Title: The Binary NH3-H2O Bubble Reactor

Author: Johan Enslin

Company: Heat Recovery Micro Systems CC

Country: South Africa

Introduction:

Various forms of the REHOS cycle have been described in many previous publications to make the principles of operation clear. In this regard we refer to the latest two documents [7] that comprehensively describe the Simplified REHOS Cycle, designed with only a single NH3-H2O bubble reactor used for both absorption and desorption functions. The referenced paper [9] do a thorough analysis of the process variables as calculated for the Simplified REHOS Cycle, but only calculate the variables around the bubble reactor. Only inputs and outputs of the reactor are balanced in mass-, species-, and heat balancing equations, treating the total reactor operation as a single, internally balanced component of the REHOS cycle.

Due to the complexity of heat and mass exchange in the bubble reactor in operation, it was pointed out to me that the reactor internal processes use different media for different vertical positions inside the reactor, due to the change in ammonia concentration with changing temperatures along the vertical temperature gradient. Density differences due to concentration and temperature differences of the zeotropic mixture would cause slow migrationary vertical up flow of NH3-rich vapor bubbles, surrounded by an entrained mass of high concentration NH3 in aqua mixture. This slow migratory vertical up flow of the ammonia-rich mixture, is in direct contact with the equally slow migratory down flow of the ammonia-lean mixture, giving rise to mass-, species-, and heat transfer between the two vertical migratory flows. In area's which are sub-cooled due to the extraction of heat, by heat exchanger coils, for example, would absorb more vapor, generating more absorption heat than other, non-subcooled regions.

To illustrate proper internal mass-, species-, and heat balance it would be required to slice the reactor up into various segments horizontally, forming a new segment for each vertically spaced horizontal disc as shown in Figure 2. The mass-, species-, and heat balance calculations should be done for each different slice or segment separately, to ensure that each segment stay in balance before treating the reactor as a single component in saturated balance and considering inputs and outputs of the reactor only for the external process flows making up the REHOS thermodynamic cycle.

This document describe the calculations done on a NH3-H2O bubble reactor used for a typical Simplified REHOS cycle as sketched in Figure 1, below.

Formulas for the calculation of all process parameters like temperature, pressure, enthalpy as well as NH3 concentration are provided. All these formulas were solved in an Excel Spreadsheet, linked to two files of lookup tables for Saturated Steam, Saturated and Superheated (at 10 Bar Absolute) Ammonia, as well as lookup table process data for saturated NH3 in Aqua solutions with several different concentrations of ammonia. Over years the lookup table data, referenced in [1] to [5], crosschecked and double checked with numerous other sources have been compiled. The excel files with these "Steam Tables", as I call them, have become quite large over the years, also carrying information on various other substances, making them too large to transfer by e-mail. The REHOS cycle is made possible by a few physical phenomena found in working with a vertical column of a zeotropic binary solution of NH3 dissolved in water.



From a publication made for the Kalina cycle, by L. Kielasa et al [8] made in 1996 already, ammonia-water mixtures have four primary differences from the pure NH3 and H2O state. The third primary difference mentioned in this paper, spell out that "A binary mixture has thermo-physical properties that causes mixed fluid temperatures to increase or decrease without a change in heat content. The temperature of pure substances like NH3 or H2O cannot change without a change in energy." This have the result that two media streams mixing and un-mixing have an effect on the temperatures as follows: When an ammonia-rich media stream mix with an ammonialean stream, heat is released (as the mixing process is exothermic), called the heat of solution (or enthalpy of solution), causing the so-formed mixture stream to rise in temperature well above the temperatures of the individual input streams. Also, when a strong solution of ammonia in water is separated into the nearly pure ammonia and nearly pure water separate streams, heat is absorbed (as the desorption process is endothermic), causing the formed liquid streams to decrease in temperature, well below the temperature of the original strong solution.

In the REHOS configuration, nearly pure NH3 vapor is bubbled through the reactor, from the bottom up. The absorption taking place in the reactor bottom would generate heat, raising the reactor bottom temperature. The heat of solution of NH3 into a leaner mixture of NH3 in aqua would also contribute to this temperature raising at the reactor bottom. Nearly pure NH3 liquid (as well as some vapor) is removed from the reactor top, therefore decreasing the temperature at the reactor top, due to the flashing heat extraction from the top of the reactor, but also due to the endothermic reaction of desorption of ammonia and water in the top end of the reactor.

The Bubble Reactor:

For calculation purposes we have sliced the vertical reactor column in a number of horizontal disc's or segments and ran the mass-, species-, and heat balance formula's for each segment individually. We assumed steady-state conditions with completely saturated, stabilized mixture upflows, with the complete reactor at a constant saturation pressure of 200 kPa Abs, and, being saturated, each segment also has a percentage saturated vapor present in the segment. The lean mixture downflow from each segment is subcooled with a few degrees, as can be seen in table 1, below.

Heat added into a segment (by the various in-, and outflows as well as external heat input via heat exchanger coils extending into the reactor) cause the vapor content (quality x) of the inflow stream and outflow stream to vary, but not the temperature and bulk segment NH3 concentration. If extra heat is added into a segment, the heat balance internally cause the upflow stream quality (x), to be higher than the inflow stream. Should heat be extracted from a segment (-Q added), the opposite is true. The upflow stream quality (x), in this case would be lower than the inflow stream. The quality (x) in the various streams are also influenced by the chosen vapor flow @ A, as well as the subcooling of the downflow streams.

The calculation results are listed in Table 1, below, and each segment bulk temperature and NH3 concentration is also added to the sketch in Figure 2 below. In Figure 2, the



inflow and outflow streams are drawn as arrows, but an identifying letter of the alphabet next to it. Looking at Table 1, it is clear that due to the heat input (Q_1) into segment 1, the quality (x) at stream C, (which is the rich mixture outflow stream leaving segment 1), is higher than the quality (x) at stream E, (which is the rich mixture inflow stream entering segment 1 from segment 2). Also, due to the large heat extraction from the reactor in segment 10, (the heat added Q_6 is a large negative number), the quality (x) of the stream U, leaving segment 10, is lower than the quality (x) for stream W entering segment 10 from below.

Note that the vapor outflow stream A, is chosen fairly high (40% of the liquid outflow stream B) for this example calculations as displayed in Table 1, but this flow stream is

	Mass Flow	Temp	Enthalpy	Quality	% NH3 in	Subcool
	(kg/s)	(Celsius)	(J/kg)	(x)	Aqua	(Celsius)
Α	3.461E-02	-19	1.127E+06	100.00%	100.00%	
В	8.653E-02	-19	-5.449E+04	0.00%	99.99%	
С	5.689E-01	-11	-1.602E+05	3.90%	75.30%	
D	4.478E-01	-19	-2.802E+05	0.00%	68.62%	12
E	1.186E+00	-3	-2.182E+05	0.78%	63.50%	
F	1.065E+00	-9	-2.652E+05	0.00%	59.35%	10
М	3.324E+00	29	-9.107E+04	0.32%	39.44%	
N	3.203E+00	26	-1.019E+05	0.00%	37.15%	7
0	3.700E+00	37	-4.495E+04	0.24%	35.00%	
Р	3.579E+00	34	-5.309E+04	0.00%	32.80%	7
U	4.997E+00	61	1.126E+05	0.31%	22.71%	
V	4.876E+00	59	1.105E+05	0.00%	20.79%	6
W	5.431E+00	69	1.887E+05	1.94%	18.90%	
Х	5.310E+00	67	1.664E+05	0.00%	17.05%	6
Y	8.653E-06	26	1.277E+05	0.00%	99.99%	
Z_turb	8.424E-02	-19	1.186E+06	100.00%	99.99%	
Z_comp	3.689E-02	-19	1.127E+06	100.00%	99.99%	
Heat Absorbed from the Environment Q_1 10649 Watt						
Regenerative Heat Extracted from Q6 -117818 Watt						

Table 1

used to maintain stability and ensure vapor stays present in each segment, mainly. In fact in reality it would be required mainly for starting purposes to establish the NH3 concentration-, and vertical temperature gradient. When the reactor has been stabilized and saturated in all segments, and the temperature gradient stable, this vapor outflow stream A can be decreased to a smaller value, just for maintaining vapor presence in each segment of the reactor, as the major vapor inflow stream Z would come from the turbine exhaust as low pressure vapor, equaling the liquid outflow stream B. From the balancing equations in each individual segment, it is clear that with a decrease in vapor mass flow stream A, would cause a corresponding increase in the liquid flow stream B. For this example reactor, the temperatures of the bulk mass inside each segment was chosen, ranging from -19°C for segment 0 at the top of the reactor, to 69°C for segment 11 at the bottom of the reactor, each segment 8°C higher in temperature, from the top downward. The NH3 concentration in the bulk mass of each segment was chosen from the lookup tables to reflect the correct (200 kPa Abs) saturation pressure at the chosen temperature. Enthalpy values of each named stream comes from the look-up tables of the corresponding NH3 saturation table of the correct concentration at the chosen temperature of the segment bulk.

From segment 0, it should be clear that the desorbed, lean downflow stream D would be at a lower concentration NH3, but the temperature is likely to be the same as the bulk segment 0 temperature, in other words, the downflowing stream D is subcooled by 12°C. It is this subcooling that enable vapor bubbles to be absorbed in the next downstream segment 1, creating the bubble heating effect required to desorb NH3 from the segment. Enthalpy values as listed in table 1 for the subcooled downflow streams are correctly listed for the temperatures of the subcooled streams, and not for the saturated values like all other enthalpy values listed in table 1. Similar to the explanation above, all the lean downflow streams leaving each segment is subcooled by some degrees, eg. stream F is subcooled by 10°C, stream N and P is subcooled by 7°C and stream V and X is subcooled by 6°C, as can be seen from the table 1 results, above. Desorption therefore take place in each segment of the reactor, at different temperatures and NH3 concentrations, enabling the continuous flow of NH3 vertically upwards in the reactor. In each segment, the saturated, NH3-rich upflow therefore absorb vapor and generate heat while flowing upwards, while the lean, downflow subcooled liquid is heated in each segment by the heated counter-flow stream. Look at segment 6 as the example, listed in table 1. The bulk temperature of segment 6 is 29°C, and the heated stream O enter the segment at 37°C. The hot stream is cooled by 8°C in flowing upwards through segment 6, from 37°C entering as stream O, cooled to 29°C exiting segment 6 as stream M, while the subcooled, lean downwards flowing stream enter segment 6 at 26°C of stream N, and is being heated by 8°C to 34°C exiting segment 6 as stream P.

In the balanced reactor as a whole, the average temperature difference between the NH3rich stream upflow temperature and the NH3-lean stream downflow calculate to 3.64° C averaging all segments. The overall lean downflow stream subcooling calculate to 7.64° C, while the average density of the vapor-filled upflow stream calculate to 430 kg/m3, while the lean mixture, vapor-free downflow stream average density is 811 kg/m3 for this example balancing calculations where the results are partially listed in table 1. Heat added into the reactor as Q_1 to the amount of 10649 Watt is extracted from ambient conditions (25° C) with the LMTD for the heat exchanger is 36° C, as the heat exchanger coil is inserted in segment 1, with a bulk temperature of -11° C. The LMTD of the evaporator is 35° C, as the pumped, 10 Bar Abs pressure is evaporated at 26° C in segment 10, where the bulk temperature is 61° C. The LMTD for the superheater calculate to 28° C, as the heat exchanger coil is immersed in segment 10 with a temperature of 61° C and the superheated outlet vapor temperature is 33° C. The heat extracted from the reactor in segment 10 amount to 117818 Watt, and the value of Q6 reflect the negative value, as this heat is removed from the reactor. The balanced condition for the reactor as listed in table 1 represent a turbine output power of 10000 Watt, calculating with a turbine with isentropic efficiency of 70%.

Heat balance is achieved by adjusting the quality (x) of the outflow stream in the segment so that the heat of evaporation/condensation at the segment bulk temperature add or subtract to the mass of vapor produced/condensed. In flow streams where the quality falls between 0% (fully liquid flow) and 100% (fully vapor flow), (0% < x < 100%), the enthalpy was calculated using the correct mass of liquid and vapor present in the flow stream. The calculation results are listed in Table 1 above as generated in Excel, where the mass-, species-, and heat balance calculations were done for each segment individually as well as for the reactor over-all.

Nomenclature:

 M_A = Mass flow in kg/s at position A. (Subscript reflect position, A, B, C etc.)

- P_A = Pressure in Pa Abs at position A.
- T_A = Temperature in °Celsius at position A.
- ρ_A = Media density in kg / m^3 at position A.
- H_A = Enthalpy in J/kg at position A. (Enthalpy of all lookup tables (H_2O and NH_3) have been adjusted for liquid at 0°C to have an enthalpy of zero J/kg.)

 H_{vE} = Vapor enthalpy of the solution at position E.

 H_{IE} = Liquid enthalpy of the solution at position E.

 $\% NH3_A$ = Concentration ammonia in media at position A.

(Turbine_Power) = Isentropic turbine expansion power in Watt.

(Liquid_Heat) = Heat Energy for the heating of liquid, in Watt.

(Evap_Heat) = Heat Energy for the evaporation of liquid into vapor, in Watt.

(Sht_Heat) = Heat Energy for the superheating of saturated vapor, in Watt.

All the equations for mass-, species-, and heat balance are listed below in each segment respectively. Not all segments are shown, but only the topmost and bottommost, as well as segments with external heat input/extract segments. These should all be solved together for proper balancing of the specific segment as well as for the overall reactor.

Segment 0: Equation Chapter (Next) Section 1

Mass Balance:

$$M_A + M_B + M_D = M_C \tag{1.1}$$

Species Balance:

$$M_{A}.\% NH_{A} + M_{B}.\% NH3_{B} + M_{D}.\% NH3_{D} = M_{C}.\% NH3_{C}$$
 (1.2)

Heat Balance:

$$M_{A}.H_{A} + M_{B}.H_{B} + M_{D}.H_{D} = M_{C}.H_{C}$$
(1.3)

Segment 1:Equation Section (Next)

Mass Balance:

$$M_C + M_F = M_E + M_D \tag{2.1}$$

Species Balance:

$$M_{c}.\% NH3_{c} + M_{F}.\% NH3_{F} = M_{E}.\% NH3_{E} + M_{D}.\% NH3_{D}$$
 (2.2)

Heat Balance:

$$M_{C} \cdot H_{C} + M_{F} \cdot H_{F} = M_{E} \cdot H_{E} + M_{D} \cdot H_{D} + (Q_{-1})$$
(2.3)

Segment 6:Equation Section (Next)

Mass Balance:

$$M_M + M_P = M_O + M_N \tag{3.1}$$

Species Balance:

$$M_{M}.\% NH3_{M} + M_{P}.\% NH3_{P} = M_{O}.\% NH3_{O} + M_{N}.\% NH3_{N}$$
(3.2)

Heat Balance:

$$M_{M}.H_{M} + M_{P}.H_{P} = M_{O}.H_{O} + M_{N}.H_{N}$$
(3.3)

Segment 10:Equation Section (Next)

Mass Balance:

$$M_U + M_X = M_W + M_V \tag{4.1}$$

Species Balance:

$$M_{U}.\% NH3_{U} + M_{X}.\% NH3_{X} = M_{W}.\% NH3_{W} + M_{V}.\% NH3_{V}$$
(4.2)

Heat Balance:

$$M_{U} \cdot H_{U} + M_{X} \cdot H_{X} = M_{W} \cdot H_{W} + M_{V} \cdot H_{V} + (Q_{-}6)$$
(4.3)

Segment 11:Equation Section (Next)

Mass Balance:

$$M_{W} = M_{X} + M_{Y} + M_{Z_{turbine}} + M_{Z_{comp}}$$

$$(5.1)$$

Species Balance:

$$M_{W}.\% NH3_{W} = M_{X}.\% NH3_{X} + M_{Y}.\% NH3_{Y} + M_{Z_{turbine}}.\% NH3_{Z_{turbine}} + M_{Z_{comp}}.\% NH3_{Z_{comp}}.$$
(5.2)

Heat Balance:

$$M_{W}.H_{W} = M_{X}.H_{X} + M_{Y}.H_{Y} + M_{Z_{turbine}}.H_{Z_{turbine}} + M_{Z_{comp}}.H_{Z_{comp}}$$
(5.3)

Overall Reactor as One Single Component:Equation Section (Next)

Mass Balance:

$$M_A + M_B = M_Y + M_{Z_turbine} + M_{Z_comp}$$
(6.1)

Species Balance:

$$M_{A}.\% NH3_{A} + M_{B}.\% NH3_{B} = M_{Y}.\% NH3_{Y} + M_{Z_{turbine}}.\% NH3_{Z_{turbine}} + M_{Z_{comp}}.\% NH3_{Z_{comp}}.$$
(6.2)

Heat Balance:

 $M_{A} \cdot H_{A} + M_{B} \cdot H_{B} = M_{Y} \cdot H_{Y} + M_{Z_{turbine}} \cdot H_{Z_{turbine}} + M_{Z_{comp}} \cdot H_{Z_{comp}} + (Q_{1}) + (Q_{6})$ (6.3)

The heat (Q_1) that need to be added to the reactor for overall heat balancing, represent the turbine energy used, where the liquid stream B is pumped externally to a high pressure (10 Bar Abs in this example) before heat exchanger coils extract the heating, evaporation and superheating energy from the reactor segment 10 (the large negative value in Q_6) where the segment bulk temperature is 61°C. The superheated output vapor leaves the reactor at 33°C while the evaporation take place at 26°C.

From this complete overall heat balance, it should be clear that the energy in the turbine exhaust (as well as the compressor output) is completely regeneratively re-used in the reactor. No heat-rejection is required in the REHOS cycle using the regenerative reactor, making the thermodynamic efficiency of converting heat to power extremely high.

Also, the heat input from the environment, (Q_1) that need to be added with a heat exchanger into the reactor, is coming into segment 1 in this example, where the segment bulk temperature is -11°C. Ambient water may therefore be used as heat source, as the heat will then spontaneously flow from the ambient ~ 25°C to the colder segment 1. This is only the example calculation of course, and external heat may in fact be added in any segment anywhere along the length of the reactor with exactly the same result. As all segments are saturated and have excess vapor available, adding heat in any segment would just increase the quality (x) of the mixture in that segment, and not affect the temperatures or ammonia concentration at all! Also, the heat exchange coils absorbing the regenerative heat from the reactor for heating, evaporating and superheating the liquid stream B may be put into any segment of the reactor (it is shown in this example as segment 10, having a temperature of 61°C) with the same effect. These coils could therefore be placed in a lower (hotter) segment for higher rate of heat transfer, or placed higher up in the reactor where the temperature is lower, with exactly the same result. It does not change the temperature or ammonia concentration in the reactor at all.

The REHOS cycle make use of the bubble reactor as a gravitational liquid density separator, because of the importance of keeping the turbine exhaust backpressure as low as possible (being only the hydraulic pressure of the reactor liquid column to overcome), but other logical applications of the zeotropic binary bubble reactor may not necessarily have this requirement.

Figure 3



Should you want to use this described bubble reactor as an air de-humidifier, for example, the gravitational density separation may as well be replaced with centrifugal force, making the various flow migrations in the reactor much faster, using much greater separation forces. The reactor cold top would then be used to cool down air, condensing water vapor from it, and the hot radially furthest from the rotation centre reactor edge

would then re-heat the dried air again to ambient. Such a dehumidifier would have an extremely low energy consumption, and could therefore practically be built into units providing water from the air at very low cost! Windmills, traditionally used for pumping water from an underground source, may power the rotation of the de-humidifier, so as to provide water extracted from the humidity in the air.....



Figure 4

In figure 3 above, a simple reactor similar to the example reactor with detailed balancing calculations shown in the first part of this document is shown. In this reactor, used as a de-humidifier (or air conditioner) extracting heat (Q_cold) from ambient air. The heat exchanger enter the reactor at a temperature below 0° C, (maybe -11°C like our previous example), condensing the water vapor from the humid air. The resulting cold air may be used for air conditioning, while the hot side of the heat pump raise the temperature of a heat exchanger to over 100°C.

The energy used by this type of heat pump, using a zeotropic binary liquid column as reactor fitted with a standard blower (compressor) is extremely low, due to the low compression ratio. The compressor only has to produce a pressure high enough to overcome the liquid column hydraulic backpressure. This was already described in my paper [6] presented in July 2017. In a typical example calculation operating the reactor at 4 Bar Abs, the heat pump so formed may have a COP in excess of 200, making the heat of solution type of heat pump extremely cost-effective.

To increase the performance even higher, the standard compressor may be replaced with a vapor injector type compressor, as this type of compressor can easily deliver the required differential pressure. Using a injector type compressor like figure 4 above, have the added advantage that the power requirements to pump liquid is a lot less than compressing vapor. In addition, the high pressure drive vapor required by the injector nozzle, could utilize the regenerative concept of extracting the heat required for evaporation from the reactor hot bottom. This have the result that the fully regenerative REHOS heat pump so formed, have a calculated COP in the order of 1000, increasing the performance by a factor of 5.

Using a REHOS heat pump for a de-humidifier as sketched in figure 4, below, can extract water from the ambient air at an extremely low energy (and therefore cost) requirement. My own calculations prove to me a water from air extract cost of (for electricity) about 20% of the current municipal water cost. This could definitely me made into a commercial product for draught-stricken countries, and could be built on large scale also for agricultural use.

Apart from the REHOS cycle optimized for electricity production from ambient environmental heat, the Binary NH3-H2O Bubble Reactor can be used in multiple other applications like for example, agricultural water pumps powered by the ambient heat in the water it is pumping and many others.

The REHOS technology can really solve a lot of global interest problems, like low cost water in draught-stricken countries, low cost power for all across the globe, decarbonization of the power generation sector globally, as well as low cost non-fossil combustion mobility in land and air mobility. This list is only limited by our imagination......

References

- 1. Thermophysical Properties of NH3 + H2O solutions for the industrial design of absorption refrigeration equipment, by Dr Manuel R. Conde-Petit (M. Conde Engineering, Zurich Switzerland) 2004.
- 2. Evaluation of thermodynamic properties of ammonia-water mixture up to 100 bar for power application systems, by N. Shankar Ganesh and T. Srinivas of the Vellore Institute of Technology, Vellore-632014, India. This paper was published in Journal of Mechanical Engineering Research Vol. 3. (1), pp. 25-39, January, 2011.
- 3. Analysis of Absorber Operations for the 5 kW Ammonia/Water Combined Cycle by Sirisha Devi Govindaraju as Thesis Presented to the Graduate School of the University of Florida in Partial Fulfillment of the requirements for the Degree of Master of Science, 2005.
- 4. Thermodynamic Properties of Water including Vapor, Liquid and Solid Phases, by J.H. Keenan, F.G. Keeyes, P.G. Hill, J.G. Moore and published by John Wiley & Sons Inc 1969.
- 5. Thermodynamic Properties of Ammonia by Lester Haar and John S. Gallager, published in J. Phys. Chem. Ref. Data, Vol. 7, No. 3, 1978.
- 6. Paper presented at PowerGen Africa Conference July 2017 and published in the conference proceedings titled "Introducing a novel thermodynamic cycle (patent pending), for the economic power generation from recovered heat pumped from the huge global thermal energy reservoir called earth" by Johan Enslin, Heat Recovery Micro System CC. This paper is also accessible from my website http://www.heatrecovery.co.za/.cm4all/iproc.php/PowerGen-Africa 2017 Proceedings Speaker0 Session19149_1.pdf
- 7. A Paper titled "The Simplified REHOS Cycle.pdf" was written by Johan Enslin in August 2017 and published on my website http://www.heatrecovery.co.za/.cm4all/iproc.php/The Simplified REHOS Cycle.pdf
- 8. An Introduction to the Kalina Cycle, reprinted by Henry A. Mlcak, PE, first published in PWR- Vol.30, Proceedings of the International Joint Power Generation Conference, with editors: L. Kielasa and G.E. Weed, Book No. H01077-1996.
- 9. A Paper titled "Clarifying Process Parameters for the REHOS Cycle Concept_rev3.pdf" was written by Johan Enslin in October 2017 and published on my website <u>http://www.heatrecovery.co.za/.cm4all/iproc.php/Clarifying Process</u> Parameters for the REHOS Cycle Concept_rev3.pdf