Study on performance of hybrid adsorption-compression type II heat pumps based on ammonia-salt adorption

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ABSTRACT: Sorption heat pumps based on monovariant reactions, such as ammonia-salt systems can operate at low driving temperatures and achieve high power densities in comparison with multi-variant sorption systems. The disadvantage of monovariant systems, however, is the inflexibility towards required temperature levels. Where multivariant systems scale over a large range of temperatures, for the monovariant system the temperature range is limited by the discrete transition from (fully) adsorbed to desorbed state. To increase flexibility towards changes in operating temperatures of the monovariant sorption systems, the extension of such systems with a compressor has been studied. Focus of this research is on the use of ammonia-salts for type II heat pump for upgrading low temperature industrial waste heat to low-medium pressure steam. At ECN a system based on LiCl-MgCl$_2$ ammonia-reactions has proven to achieve sufficient temperature lift (>50ºC) and cyclic stability (>100 cycles) but requires a minimum temperature of 120ºC for proper operation. To add flexibility to this system, i.e. to be able to use waste heat below 120ºC, the performance of a hybrid variant containing both thermally-driven sorption reactors as well as a compressor has been evaluated.

This evaluation focuses on extension in temperature range, and exergy efficiency and economic consequences of such a hybrid system. In addition, the possibility to use other ammonia-salt combinations has been investigated. The conclusions are that hybrid systems can reduce primary energy consumption and be economically feasible. It also shows that other salt combinations than LiCl-MgCl$_2$ could be more suitable for a hybrid thermo-chemical adsorption-compression system.

Keywords: sorption, hybrid, compression, heat pump, ammonia

NOMENCLATURE

Symbol	Description
COP	Coefficient of Performance (-)
C_p	specific heat capacity (J mol^{-1} K^{-1})
H	enthalpy (J mol^{-1})
hc	inert thermal mass (4 J g$_{salt}^{-1}$ K^{-1})
k	isentropic exponent (1.319)
m	molar mass (g mol^{-1})
n	theoretical amount of ammonia reacting per amount of salt(molmol^{-1})
N	amount (euros kWh^{-1})
p	power density (W g^{-1})
P	pressure (Pa)
PER	primary energy ratio (J primary energy per J useful heat)
PES	primary energy savings (J primary energy per J useful heat)
Q	heat (J mol^{-1})
R	gas constant (8.314 J K^{-1} mol^{-1})
s	savings (€kW^{-1} year^{-1})
S	entropy (J mol^{-1} K^{-1})
t	time (s)
T	temperature (K)
w	work (J mol^{-1})

Greek letters	Description
Δ	change
η	efficiency
ϕ	ratio

Subscripts	Description

ads	adsorption of ammonia
c	cycle
des	desorption of ammonia
dis	discharge cycle
el	electricity
h	high/output (temperature)
hts	high temperature salt
i	isentropic
l	low/ambient (temperature)
lts	low temperature salt
m	medium/waste heat (temperature)
o	operating (time)
reg	regeneration/charge cycle
st	steam
x	exergy

1. INTRODUCTION

Large quantities of energy are used in industry and released as waste heat to the environment. A study by Spoelstra [1] shows that the chemical industry and refineries in The Netherlands actively releases 160 PJ per year of waste heat in the temperature range of 50°C to 160°C (see *Figure 1*). Upgrading this heat to medium pressure steam (with a temperature of 180 to 220°C), is an interesting option for waste-heat reuse. Existing technologies for such reuse are, however, very limited. Commercially available, industrial compression heat pumps are, with some exceptions, limited to a maximum output temperature of approximately 130°C and sorption based, heat-driven heat pumps type II require a relative high waste heat temperatures of 120°C or more, for a reasonable temperature lift. Measurements on lab-scale prototypes show a maximum temperature-lift of 70°C for an adsorption based type II heat pump, provided the available source heat temperature is at least 130°C [2]. As shown in *Figure 1*, the energy savings potential at such waste heat temperatures is limited to approximately 20 PJ per year. Lowering the required waste-heat temperature would unlock a significant greater amount of waste-heat and thereby creating a larger energy-savings potential.
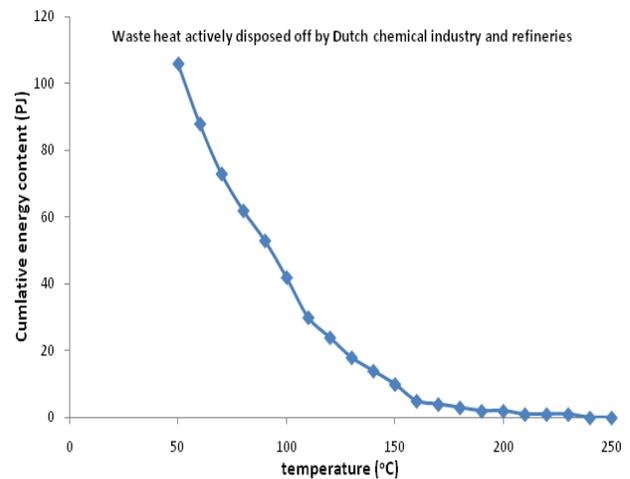
Figure 1. Cumulative energy content (PJ) of disposed waste heat as a function of waste-heat temperature for chemical industry and refineries in The Netherlands [1].

To operate a heat-driven sorption system using lower temperature heat, multi-stage cycles can be used. These cycles will, however, have a low COP and the sorbent reactors will be significantly larger and thus more costly compared to a single-stage heat pump. An alternative solution would be to equip the heat-driven system with a work-driven compressor. This compressor could be placed either in the low temperature, regeneration cycle, or in the high-temperature, discharge, cycle or in both. *Figure 2* shows the (theoretical) effect of a hybrid double-compressor adsorption system: a significant reduction in required waste heat temperature can be achieved. It also allows the use a larger variety of salts as the compressor can be used in either or both the discharge and the regeneration cycle of the process. The drawback of such a system is the necessity of work input (mechanical or electric).

The goal of this study is to determine which system configurations are possible and to determine their performance factors such as temperature (lift), efficiencies (both heat and work), exergy and power density.
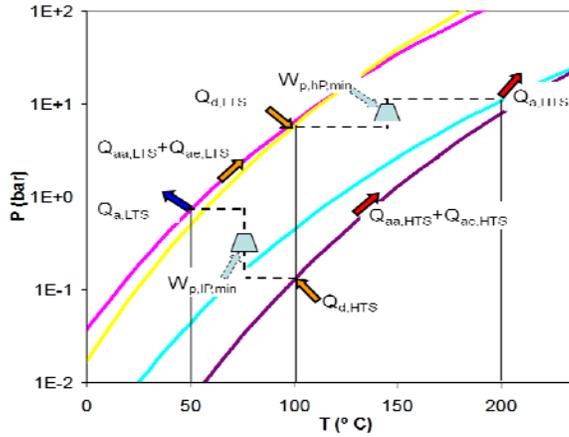

Figure 2. Example of hybrid solid-sorption cycle based on a double-compressor ammonia-salt system.

2. MATERIALS & METHODS

Although various combinations of sorbents (both liquid as well as solid) and sorbates can be used in a hybrid cycle, it was decided to limit our analysis to ammonia-salt reactions due to our experience with such reactions. Based on literature data [3,4,5] and our in-house experience, 47+1 ammonia-salt reactions with their subsequent enthalpy and entropy values were selected for further analysis. The +1 refers to evaporation/condensation of pure ammonia. The performance of hybrid configurations with a compressor at low pressure/low temperature, at high pressure/temperature or combined has been calculated.

The model calculation follows a stepwise approach. The first step is to calculate the equilibrium pressures for the low temperature salt (lts) and the high temperature salt (hts), based on the chosen temperatures and the thermodynamic data of the salts:

$$P = e^{-\frac{\Delta H}{RT} + \frac{\Delta S}{R}}$$

yielding $P_{ads,lts}(T_l)$, $P_{ads,hts}(T_h)$, $P_{des,lts}(T_m)$ and $P_{des,hts}(T_m)$, the *ads*orption and *des*orption reactions equilibrium pressures for the low temperature salt (lts) and the high temperature salt (hts) at given low (T_l), medium (T_m) and high temperature (T_h). Only for LiCl(1-3)NH$_3$ and MgCl$_2$(2-6)NH$_3$ salt reactions, separate adsorption/desorption data was available and used for calculation of the pressures. From these pressures, the pressure

ratios for the *reg*eneration and *dis*charge cycle are calculated:

$$\phi_{reg} = \frac{P_{ads,lts}}{P_{des,hts}}, \quad \phi_{dis} = \frac{P_{ads,hts}}{P_{des,lts}}$$

Using these pressure ratios, the mode of operation can be determined: for all salt reactions with both (regeneration and discharge) pressure ratios smaller than 1, the sorption reaction will occur spontaneous, higher than 1 a compressor with a pressure increase equal (or larger) than the pressure ratio will be required for operating the cycle.

At this moment the number of salt combinations is greatly reduced by implying limits on pressures and pressure ratio. A maximum working pressure of 60 bars was applied. This maximum pressure was chosen to avoid construction issues and too large losses due to open gas volumes in the system. A lower pressure limit of 0.1 bars is applied to avoid too limited driving force to move the gas from the LTS to the HTS reactor and vice versa. Furthermore, a maximum pressure ratio limit of 3 was applied. This value was chosen because the required work, in terms of required *primary* energy, for pressure ratios above 3, starts nearing the amount of primary energy saved by the hybrid heat pump. A pressure ratio of 3 is also considered the upper limit for dynamic compressors, which are in general more efficient than positive displacement compressors.

In the next the work required by the compressor is determined. The compressor work for the regeneration cycle is calculated using:

$$W_{reg} = \frac{RT_l}{\eta_H} \frac{k}{k-1} \left[\phi_{reg}^{\frac{k-1}{k}} - 1 \right]$$

An isentropic efficiency of 0.75 was used. This value has been estimated from literature information [6]. The compressor output temperature is then given by:

$$T_{u,gen} = T_l \left[1 + \frac{\phi_{reg}^{\frac{k-1}{k}} - 1}{\eta_H} \right]$$

Similar equations were derived for the compressor work of the discharge cycle. The next step involves determining the heat losses and the subsequent net heat output and COP values. The heat losses consist of losses due to heating up the ammonia (difference between T_w and target temperature, multiplied by heat capacity of ammonia) and heat losses due to heating up the sorbent reactor. The heat losses of the reactor are related to heating of the salt and of the inert reactor-material. The con-

tribution of this inert mass (tubes, fins, thermal oil/steam) has been set to 4 J K^{-1} per g of salt. This is comparable with the inert mass-salts ratios used in an ECN prototype heat transformer [2]. The required amount of salt has been corrected using a bed loading factor, the fraction of reacting salt used per cycle, which was set to 0.7. Altogether this results in the following heat loss of the hts-reactor in the discharge cycle (J per mol NH$_3$):

$$Q_{loss,hts,dis} = C_{p,NH_3}(T_h - T_{w,dis}) + \frac{n_{hts} \cdot m_{hts}}{n_{hts}}(C_{p,hts} + hc) \cdot (T_h - T_m)$$

Similar equations were derived for the low temperature reactor and the regeneration cycle. The heat output is now given (in J per mol NH$_3$) as the difference between sorption enthalpy and heat loss:

$$Q_{out,dis}(T_h) = \Delta H_{hts} - Q_{loss,hts,dis}$$
$$Q_{in,dis}(T_m) = \Delta H_{lts} + Q_{loss,lts,dis}$$
$$Q_{in,reg}(T_m) = \Delta H_{hts} - Q_{loss,hts,reg}$$
$$Q_{out,reg}(T_l) = \Delta H_{lts} + Q_{loss,lts,reg}$$

From the work and the net heat input and output the COP values can be calculated for both heat and work input:

$$COP_h = \frac{Q_{out,dis}}{Q_{in,dis} + Q_{in,reg}}$$
$$COP_w = \frac{Q_{out,dis}}{w_{dis} + w_{reg}}$$

The overall exergy efficiency is calculated from the net heat and work flows (T_l is assumed ambient temperature):

$$\eta_{ex} = \frac{Q_{out,dis} \cdot \left(\frac{T_h - T_l}{T_h}\right)}{(Q_{in,dis} + Q_{in,reg})\left(\frac{T_m - T_l}{T_m}\right) + w_{dis} + w_{reg}}$$

To calculate the power density a total cycle (= discharge + regeneration) time, of 3600 seconds has been assumed, yielding the power density, p (W per g sorbent):

$$p = \frac{Q_{out,dis}}{\left(\frac{n_{lts} \cdot m_{lts}}{n_{lts}} + \frac{n_{hts} \cdot m_{hts}}{n_{hts}}\right) t_o}$$

Using the hybrid heat pump performance and some typical prices and efficiencies for electricity and steam production (see *Table 1*), the primary energy ratio (*PER*), primary energy savings (*PES*) and annual savings (s) can be calculated:

Table 1. Parameters for economic analysis

parameter	value	
efficiency steam production, η_{st}	0.85	J$_{steam}$ per J$_{primary}$
efficiency electricity production, η_{el}	0.45	J$_{electricity}$ per J$_{primary}$
steam price, N_{st}	0.039 € kWh^{-1}	
electricity price, N_{el}	0.065 € kWh^{-1}	
operating time, t_o	8000 hours per year	

$$PER = \frac{COP_w}{\eta_{el}} , PES = \eta_{st}^{-1} - PER$$

$$s = t_o \left(N_{st} - \frac{N_{el}}{COP_w}\right)$$

3. RESULTS

Table 2 shows the results for the salt-combination LiCl(1-3)NH$_3$-MgCl$_2$(2-6)NH$_3$, which is currently researched at ECN for application in heat driven heat pump type II. It contains the pressure ratios for various temperature combinations with on the top part the results for ambient temperature versus the waste heat temperature (middle) and the bottom part the waste heat temperature versus the output temperature. The results show heat-driven application (green area) is only possible for relatively high waste heat temperatures of at least 110°C (with 20°C ambient temperature and a maximum output temperature of 190°C). The white area (pressure ratios between 1 and 3) shows the conditions in which a compressor with a pressure ratio up to 3 can be used. A compressor reduces the minimum waste heat temperature to 90°C and/or increases the output temperature up to 230°C. The red areas show compressor ratios exceeding 3.

Table 2. Results LiCl(1-3)NH₃-MgCl₂(2-6)NH₃ heat pump configuration: top: temperatures and resulting pressure(ratio)s, bottom: detailed results for 30 °C ambient and 100 °C waste heat temperature.

T_l (°C)	$P_{ads,lts}$ (bar)	ϕ_{reg}			
20	0.14	3.2	1.8	1.1	0.6
30	0.25	5.8	3.3	1.9	1.2
40	0.43	10.2	5.8	3.4	2.0
50	0.73	17.1	9.7	5.7	3.4
$P_{des,hts}$ (bar)		0.04	0.08	0.13	0.21
T_m (°C)		80	90	100	110
$P_{des,lts}$ (bar)		2.38	3.78	5.85	8.86
150	2.68	1.1	0.7	0.5	0.3
170	4.88	2.0	1.3	0.8	0.6
190	8.43	3.5	2.2	1.4	1.0
210	13.9	5.9	3.7	2.4	1.6
230	22.1	9.3	5.9	3.8	2.5
T_h (°C)	$P_{ads,hts}$ (bar)	ϕ_{dis}			

T_m (°C):	100						
		COP_h	COP_w	η_x	PER	PES	s
T_l (°C)	T_h (°C)				$J_{primary}/J_{useful}$		€ kW⁻¹ year⁻¹
30	150	0.32	11.7	0.42	0.19	0.99	272
	170	0.28	10.1	0.41	0.22	0.96	265
	190	0.25	5.9	0.37	0.38	0.80	228
	210	0.23	3.5	0.34	0.63	0.54	169
	230	0.21	2.4	0.30	0.93	0.25	97

The second part of *Table 2* shows more detailed results for 100°C waste heat and 30°C ambient temperature. As can be expected, the COP_h and COP_w decreases with increasing output temperatures. Up to 190°C output temperature, the savings exceed 200 euros per kW per year, still 2/3rd of the amount that would be saved with a pure heat-driven system (=312 euros per kW per year).

These calculations were conducted for all 48x48 combinations of ammonia salt reactions, yielding a large array of data. From this data, a selection was made of the most favorable salt combinations for application in a hybrid heat pump. This selection was made on calculated COP values and the number of possible combinations (i.e. the number of 'white' and 'green' fields in the table) within limits regarding pressure ratios (a maximum of 3), pressure levels (between 0.1 and 60 bars) and temperature levels (T_l = 20 to 50°C, T_m = 60 to 110°C and T_h = 150 to 230°C). The results of this procedure are shown in *Table 3*. For the heat-driven configuration 11 salt-combinations could be used whereas the single and double compressor configurations yield respectively 38 and 19 useable salt-combinations. Adding the compressor also increases the specific heat output, maximum COP and maximum output temperature. From this table is it clear that applying a compressor can also significantly reduce the waste-heat temperature required for a heat pump type II cycle.

Table 3. Overview of results for heat-driven, single and double compressor systems.

	heat driven	single compressor	double compressor
# of salt combinations	11	38	19
# of operating conditions	31	241	175
Max. heat output (W per g salt)	0.08	0.13	0.12
Max. COP_h	0.25	0.32	0.33
Min. T_m (°C)	90	70	60
Max. T_h (°C)	210	220	230

Table 4 shows the temperature interval and the average COP_h value of the salt combinations that yield the best performance, either in terms of applicable temperature range ('flexibility') or in terms of energy efficiency. For hybrid operation (both single and double compressor configuration) the ammonia-salt reactions $CaCl_2(4-8)NH_3$ with $MnCl_2(2-6)NH_3$ and $CaCl_2(4-8)NH_3$ with $MnSO_4(2-6)NH_3$ are most favored. The $MnCl_2$ combinations can be used for a large temperature range, both in terms of waste heat temperature as well as useful heat output temperature, whereas the combination with

MnSO$_4$ achieves high efficiencies in a smaller temperature range.

Table 4. Most favorable ammonia-salt reactions for heat-driven and hybrid systems.

ammonia salt reaction		T_l	T_m	T_h	COP_h
lts	hts	°C	°C	°C	-
heat-driven					
MnCl$_2$(2-6)NH$_3$		30	110	180-200	0.22
MnSO$_4$(2-6)NH$_3$	NiCl$_2$(2-6)NH$_3$	40	100-110	170-210	0.19
ZnCl$_2$(2-4)NH$_3$		40-50	100-110	170-180	0.25
ZnCl$_2$(4-6)NH$_3$	MgCl$_2$(2-6)NH$_3$	30	110	180	0.25
single compressor					
CaCl$_2$(4-8)NH$_3$	MnCl$_2$(2-6)NH$_3$	30-50	80-110	150-210	0.18
	MnSO$_4$(2-6)NH$_3$	30-40	80-90	150-160	0.32
double compressor					
CaCl$_2$(4-8)NH$_3$	MnCl$_2$(2-6)NH$_3$	30-50	60-100	130-200	0.20
	MnSO$_4$(2-6)NH$_3$	40-50	80-90	150-160	0.33

4. DISCUSSION AND CONCLUSIONS

The results show ammonia-salt reactions in combination with a compression step yield a significant larger range of waste heat and output temperatures for which a heat pump type II cycle can be applied. Using realistic and achievable values for heat losses, compressor efficiencies and cycle times show acceptable COP values and power densities. Although the savings in energy costs are obviously lower compared to a heat-driven system as electricity is required for the compressor work, the savings of a hybrid system are only 30% less than for a heat-driven system. Given that an entirely heat-driven system for low waste heat temperatures would require multistage, thus double the number of reactor and low COP_h, it can be expected that a hybrid system would be a very competitive alternative.

However, there are also some aspects that have not been addressed in this study. These include the possible irreversibility of salt reactions, the temperature gradients required for transferring heat into/from the salt reactors, the aspect of combining a batch-operated process (adsorption heat pump cycle) with a continuous process (compression) and the lack of a detailed cost calculation for a hybrid heat pump to determine whether the financial benefits outweigh the costs. These issues will be addressed in future research projects. Several of these aspects can be dealt with: the irreversibility of ammonia-salt reactions is not uncommon but the salt-reactions used are of pure salts only. Research by Kato [7] shows that salt-mixtures can yield intermediate pressure-temperature relations, which can replace salts that show irreversibility. This way also the material costs for the heat pump can be reduced: by replacing expensive salts by mixtures of cheap salts. Problems related to combin-

ing batch and a continuous process can be minimized by using multiple reactors. This would also allow more efficient operation thus higher COP_h and COP_w due to heat recuperation between sorption cycles. The final conclusion therefore is that the calculations in this paper show that hybrid heat pump technology using a mono-variant salt-reaction can provide a useful alternative for relatively low temperature heat that is currently disposed off in the environment as waste product.

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