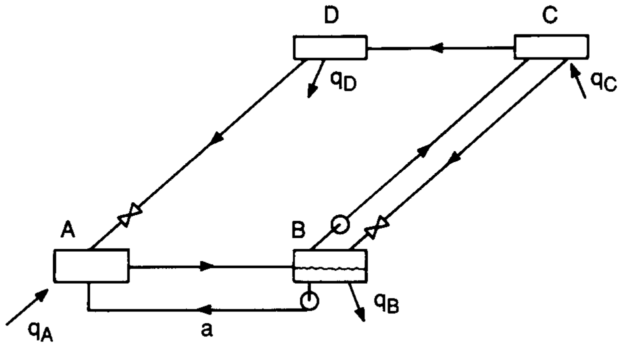

Figure 14 Process scheme of an absorption heat pump with a nonmiscible auxiliary fluid. This fluid evaporates together with the ammonia and condenses in the absorber. It is recirculated to the evaporator through its own circulation pump

The cycle is based on the single-stage absorption heat pump as shown in Figure 10. The working fluid mixture is water and ammonia. Now a third fluid is introduced into the evaporator: this fluid is condensable in the temperature and pressure range of the heat pump, and is not miscible with water and ammonia. The fluid may be a hydrocarbon, for example. The auxiliary fluid and the ammonia both evaporate inside the evaporator. Each establishes a partial pressure according to its vapor pressure at the evaporator temperature. The total pressure is the sum of the two partial pressures. When the vapor mixture is admitted into the absorber, the ammonia is absorbed while the auxiliary fluid is enriched in the remaining vapor. Since the total pressure does not change, the partial pressure of the auxiliary fluid increases until condensation commences. Due to the immiscibility, the auxiliary fluid is collected at the absorber exit and recirculated by means of a pump to the evaporator. In order for the absorption process to continue the absorber has to be subcooled below the saturation temperature of the conventional cycle or the ammonia concentration of the absorbent has to be reduced. Thus a trade-off is encountered between an increased COP and a decreased temperature lift. Prototype units have shown an increase in COP of 14%.[53]

The auxiliary fluid can also be used to reduce the generator temperature for a given temperature lift from evaporator to absorber. Another application are heat transformers.

Use of noncondensable auxiliary fluids, replacement of the solution pump

The absorption heat pumps just discussed use no compressor or turbine, just heat exchangers and liquid feed pumps. This represents a major advantage absorption systems have over their competitors, mechanical vapor compression, since a lack of moving parts means usually high reliability. The only moving parts in the absorption heat pumps are optional flow control valves and liquid feed pumps. But even those can be eliminated.

This is accomplished by using a noncondensable gas, usually hydrogen, in addition to the ammonia/water mixture. The hydrogen serves the purpose of maintaining the total pressure at a constant level. Thus the total pressure in the evaporator and the condenser is the same, while the ammonia partial pressure changes according to the temperature conditions. The need for a pump for maintaining the pressure difference is eliminated. Nevertheless the fluid has to be circulated between generator and absorber. This is accomplished by designing a generator with a thermo–syphon or vapor bubble pump that is driven by the heat supplied to this part of the system (Figure 15). This absorption system has no moving parts at all. This

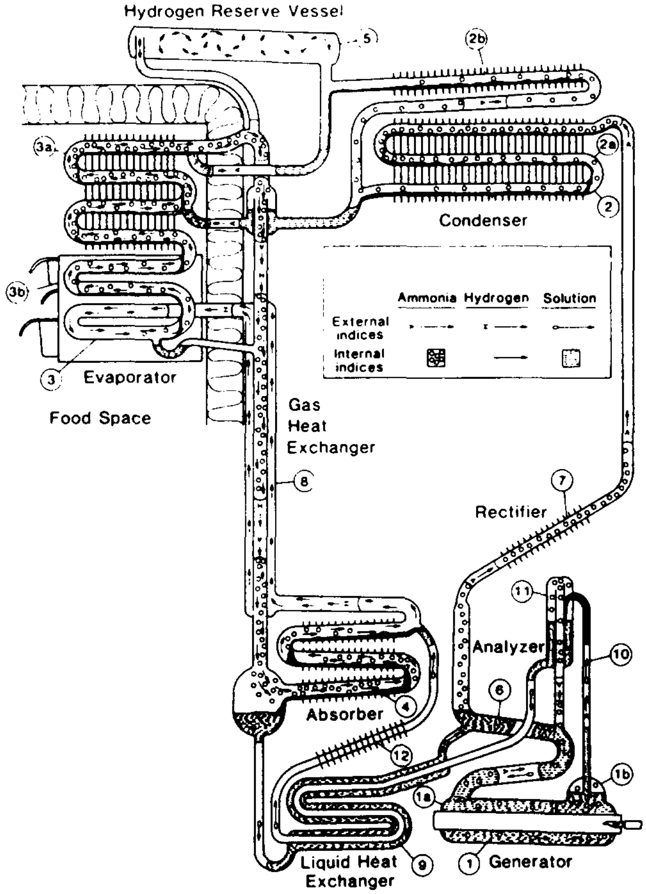

Figure 15 Process scheme of an absorption heat pump with a noncondensable auxiliary gas, usually hydrogen. While the total pressure in the entire system is constant, the partial pressure of the ammonia varies as required in an absorption system

concept was first patented in 1899 but never worked satisfactorily because air was used as the auxiliary gas as described in Ref. 37. The air caused a high mass transfer resistance. In the 1920's the idea was rediscovered and hydrogen was used successfully. Refrigerators of this design, which are perfectly quiet, are still sold in large numbers for recreational vehicles and hotel rooms, and to users without electricity. So far the principle was restricted to small capacities such as refrigerators. The challenge in the design for larger systems is two-fold. The first is the development of a thermo–syphon which reliably produces high liquid flow rates; the second challenge is the design of a gas heat exchanger that precools the hydrogen on its way back to the evaporator, with negligible pressure drop. Recently, however, a module was developed and tested for residential heating applications that has a heating capacity of 3 kW.[54] For safety reasons, the auxiliary gas is helium.

Using a noncondensable auxiliary gas is a concept that takes advantage of the thermodynamic properties of fluids to modify a combination of Rankine cycles to a heat pump without any moving part.

Improving heat and mass transfer: the rotating heat pump

Another remarkable concept relating to moving parts and at the same time to heat transfer enhancement consists of a rotating absorption heat pump.[55] This concept yields a number of advantages. All important heat transfer surfaces in the absorber, generator, and condenser are discs rotating about their center axes. As a consequence, the liquid film spreads out very thin and achieves a highly turbulent flow, enhancing heat and mass transfer considerably. Thus this concept uses a working fluid combination that otherwise has poor transport properties. In this case it is an aqueous solution of a mixture of alkali hydroxides, and the refrigerant is water. The major advantage of this fluid is the temperature lift capability, which is not limited by crystallization. The heating water is admitted through the rotating axis, and the heat pump acts as its own evaporator fan circulating air. The solution pump is built into the rotating system by just providing a liquid pick-up at the circumference of a heat exchange area.

Combinations of a single compressor with solution circuits

So far building blocks were combined to a simple vapor compression system and to a number of single and multi-stage absorption systems. They can also be combined into more complex vapor compression systems which may have some surprising features. When a second solution circuit of different mixture concentration is added to a vapor compression system with solution circuit, then the system shown in Figure 16 is obtained. Refrigerant vapor is supplied from two evaporators to the compressor suction side, while the high pressure vapor is supplied simultaneously to two absorbers. The low temperature desorber and the high temperature absorber exchange heat with an external source and sink, while the low temperature absorber supplies all of its heat to the high temperature evaporator. Again internal heat exchange is employed. This cycle incorporates one compressor and two solution circuits. While the pressure and temperature values within each solution circuit are determined by the circulating mixture and its composition, the combined system represents a cycle which operates between the lowest temperature (heat source) and a highest temperature (heat sink). However, the compressor encounters a pressure ratio which is very small. The pressure difference is just the same as for the single-stage cycle which would pump heat only across half the temperature lift, for example, between the heat source temperature and the intermediate temperature level (Figure 16). This cycle allows operation across a large temperature lift at very moderate pressure ratios, a feature which could be achieved by a working fluid of a very low slope of its vapor pressure curve. According to Figure 3 and Trouton's Rule, such a fluid does not exist. However, its effect can be simulated by the cycle.

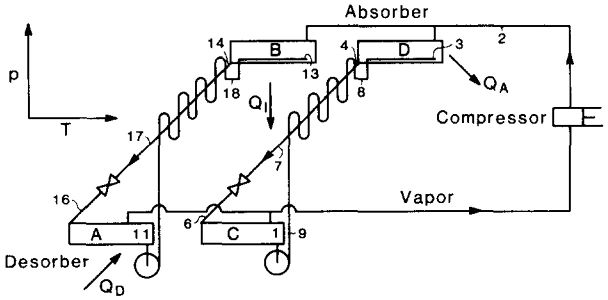

Figure 16 Process scheme of a vapor compression heat pump with two solution circuits. This unit pumps heat from desorber A to absorber D with a large temperature lift, while the pressure difference the compressor has to overcome is imposed by a temperature lift from only A to B

This configuration is a solution to the third shortcoming of the conventional Rankine cycle, high pressure ratios, as mentioned in the introduction.

The slope of vapor pressure curves is proportional to the latent heat of evaporation. This is true for the effective vapor pressure curve of the two-stage cycle as well. For each unit of vapor generated by introducing heat from the heat source, the compressor has to compress approximately twice as much vapor, since the additional quantity is delivered from the internal heat exchange process. That is equivalent to a fluid with a latent heat that is only half as large than for a conventional fluid in a conventional cycle. The advantage of a low pressure ratio of the moderately sloped effective vapor pressure curve is achieved by reduced capacity or increased mass flow rate. This cycle has been analyzed and is now being built on a laboratory scale in two groups[49,56,57] with emphasis on different aspects.

The concept of the vapor compression heat pump with two solution circuits can be merged with the concept of a one solution circuit. One obtains a system in which the concept absorber/desorber heat exchange is realized in a similar way as in the absorption heat pump shown in Figure 13. The corresponding vapor compression system is shown in Figure 17. The absorber supplies not only heat to the heat sink but also to the desorber. Only one solution pump is left, and the liquid/liquid heat exchanger is eliminated. This represents a vapor compression heat pump of a potentially very low pressure ratio and with large gliding temperature intervals.[58] This cycle is an extension of the concept referred to as a "blend cascade" which is used in the liquefication of natural gas.[59,60]

Another option is to combine two solution circuits and a compressor in the manner that "temperature transformation" is obtained (Figure 18). In this case, the compressor works on a given temperature level while the heat pumping is performed on two entirely different temperature levels.[49,61] Vapor is generated in the desorber out of a mixture (e.g., ammonia/water) and compressed by the compressor. The high side pressure is selected in such a way that the heat of condensation of the vapor within the condenser can be used to further generate vapor in the desorber. The remaining solution in the desorber is pumped through a liquid/liquid heat exchanger into the absorber, while the condensate leaving the condenser is pumped into the evaporator. The pressure in the evaporator and absorber is the same (Figure 18). The actual value of this pressure is determined by the composition of the mixture and the desired temperature levels of the heat pump process.

The evaporator of the heat pump absorbs heat from an outside high temperature source, while the absorber rejects heat by absorbing vapor supplied by the evaporator into the liquid mixture pumped from the desorber through the liquid/liquid heat exchanger. The solution with the high working fluid concentration leaves the absorber and returns through the other side of the liquid/liquid heat exchanger and the expansion valve into the desorber.

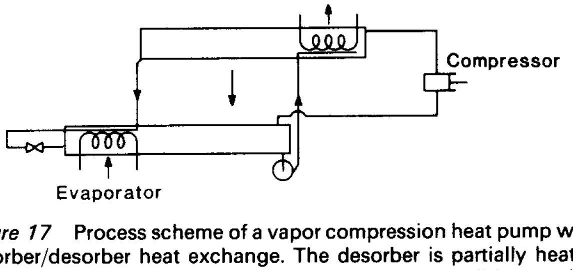

Figure 17 Process scheme of a vapor compression heat pump with absorber/desorber heat exchange. The desorber is partially heated by the absorber in the range where the temperature glides overlap

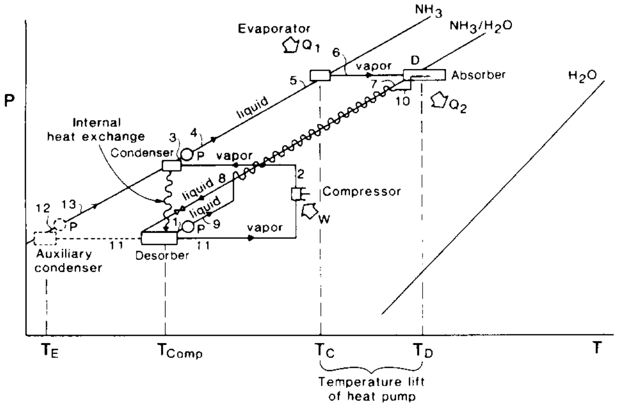

Figure 18 Process scheme of a vapor compression heat pump with temperature transformation. While the compressor works on a given temperature level, T_{comp}, the heat pumping occurs between T_C and T_D. Thus compressor and heat pumping temperature levels are decoupled

In a conventional heat pump, the compressor conveys vapor from the evaporator to the condenser of the same solution circuit, the same one that does the heat pumping. Here the compressor conveys vapor from one solution circuit to the next, while the actual heat pump process returns the vapor to the original solution circuit. Due to this measure, the compression process and the heat pump process are decoupled. This enables one to select the temperature levels for the actual heat pump process (almost) independently of the temperature level of the compressor suction gas.

Solid/vapor systems

In these Rankine cycles the absorbent is actually a solid material. Although the phase change process is now between a vapor and a solid phase, the thermodynamic principle that is employed, the vapor pressure decrease, is equally important. Solid/vapor systems have to be operated in a discontinuous fashion. Figure 19 shows a bed of zeolite that acts as an absorber for water. As the zeolite bed absorbs water vapor, it has to be cooled. Its temperature can be up to 100°C higher than that of the evaporator which generates the vapor. Thus a temperature lift of 100°C is possible, which is larger than what is available with most liquid/vapor systems. When the zeolite is saturated with water the process can be reversed. By heating the zeolite bed the water vapor is desorbed and condensed in the heat exchanger that used to be the evaporator. Thus the function of the pair of heat exchangers in Figure 19 is reversed. A quasi-continuous mode can be achieved when two or more such pairs are in operation with a suitable phase shift. This concept can be used as a heat or cold storage device. When the water and zeolite are separated they can be stored at any temperature for any length of time. When heat is needed (or cooling capacity) then the water is evaporated, providing cooling, and absorbed in the zeolite bed, providing heat. In the case of heat storage, the evaporator would pick up heat from the surroundings; in the case of cold storage, the heat of absorption could be rejected as waste heat. Another option is to operate the storage device as a heat pump or heat transformer. In this case the storage unit would be charged at temperature levels that are different from the levels at which the heat is required. A summary of the options and their implications is given in Ref. 62.

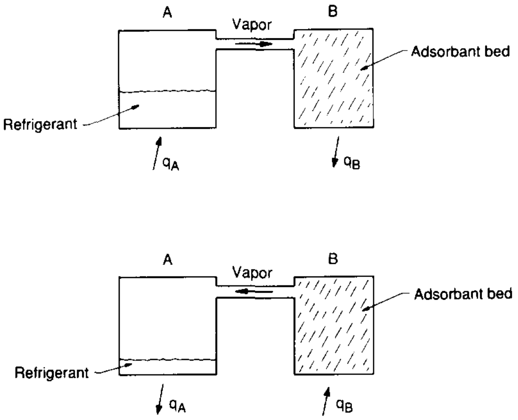

Figure 19 Scheme of a solid/vapor adsorption system for heat pumping, transformation and/or energy storage. The same pair of a refrigerant reservoir and a solid adsorbent bed change in a timely sequence their tasks from an evaporator/absorber pair to a condenser/desorber pair. The sequence can be interrupted for energy storage

Other fluids have been proposed for solid/vapor absorption systems as well. The refrigerants are generally the same fluids that are found in other applications. The solid adsorbents are zeolites, active carbons, salts, and lastly metals, with hydrogen as the refrigerant. Salt/ammonia systems were historically used in household refrigerators.[37] In a recent development such fluid pairs have been suggested for heat pumping and refrigeration applications.[63] Salt methanol systems were investigated as well.[64] Also recently, two groups have developed independently–solid/vapor heat pumps that employ absorber/desorber heat exchange[65] with the help of a heat transfer fluid that circulates between two adsorbent beds and a heat source and heat sink. An important feature is the use of a thermal wave that propagates through the beds and enables two-stage features.

Other Rankine cycle combinations

The examples discussed here represent only a small portion of the Rankine cycles that are available in theory or have been investigated or tested in more detail. The area of heat, cold, or energy storage has only been mentioned. Also power generation processes were not discussed in detail. Applications of working fluid mixtures in power generation are restricted to bottoming cycles, since most fluid mixtures are not thermally stable at high temperatures. However, work has been performed in this area for bottoming cycles.[66–70] The concepts of lower (or higher) pressure ratios and of temperature transformation have not been investigated. They have the potential for improving efficiency, or shifting operating conditions of turbines to more desirable temperature and pressure levels.

Research needs

The research needs can be divided into two major areas. The first relates to working fluids. There is continuous need for fluids which are safe, non-corrosive, non-toxic, and stable at as high a temperature as possible. The latent heat should be high, to reduce the mass flow rate, but the specific heat should be small to minimize losses in liquid/liquid heat exchangers and expansion valves. It has been shown that in order to compare fluids essentially one nondimensional number

$$\frac{c_{\mathrm{pl}}^{*}T}{Q_{\mathrm{lat}}}$$

is quite helpful, the ratio of liquid specific heat, c_{pl}, multiplied by the absolute temperature, T, divided by the latent heat Q_{lat}. It is a measure of the largest loss in a heat pump cycle which is associated with the expansion process.[71]

The second area is the development and testing of advanced cycles, a subject matter that is only at the beginning of being explored. A method of finding new cycles has been outlined in Refs. 44 and 49.

Other research areas are transport properties, corrosion inhibitors, and additives that increase heat and mass transfer or shift crystallization limits.

With regard to heat transfer the following issues are of concern. Mixtures require counterflow heat exchangers, but in many applications, such as air-conditioning, crossflow heat exchange is customary, for example when heat between the evaporating refrigerant and air is exchanged. The development of a compact and efficient counterflow heat exchanger is under way.[72] Furthermore, in the case of internal heat exchange one faces the difficulty that in many applications (such as desorber/absorber heat exchange) falling film heat exchangers would be preferable, but do not allow counterflow. New solutions have to be found. In general, more sophisticated cycles often require additional heat exchange area. In order to stay competitive, compact heat exchangers with enhanced surfaces of small volume and weight are desired. Multiple pass heat exchangers would be of advantage. Lastly, methods should be devised that allow to eliminate or weaken the influence of the nonlinearity of the temperature profiles.

Conclusions

The concept of building blocks for generalized Rankine cycles provides many possibilities for the development of efficient energy conversion systems for a variety of general and specialized applications. All opportunities and shortcomings arise from the interaction of fluid properties with the cycle, heat transfer conditions, and the application. The potential the cycles provide beyond today's state-of-the-art and research programs can best be employed when significant progress is made in the development of new fluids and heat exchange concepts.

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