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Corresponding Author: Prof. Mahmoud Bourouis, Ph.D.

Corresponding Author's Institution: Rovira i Virgili University

First Author: Francisco Táboas, Ph.D.

Order of Authors: Francisco Táboas, Ph.D.; Mahmoud Bourouis, Ph.D.; Manel Vallès, Ph.D.

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The results show that $NH_3/(LiNO_3+H_2O)$ and $NH_3/LiNO_3$ working mixtures have higher values of COP as compared to NH_3/H_2O working mixture, the differences being more pronounced at low generation temperatures. If the activation temperature is set to 85ºC, the minimum evaporation temperatures that can be achieved are -18.8ºC for the cycle with $NH_3/LiNO_3$, -17.5ºC for the cycle with $NH_3/(LiNO_3+H_2O)$ cycle and -13.7ºC for the NH_3/H_2O cycle at a condensing temperature of 25ºC. Also, for the $NH_3/(LiNO_3+H_2O)$ working fluid mixture, it has been demonstrated that the absorption refrigeration cycle can be operated without a distillation column and in this case the water content in the refrigerant stream entering the evaporator is less than 1.5 % in weight at the operating conditions selected.

Ammonia/water and ammonia/salt mixture absorption cycles analysis for refrigeration purposes in fishing ships

Francisco Táboas[a], Mahmoud Bourouis[b, 1], Manel Vallès[b]

[a] Universidad de Córdoba, Campus de Rabanales, Edificio Leonardo da Vinci, 14014 Córdoba, Spain.

[b] CREVER – Universitat Rovira i Virgili, Av. Països Catalans No. 26, 43007 Tarragona, Spain

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Highlights:

- Ammonia absorption systems can provide refrigeration necessities for fishing ships.
- Absorption refrigeration systems reduce the energy consumption of fishing ships.
- The NH_3 / ($LiNO_3$+H_2O) mixture is recommended for absorption refrigeration cycles.

Nomenclature:

f: Circulation ratio

h: Enthalpy (kJ·kg^{-1})

$\dot{m}$: Mass flow rate (kg s^{-1})

P_{high}: Condenser pressure (Pa)

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[1] Phone: +34 977 55 86 13, Fax: +34 977 55 96 91.

P_{low}: Evaporator pressure (kPa)

$\dot{Q}$: Heat duty (kJ·s^{-1})

reflux: Reflux ratio

T: Temperature (ºC)

x: Ammonia mass fraction

Greek symbols

η: Efficiency

ρ: Density (kg·m^{-3})

ξ: Vapour mass fraction

Subscripts:

ABS: Absorber

COND: Condenser

EVAP: Evaporator

COP: Coefficient of performance

GEN: Generator

LVHX: Liquid-vapour heat exchanger

iso: Isentropic efficiency

rect: Rectification

sat: Saturation state

SHX: Solution heat exchanger

stripping: stripping section

rectifying: rectifying section

Abstract

In this work, the use of waste heat energy of jacket water in diesel engines of fishing ships was analysed for use as a heat source for absorption refrigeration systems. The thermodynamic simulation of an absorption refrigeration cycle with three different working fluid mixtures that use ammonia as a refrigerant was carried out. This analysis was assessed in terms of the cooling demand and cycle performance as a function of the evaporator, condenser and generator temperatures. Moreover, the need for rectifying the vapour stream leaving the generator was analysed together with the drag of the fraction of non-evaporated liquid to the absorber.

The results show that $NH_3/(LiNO_3+H_2O)$ and $NH_3/LiNO_3$ working mixtures have higher values of COP as compared to NH_3/H_2O working mixture, the differences being more pronounced at low generation temperatures. If the activation temperature is set to 85ºC, the minimum evaporation temperatures that can be achieved are -18.8ºC for the cycle with $NH_3/LiNO_3$, -17.5ºC for the cycle with $NH_3/(LiNO_3+H_2O)$ cycle and -13.7ºC for the NH_3/H_2O cycle at a condensing temperature of 25ºC. Also, for the $NH_3/(LiNO_3+H_2O)$ working fluid mixture, it has been demonstrated that the absorption refrigeration cycle can be operated without a distillation column and in this case the water content in the refrigerant stream entering the evaporator is less than 1.5 % in weight at the operating conditions selected.

1. Introduction

The reduced profitability of the fishing activity due to the continuous rise in the price of fossil fuel is a problem for fishing ships the world over. According to the European Commission in 2000, the world’s fishing fleets were responsible for around 1.2% of the total global fuel consumption, corresponding to 0.67 litres of fuel per Kg of live fish and shellfish landed. In 2008, the EU fishing fleets consumed 3.7 billion litres of fuel, representing 25% of the value of landings.

Almost all types of fishing ships, from small boats to large fishing factories, use some type of refrigeration to preserve their catch. The methods range from the daily loading of ice to installations of sophisticated equipment for low-temperature freezing and cold storage. In large ships, cooling systems are used to produce onboard ice, cool tanks with sea water to store fish and cold stores to maintain the desired temperature to freeze the captures.

Refrigeration requirements in fishing ships vary widely depending on the application. Catches can be conserved on ice, in refrigerated seawater or ice can be produced on the ships. In most applications, the evaporator temperature varies from just below 0 ºC to -25 ºC. The condenser temperature depends on the sea water temperature and is in the range of 15 to 31ºC.

During the operation, the diesel engines of the fishing ships do not stop, and can deliver a large amount of waste heat energy trapped in the jackets of the engine and in the exhaust gases. Sorption machines are proposed in literature to utilise the large amount of waste heat energy in the diesel engines of fishing ships for air conditioning (Tse et al. [1]) or refrigeration (Wang et al. [2], Fernández-Seara et al. [3]).

Wang and Wang [4] analysed the developments reported in the literature related to the use of sorption technologies for refrigeration purposes in fishing ships. The authors concluded that sorption technologies were still not adapted for use on fishing ships and that solid sorption and NH_3/H_2O absorption systems have high potential for utilising the waste heat energy.

Fernandez-Seara et al. [3] demonstrated the ability of ammonia-water absorption refrigeration systems to provide onboard cooling using a gas-to-thermal fluid heat recovery system from engine exhausts on a fishing boat. Synthetic oil was used as a heat transfer fluid. The heat energy recovered from the engine exhaust gasses was 16.6 kW and the cooling capacity of the system was 8.33 kW. The authors reported that nowadays mechanical refrigeration is adopted for use in traditional fishing ships, which use crushed ice for caught fish preservation as it melts less quickly. However, these ships do not use any heat recovery system. They reported that in these fishing ships the hold capacity ranges from 80 to 150 m^3 and the refrigeration needs are from 5 to 10 kW while the hold and evaporation temperature are 0^{o}C and -10^{o}C, respectively. Ice production is not considered. Four-stroke diesel engines with a power in the range of 700 to 1200 kW are fitted in these fishing ships. Thus, a large amount of waste heat energy is available in the exhaust gasses which can be recovered using a gas-to-thermal fluid heat recovery system and can be utilized in the absorption refrigeration systems to provide the cooling needs of the fishing ships.

Peranic et al. [5] designed and compared the ammonia compression refrigeration system and the ammonia-water absorption refrigeration system powered by the heat recovered from the engine exhaust gasses of a medium size fishing boat for sea water refrigeration. They reported that the exhaust gasses from the engine have a temperature of 400^{o}C and carry 30% of the total heat power input of the fuel while the outgoing heat with cooling water is 28%. The available exhaust gas heat energy in the fishing boat investigated with a 700 kW diesel engine was 425 kW. Thus, the waste heat can be recovered and utilized in the absorption refrigeration system with an increase in energy efficiency compared to compression cycles.

There are technical problems to implement absorption technologies ships, mainly in the handling of liquids in an accelerated motion system. The falling film configuration usually used in the thermal components of commercial absorption machines can be broken by the continuous movement, which negatively affects heat and mass transfer processes. Safarik et al. [6] reported about a water/LiBr absorption refrigeration machine that was adapted to the requirements of marine necessities and used to provide HVAC in cargo ships. The waste heat energy usually available from the main engine or the diesel generator was used to power the absorption refrigeration machine. Several internal adjustments were made in order to avoid the refrigerant mixing with the solution in certain conditions at sea and to enable the chiller to cope with static and dynamic heel. The absorption machine of a nominal capacity of 140 kW was tested at a German naval test facility under realistic marine conditions. A reduction of about 14 % was observed in the COP of the system compared to normal operation when the chiller was continuously operated at +/-20°dynamic heel. The authors reported that the installation cooling capacities in a common cargo ship vary from about 150 kW to 500 kW and consume 5% to 15% of the onboard power supply during sea operation. They reported that absorption chillers for marine application must operate reliably even in heavy swell (+/-22.5° dynamic, 15° static) and must be mechanically strong to withstand (+/- 0.8 g) accelerating force and vibrations.

The higher pressure of a NH_3/H_2O working pair allows for the use of bubble absorbers and generators of the plate heat exchanger type that are considered to be less affected by the inclination angle of the machine. Cerezo et al. [7] and Táboas et al. [8] studied the absorption and desorption processes with the NH_3/H_2O mixture using plate heat exchangers at operating conditions of interest for absorption refrigeration cycles. The experimental results showed the feasibility of absorption cycles employing plate heat exchangers. The drawback of using the NH_3/H_2O working fluid mixture in absorption cycles is that the vapours leaving the generator have to be rectified before entering the condenser. So, a distillation column is needed at the top of the generator. However, as

Fernández-Seara et al. [3] pointed out, the distillation column operation can also be affected by the inclination of the ship and by deficiently purified ammonia with a significant water content which can reach the evaporator where the water tends to accumulate leading to reduce the efficiency of the cycle.

The $NH_3/LiNO_3$ working fluid mixture has been proposed in literature in order to avoid the use of distillation columns in ammonia based absorption refrigeration machines. The use of this working fluid mixture reduces the temperature required for the heat source, which makes it suitable for solar cooling applications. The thermodynamic analysis of the absorption refrigeration cycle employing $NH_3/LiNO_3$ as a working fluid mixture predicts a higher COP as compared to a NH_3/H_2O mixture (Chinnappa [9], Antonopoulos and Rogdakis [10], Heard [11], Ayala et al. [12], Sun [13], Rivera and Rivera [14]).

Despite the advantages of the $NH_3/LiNO_3$ mixture, absorption cycles with this working fluid have not yet been commercially implemented. The experimental results obtained are below expectations. In experiments Rivera and Best [15] obtained the heat transfer coefficients in boiling conditions for $NH_3/LiNO_3$ and NH_3/H_2O mixtures. These authors reported that the heat transfer coefficient of ammonia $NH_3/LiNO_3$ is two to three times lower than that of NH_3/H_2O. Heard [11] mentioned that the reduction in the achieved values of the COP and cooling capacity against the expected ones is mainly due to the low efficiency of the absorption process, penalized by the high viscosity of the solution. Zacarías [16] tested a single-effect absorption refrigeration machine and obtained efficiencies in the absorber, generator and solution heat exchanger between 30 and 60% lower than those provided by the simulation model. Oronel et al. [17] measured the boiling heat transfer coefficients with a $NH_3/LiNO_3$ mixture in a plate heat exchanger and compared the results with the data of Táboas et al. [8] obtained with NH_3/H_2O in the same set-up, showing that heat transfer coefficients with $NH_3/LiNO_3$ mixture were about 60% lower.

The addition of water to the binary mixture of $NH_3/LiNO_3$ to improve heat and mass transfer processes was first proposed by Ehmke and Renz [18] and Bokelmann and Steimle [19] from the University of Essen.

Ehmke and Renz [18] studied the effect of water on the solubility and viscosity of the ternary working pair $NH_3/(LiNO_3+H_2O)$, and suggested an optimal water mass fraction of between 0.20 and 0.25 in the absorbent mixture $(LiNO_3+H_2O)$. The authors also determined and correlated the density and vapour pressure of the solutions with a 0.25 water mass fraction in the absorbent mixture.

Bothe [20] presented an experimental study comparing the performance of an absorption heat pump employing NH_3/H_2O and $NH_3/(LiNO_3+H_2O)$ as working fluid mixtures. The author reported higher operation temperatures and significant COP improvements for the ternary mixture as compared to the binary mixture, in heat pump applications. It was also observed that there is no need for rectification, which increases the cooling capacity. Rivera et al. [21] compared the performance of a solar powered intermittent absorption refrigeration system with the binary mixture $NH_3/LiNO_3$ and ternary mixture $NH_3/(LiNO_3+H_2O)$. The authors concluded that the amount of ammonia vapours produced during the generation is higher for the ternary mixture with water concentrations of 20% and 25% in the absorbent. Also, it was found that with the ternary mixture, the solar coefficients of performance were up to 24% higher than those obtained with the binary mixture, varying from 0.066 to 0.093 and, with the ternary mixture the initial generation temperatures were up to 5.5 °C lower than those required for the $NH_3/LiNO_3$ mixture. No traces of water in the ammonia vapour were observed in the experiments carried out.

Recently, Oronel et al. [22-23] carried out an experimental study on the absorption and desorption processes with $NH_3/LiNO_3$ and $NH_3/(LiNO_3+H_2O)$ mixtures in a plate heat exchanger. The authors reported significant improvements in the absorption and desorption processes with the ternary mixture as compared to the binary mixture. Therefore, absorption chillers for fishing ships can be built using plate heat exchangers in all thermal components, reducing the chiller size and the refrigerant charge.

Regarding the thermophysical properties of the ternary mixture, Libotean et al. [24-25] performed experimental measurements and developed equations for calculating vapour/liquid equilibrium and transport properties of the ternary mixture $NH_3/(LiNO_3+H_2O)$ with a water content of 20, 25 and 30% in the absorbent. The recent solubility data compiled by Eysseltova and Orlova [26] also confirmed that the addition of water improves the solubility of the solution, making the ternary mixture more suitable for high generation temperatures or low cooling temperatures.

The ternary mixture $NH_3/(LiNO_3+H_2O)$ can be used as a working fluid mixture in the absorption refrigeration cycle utilizing waste heat energy available in diesel engines of fishing ships because of the above-mentioned advantages. Firstly, the $NH_3/(LiNO_3+H_2O)$ absorption refrigeration cycle is simpler than the NH_3/H_2O absorption refrigeration cycle and, secondly, the required driving temperatures of the $NH_3/(LiNO_3+H_2O)$ cycle are lower than those employing NH_3/H_2O and similar to those of $NH_3/LiNO_3$ cycle. The major advantage of the absorption refrigeration cycle with the ternary mixture over the conventional NH_3/H_2O absorption cycle is the ability to operate without a distillation column, since the operation of these columns may be affected in motion. In comparison with the binary mixture $NH_3/LiNO_3$, heat and mass transfer coefficients achieved with the ternary mixture are higher, which would result in smaller heat exchangers.

This work discusses the feasibility of using $NH_3/(LiNO_3+H_2O)$ as a working fluid in a single-effect absorption refrigeration cycle at operating conditions of interest for fishing ships, and the results are compared with those obtained with $NH_3/LiNO_3$ and NH_3/H_2O as working fluids in the same absorption cycle. This comparison is performed not only according to the driving temperature [Libotean et al. [27]), but also in relation to the coefficient of operation (COP). Moreover, other aspects related with the cycle operation were analyzed, namely: (i) The need for rectifying the vapour stream leaving the generator and the drag of the fraction of non-evaporated liquid to the absorber, (ii) The influence of the evaporator temperature glide on the COP of the cycle; (iii) The feasibility of using the jacket water as the heat source for absorption refrigeration in fishing ships.

2. Mathematical model

A computer simulation model has been developed, in the Engineering Equation Solver (EES) environment, to predict the performance of a single-effect absorption refrigeration cycle using three working fluids, namely, NH_3/H_2O, $NH_3/LiNO_3$ and $NH_3/(LiNO_3+H_2O)$.

Figure 1.a shows a schematic configuration of the single-effect absorption cycle with $NH_3/LiNO_3$ and $NH_3/(LiNO_3+H_2O)$ working fluid mixtures, since the ternary mixture is intended for use without vapour rectification. In the case of an absorption cycle with a NH_3/H_2O working fluid mixture, the thermodynamic model of the cycle includes a distillation column with total condensation, as shown in Figure 1.b.

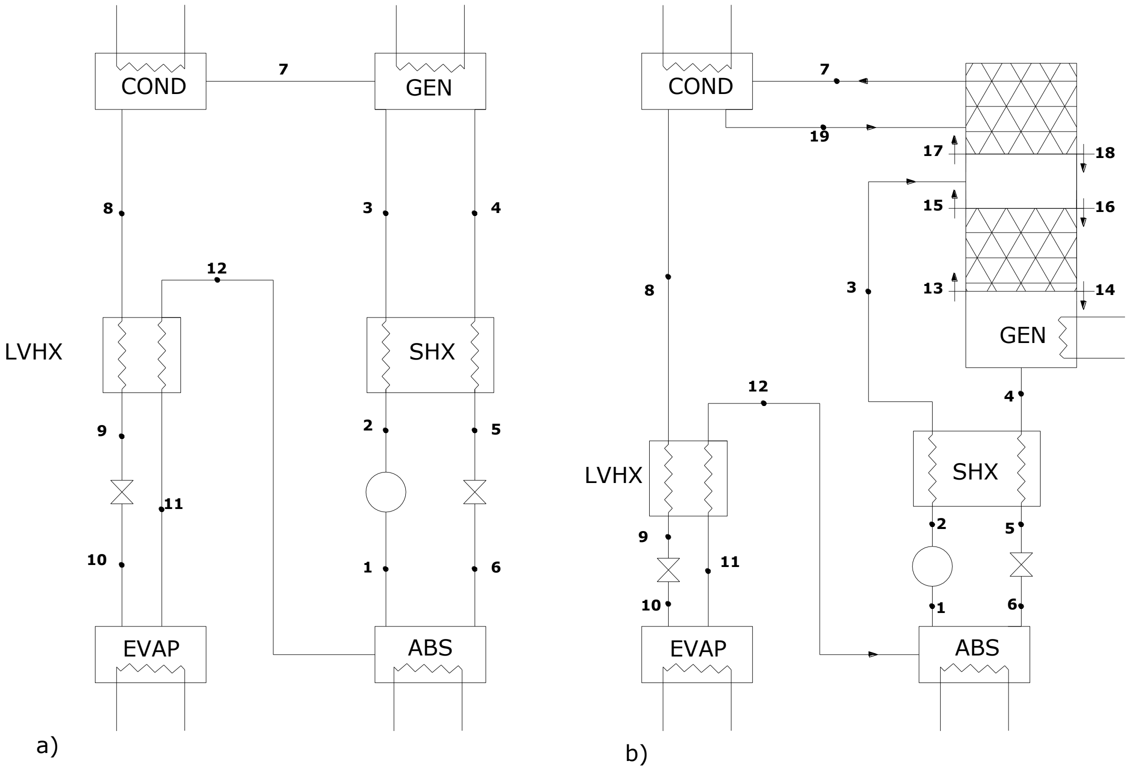

Figure 1. Diagrams of the considered absorption cycles with: (a) $NH_3/(LiNO_3+H_2O)$ and $NH_3/LiNO_3$, (b) NH_3/H_2O

The mathematical model is based on the application of global mass, species and energy balance equations. In formulating the model, the following assumptions have been made:

- Heat losses to the environment are negligible.
- Pressure losses in all the devices and tubes are not considered except for pump and expansion valves.
- The liquid leaving the condenser (stage 8) is saturated.
- The solution leaving the generator is saturated (stage 4).

For absorption cycles with $NH_3/(LiNO_3+H_2O)$ and $NH_3/LiNO_3$:

- The vapour leaving the generator (stage 7) is saturated and in thermal equilibrium with the solution leaving the generator (stage 4).

For absorption cycle with NH_3/H_2O:

- The vapour leaving the distillation column (stage 7) is saturated at the pressure of the condenser.
- The liquid and the vapour streams inside the column are saturated.

In addition to the typical efficiencies of the solution and liquid/vapour heat exchangers, absorber efficiency was also considered. In common practice, the absorber is oversized and the solution leaving the absorber has some degree of subcooling. The effectiveness of the absorption process was calculated by using Eq. (1):

$$\eta_{ABS} = \frac{x_1 - x_6}{x_{sat}\left(T_1, P_{low}\right) - x_6} \qquad \text{Eq. (1)}$$

When ammonia refrigerant with a small amount of water is evaporated in an evaporator controlled by a thermostatic expansion valve, some liquid fraction may be present at the evaporator outlet. The presence of this liquid (mainly water) can be controlled by adjusting the temperature glide of the thermostatic expansion valve. For low values of the temperature glide, the liquid fraction leaving the evaporator will be higher, reducing the cooling effect and consequently reducing the COP. However, the use of a high temperature glide needs lower evaporation temperatures that also lead to low values of COP.

In the present work, a temperature glide of 10 K in the evaporator is considered. Also it is assumed that the remaining liquid in the evaporator is dragged by the vapour flow to the absorber through the liquid–vapour heat exchanger.

The input variables for the distillation column were the reflux ratio and the Murphree efficiencies of the stripping and rectifying section.

The reflux ratio is defined by Eq. (2):

$$reflux = \frac{\dot{m}_{19}}{\dot{m}_7} \qquad \text{Eq. (2)}$$

The Murphree efficiencies of the rectifying and stripping sections can be defined for the liquid or vapour phase, though they are usually defined for the vapour phase [Zavaleta and Simoes [28]. In the stripping section the Murphree efficiency of the vapour phase is as Eq. (3):

$$\eta_{stripping} = \frac{x_{15} - x_{13}}{x_{T_{15}=T_{14}} - x_{13}} \qquad \text{Eq. (3)}$$

And in the case of the rectifying section, it was defined as Eq. (4):

$$\eta_{rect,vapour} = \frac{x_7 - x_{17}}{x_{T_7=T_{19}} - x_{17}} \qquad \text{Eq. (4)}$$

The equations of the mathematical model are as follows:

Absorber

$$\dot{m}_{12} + \dot{m}_6 = \dot{m}_1 \qquad \text{Eq. (5)}$$

$$\dot{m}_{12} \cdot x_{12} + \dot{m}_6 \cdot x_6 = \dot{m}_1 \cdot x_1 \qquad \text{Eq. (6)}$$

$$\dot{Q}_{ABS} = \dot{m}_{12} \cdot h_{12} + \dot{m}_6 \cdot h_6 - \dot{m}_1 \cdot h_1 \qquad \text{Eq. (7)}$$

$$\eta_{ABS} = \frac{x_1 - x_6}{x_{sat}\left(T_1, P_{low}\right) - x_6} \qquad \text{Eq. (8)}$$

Solution heat exchanger

$$\dot{m}_2 \cdot \left(h_2 - h_3\right) + \dot{m}_4 \cdot \left(h_4 - h_5\right) = 0 \qquad \text{Eq. (9)}$$

$$\eta_{SHX} = \frac{\dot{m}_4 \cdot \left(h_4 - h_5\right)}{\min\left(\dot{m}_4 \cdot \left(h_4 - h_{T_5=T_2}\right); \dot{m}_2 \cdot \left(h_{T_3=T_4} - h_2\right)\right)} \qquad \text{Eq. (10)}$$

Pump

$$\eta_{pump} = \frac{1}{\rho_1} \cdot \frac{P_{high} - P_{low}}{\left(h_2 - h_1\right)} \qquad \text{Eq. (11)}$$

Expansion valve

$$h_9 = h_{10} \qquad \text{Eq. (12)}$$

Liquid/vapour heat exchanger

$$\dot{m}_8 \cdot (h_8 - h_9) + \dot{m}_{11} \cdot (h_{11} - h_{12}) = 0 \qquad \text{Eq. (13)}$$

$$\eta_{LVHX} = \frac{\dot{m}_{12} \cdot (h_{12} - h_{11})}{\min\left(\dot{m}_8 \cdot \left(h_8 - h_{T_9=T_{11}}\right); \dot{m}_{11} \cdot \left(h_{T_{12}=T_8} - h_{11}\right)\right)} \qquad \text{Eq. (14)}$$

Evaporator

$$\dot{Q}_{EVAP} = \dot{m}_{11} \cdot h_{11} - \dot{m}_{10} \cdot h_{10} \qquad \text{Eq. (15)}$$

In the case of the generator and condenser, the mass, energy and species equations have different formulations, depending on the fluid mixture. These equations are summarized in Table 1 for the selected three working fluid mixtures.

Table 1. Mass, species and energy balance equations in the generator and condenser for the considered fluid mixtures

	$NH_3/LiNO_3$ and $NH_3/(LiNO_3+H_2O)$	NH_3/H_2O
CONDENSER	Eq. (16) $\dot{m}_8 = \dot{m}_7$	Eq. (18) $\dot{m}_7 = \dot{m}_8 + \dot{m}_{19}$
	Eq. (17) $\dot{Q}_{COND} = \dot{m}_7 \cdot h_7 - \dot{m}_8 \cdot h_8$	$\dot{Q}_{COND} = \dot{m}_7 \cdot h_7 - \dot{m}_8 \cdot h_8 - \dot{m}_{19} \cdot h_{19}$ Eq. (19)
GENERATOR	Eq. (20) $\dot{m}_3 = \dot{m}_4 + \dot{m}_7$	Eq. (23) $\dot{m}_{14} + \dot{m}_{13} = \dot{m}_4$
	Eq. (21) $\dot{m}_3 \cdot x_3 = \dot{m}_4 \cdot x_4 + \dot{m}_7 \cdot x_7$	Eq. (24) $\dot{m}_{14} \cdot x_{14} = \dot{m}_{13} \cdot x_{13} + \dot{m}_4 \cdot x_4$
	$Q_{GEN} = \dot{m}_4 \cdot h_4 + \dot{m}_7 \cdot h_7 - \dot{m}_3 \cdot h_3$ Eq. (22)	$\dot{Q}_{GEN} = \dot{m}_{13} \cdot h_{13} + \dot{m}_4 \cdot h_4 - \dot{m}_{14} \cdot h_{14}$ Eq. (25)

Moreover, for the absorption cycle with NH_3/H_2O, the distillation column adds the following equations, at the stripping, rectifying and column feed sections of the distillation column.

Stripping section

$$\dot{m}_{13} + \dot{m}_{16} = \dot{m}_{14} + \dot{m}_{15} \qquad \text{Eq. (26)}$$

$$\dot{m}_{13} \cdot x_{13} + \dot{m}_{16} \cdot x_{16} = \dot{m}_{14} \cdot x_{14} + \dot{m}_{15} \cdot x_{15} \qquad \text{Eq. (27)}$$

$$\dot{m}_{13} \cdot h_{13} + \dot{m}_{16} \cdot h_{16} = \dot{m}_{14} \cdot h_{14} + \dot{m}_{15} \cdot h_{15} \qquad \text{Eq. (28)}$$

$$\eta_{stripping} = \frac{x_{15} - x_{13}}{x_{T_{15}=T_{14}} - x_{13}} \qquad \text{Eq. (29)}$$

Rectifying section

$$\dot{m}_{17} + \dot{m}_{19} = \dot{m}_{18} + \dot{m}_{7} \qquad \text{Eq. (30)}$$

$$\dot{m}_{17} \cdot x_{17} + \dot{m}_{19} \cdot x_{19} = \dot{m}_{18} \cdot x_{18} + \dot{m}_{7} \cdot x_{7} \qquad \text{Eq. (31)}$$

$$\dot{m}_{17} \cdot h_{17} + \dot{m}_{19} \cdot h_{19} = \dot{m}_{18} \cdot h_{18} + \dot{m}_{7} \cdot h_{7} \qquad \text{Eq. (32)}$$

$$reflux = \frac{\dot{m}_{19}}{\dot{m}_{7}} \qquad \text{Eq. (33)}$$

$$\eta_{rect,vapour} = \frac{x_{7} - x_{17}}{x_{T_{7}=T_{19}} - x_{17}} \qquad \text{Eq. (34)}$$

Column feed section

$$\dot{m}_{17} = \dot{m}_{15} + \dot{m}_{3} \cdot \xi_{3} \qquad \text{(Eq. 35)}$$

$$\dot{m}_{17} \cdot x_{17} = \dot{m}_{15} \cdot x_{15} + \dot{m}_{3} \cdot \xi_{3} \cdot x_{3,vapour} \qquad \text{(Eq. 36)}$$

$$\dot{m}_{17} \cdot h_{17} = \dot{m}_{15} \cdot h_{15} + \dot{m}_{3} \cdot \xi_{3} \cdot h_{3,vapour} \qquad \text{(Eq. 37)}$$

$$\dot{m}_{16} = \dot{m}_{18} + \dot{m}_{3} \cdot \left(1 - \xi_{3}\right) \qquad \text{(Eq. 38)}$$

$$\dot{m}_{16} \cdot x_{16} = \dot{m}_{18} \cdot x_{18} + \dot{m}_{3} \cdot \left(1 - \xi_{3}\right) \cdot x_{3,liquid} \qquad \text{(Eq. 39)}$$

$$\dot{m}_{16} \cdot h_{16} = \dot{m}_{18} \cdot h_{18} + \dot{m}_{3} \cdot \left(1 - \xi_{3}\right) \cdot h_{3,liquid} \qquad \text{(Eq. 40)}$$

The nominal operating conditions considered for the cycle simulation are summarized in Table 2.

Table 2. Nominal operating conditions considered for the cycle simulations

Pump efficiency, $\eta_{pump,iso}$	0.5
Solution Heat exchanger efficiency, η_{SHX}	0.7
Liquid-Vapour Heat exchanger efficiency, η_{LVHX}	0.7
Absorber efficiency, η_{ABS}	0.7
Generator temperature, T_4 (ºC),	85
Absorber outlet temperature, T_1 (ºC)	25
Condenser outlet temperature, T_8 (ºC)	25
Evaporator temperature, T_{10} (ºC)	-15
Glide at the evaporator, ΔT_{evap} (ºC)	10
Water content in the absorbent M (only the ternary cycle)	0.2
Efficiency stripping, $\eta_{stripping}$ (only the NH_3+H_2O cycle)	0.9
Efficiency rectifying, $\eta_{rectifying}$ (only the NH_3+H_2O cycle)	0.9
reflux ratio (only the NH_3+H_2O cycle)	0.2

3. Thermophysical properties

The thermodynamic and transport properties for NH_3/H_2O mixture were obtained from the equation of Ibrahim and Klein [29] implemented in the EES. For $NH_3/LiNO_3$ and $NH_3/(LiNO_3+H_2O)$ mixtures, vapour-liquid equilibrium was obtained from the correlations reported by Libotean et al. [24], while density was calculated using the correlations of Libotean et al. [25].

The liquid enthalpy for $NH_3/LiNO_3$ and $NH_3/(LiNO_3+H_2O)$ mixtures was obtained following the method of Haltenberger [30] used by McNeely [31]. This method was developed for binary mixtures with only one component in the vapour phase. In the case of the ternary mixture, the procedure used was the same, considering that the water content in the vapour phase was very small. In addition, it should be noted that the enthalpy reference value for ammonia is 0 kJ/kg at 0ºC, and the reference state for the

NH_3/$LiNO_3$ and NH_3/($LiNO_3$+H_2O) mixtures is 0 kJ/kg at 0ºC with an ammonia mass fraction of 0.5.

Figures (2.a) and (2.b) show the Dühring diagram for NH_3/$LiNO_3$ and NH_3/($LiNO_3$+H_2O), respectively, using the vapour-liquid equilibrium correlations of Libotean et al. [24]. Figure 2.a also shows the solubility curves drawn from the data reported by Linke [32].

In the case of the ternary mixture, Eysseltova and Orlova [26] recompiled data for the solubility curves. In the present work, the water content in the absorbent was set to 20% in weight for the ternary mixture. As the conditions are based on the data of Eysseltova and Orlova [26], the ammonia mass fraction should be below 0.15 for the ternary mixture to crystallize on the temperature range between 5 and 35 C°. Consequently, the risk of crystallization for the ternary mixture is even lower than that of NH_3/$LiNO_3$ mixture.

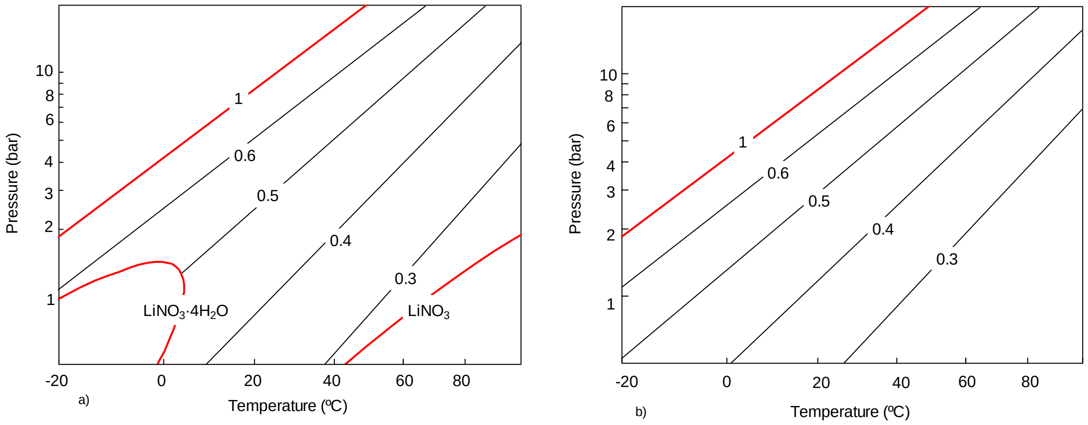

Figure 2. Dühring Diagram for: (a) NH_3/$LiNO_3$ from the data of Libotean et al. [24], and solubility curves obtained with the interpolated data from Linke [32], (b) NH_3/($LiNO_3$+HO_2) from the data of Libotean et al. [24] for a water content of 20% in weight in the absorbent

4. Results

The main parameters of the cycle state points for the nominal case study are reported in Table 3. The feasibility of using $NH_3/(LiNO_3+H_2O)$ as a working fluid in a single-effect absorption refrigeration cycle for fishing ships is discussed in this paragraph together with a comparison with the binary mixtures $NH_3/LiNO_3$ and NH_3/H_2O.

4.1. Water content in refrigerant

Figure 3 shows the ammonia mass fraction of the vapour stream entering the condenser as a function of generator temperature with the conditions specified in Table 1. For the NH_3/H_2O cycle, the assumption of Murphree efficiencies of 0.9 gives an ammonia mass fraction higher than 0.998. Figure 3 reveals, that for the considered operating conditions, the $NH_3/(LiNO_3+H_2O)$ mixture may be used in a single effect cycle without rectification giving a maximum water content of 1.5% in the refrigerant stream at a generator temperature of 110 °C. If a plate heat exchanger is used as evaporator and the feeding to the evaporator is controlled by a thermostatic valve, the refrigerant evaporation will usually not be completed and the non-evaporated liquid will be dragged by the refrigerant vapour leaving the evaporator with a high velocity. This amount of liquid can be dragged out with a moderate temperature glide in the evaporator subsequently avoiding water accumulation in the evaporator (Fernández-Seara and Sieres [33]).

Table 3. State points for the cycle simulations at nominal operating conditions

	Stream	1	2	3	4	5	7	8	10	11
NH_3/H_2O	T (°C)	25.0	25.2	63.8	85.0	43.4	44.7	25.0	-15	-5.0
	P (kPa)	235.8	1002	1002	1002	1002	1002	1002	235.8	235.8
	m (kg s^{-1}) 10^{3}	111.00	111.00	111.00	102.69	102.69	10.36	8.31	8.31	8.31
	x	0.432	0.432	0.432	0.386	0.386	0.998	0.998	0.998	0.998
	h (kJ kg^{-1})	-123	-121.2	50.27	153.3	-32.04	1340	116.3	60.88	1266
$NH_3/LiNO_3$	T (°C)	25.0	25.2	62.1	85.0	43.5	85.0	25.0	-15	-5.0
	P (kPa)	236.2	1003	1003	1003	1003	1003	1003	236.2	236.2
	m (kg s^{-1}) 10^{3}	114.50	114.50	114.50	106.11	106.11	8.33	8.33	8.33	8.33
	x	0.457	0.457	0.457	0.414	0.414	1.0	1.0	1.0	1.0
	h (kJ kg^{-1})	111	111.7	221.9	325.7	206.9	1446	117.7	68.99	1269
$NH_3/(LiNO_3+H_2O)$	T (°C)	25.0	25.5	63.3	85.0	43.7	85.0	25.0	-15	-5.0
	P (kPa)	235.2	235.2	235.2	999.2	999.2	999.2	999.2	235.2	235.2
	m (kg s^{-1}) 10^{3}	120.39	120.39	120.39	112.08	112.08	8.31	8.31	8.31	8.31
	x	0.435	0.435	0.435	0.393	0.393	0.393	0.996	0.996	0.996
	h (kJ kg^{-1})	124.9	126.3	247.8	350.1	219.7	1455	114.7	49.36	1254

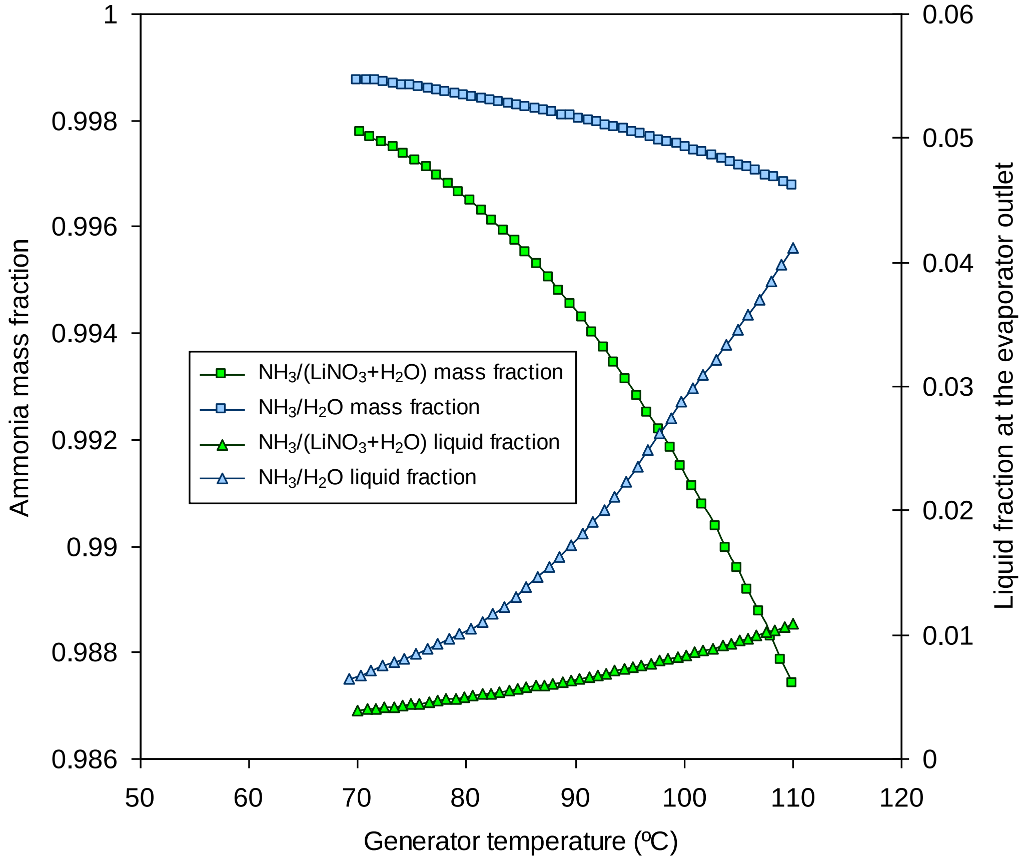

Figure 3. Mass fraction of ammonia in the vapour stream entering the condenser at different generator temperatures and the corresponding liquid fraction at the evaporator outlet

4.2. Influence of the generation temperature on the cycle COP

Figure 4 shows the influence of the generator temperature on the COP using the three working fluid mixtures under the operating condition specified in Table 1. The maximum COP of the cycle is obtained for a $NH_3/(LiNO_3+H_2O)$ working mixture, with quite similar results obtained for the $NH_3/LiNO_3$ working mixture. The trend of the graph shows that $NH_3/(LiNO_3+H_2O)$ and $NH_3/LiNO_3$ working mixtures have higher values of COP as compared to NH_3/H_2O working mixtures. At low generator temperatures, the differences in COP between these two mixtures and the NH_3/H_2O

mixture are noticeable. The trend shows an abrupt increase in the COP with an increase in generator temperature at lower generation temperatures up to 80ºC, however, the increase in COP is less for the generator temperature between 80ºC and 90ºC. The generator temperature does not have a prominent effect on the COP of cycles above 90ºC. At higher generator temperature the COP of both $NH_3/(LiNO_3+H_2O)$ and $NH_3/LiNO_3$ working mixtures is similar and higher than the NH_3/H_2O working mixture. Also, Figure 4 shows that absorption refrigeration cycles employing $NH_3/(LiNO_3+H_2O)$ and $NH_3/LiNO_3$ working mixtures have lower minimum activation temperatures as compared to the NH_3/H_2O working mixture.

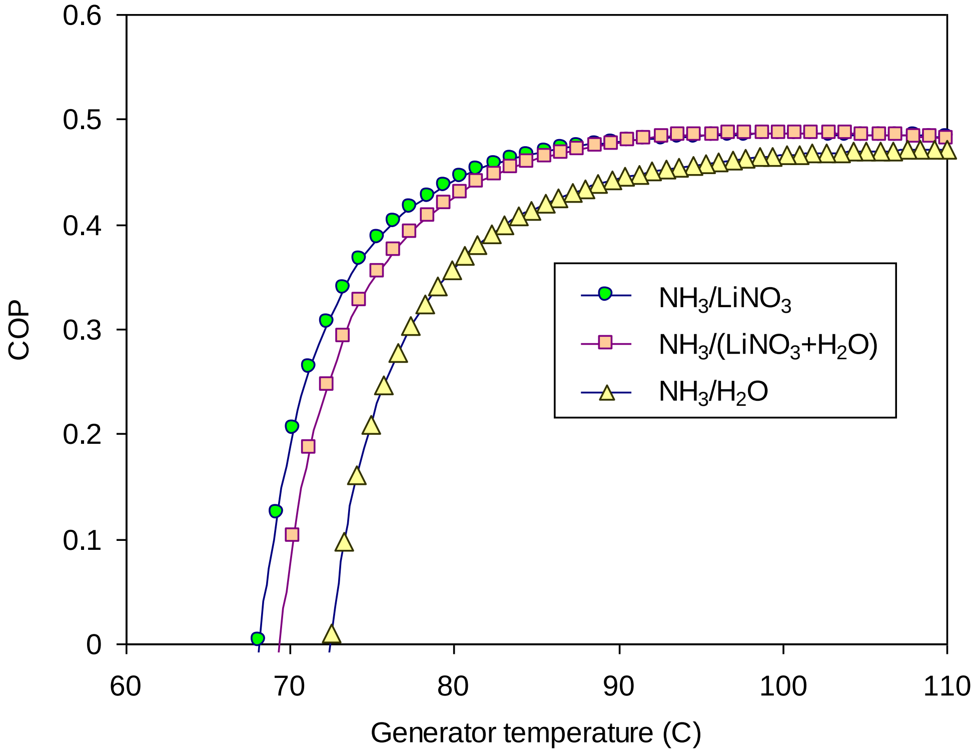

Figure 4. COP versus generator temperature for the considered working fluid mixtures

4.3. Circulation ratio

Another parameter of interest to analyse the feasibility of an absorption cycle is the circulation ratio, which is defined as the ratio of the mass flow rate of the basic solution leaving the absorber to the mass flow rate of the vapour stream entering the condenser (Eq. (41).

$$f = \frac{\dot{m}_1}{\dot{m}_7} \qquad \text{Eq. (41)}$$

A high circulation ratio involves high pump consumption which implies a high electrical consumption, eliminating the advantage of absorption cycles compared with vapour compression cycles.

The differences between the three cycles considered in terms of circulation ratio are small, the NH_3+H_2O cycle having the lowest circulation ratio. For temperatures higher than 85 ºC, the circulation ratio is lower than 15 for all the cycles. Taking into account the viscosities of the three mixtures, the expected pump energy consumption will be lower for the NH_3/H_2O mixture due to its lower viscosity.

4.4. Minimum evaporation temperature

The minimum evaporation temperature of the cycle depends on the absorption-condensation temperature and the generation temperature. The cycle generation temperature could be around 85ºC, if only the heat of engine jacket water is used. However, the absorption and condensation temperatures depend on the seawater temperature, which can reach temperatures as high as 31ºC (Peranić et al. [5]).

Figures 5a and 5b show the COP variation versus the evaporation temperature for the three mixtures at a constant generation temperature of 85 ºC with a condensation temperature of 25 and 30 ºC.

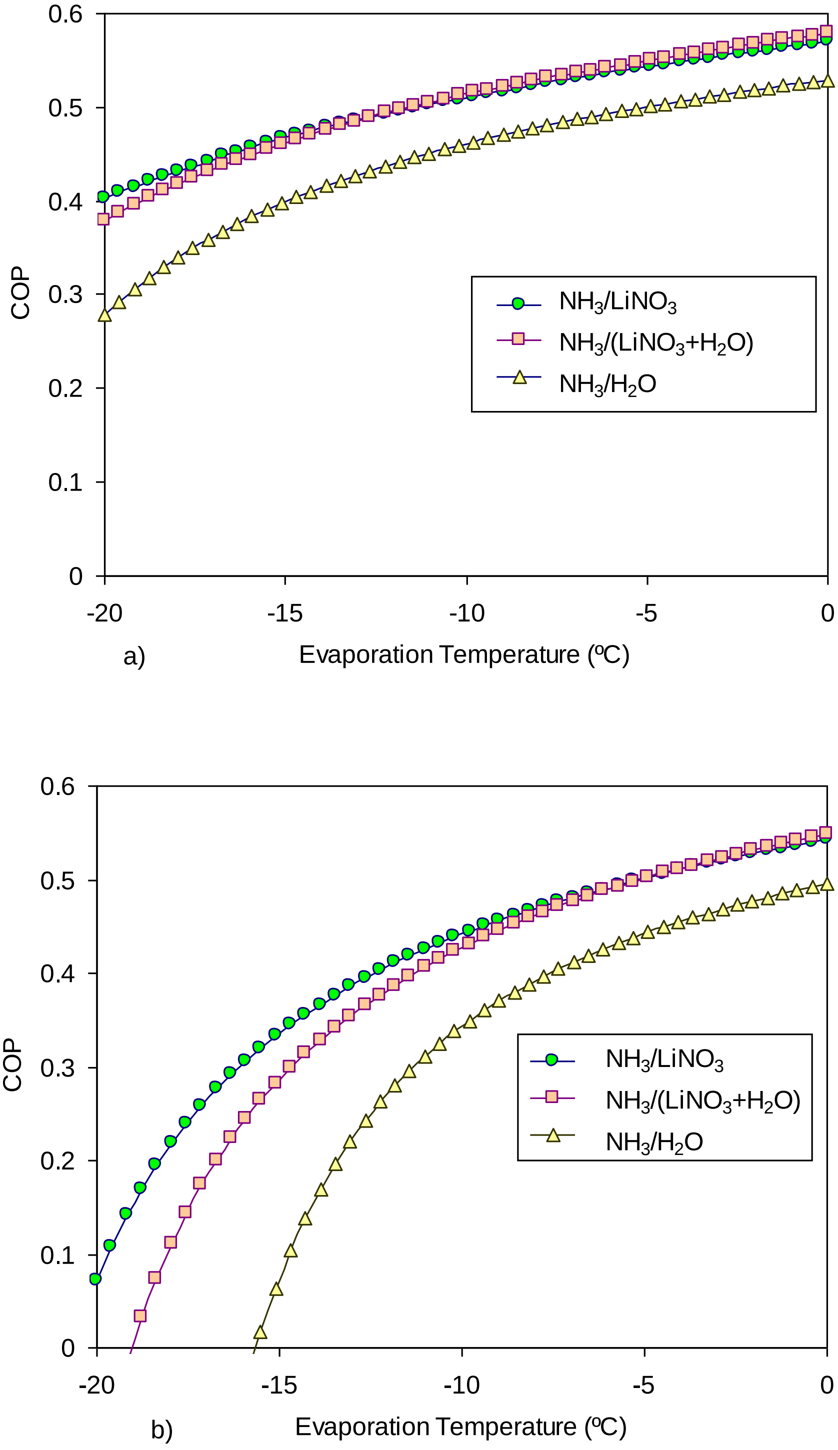

Figure 5. COP versus evaporation temperature for the considered working fluid mixtures at a constant condensing temperature of: (a) 25ºC, (b) 30ºC

As observed from Figure 5a, all the absorption cycles can operate at a condensation temperature of 25 °C for the considered evaporation temperature range, but the NH_3/H_2O cycle has a COP lower than 0.4 for evaporation temperatures lower than -15ºC. In the case of a condensation temperature of 30ºC (Figure (5b)), the NH_3/H_2O cycle cannot operate at -15ºC, but the $NH_3/(LiNO_3+H_2O)$ and $NH_3/LiNO_3$ cycles still achieve COP values higher than 0.3.

4.5. Influence of the evaporator temperature glide on the cycle COP

The temperature difference between bubble and dew point increases significantly with the water content in the refrigerant. For a bubble point of -15ºC, if the water content in the refrigerant is 1%, this temperature difference is 48.8 ºC. However, with a 5% of water, this temperature difference increases up to 71.1 ºC.

Hence, in a NH_3/H_2O absorption machine without a distillation column it is impossible to accomplish the complete evaporation of the refrigerant in the evaporator with a reasonable temperature glide in the evaporator. In this work, the evaporator is considered a once-through evaporator, where liquid accumulation does not occur because it is drained by the vapour flowing through the evaporator.

Figure 6 evaluates the influence of the glide temperature on the COP of the cycle. The evaporator inlet temperature was maintained constant at -15ºC. In the $NH_3/LiNO_3$ cycle, the influence of temperature glide is negligible as should be expected. In the $NH_3/(LiNO_3+H_2O)$ and NH_3/H_2O cycle for a temperature glide up to 3 ºC, the influence on the COP is noticeable. This indicates that these two cycles are feasible at temperature glides greater than 3ºC.

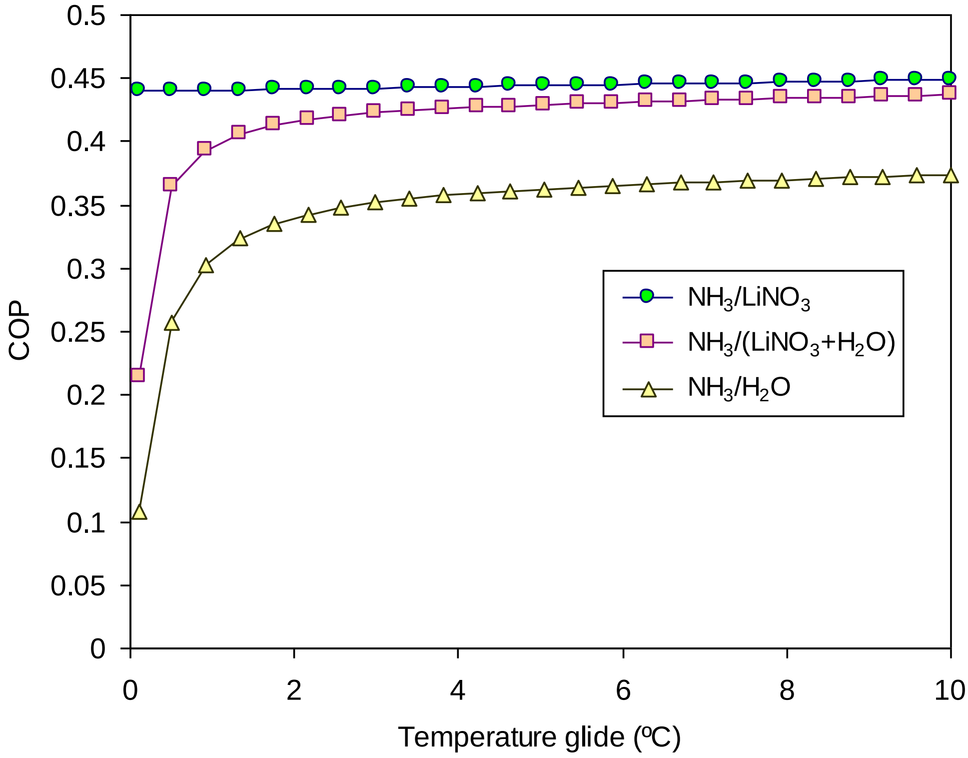

Figure 6. COP versus temperature glide in the evaporator for the considered working fluid mixtures

4.6. Jacket water as the heat source for absorption refrigeration in fishing ships

Hot Jacket water in diesel engines is a source of heat energy preferable to that of exhaust gases because hot gas heat exchangers (HGHX) tend to be huge, increasing the installation cost and have high fouling rates. To take advantage of the waste heat of jacket water, the absorption cycle should be capable of providing the cooling requirements with the temperature available at this heat source.

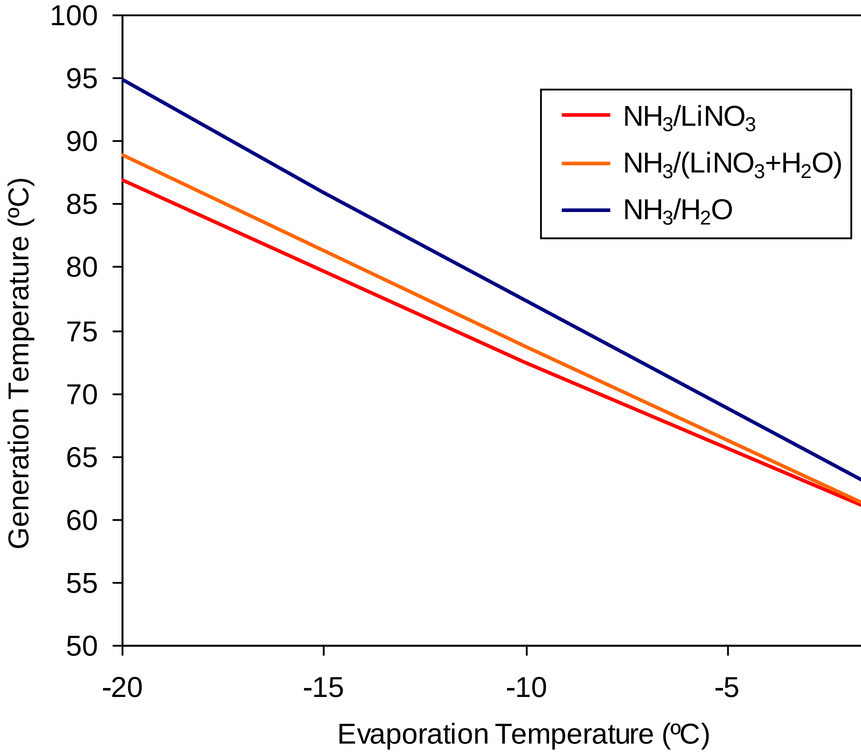

Figure 7. Minimun generation temperature for the considered working fluid mixtures

Figure 7 shows the results for the minimum activation temperature at 90% of the maximum COP for the three working fluid mixtures considered, at a condensation temperature of 25ºC. It can be observed that the minimum activation temperatures are quite similar for the $NH_3/LiNO_3$ and $NH_3/(LiNO_3+H_2O)$ absorption refrigeration cycles. In the case of the NH_3/H_2O absorption cycle the minimum activation temperature is somewhat higher. If the activation temperature is set to 85ºC, the minimum evaporation temperature that can be achieved is -18.8ºC for the $NH_3/LiNO_3$ cycle, -17.5ºC for the $NH_3/(LiNO_3+H_2O)$ cycle and -13.7ºC for the NH_3/H_2O cycle.

At low evaporation temperatures, the differences between the COP and activation temperature of the absorption refrigeration cycles with the three working fluid mixtures considered are more significant (Figs. 5 and 7). For instance, when the evaporation temperature of the cycle is 0ºC, the minimum activation temperature of the cycle with the ternary mixture is 58.8 ºC, equal to the activation temperature of the $NH_3/LiNO_3$ cycle, while the activation temperature of the NH_3/H_2O cycle is 1.5 ºC higher. However, at an evaporation temperature of -20ºC, the minimum activation temperature of the cycle with the ternary mixture is 88.8 ºC, while the activation temperature of the NH_3/H_2O cycle is 7.9 ºC higher than $NH_3/(LiNO_3+H_2O)$ cycle and that of the $NH_3/LiNO_3$ cycle is 2ºC lower than the $NH_3/(LiNO_3+H_2O)$ cycle.

5. Conclusions

The $NH_3/LiNO_3$, NH_3/H_2O and $NH_3/(LiNO_3+H_2O)$ absorption refrigeration cycles were analysed in this study to evaluate the feasibility and implementation of absorption machines driven by waste heat sources in fishing ships. The main results are summarized below.

- The $NH_3/(LiNO_3+H_2O)$ absorption refrigeration cycle can be operated without a distillation column, in this case the calculated water content in the refrigerant entering the evaporator is less than 1.5 % in weight for the operating conditions selected. If the evaporator is of the dry type and thermostatically controlled, the refrigerant evaporation will usual not y be completed and the non-evaporated liquid will be dragged by the refrigerant vapour leaving the evaporator at a high velocity.
- The maximum COP is obtained for the $NH_3/(LiNO_3+H_2O)$ cycle, followed by the $NH_3/LiNO_3$ cycle. The activation temperature analysis shows that these two working fluid mixtures are suitable for low grade waste heat. At a generation temperature of 85ºC and condensation/absorption temperatures higher than

30ºC, the NH_3/H_2O cycle cannot be operated at evaporation temperatures lower than -10 ºC.

- Jacket water of fishing ship diesel engines deliver high amounts of waste heat energy but at low temperatures. This heat is easier to recover than exhaust gases but requires an absorption cycle able to operate with low activation temperatures. The minimum evaporation temperature that can be achieved with a heat source at 85ºC was found to be -17.5ºC for the $NH_3/(LiNO_3+H_2O)$ cycle when the condensing temperature is 25ºC.

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nitrate+water) working pairs for solar absorption chiller, In Proceedingd of International Sorption Heat pump Conference, Seoul (Korea).

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Figures Caption

Figure 1.	Diagrams of the considered absorption cycles with: (a) $NH_3/(LiNO_3+H_2O)$ and $NH_3/LiNO_3$, (b) NH_3/H_2O
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Figure 6.	COP versus temperature glide in the evaporator for the considered working fluid mixtures
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Tables Caption

Table 1	Mass, species and energy balance equations in the generator and condenser for the considered fluid mixtures
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Table 3	State points for the cycle simulations at nominal operating conditions