# RE-EVALUATION OF THE HONIGMANN-PROCESS: THERMO-CHEMICAL HEAT STORE FOR THE SUPPLY OF ELECTRICITY AND REFRIGERATION

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## ABSTRACT

An invention for thermo-chemical energy storage and conversion from the 19th century has been considered for use at present time. The vapor depression related to the vapour-liquid or vapour-solid equilibrium of solutions, sorbents, or monovariant chemical reactions is utilized to operate an expansion machine. Moreover, the process can be used for cooling or heat pumping. The energy which drives the process can be low-grade heat. The flexibility in operation is pointed out, and the outline of an experimental setup to investigate the process behavior is described. Integral energy balances allow the approximate calculation of mechanical energy density and efficiency, which show interesting values of $\rho_{mech} = 1{,}4 - 17{,}5\ Wh/kg$ and $\eta_{mech} = 0{,}04 - 0{,}10$ in the case of use of near-ambient (120°C) temperature heat.

## INTRODUCTION AND BASICS OF THE PROCESS

A thermo-chemical energy storage is unique, because it can be used for energy conversion also. It can be charged either with input of heat or mechanical work. In the discharging phase the user is provided with heat, refrigeration, or mechanical work at any desired moment and in any combination. This store could be a central device within a modular energy supply, which is especially suited for the use of transient renewable energy sources or waste heat.

The so called Honigmann-process is based on the vapour pressure depression of a concentrated solution or adsorbed vapour in comparison to the pure working fluid. Built on this, the process was invented and filed for patent in 1883 by Moritz Honigmann (1). In Berlin and Aachen so-called 'fireless locomotives' were successfully used for public transport. With today's challenges of energy supply in mind, a re-evaluation of the process seems to be on time.

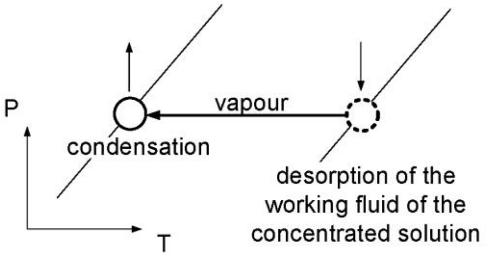

**Figure 1a: Desorption with heat input**

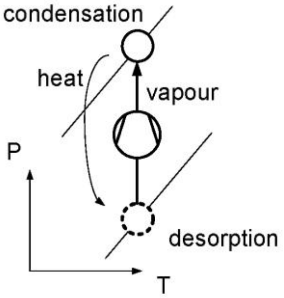

**Figure 1b: Desorption with work input**

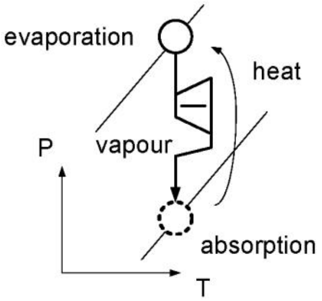

**Figure 2a: Honigmann – supply of electricity**

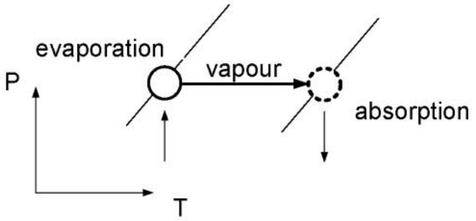

**Figure 2b: Production of cold**

In Figures 1 and 2 the different process steps are shown in a simplified pressure-temperature diagram with qualitatively depicted isosteres (Dühring or Van’t Hoff). The line at the left side is the vapour pressure line of the pure working fluid. The dotted circle in each case represents an absorber or desorber. The solid circle represents an evaporator or condenser. The production of cold can be accomplished in the way of classical batch absorption cooling (Figure 2b): working fluid is evaporated at a low temperature. The vapor is absorbed into the solution at the same vapor pressure, and the heat of absorption is released at an elevated temperature. This means discharging the storage.

The discharging in Honigmanns power producing way is shown in Figure 2a: The concentrated solution (originally sodium hydroxide) is allowed to exchange heat with the evaporator which contains, e.g., water. If the water and the solution are at approximately the same temperature the vapour pressure will be different, and work can be produced across this pressure difference in an expansion machine (Figure 2a). After doing work the steam is absorbed into the solution. Heat of absorption is released, flows to the evaporator and subsequently evaporates more water. Work is being produced from the storage with (ideally) no input or output of heat.

During this process, the solution is diluted continuously and the vapour pressure depression decreases, so that less work can be produced from a given absorbed mass. The solution then needs to be regenerated. This is the process when the store is recharged. Technically this can be accomplished by applying heat and condensing the produced steam by use of cooling water (Figure 1a). Other ways for regeneration are with the help of a compressor and reversing the Honigmann process (Figure 1b), or maybe even through electrolysis.

The process can be realised with all known and unknown absorbents and adsorbents. To name a few, there are water and sulphuric acid ($H_2SO_4$), lithium chloride (LiCl), lithium bromide (LiBr), calcium chloride ($CaCl_2$), zeolith, or silicagel, or ammonia ($NH_3$) with water, ammoniates, activated charcoal, and so on.

Isshiki et al. (2) have built several vehicles with water/LiCl working with the Honigmann process. Apart from this activity no other recent work on the process is known to the authors.

## EXPERIMENTAL PLANT

An experimental plant according to the flow chart in Figure 3 will be erected at TU Berlin. The absorber/desorber AD and the evaporator/condenser EC are separated. During the work producing process the two tanks are thermally connected by a circulating heat transfer fluid. This setup differs from the integrated heat exchanger design of the Honigmann machine in the 19th century. At that time the solution vessel was connected to the water tank with heat exchanger tubes that were immersed into the solution. The separation adds though several degrees of freedom for the experimental campaign and also permits to use the same vessels for the regeneration period.

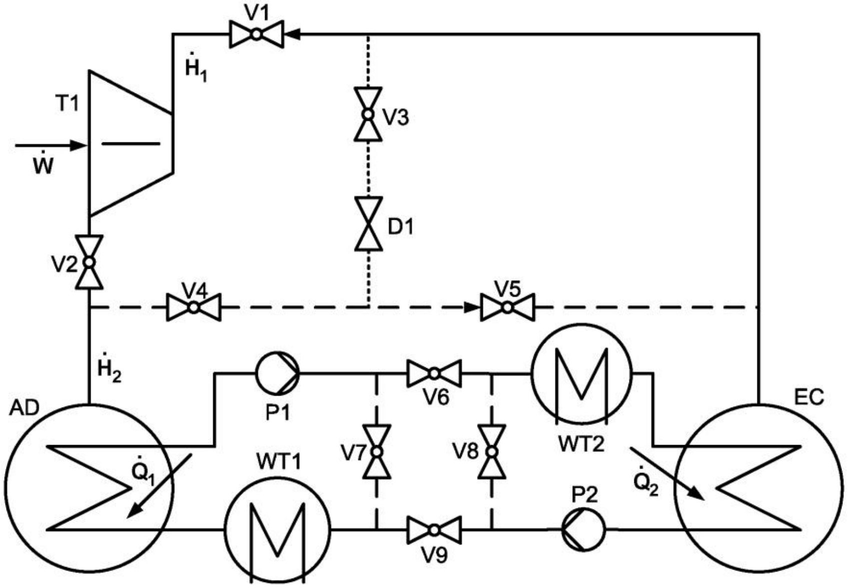

**Figure 3: Flow chart of the Experimental Setup**

During the work producing process heat $\dot{Q}_1^{Abs}$ is transferred from the hot solution in absorber AD to the heat transfer fluid. This fluid is pumped by pump P1 first to the heat exchanger WT2 and then to the evaporator EC where heat $\dot{Q}_2^{Evap}$ is released. The fluid afterwards flows back to the absorber, passing heat exchanger WT1. Valves V7 and V8 are closed. In evaporator EC steam is generated which flows through the expansion machine T1 and does work. The steam then is directed into absorber AD, where it is absorbed by the solution and more heat is released. Valves V3, V4 and V5 are closed.

With heat exchanger WT1 or WT2 additional heat can be added to the system or it can be rejected. This probably is necessary to close the energy balance. It also permits to control the conditions in the vessels. In addition, for, e.g., heat exchanger testing an adjustable throttle D1 can be used.

For the regeneration process only valves V4, V5, V7 and V8 are open. The heat transfer fluid is pumped in two different circuits. Pump P1 pumps fluid to heat exchanger WT1. There it takes up heat and flows to desorber AD. The hot fluid regenerates the solution ($\dot{Q}_1^{Des}$). Vapour coming from the desorber flows to the condenser EC. The condenser is cooled by a second heat transfer fluid circuit and heat $\dot{Q}_2^{Cond}$ is released. It is pumped by pump P2 and cooled at heat exchanger WT2.

In the case of liquid absorbents it is necessary to add storage tanks to the main heat exchangers and to circulate the absorbent through the absorber/generator. For solid adsorbents a storage vessel would be required for the evaporator/condenser only.

## ENERGY BALANCES FOR THE MAIN COMPONENTS

In the following basic investigations on energy balances will be presented for the main components of the system, this means for the absorber/desorber AD, the evaporator/condenser EC and the expansion machine T1. For understanding of the main features a regeneration process with heat input and the Honigmann process with work output have been combined to form a closed cycle process (Figure 4). Isobaric desorption at $p^{LV}(T^{Cond})$ and isothermal absorption are assumed. In addition, the condensate is preheated with $\dot{Q}_2^{Heat}$ before starting the evaporation. The diluted solution is cooled isosterically before starting the desorption ($\dot{Q}_1^{Cool}$ ). The work for liquid pumping is neglected. Taking into account these and other assumptions described below, the sum of in- and outgoing heat and work into the closed system must be zero according to the first law of thermodynamics.

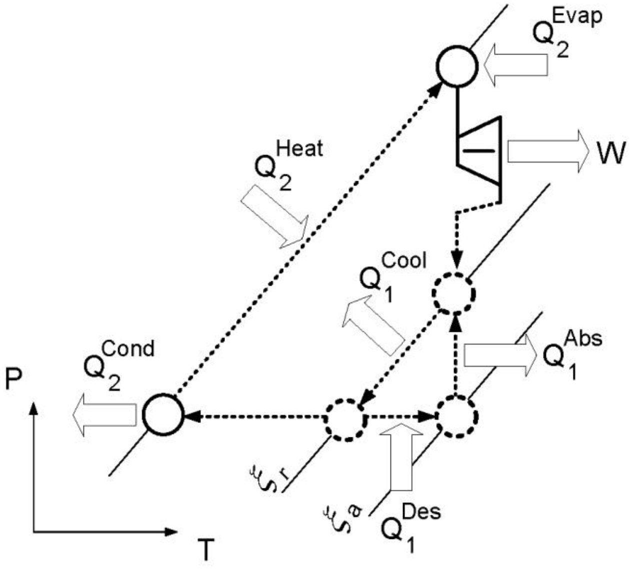

**Figure 4: Closed Cycle Process**

According the first law of thermodynamics the change of the inner energy of the solution $U_{AD}$ in component AD equals the enthalpy flow $\dot{H}_2$ and heat flow $\dot{Q}_1$ :

$$\frac{dU_{AD}}{dt} = \dot{H}_2 + \dot{Q}_1 . \qquad [1]$$

This includes the neglection of the kinetic and potential energy. In the following it is assumed, that the amount of working fluid (absorbent) in the gas phase is pure working fluid, so that the inflow $\dot{m}_2$ equals the change in working fluid content, $\frac{dm_W}{dt}$. With the additional assumption of an ideal liquid, and that the amount of vapour in component AD is negligible we get $h_{AD} \triangleq u_{AD}$ and write:

$$\frac{d\big(h_{AD} * (m_W + m_A)\big)}{dt} = h_2 * \dot{m}_W + \dot{Q}_1 \,. \tag{2}$$

$h_{AD}$ is the specific enthalpy of the liquid solution. It is determined with the property data as $h_{AD} = h_{AD}^{L}(p^{LV}(\xi, T)\,, T)$. For the calculations we assume the solution to be in equilibrium, in order to determine the vapour pressure $p^{LV}$ from temperature $T$ and mass fraction $\xi$ which, in turn give $h_{AD}$. The mass of the solution is sum of the mass of the pure absorbent $m_A$ and the mass of the working fluid $m_W$. The total mass increases or decreases with the incoming or outgoing mass flow $\dot{m}_W$. Both, $m_W$ and $\dot{m}_W$ are dependent on time. In case of absorption $h_2$ depends on the expansion process in the turbine. In the calculations below we start the expansion with saturated vapour at pressure $p^{LV}(T^{Evap})$ in the evaporator and assume isentropic expansion. The pressure at the end of the expansion is the vapour pressure of the solution $p^{LV}(\xi, T^{Abs})$. The expanded vapour will have a liquid and a gas component. The quality depends on the expansion process. In case of desorption the enthalpy $h_2$ of the mass flow $\dot{\mathrm{m}}_{\mathrm{W}}$ equals the enthalpy of the water vapour at the vapour pressure and temperature $h_2^{Des} = h_{AD}^{V}(p^{LV}(\xi, T)\,, T)$. During absorption the heat of absorption $\dot{Q}_1 = \dot{Q}_1^{Abs}$ is released to the heat transfer fluid. For the regeneration process $\dot{Q}_1 = \dot{Q}_1^{Des}$ is needed to regenerate the solution and represents the driving energy of the process.

Applying the product and chain rule we get [3] for the isothermal absorption and [4] for the isobaric desorption.

$$\left[\underbrace{\left(\frac{\partial h_{AD}^{Abs}}{\partial T}\right)_{\xi} * \frac{dT}{dt}}_{0\ (T\ is\ constant\ )} + \left(\frac{\partial h_{AD}^{Abs}}{\partial \xi}\right)_{T} * \frac{d\xi}{dt}\right] * (m_W + m_A) + \ h_{AD}^{Abs} * \ \dot{m}_W = h_2^{Abs} * \ \dot{m}_W + \ \dot{Q}_1^{Abs}, \tag{3}$$

$$\left[\underbrace{\left(\frac{\partial h_{AD}^{Des}}{\partial p^{LV}}\right)_{\xi} * \frac{dp}{dt}}_{0\ (p\ is\ constant\ )} + \left(\frac{\partial h_{AD}^{Des}}{\partial \xi}\right)_{p^{LV}} * \frac{d\xi}{dt}\right] * (m_W + m_A) + \ h_{AD}^{Des} * \ \dot{m}_W = h_2^{Des} * \ \dot{m}_W + \ \dot{Q}_1^{Des}. \tag{4}$$

The definition of the mass fraction $\xi = \ m_W/(m_A + m_W\ )$ is solved for $m_W$:

$$m_W(t) = \ \frac{\xi(t) * m_A}{1 - \xi(t)}\,. \tag{5}$$

And the derivative with respect to time gives:

$$\frac{dm_W(t)}{dt} = \dot{m}_W(t) = \ \frac{m_A}{\big(1 - \xi(t)\big)^2} * \ \frac{d\xi}{dt}\,. \tag{6}$$

We replace $m_W$ and $\dot{m}_W$ in [3] and [4] with these expressions and integrate over time. Afterwards we can apply the substitution rule and get an expression for the heat of absorption or desorption [7] that is dependent on $\xi$ only and not on time. With the knowledge of the property data this can be solved by numerical integration.

$$Q_1^{Abs/Des} = \int_{\xi_{start}}^{\xi_{end}} \left[\left(\frac{\partial h_{AD}}{\partial \xi}\right)_{\mathrm{T/p^{LV}}} * (1 - \xi) + (h_{AD} - \ h_2)\right] * \ \frac{m_A}{(1 - \xi)^2}\ \ d\xi\,. \tag{7}$$

After absorption the diluted solution in component AD is now at a higher temperature and pressure than it should be at the beginning of the desorption. To obtain the original state, the solution has to be cooled with the release of heat $Q_1^{Cool}$ at constant mass fraction and mass:

$$Q_1^{Cool} \ = \ \big(h_{AD}^{Des,start} \ - h_{AD}^{Abs,end}\big) * (m_W + m_A). \tag{8}$$

The energy balance for the evaporator/condenser EC is given by [9] and treated in the same way as for component AD:

$$-\frac{dU_{EC}}{dt} = -\dot{H}_1 + \dot{Q}_2 \,. \qquad [9]$$

Comparable to equation [2], the inner energy $U_{EC}$ is substituted by the enthalpy of the condensate $h_{EC} * m_W^{EC}$, and the enthalpy flow $\dot{H}_1$ is replaced by $h_1 * \dot{m}_W$. The enthalpy $h_{EC}$ of the pure working fluid is the enthalpy of saturated liquid at the boiling temperature $T^{LV}$. For the evaporation this is $h_{EC}^{Evap} = h_{EC}^{L}(T^{Evap})$ and for the condensation $h_{EC}^{Cond} = h_{EC}^{L}\left(T^{Cond}\right)$. In both cases temperature and pressure, and therefore also the specific enthalpy, are taken as constant. $h_1$ is the specific enthalpy of the incoming or outgoing vapour flow. During evaporation it is $h_1^{Evap} = h_1^{V}(T^{Evap})$. For the condensation it is the outgoing vapour of the desorber AD with a higher temperature than the saturated vapor of the pure working fluid. Therefore it is $h_1^{Cond} = h_2^{Des} = h_{AD}^{V}(p^{LV}(\xi, T), T)$. Finally we get:

$$Q_2^{Evap/Cond} = \int_{\xi_{start}}^{\xi_{end}} (h_1 - h_{EC}) * \frac{m_A}{(1-\xi)^2}\, d\xi \,. \qquad [10]$$

After the condensation of the desorbed working fluid the condensate needs to be heated to the temperature of evaporation:

$$Q_2^{Heat} = \left(h_{EC}^{Evap} - h_{EC}^{Cond}\right) * m_W^{EC} \,. \qquad [11]$$

Finally, for the expansion machine the power output is:

$$\dot{W} = -\,(h_1 - h_2) * \dot{m}_W \,. \qquad [12]$$

The produced work then equals:

$$W = -\int_{\xi_a}^{\xi_r} \left(h_1^{Evap} - h_2^{Abs}\right) \frac{m_A}{(1-\xi)^2}\, d\xi \,. \qquad [13]$$

## RESULTS AND DISCUSSION

For a numerical example LiBr/$H_2O$ has been chosen as a working pair. A very small change in mass fraction of $d\xi = 0{,}01$ was assumed to show the main characteristics of the process. The absorption and evaporation take place at $T^{LV} = 120°C$ and the condensation and desorption at $p^{LV} = 0{,}3\ bar$. The masses have been chosen in such a way that 1 kg of water is expanded in the machine in one complete cycle. The calculations have been carried out with one integration step only and the help of diagrams. The accuracy of the results therefore is in the range of the reading accuracy. The results are listed in Table 1.

| *symbol* | *value [kJ]* |
|---|---|
| $Q_1^{Abs}$ | -2300 |
| $Q_2^{Evap}$ | 2200 |
| $Q_1^{Cool}$ | -200 |
| $Q_1^{Des}$ | 2800 |
| $Q_2^{Cond}$ | -2400 |
| $Q_2^{Heat}$ | 200 |
| $W$ | -300 |

**Table 1: Results of the calculations**

The values for $Q_1^{Abs}$ and $Q_2^{Evap}$ show the characteristic of Honigmann. $Q_1^{Abs}$ is in the same range or even larger than $Q_2^{Evap}$. This is the premise that the process can run independently during the work producing period without additional heating from the outside. The surplus of $Q_1^{Abs}$ can be used to heat the working fluid in EC ($Q_2^{Heat}$).

With these results we can calculate the mechanical efficiency of the system. It is defined as the work output divided by the heat input during the recharging process of the accumulator and the remaining heat for heating up the water:

$$\eta_{mech} = \frac{W}{Q^{Input}} \qquad [14]$$

with $Q^{Input} = Q_1^{Des} + Q_2^{Heat} + (Q_1^{Abs} + Q_2^{Evap})$. The mechanical efficiency for this example is $\eta_{mech} = 300\,kJ/2900\,kJ = 0{,}1$. Heat losses to the ambient have been neglected. The work is calculated with the assumption of isentropic expansion. The Carnot efficiency with $\eta_{Carnot} = (393K - 342K)/393K = 0{,}13$ is higher, because the cycle is not inherently reversible.

The mechanical energy density is defined as the work $W$ produced by the expansion machine during one charging cycle normalized by the mass of the solution rich in working fluid $m_r$:

$$\rho_{mech} = \frac{W}{m_r}\,. \qquad [15]$$

For the mechanical energy density we obtain $\rho_{mech} = 300\,kJ/60\,kg = 1{,}4\,Wh/kg$. This number does not take into account the weight of the heat exchangers, vessels and connecting pipes etc. For a similar example with a larger change in mass fraction of $d\xi = 0{,}3$ (and a lower desorption temperature) we obtain $\rho_{mech} = 130\,kJ/2\,kg = 18\,Wh/kg$, which is much higher. The efficiency decreases though ($\eta_{mech} = 130\,kJ/3200\,kJ = 0{,}04$), since in the area of high dilution, the vapour pressure depression decreases and less work can be produced from the same mass flow.

## FINDINGS AND SUMMARY CONCLUSIONS

First integral energy balances for the main components of the Honigmann-Engine demonstrate the potential of the process. Even if the process is operated with near ambient heat (120°C) the conversion efficiency will amount to around 10%. The storage capacity will be comparable to conventional batteries, but the charging is done by heat and not by electricity. The technology must be evaluated regarding the whole system since the flexibility for the charging process and the different possibilities for the use of the energy are unique in this combination. Moreover, the working pair can be chosen so as to optimize the process for a given application. Experiment will be performed in the future.

## NOMENCLATURE

| *symbol* | *meaning* | *symbol* | *meaning* |
|---|---|---|---|
| $W, \dot{W}$ | work, power | $\xi$ | mass fraction |
| $Q, \dot{Q}$ | heat, heat flow | $\xi_r, \xi_p$ | mass fraction of the rich/poor solution |
| $U$ | inner energy | $\rho_{mech}$ | mechanical energy density |
| $H, h$ | enthalpy, specific enthalpy | $\eta_{mech}$ | mechanical efficiency |
| $T$ | temperature | $Abs$ | ab- or adsorber |
| $p^{LV}$ | vapour pressure | $Des$ | desorber |
| $t$ | time | $Cond$ | condenser |
| $m, \dot{m}$ | mass, mass flow | $Evap$ | evaporator |
| $m_r$ | mass of the solution rich in working fluid | $AD$ | absorber/desorber |
| $m_W$ | mass of the working fluid | $EC$ | evaporator/condenser |
| $m_A$ | mass of the pure ab-/adsorbent | | |

## REFERENCES

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(2) Isshiki N et al, 1996, Absorption steam tricycle driven by concentrated solar heat energy, Proceedings of ‘Ab-Sorption 96’, Canada, pp 661-667