MEASUREMENT RESULTS FOR THE NOVEL NH_3 - $NiCl_2(NH_3)_{2/6}$ REACTION COOLING DEVICE

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ABSTRACT

Due to their periodic operation, reaction cooling devices are more restricted in use than conventional absorption cooling devices. In addition, a higher heat of reaction as compared to the heat of absorption contributes to a lower theoretical COP of such devices. Despite of that, there are some niches, e.g. cascading sorption cycles, where reaction devices can be used for cooling and in parallel for heating purposes and have a chance to be competitive.

In this paper, experimental results of a device, working with two reactors in counter-phase, will be presented. The device has been built and tested as a part of a cascading triple-effect sorption device, with the function of increasing the COP of the cooling system. As working pair the reversible reaction between NH_3 and $NiCl_2(NH_3)_{2/6}$ has been used.

In this paper we will restrict ourselves to the discussion of the experimental results of the reaction device only. The cyclic operation of the device will be presented in detail. In addition, the COP of the device will be discussed. It is about 0,17, which is much higher than the COP of similar experimental devices with the same working pair. Still there are some irreversibilities, e.g., in form of heat losses, which have to be taken into the consideration for the design of the next generation of reaction cooling devices.

KEYWORDS

Reaction cooling device, sorption cycle, cooling, measurement results

1. INTRODUCTION

Reaction cooling devices are limited in use if compared to the other sorption cycles, i.e. absorption and adsorption cooling devices. Usually the processes require higher temperature levels of the driving heat, which brings about an increase in the heat losses to the environment. Additionally, the higher heat of reaction as compared to the heat of absorption limits the theoretical COP of single-effect reaction device, operating with two reactors in phase-shift [1,2].

One interesting application is to use the reaction cooling device as a heat transformation device at higher temperature levels (above 200°C), where the efficient absorption devices can not be used. The goal of the project which is reported on here was to perform a successful coupling of an absorption and reaction cooling device with the intention of improving overall sorption system efficiency.

This was not the first successful coupling of the continuously operating absorption device and discontinuously operating solid-gas sorption cooling device. The first experimental two-stage cascading device [3] was a combination of a single-effect $LiBr/H_2O$ cooling device and a zeolite/H_2O adsorption cooling device. It had a COP around 1,2, which was considered high at that time. Due to a very complex operation these combined systems did not achieve much more attention at that time.

Coupling of absorption and reaction cooling device in a cascade was not attempted before. In this case a double-effect $LiBr/H_2O$ cooling device is the bottoming part with a $NiCl_2(NH_3)_{2/6}/NH_3$ solid sorption cooling device working as the topping part (Figure 1) [4,5,6]. In contrast to the first coupling device [3] two different refrigerants are used. The reason of using ammonia is the fact that the high evaporation pressure of ammonia alleviates problems with the heat and mass transfer in the solid sorption device.

Driving heat for the cascade is brought into the system in the reaction device, heating the reactor that is performing the decomposition of $NiCl_2(NH_3)_6$ into NH_3 and $NiCl_2(NH_3)_2$ (reactor R2 in Figure 1). The reactor R1 at the same time is in the synthesis phase. Heat of reaction, which is released due to the synthesis of 4 moles of NH_3 and $NiCl_2(NH_3)_2$, is transferred to the bottoming absorption device. It is the driving heat for the $LiBr/H_2O$ device. The heat transfer between the devices is performed by a loop-type heat pipe.

To increase the quantity of heat gained at the reactor R1, two internal heat exchangers, HX1, HX2, are installed. Cooling energy is gained in both parts of the cascade, periodically with the reaction device and continuously with the absorption device.

With the use of two or more reactors, which would operate alternatively, a kind of quasi-continuous mode of operation is achieved. Due to the high cost of reactors, the systems with more than two reactors are usually not considered. Despite the possibility to achieve a quasi-continuous operation of the topping part, a kind of heat storage has been installed in the cascaded device [4]. This was performed in the bottoming part by storing the cooling energy internally, indirectly in a form of

additionally separated water and strong $LiBr/H_2O$ solution. It was shown by Berlitz et al. [4] that for the internal 'cold' storage volumetrically only about 10% of storage for hot oil at 150°C is needed to compensate the time (1/3 of reaction phase time), when topping part does not produce the driving heat for the bottoming part.
In the following the experimental reaction cooling device will be briefly presented.

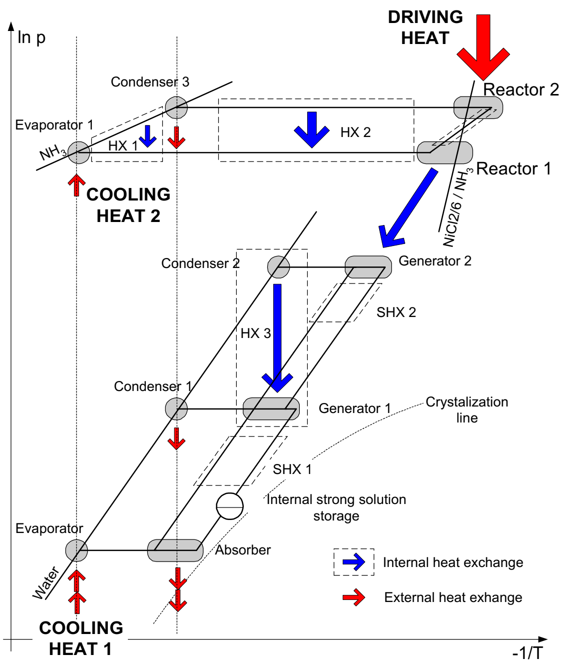


Figure 1: Cascading sorption cooling cycle in p-T diagram [7].

2. EXPERIMENTAL REACTION COOLING DEVICE

To understand the dynamics in the reaction device, the course of the process in the reactors will be presented first (Figure 2). Basically it can be divided into two successive phases, sensible and reaction phase. During the sensible phase the reactor is heated up for the next decomposition phase or cooled down for the synthesis phase. The reaction phase represents the main part of the cycle. It defines the cooling and heating power of the topping device.

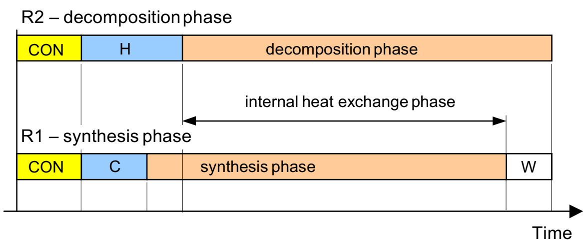


Figure 2: Division of the solid-gas cycle into the basic phases. CON: connection phase, C: cooling phase, H: heating phase, W: waiting phase [7].

Usually there is an additional connecting phase, which serves for the internal heat recovery between the two reactor vessels after the finished reaction phase (CON in Figure 2). Its purpose is to lower the quantity of driving heat.
As it can be seen in Figure 2 a phase, which we will call a waiting phase (W in Figure 2), is required to finish both reaction phases in the reactors to the same extent (as long as the phases are not self-adjusting). The internal heat exchange phase, which is also shown, is the time, when the two internal heat exchangers, HX1 and HX2, are in function.
If compared with the continuous cooling energy production of the absorption device, there are several phases beside the synthesis phase, which is the only one used for cooling. For the connection phase it can be said that it brings about an improvement of the COP. But on the other side, it negatively influences the external cooling power of the device. The sensible phase and the waiting phase, which results from the change in function of the reactors, are not beneficial for the efficiency. Therefore, to minimise the effect of periodic operation of the device and to improve the cooling efficiency of the device these phases should be reduced as far as possible.
The sensible phase can be efficiently reduced by decreasing the inert mass of the reactors. It has been found out that the inert ratio, which is a ratio of inactive mass to the mass of active salt ($NiCl_2$) that was used in the construction of the device, is about 7. The waiting phase results from the dynamics of both reactors and could be reduced by controlling the temperature of the reaction. When the reactor was in the decomposition phase the heating has been switched on/off. During the synthesis phase the heat rejection has been controlled by the mass flow of the condensate in the heat pipe.
In Figure 3 the scheme of the reaction cooling device which was designed and built in CNRS-IMP, Perpignan, is presented. The main part of the device are the reactors, which consist of 27 vertical reaction tubes each. In the middle of each tube the evaporator of the heat pipe is located. The rest is filled with the graphite matrix composed of a compressed expanded graphite that has been impregnated with the reactive salt. The heating of the reactors is performed by external heating of the reactor tubes. In our case hot air, which is circulating through the reactor, is used instead of flue gas.
The refrigerant enters and leaves the reactor tubes at their upper part. With a proper switching of the connections with the evaporator and condenser the specific reaction, synthesis or decomposition, can occur in the reactors.

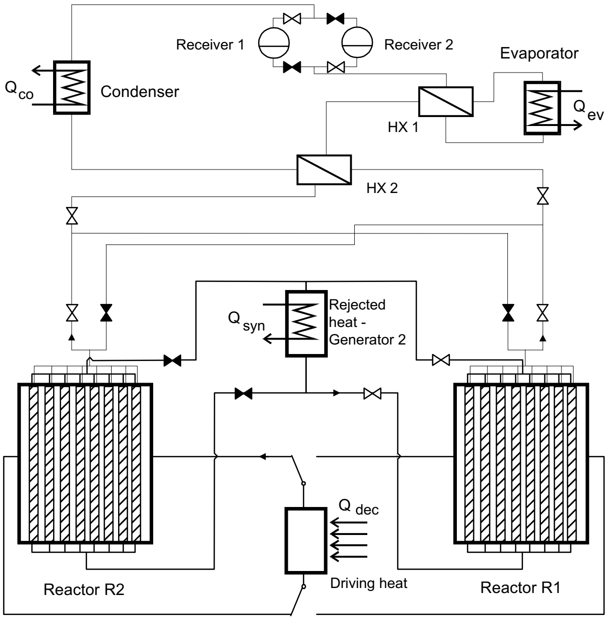


Figure 3: Reaction cooling cycle with two reactors operating in counter-phase. The reactor R1 is in the synthesis phase, reactor R2 in the decomposition phase. HX1 represents the internal liquid-gas heat exchanger, HX2: the gas-gas heat exchanger, ⋈ ***- opened valve,*** ⧓ ***- closed valve.***

In the following the cyclic operation of the device will be presented. The emphasis will be laid on the pressure and temperature conditions in the reactors. In the analysis of the calculated data, we will restrict ourselves to the heat flows and the cooling efficiency COP.

3. CYCLIC OPERATION OF THE REACTION COOLING DEVICE

The first task was to establish the time course of the process phases, to make the evaluation of the process data possible. This was required for a later determination of the averaged values and quantities of heat, which were used for the determination of internal process and of the performance of the reaction device.
The operation of the device has been cut into half-cycles, in which the reactors performed one reaction phase. In this way the dynamics in each reactor could be observed and analysed. Each half-cycle has been further divided into single phases as presented in Figure 2. This has been performed with the analysis of the pressure and temperatures in the system.

3.1 Temperature and pressure levels in reactors

The two reactors of the topping device operate cyclic, constantly switching between the decomposition and synthesis phase. To present clearly the cyclic operation of the experimental topping device during a longer period, the course of the mean temperatures in the reactors are presented first (Figure 4). The mean temperatures represent the average external temperature of the reactor tubes in the single reactor.

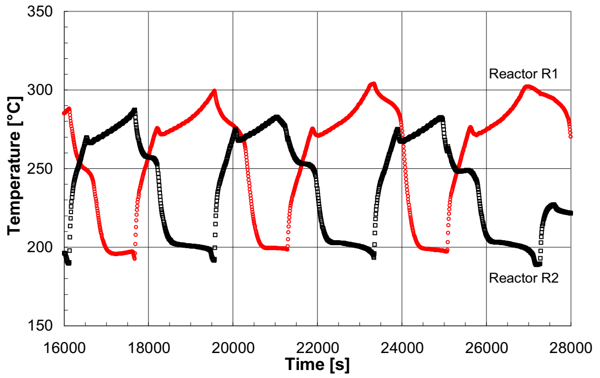
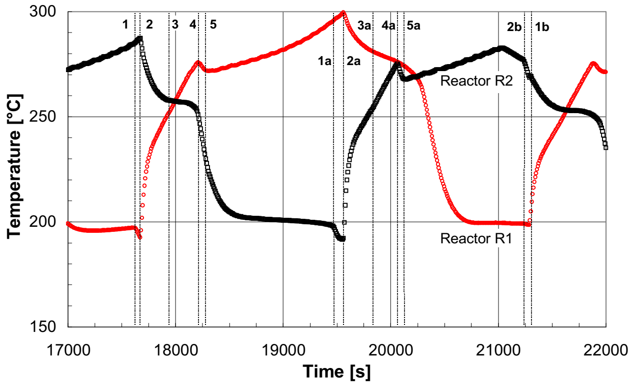


Figure 4: Mean temperature levels in the reactors over six successive half-cycles.

In Figure 4 six successive half-cycles of the same day measurement are presented, together with the connection and heating/cooling phases. As it can be seen the temperatures in reactors R1 and R2 change in a range between 200°C and 300°C, depending on the reaction phase. During the synthesis phase a rather constant temperature level is noted, which can be linked with the constant heat transfer to the bottoming absorption device. The temperature during the decomposition phase increases due to the insufficient heat transfer from the hot air, which is used to heat up the reactor tubes. With higher temperature of the reactors, the reaction process is intensified. Consequently, the duration of the reaction phase is reduced. In case of a more constant temperature, the phase would be longer and the operation of the reactors would be less adjusted. As a result the external cooling power and COP would decrease.
For the following discussion we chose a single reaction cycle, with the emphasis on the first half-cycle.

<u>**3.1.1 Connection phase.**</u> In our case the first half-cycle starts when the reactors are directly connected (let us start at 17600s – Point 2 in Figure 5). At this point the synthesis reactor R1 is at the lowest and the decomposition reactor R2 at the highest temperature level. Some deviations can occur due to the waiting phase, which could not be successfully eliminated. In the case that is presented in Figure 5 the reactor R1 has to wait on R2 to finish the decomposition phase. This results in a small temperature drop in the reactor, because the synthesis reaction is terminated and no further heat of reaction is released (between 1 and 2 in Figure 5). The waiting phase appears due to the fact that the reactor has to decompose to such an extend that in the next synthesis phase it would satisfy the required cooling energy. In the case when we would stop the decomposition phase at Point 1 the reactor would react with less ammonia in the next phase, which would result in irregular allocation of the ammonia in the reactors. This would lead to additional irregularities in the operation of reaction cooling device.

After the direct connection between the reactors, they tend towards the equilibrium temperature at the pressure, which was reached after the pressure equalisation. After 4-5min. of the connection phase, the reactors are disconnected again (3 in Figure 5).



1 – end of synthesis phase, possible start of the connection phase, 2 – end of decomposition phase, possible start of the connection phase, 3 – end of connection phase, 4 - start of decomposition phase, 5 – start of synthesis phase. Indexes a, b – represents the same points in subsequent half-cycles.

Figure 5: Comparison of the temperature in the reactors. For the discussion a cycle is divided into the phases [7].

To present the process more clearly the pressure levels in all main heat exchangers will be discussed in parallel (Figure 6). If we closely look at the measured pressure levels in the evaporator, condenser, and in both reactors (Figure 6), we can easily distinct between the phases in the process.

At the beginning of the connection phase the pressure in the reactors R1 and R2 is equalised. Due to the direct connection between the reactors, the ammonia vapour flows from the reactor R2 to react in R1. As a result the pressure level decreases. The end of the connection phase can be noticed by the differentiation between the pressure levels in the reactors (3 in Figure 6).

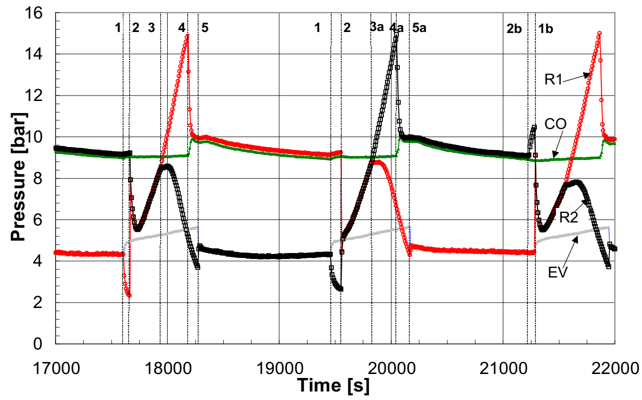


Figure 6: Pressure in the evaporator (EV), condenser (CO) and in the reactors during one complete reaction cycle. Abbreviations are explained in Figure 5 caption [7].

__3.1.2 Sensible heating/cooling phase.__ When the connection phase is over, the reactor with finished synthesis (R1) is further heated up, which causes the increase in the pressure and temperature in the reactor.

On the other side the reactor R2 has to be further cooled down. During the cooling down phase, the heat pipe loop is functioning to accelerate the cooling process.

__3.1.3 Reaction phase.__ The decomposition phase in the reactor R1 begins when the pressure is noticeably higher than in the condenser (4 in Figure 6). After the opening of a valve, which is connecting the condenser section with the reactor R1, the pressure in the reactor drops to the condenser pressure level. This level is followed until the end of the decomposition phase. Start of the phase can be seen as a small temperature drop in reactor R1 also (4 in Figure 5).

On the other side, when the pressure in reactor R2 drops below the pressure in the evaporator, the synthesis phase in the reactor R2 begins (5 in Figure 6). After the connection of the evaporator and reactor R2 the pressure in the reactor equalises with the pressure in the evaporator. The end of decomposition phase, which denotes the end of the first half-cycle, is over at Point 2a in Figure 6.

The first-half of complete cycle is over when both, synthesis and decomposition phase are finished (2a in Figure 5). In the next half-cycle, roles are exchanged between the reactors R1 and R2.

__3.1.4 Waiting phase.__ In Figure 6 the waiting phase, which denotes the time between the end of reaction phases, is periodically present between the points 1 and 2.

In the first half-cycle, the reactor R1 with finished synthesis, had to wait on reactor R2 to finish the decomposition to the adequate level. Let us observe the pressure in the reactor R1 from the same starting-point like before (1 in Figure 6). It can be seen that the pressure in the reactor decreases at the end of synthesis phase, while the pressure in the evaporator increases. The pressure drop in the reactor R1 is linked with the temperature drop and it is a result of a tendency to the reaction equilibrium in the reactor. Namely, at the end of the synthesis there is still some salt that did not react with ammonia. This salt reacts with the rest of ammonia vapour in the reactor causing the decrease in pressure.

In the reactor R2 the decomposition phase is not over at Point 1 in Figure 6. The end of phase can be observed as a pressure drop in the reactor due to the connection with the other reactor R1 (2 in Figure 6).

During the second half-cycle the reactor R2 (1a-2a in Figure 6), which finished the synthesis phase, had to wait on the reactor R1. Differently is in the third half-cycle (1b-2b in Figure 6), where the reactor R2 had to wait on the R1 to finish the synthesis phase. Because at the end of the decomposition phase the valves are closed and the reactor is still hot, the pressure in R2 increases rapidly. This is due to ammonia vapour, which is additionally released.

3.2 Measurement results in pressure-temperature diagram

To imagine the operation range of the experimental reaction device the results for both reactors, which are presented above, are plotted in a pressure-temperature diagram (Figure 7). The conditions in the reactor R1 are presented with circle marks and conditions in the reactor

R2 with cross marks. To be better imagined, the equilibrium reaction line [8], is presented also.

Two regions can be clearly seen in the Figure 7. On the left side of the equilibrium line the synthesis phase region, and on the right side the decomposition phase region. The difference between two measurement points in Figure 7 equals to the scan rate of 8s.

For a more detailed discussion we will follow the conditions in the reactor R1, which starts with the finished synthesis, first (1, R1 in Figure 7). After the connection with the reactor R2 the pressure increases in a matter of seconds (R1). In this moment the additional ammonia vapour flows from the already decomposed reactor R2. The vapour reacts with the salt in the reactor R1 and the pressure starts to decrease after the first shock. With the connection between the reactors also the external heating with the hot air switches to the reactor R1. As a result the temperature of the R1 increases during the connection phase (1-3, R1 in Figure 7). After a certain time period a minimum pressure is reached. At this point the heating of R1 overcomes the contribution of the reaction process so that the pressure starts to increase again.

When the connection phase is finished, the reactor R1 is further heated up (3-4, R1 in Figure 7). During this phase the conditions in the reactor follow the equilibrium line (solid line in Figure 7). The difference to the equilibrium line is assumed to be the result of the reactor temperature measurement, which is performed on the external side of the reactor tubes. Thus the measured decomposition temperature is higher than the temperature of the decomposition process. On the other side, the mean temperature of the reactor tubes during the synthesis phase is also different to the mean process temperature. It depends on the heat transfer conditions during the reaction phase.

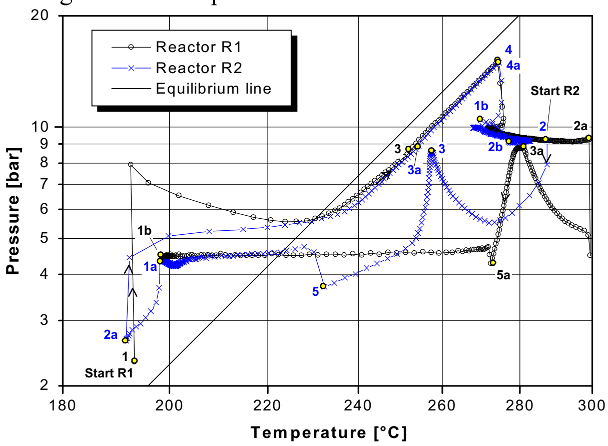


Figure 7: Pressure and temperature conditions during one cycle of the device. The circle marks represents the conditions in the reactor R1 and the cross marks the conditions in the reactor R2 [7]. The abbreviations are explained in Figure 5 caption.

At Point 4 the decomposition phase starts (4-2a, R1 in Figure 7). After the connection with the condenser, the pressure in the reactor R1 decreases to the condensation level of 10 bar. At this point the temperature and pressure level in the reactor are far enough from the equilibrium so that the reaction, the decomposition of salt is intense enough. The temperature in the reactor decreases for 5-8K in the beginning, which can be explained with the sudden transfer of ammonia released from reactor. At this point the external driving heat does not meet all needs for the decomposition of salt and for the sensible heating of the reactor. After a while, the temperature stabilises also and with the time slowly increases.

On the other side, in the reactor R2, the pressure during the connection phase does not decrease as much as in the R1 (2-3, R2 in Figure 7). This indicates that there is still a lot of ammonia in the reactor R2, which could be freed by reaction. It reacts in the R1 slowly at a rate, which is defined by the reactor R1. That explains the pressure drop after the equalisation also. If we compare the first connection phase (1-3, R1 and 2-3, R2 in Figure 7) with the second one (2a-3a, R1 and R2 in Figure 7) it can be noticed that in the second one there is no pressure drop after the pressure equalisation. It can be concluded that the ammonia is not equally distributed between the R1 and R2 at the beginning of the first cycle. This phenomenon was noticed frequently during the measurements.

In the next phase the reactor R2 is slowly cooling down (3-5, R2 in Figure 7). It takes some time that the heat pipe starts to reject the heat from the reactor effectively. This can be noticed as a slight increase in the temperature gradient. When the pressure is lower than the evaporation pressure, the synthesis phase starts (5-1a, R2 in Figure 7). At the beginning of the synthesis phase the pressure is equalised with the evaporation pressure, which can be seen as a quick increase in the pressure level.

Afterwards the reactor has to be cooled down first to begin with the synthesis. It can be seen that the temperature gradient does not change much until the process temperature reaches the equilibrium line. Then the gradient reduces due to the fact that the heat of synthesis is released by the reaction process. After a few minutes the conditions in the reactor stabilise, which can be denoted in Figure 7 as a concentration of the measured points.

The synthesis phase finishes before the decomposition does and therefore the reactor R2 has to wait on the reactor R1 to finish (1a-2a, R2 in Figure 7). During this time the heat is not rejected from the reactor and therefore it slowly cools down.

After the point 2a in the reactors, the connection phase starts again. This time the reactors have changed the roles. The R1 performs the synthesis phase and the R2 the decomposition phase. Similar patterns can be noticed in the second half-cycle as in the first one, although there are some changes connected with the different reacted quantities of ammonia in the reactors.

3.4 Level measurement

Next, very interesting measured data, is a level of ammonia in the receivers. In Figure 8 the measured level of the liquid ammonia in the receivers, which are mounted after the condenser, are presented.

During the decomposition phase the level increases, while during the synthesis phase it decreases. The slope of the plot gives us a rough estimate of the heat rate for

the synthesis and decomposition phase. It can be seen that for the synthesis phase, the level change rate can be taken as linear. This can be explained with the quite constant heat transfer to the bottoming device.
In the decomposition reactor the slope is slightly parabolic. The decomposition rate slows down with the time, due to the smaller quantity of ammonia, which can be decomposed. The slope of the level during the decomposition can be controlled with the temperature of the hot air on the external side of the reactor.
Small changes of the level at the end and at the beginning of the reaction phases are linked with the sudden pressure changes in the receivers, which causes the shift of the ammonia level.

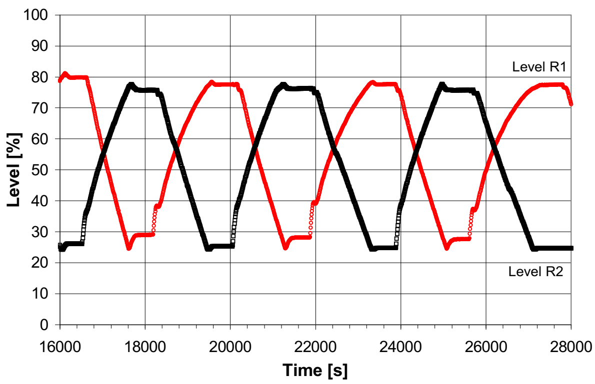


Figure 8: Comparison of the measured levels in the ammonia receivers [7].

4. CALCULATED VALUES

In the following the calculated values for heat flows at main heat exchangers and the COP will be presented (Table 1). In addition, the measured change in the level of the ammonia in the receivers is presented also. In the Table 1 half-cycles for the three day-measurements are presented. In the last line, the results are averaged in dependency on the reaction phase in the reactors.

4.1 Heat flows

The heat flows at the evaporator and condenser were calculated from the measured temperatures and mass flow on the external side of the heat exchangers. The heat flows to the reactor in the decomposition phase is taken as the electrical power, which is used to heat up the hot air.
More difficult was the determination of the heat at the synthesis reactor. Because the mass flow at the heat pipe has not been measured, another approach was used. The heat flow was calculated from the measured values, which were available on the side of condenser of the heat pipe. In our case the condenser of the heat pipe was the internal side of the tubes in the generator G2 of the absorption device [7].
In Figure 9 the time course of the heat flows at the evaporator, condenser and in the reactors is presented.
From the results for the heat flow at the condenser a short, but high increase can be seen in the beginning of each half-cycle (CO in Figure 9). This is a result of the condensation of large quantities of ammonia, which came from reactor at the beginning of the decomposition phase. It correlates with the pressure drop in the reactor (after 4, 4a in Figure 7). When the present ammonia is condensed, the condenser returns to the normal operational conditions.

Table 1: Calculated values from the measurements on the reaction device [7].

Nr.	PHASE	Q_{ev} [kJ]	Q_{co} [kJ]	Q_{dec} [kJ]	Q_{syn} [kJ]	Q_{loss} [kJ]	ΔQ [kJ]	ΔL_1 [%]	ΔL_2 [%]	COP [-]
1	**R1 DEC**	6537	7486	38544	26658	5160	5777	63	71	0,17
2	**R1 SYN**	6069	8998	43872	22409	6408	12126	70	65	0,14
3	**R1 DEC**	7031	7110	35672	31115	4907	-428	61	61	0,20
4	**R1 SYN**	4533	5974	28643	17781	3815	5607	57	52	0,16
5	**R1 DEC**	5821	6247	32732	23193	6192	2921	52	53	0,18
6	**R1 SYN**	4743	6208	27546	21562	4061	458	54	53	0,17
7	**R1 DEC**	6145	6211	34976	24967	5023	4920	54	53	0,18
8	**R1 SYN**	5054	5957	30166	21908	4003	3353	54	53	0,17
9	**R1 DEC**	5820	6527	32484	25141	5299	1337	53	52	0,18
10	**R1 DEC**	4923	5302	25903	20984	3730	810	44	54	0,19
11	**R1 SYN**	4587	6451	37559	19174	5276	11245	54	52	0,12
12	**R1 DEC**	5730	5462	27535	26773	4077	-3047	49	53	0,21
13	**R1 SYN**	4447	6197	34971	19802	4858	8561	54	53	0,13
14	**R1 DEC**	5538	4665	29119	25239	4039	-812	51	53	0,19
15	**R1 SYN**	4808	6106	27886	22039	5628	-1078	54	49	0,17
16	**R1 DEC**	5557	5855	30985	23414	4175	3099	50	53	0,18
17	**R1 SYN**	5246	6252	31465	23470	4234	2756	54	54	0,17
18	**R1 SYN**	3971	5525	28945	19428	3891	4072	54	43	0,14
19	**R1 DEC**	5257	4343	22741	24374	3208	-1977	40	44	0,23
20	**R1 SYN**	2820	4935	28185	12336	3552	10182	42	43	0,10
21	**R1 DEC**	4577	5076	24351	22084	3712	-3504	44	43	0,19
22	**R1 SYN**	3955	4683	27969	17931	3806	5502	43	43	0,14
23	**R1 DEC**	5647	5262	25869	25373	4239	-3358	44	42	0,22
24	**R1 SYN**	3986	4643	29837	17096	4474	7610	44	43	0,13
25	**R1 DEC**	4338	5384	28838	22555	4577	660	41	43	0,15
26	**R1 SYN**	4119	4211	25617	19474	3240	2812	44	42	0,16
AV	**R1 DEC**	**5609**	**5764**	**29981**	**24759**	**4488**	**492**	**50**	**52**	**0,19**
AV	**R1 SYN**	**4488**	**5857**	**30974**	**19570**	**4403**	**5631**	**52**	**50**	**0,15**
AV	**MEAN**	**5048**	**5810**	**30477**	**22165**	**4446**	**3062**	**51**	**51**	**0,17**

R1 SYN: R1 in synthesis phase, R2 in decomposition phase
R1 DEC: R1 in decomposition phase, R2 in synthesis phase

On the side of the evaporator a similar effect would be expected (EV in Figure 9). Due to the fact that the synthesis conditions in the reactor usually has to be established first, the peak at the beginning of the synthesis phase does not occur. The reaction occurs rather slower at the beginning. At this point we have to stress that the pressure and temperature conditions differ between the reactor tubes in each of the reactors. The reactor tubes, which finished colder during the decomposition phase, could start at the beginning of the synthesis phase with the reaction almost instantly. The warmer reactor tubes has to be cooled down by the heat pipe evaporator first to be prepared for the synthesis phase.

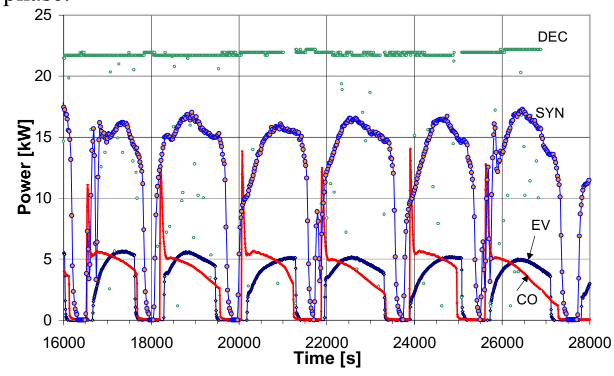


Figure 9: Heat flows on the external heat exchangers of the reaction cooling device. Abbreviations: DEC: driving heat flow, SYN: heat flow to the bottoming device, CO: heat flow at the condenser, EV: heat flow at the evaporator [7].

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For the electrical power (DEC in Figure 9) it can be seen that it is constantly in use, during the connection phase also. Small interruptions are due to the control of the driving heat temperature level. Only a few times it was switched off for a shorter period to slow down the decomposition phase with an intention to let the synthesis phase more time.

The heat released during the synthesis half-cycle (SYN in Figure 9) is in our case not fully representative for the heat flow. Because the heat transferred to the bottoming device relies on the mass flow of the solution between the generator G1 and the solution storage tank [7], a time shift is expected. In this time shift the transferred energy has to heat up the solution in the generator G2, it has to be transferred to the generator G1 and furthermore it has to be noticed on the solution flow from the generator G1.

Another time shift emerges at the end of synthesis phase, because there is still some stored heat in the transfer system. As a result the heat of synthesis, as a time dependent value, is transferred almost the whole cycle time, with a short pause during the connection phase. Because it does not present the direct heat flow from the reactor, it can be used as an averaged value only. As a particularity, some sudden changes in the heat flow can be noticed at the beginning of the heat transfer. They results from the breakdown of the solution flow in the absorption device.

In addition to the heat flows at the main heat exchangers, the heat loss (Table 1) to the environment has been estimated from the geometry data. It served for the analysis of the energy balance of the reaction device [7]. As it can be seen (Table 1) these heat losses represent of about 15% of the energy that is used for the heating of the circulating air. Therefore an increase in COP would be expected if the heat losses to the environment would be reduced.

4.2 Device efficiency

First, the energy balance has been checked for each half-cycle by the following equation

$$Q_{dec} + Q_{ev} - Q_{syn} - Q_{co} - Q_{loss} = 0 .$$

It can be noted from the results for the mean difference in the balance (ΔQ in Table 1) that a higher difference occurs, when the reactor R1 is in the synthesis phase (average for R1 SYN, Table 1). If we look at the mean quantities of heat at the single heat exchangers, a difference in the heat at the evaporator is noted. It can be seen that for about 20% less cooling heat is gained during the R1 SYN as compared to the phase, when the R1 is in the decomposition phase (R1 DEC). Additionally, the heat rejected from the R1 (R1 SYN) is lower for the 20% also. Furthermore the reactor R1 usually finishes the phase faster than the decomposition reactor R2, which is presented with the waiting phase at the reactor R1 $\tau_{Wa,R1}$.

The most important comparison parameter of the cooling sorption device is the cooling efficiency or COP.

The external COP of the reaction cooling device is defined as a ratio of the externally measured quantity of the heat at the evaporator to the driving energy brought to the reaction cooling device

$$COP = \frac{Q_{ev}}{Q_{dec}} .$$

The calculated COP of the experimental cooling device is presented in Table 1 and in Figure 10. It has a mean value of 0,17, with different values for both half-cycles. Again, this is due to the different dynamics of the reaction process in the reactors. As discussed before, the device has reached a higher efficiency, when the R1 was in the decomposition phase. In addition, a higher external cooling power has been attained.

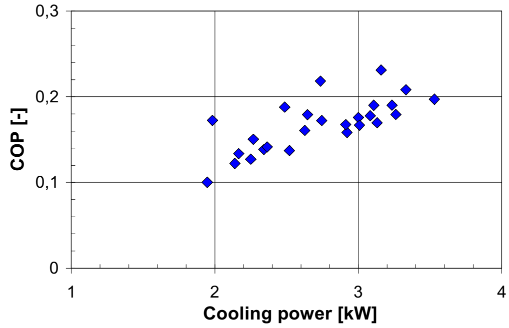

Figure 10: Efficiency of the experimental device presented in the relation to the external cooling power.

The external cooling power depends mostly on the time ratio between the synthesis phase time and half-cycle time. Less synchronous operation of the reactors would reflect in a lower time ratio. Consequently, the synthesis phase would be relatively shorter and the mean external cooling power of the device smaller.

5. CONCLUSION

In this work the preliminary measurement results on the novel reaction cooling device with two reactors working in counter-phase were presented. The emphasis was laid on the presentation of the cyclic operation of the device. It has been shown that the device operated quasi-continuously, with constant shifting of the reaction phases parallel in the both reactors. From the measurement results it has been found, that the reactor R1 produced less cooling energy than the reactor R2. The reasons could be connected with the loss of ammonia mass in the device. It has been noted during the measurements that the reacted quantity difference, which is dependent on the mass of ammonia in the system, decreased during the cyclic operation. The other possibility would be the leakage between the heat pipe and the reactive matrix in the reactor R1. This was more likely present, due to the quite large quantities of ammonia, which had to be replaced during the measurements. Another possible explanation is the presence of liquid phase in the vapour flow to the reactor R1. This can occur, when liquid ammonia, which is present in the separator, mixes with the vapour leaving the evaporator. It could be also possible that the ammonia mass was transported between the receivers, due to the malfunction of the control system.

From the analysis of the heat flows a COP of COP=0,17 resulted, which does not correspond to the expected COP value, which should be at least 0,25. It has been found that, if the difference between the operation of the device during the single half-cycles would be diminished, an increase of the COP of about 10% to the 0,19 could be reached (Table 1). In addition, minimisation of heat losses to the environment could bring another 15% increase in the COP. Still to reach the mean COP values over 0,2 a different approach to the design of the reactors would be required. Due to the numerous reaction tubes the inactive, inert mass of the reactors, which has to be cycled together with the reactive salt, is very high. With reduction of the inert mass, e.g. lower mass of the reactor tubes, inner insulation of the reactor casing, the resulting COP could be increased to the expected level.

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NOMENCLATURE

COP	[-]	coefficient of performance
p	[Pa]	pressure
Q	[J]	heat
T	[°C]	temperature
ΔL	[$kg.kg^{-1}$]	level difference

Indices

ev	evaporation
co	condensation
syn	synthesis
dec	decomposition
loss	losses