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ENTROPY PRODUCTION MINIMIZATION OF A CRHP

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ABSTRACT

Compression resorption heat pumps (CRHP) are a promising option to upgrade waste heat from industry. One way to optimize a CRHP is by minimizing the entropy production rate of the heat pump; that is to minimize the lost work of the system. In this paper a CRHP operating with an ammonia-water mixture is analysed based on an application case from the chemical industry. First, a global approach is used to analyse the entropy production rate of each of the components in the heat pump cycle. Based on the result from the global approach the component with the maximum energy dissipation in the heat pump is identified, in this case the resorber. The resorber is therefore further analysed with a detailed thermodynamic state model and entropy production is calculated using the theory of non-equilibrium thermodynamics. Measures to reduce the non-uniformity of the entropy production are then proposed based on the theory of equipartition.

Keywords: Heat pumps, entropy production minimization, plate heat exchanger, resorber, non-equilibrium thermodynamics, ammonia-water.

1. INTRODUCTION

One way to decrease the emissions and the effects of global warming is to increase the energy efficiency of processes. For many industrial processes the energy efficiency can be greatly improved by upgrading waste streams with heat pumps. For certain applications, where there is a temperature glide of the heat source and/or the heat sink, compression- resorption heat pumps (CRHP) utilizing wet compression are especially an attractive option (van de Bor et al. 2015). This paper focuses on the optimization of the performance of such a heat pump. The energetic performance is defined by the thermodynamic coefficient of performance (*COP*). In order to locate the irreversibilities in the system an entropy production analysis of the cycle is performed. This entails that a model is developed to predict the rate of entropy production in a CRHP. The model is also applied to an example case from industry. The optimal concentration of the working fluid will be selected that causes the least entropy production in the system. The component of the cycle with the highest losses will be selected and modelled in detail. The theory of non-equilibrium thermodynamics is then applied to find the distribution of entropy production in that component. Measures to reduce the non-uniformity of the entropy production are proposed with the optimization criterion of equipartition of entropy production taken into account. This is done by relating the degree of non-ideality to operating conditions and physical characteristics of the system.

2. GLOBAL APPROACH

Entropy production is a measure of the effect of irreversibilities in a system. It is the most fundamental measure of energy-dissipation (Kjelstrup et al., 2010). The entropy production rate derived from the entropy rate balance for an open system can be expressed as follows:

$$\dot{\sigma} = \sum_k \dot{m}_k s_k - \sum_j \dot{m}_j s_j - \sum_i \frac{\dot{Q}_i}{T_i}$$

Eq. (1)

In the simple model treated in this section heat exchange with the environment is ignored, so the last term drops

out of equation (1). A compression-resorption cycle consists of four components: a compressor, a resorber, a desorber and a valve. The entropy production rate of each of these components is determined using the entropy rate balance for a control volume around the component. In this section the entropy production rate is determined for each component of the heat pump, for examples see Moran and Shapiro (2010). The result provides insight into the rate of work that is lost in each component. The components can be compared to each other and the components that dissipate the most energy, and thus require closest attention in an optimization approach, can be identified. Of course, further improvement of these components is required for an optimal system.

2. 1 Application and results

The application that is used as an example to demonstrate the models that are developed is the supply of heat to a high temperature water heat pump. A water stream of 7.59 kg/s should be heated by the resorber from 89.9 °C and 1.1 bar to saturated steam at 104 °C. This results in a resorber power demand of 17.5 MW. In the desorber a waste heat stream of dodecane is cooled from 137 °C to 40 °C (T_C = 360.7 K). The required mass and heat flow of the source stream depend on the performance of the compression-resorption heat pump. They will become larger as the performance of the heat pump increases. To identify the optimum ammonia concentration for this application the calculations of van de Bor et al. (2015) are executed, together with the computation method for properties of ammonia-water of Rattner and Garimella (2015). The approach uses the following assumptions.

• No pressure drops in the heat exchangers and pipes; No heat loss to surroundings; Isentropic efficiency of the compressor of 70 %; Minimum temperature difference between the fluids in the heat exchangers is 5 K

The results at the optimum concentration are listed in table 1. From the table it is clear that the largest entropy production of the components is in the resorber.

Table 1: Performance results of the CRHP integrated in the application. Working fluid: ammonia 70 %, water 30 % (molar)

η_{is}: 70 %, $T_0 = T_C$ = 360.7 K, $\dot{m}_R$ = 10.69 kg/s

State	T, K	h, kJ/kg	s, kJ/kgK	$\dot{\sigma}$, kW/K			
Compressor in	381.2	1491	4.98	Compressor:	3.24	$\dot{W}_{lost}$	4.28 MW
Compressor out	471.3	1961	5.28	Resorber:	5.29	η_{II}	15.0 %
Resorber out	379.8	324	1.43	Desorber:	1.58	COP	3.48
Desorber in	307.9	324	1.60	Valve:	1.75		
				Total	11.86		

3. LOCAL APPROACH

It is clear from the last section that the highest losses for the considered application are in the resorber, followed by the compressor. Therefore, in this work the resorber is modelled in more detail. For the development of the entropy production model of the resorber the approach of Kjelstrup et al. (2008, 2010) is the basis. In this approach entropy production is governed by irreversibilities, as is the case physically. Falling film absorption of an ammonia-water mixture in a plate heat exchanger is considered, see figure 1. To determine the total entropy production of a control volume the different contributions should all be added up together.

$$\dot{\sigma} = \dot{\sigma}^l + \dot{\sigma}^v + \dot{\sigma}^i + \dot{\sigma}^W + \dot{\sigma}^{cm}$$

Eq. (2)

Irreversible processes that occur are heat transfer, friction and mass transfer. In this study friction is neglected, because it is not expected to play an important role in the total entropy production rate. In the condensate film as well as in the vapour, entropy production may originate from heat transfer and mass transfer (Kjelstrup et al., 2008). Since there is no concentration gradient in the vapour, nor in the liquid (see figure 2), there is no mass transfer there. Only heat transfer produces entropy and this can be expressed with the following equation.

$$\dot{\sigma}^l(x) = J_q^{'l} \frac{\partial}{\partial x}\left(\frac{1}{T^l(x,y)}\right)$$

Eq. (3)

Integration of $\dot{\sigma}^l(x)$ over the distance dx yields the total entropy production rate in the liquid region. The same equation can be used for the wall and the cooling medium as well. Since there is no temperature gradient in the vapor there is also no entropy production from heat transfer in the vapor. According to Onsager's formulation of the second law, the fluxes are a linear combination of the forces. In this case there is only one flux-force pair, so the flux equation reduces to Fourier's law for the liquid:

$$J_q^{'l} = -\lambda^l \left(\frac{\partial T^l(x,y)}{\partial x}\right)$$

Eq.(4)

The conductivity λ^l of the liquid film is calculated using the method of Conde (2004). The temperature gradients in the liquid and the wall are constant and can be estimated with:

$$\frac{\partial T^l}{\partial x} = \frac{T^l(\delta_f, y) - T^l(0, y)}{\delta_f}$$

Eq. (5)

$$\frac{\partial T^W}{\partial x} = \frac{T^W(0, y) - T^W(-\delta_W, y)}{\delta_W}$$

Eq. (6)

Although there is evaporation taking place in the cooling medium, the entropy production rate is calculated in the same way as for a single fluid with Fourier's law as a rough approximation. The temperature gradient in the cooling medium is assumed to be zero, except for the liquid boundary layer along the wall. There, the temperature gradient is assumed to be (Aarts, 2016):

$$\frac{\partial T^{cm_b}}{\partial x} = \frac{T^{cm_b}(-\delta_W, y) - T^{cm_b}(-(\delta_W + \delta_b), y)}{\delta_b^4} 4(x + \delta_W + \delta_b)^3$$
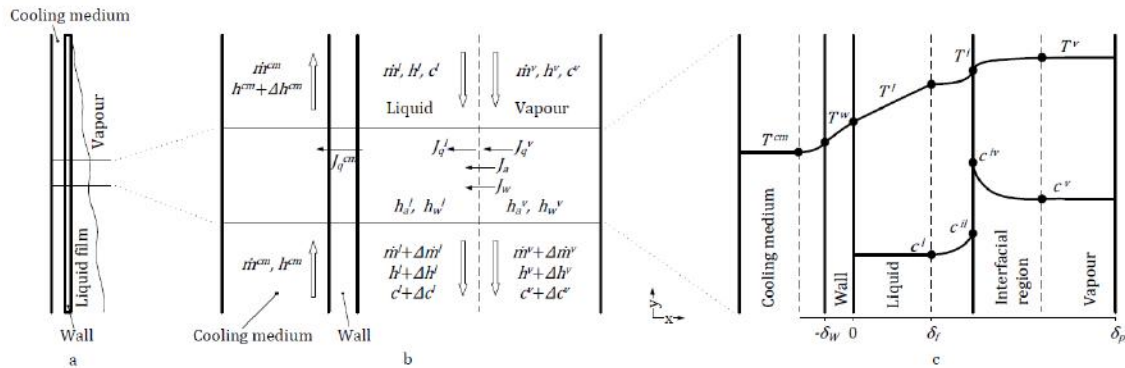
Eq. (7)

Figure 1: Three representations of the condensate film with increased detail from left to right. Parts are modified figures from Fernández-Seara et al. (2005, 2007).

The entropy production rate in the interface is derived by Kjelstrup and Bedeaux (2008) as follows:

$$\dot{\sigma}^i = J_q^{'v} \Delta_{v,l}\left(\frac{1}{T}\right) + J_a\left[-\frac{1}{T^l}\Delta_{v,l}\mu_{a,T}(T^l)\right] + J_w\left[-\frac{1}{T^l}\Delta_{v,l}\mu_{w,T}(T^l)\right]$$

Eq. (8)

Force equations can be now written in terms of resistivities as is elaborated on by Kjelstrup and Bedeaux (2008). Not all resistivities can be determined, because some of them depend on the condensation coefficient. The condensation coefficient is the fraction of molecules in the vapour that are absorbed into the liquid after collision at the interface. This coefficient is unknown for ammonia and somewhat controversial for water (Kjelstrup and Bedeaux, 2008). Instead it is suggested to write the forces in terms of temperature differences and concentration differences. And the fluxes are determined with a thermodynamic model based on that of Fernández-Seara et al. (2005, 2007). The heat transfer force can be expressed as:

$$\Delta_{v,l}\left(\frac{1}{T}\right) = \frac{T^v - T^l}{T^l T^v}$$

Eq. (9)

And the mass transfer driving forces can be derived from the chemical potential. For ammonia the driving force is the difference in chemical potential between the liquid and the vapor.

$$-\frac{1}{T^l}\Delta_{v,l}\mu_{w,T}(T^l) = -R\ln\left(\frac{(c_a\phi_a(T^l))_l}{(c_a\phi_a(T^l))_v}\right)$$

Eq. (10)

The driving force for water can be expressed in the same way. The fugacity coefficients are retrieved from Refprop (Lemmon et al., 2013).

The heat and mass fluxes are calculated with energy and mass balances, using the strategy of a model that was developed for vertical tubular absorbers by Fernández-Seara et al. (2005). Figure 2 shows a flow diagram of the iterative loops that are solved for each cell. The heat transfer coefficient of the cooling medium is obtained with a prediction method introduced by Amalfi et al. (2016). In the wall and in the liquid film it is assumed that the heat transfer takes place only by conduction. The film thickness is expressed as (Aarts, 2016):

$$\delta_f = \frac{\delta_p}{2}\frac{y^{1/4}}{L_p^{1/4}}$$

Eq. (11)

The heat transfer coefficient of the liquid and vapor side of the vapor-liquid interface are obtained with a correlation from Seader and Henley (2006) for flow across a flat place of length y. The Reynolds number that is used for the correlation is based on the length of the plate instead of the hydraulic diameter. The mass transfer coefficients are obtained using the Chilton and Colburn analogy (1934).
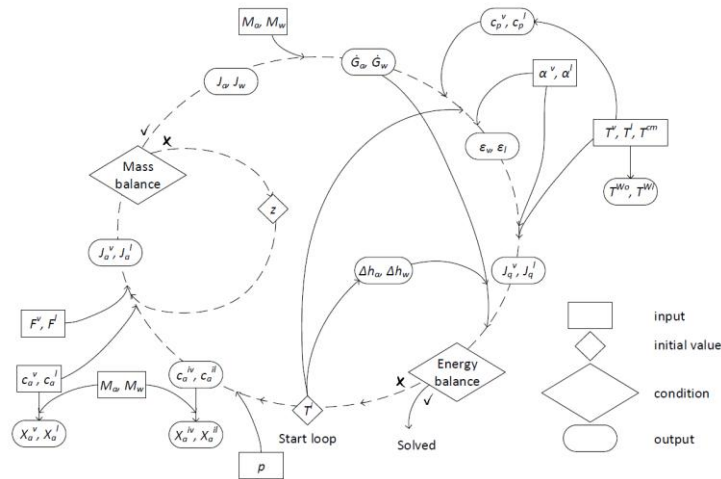
Figure 2: Flow diagram of a computational model of a segment of the resorber.

3.1 Results and discussion

The model inputs used for the resorber calculations are listed in table 2. In figure 3 the temperature profiles and the local entropy production is shown. It can be deduced that the entropy production in the resorber is not uniformly distributed. It is high at the beginning when the forces from heat and mass transfer are high.

Table 2: Resorber model inputs

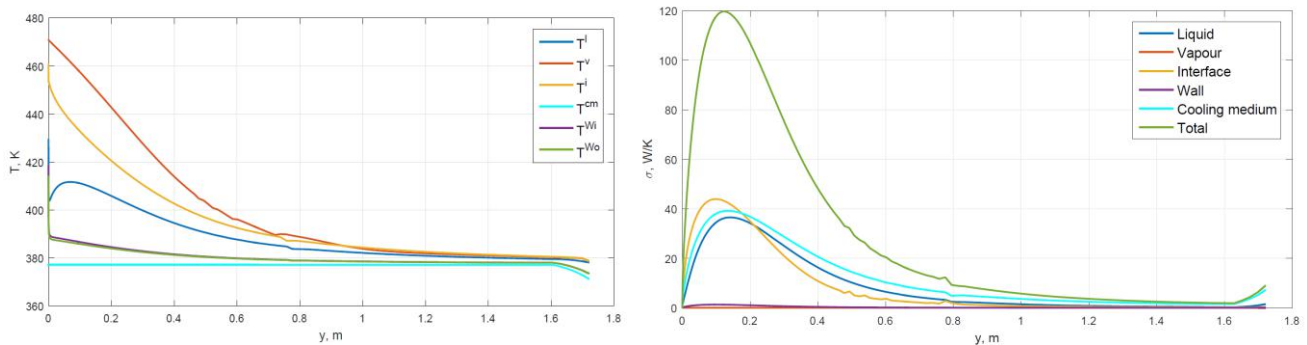| Plate charactersitics				Initial points		Other	
N_p	4250	β	50°	c_a^v	0.70 mol/mol	p	43.8 bar
A_p	1.3 m^2	α	2 mm	c_a^l	0.26 mol/mol	$\dot{m}_R$	10.7 kg/s
W_p	1.75 m	Λ	12.6 mm	T^v	477.6 K	$\dot{m}_H$	7.6 kg/s
δ_p	4 mm	λ_W	15W/m K	T^l	427.2 K	M_a	17 g/mol
δ_w	1 mm			T^{cm}	377.2 K	M_w	18 g/mol

Figure 3: The temperature profiles (left) and the local entropy production (right) along the plate.

Tondeur and Kvaalen (1987) studied equipartition of entropy production. They stated that *for a given duty, the best configuration of an exchanger, contactor, or separator is that in which the entropy production rate is most uniformly distributed.* They proceed to show mathematically, using the theory of non-equilibrium thermodynamics, for an example and in general, that the entropy production of an equipartitioned process is always smaller than of an arbitrary process when the size of the equipment and the duration of the process is kept constant. Based on their concept new configurations are suggested that may possibly increase the uniformity of the entropy production. The first configuration is to divide the process into stages: starting in the first stage with

a small mass flow and in each stage adding new hot vapour to the working fluid. Other configuration is to gradually add the vapor mass flow along the heat exchanger. The results of the local entropy production can be seen in figure 4. Even though the entropy production is more uniform along the plate the required area is larger than before. Since the inlet and outlet conditions are held constant this does also not affect the *COP* of the cycle. In the concept by Tondeur and Kvaalen (1987) the duration of the process was assumed to be a constant which is not the case here. The overall performance is therefore worse.
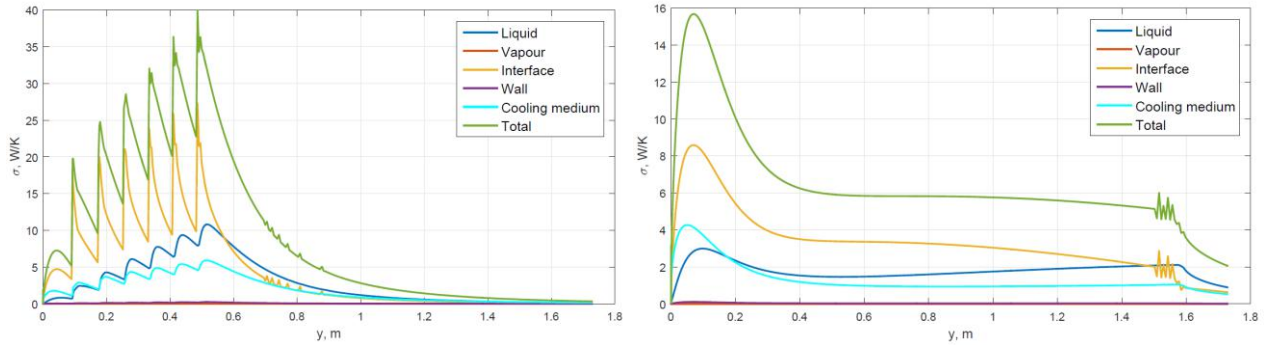

Figure 4: local entropy production along the length of the plate when the vapor mass flow is gradually added in 7 stages (left) or gradually along the heat exchanger (right).

Now the configuration is therefore kept unchanged while the duration of the process is sought to be increased to decrease the area of the heat exchanger. The resulted vapor mass flows along the length of a plate for varied plate width and plate spacing are shown in figure 5. The results confirm that with a given duty, a given total entropy production and a constant entropy production distribution, a decreased cross-sectional area in the flow direction leads to higher velocities and higher exchange rates and thus a smaller heat exchanger area. The limit of this measure will be determined by the pressure drop that is accepted for a certain application.
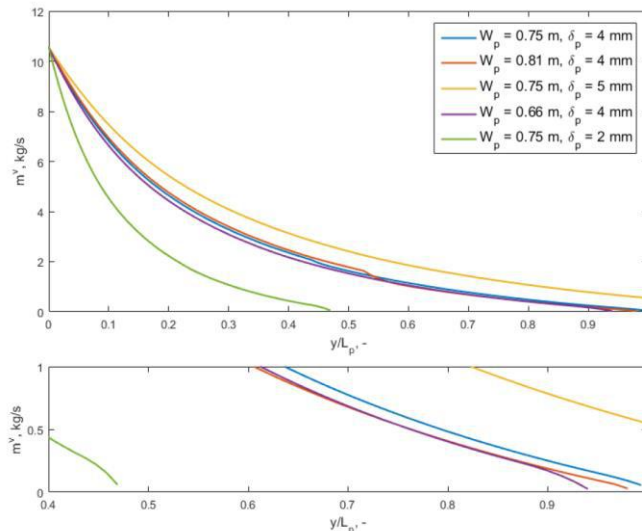

Figure 5: Vapor mass flows along the dimensionless plate length where the plate width and plate spacings have been adjusted. Bottom: detailed showing of the outlet region of the heat exchanger.

4. CONCLUSIONS AND RECOMMENDATIONS

The entropy production of the CRHP was calculated for an application from the industry and the resorber was identified as the component with the highest losses. A detailed model was therefore constructed to analyse locally the entropy production in the resorber. From that model it can be deduced that the entropy production in the resorber is not uniformly distributed. It is high at the beginning when the forces from heat and mass transfer are high. Alternative heat exchanger configurations were investigated to try to reduce this non-uniformity. One

of the alternatives investigated was to divide the process in stages and add only part of the vapor flow in the first stage, and then adding more hot-vapor in every stage until the original mass flow is reached. This however resulted in a larger heat exchanger area hence larger equipment costs. Adding continuously the vapor throughout the heat exchanger gave similar results. A reduction of the cross-sectional area of the flow direction in the heat exchanger causes the required heat exchanger area to decrease. However, the pressure drop increases and it is therefore the limiting factor. It is recommended to validate the results of the proposed model with experiments. Additionally, innovative configurations of the heat exchanger may be sought after to increase the uniformity of the distribution of the entropy production rate. However, such configuration will only cause the required area to decrease when the duration of the process remains unchanged.

ACKNOWLEDGEMENTS

NOMENCLATURE

A	Area, m^2	η	Efficiency, -
a	Amplitude of plate wave, m	ϕ	Fugacity coefficient, -
c	Molar concentration, $mol\ mol^{-1}$	Λ	Wavelength of a plate, m
c_p	Specific heat capacity at constant pressure, $J\ kg^{-1}\ K^{-1}$	λ	Thermal conductivity, $W\ m^{-1}\ K^{-1}$
COP	Coefficient of performance, -	μ	Chemical potential $J\ mol^{-1}$
F	Mass transfer coefficient, $mol\ s^{-1}\ m^{-2}$	$\dot{\sigma}$	Entropy production rate, $W\ K^{-1}$
$\dot{G}$	Mass flux, $kg\ s^{-1}\ m^{-2}$		*Sub- and superscripts*
h	Specific enthalpy, $J\ kg^{-1}$	'	Measurable
J	Flux, Wm^{-2} or $mols^{-1}m^{-2}$	*0*	Reference
L	Length, m	*II*	Second law
$\dot{m}$	Mass flow, $kg\ s^{-1}$	*a*	Ammonia
M	Molar mass, $kg\ mol^{-1}$	*b*	Boundary layer
p	Pressure, Pa	*C*	Source (application side)
N	Number, -	*cm*	Cooling medium
$\dot{Q}$	Heat transfer rate, W	*f*	film
R	Universal gas costant, $J\ K^{-1}\ mol^{-1}$	*H*	Sink (application side)
s	Specific entropy, $J\ kg^{-1}\ K^{-1}$	*i*	Interface
T	Temperature, K	*i, j, k*	Number of contribution
$\dot{W}$	Work, W	*is*	Isentropic
W	Width, m	*l*	Liquid
x	Length coordinate perpendicular to flow direction, m/ Mass concentration, $kg\ kg^{-1}$	*p*	Plate
y	Length coordinate in flow direction, m	*q*	Related to heat transfer
Z	Molar flux ratio (ammonia to total), -	*R*	Refrigerant, working fluid
	Greek symbols	*rev*	Reversible cycle
α	Heat transfer coefficient, $Wm^{-2}K^{-1}$	*v*	vapor
β	Chevron angle, °	*W*	Wall
Δ	Difference	*w*	*Water*

| δ | Thickness / distance, m | | *Abbreviations* |
| ε | Heat transfer correction factor, - | CRHP | Compression-resorption heat pump |

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