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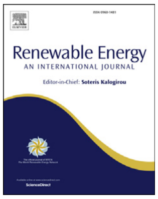

An alternative approach towards absorption heat pump working pair screening

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ABSTRACT

The successful market penetration of modern absorption heat pumps (AHP) today is critically dependent on their thermodynamic performance as well as other key factors like cost, reliability and inherent safety. Conventional AHPs have a proven record in the first two aspects but crucial shortcomings in the last two. For this reason it has been imperative to search for alternative working pairs that could potentially provide comparable performance while also satisfying the rest of the conditions to the best extent possible. As part of a systematic approach towards this direction, a detailed cycle analysis was performed, utilizing an idealized AHP system containing a real working pair, which enabled the identification of five dimensionless parameters and key thermophysical properties that influence the system's thermodynamic efficiency and the circulation ratio. In order to validate those findings, these parameters were calculated and compared between conventional and alternative AHP refrigerants. It turned out that low molecular weight ratios between absorbent and refrigerant have a beneficial effect on both coefficient of performance and the circulation ratio. Furthermore, both the refrigerant acentric factor and the absorbent vaporization enthalpy shall be minimized to obtain better performance.

1. Introduction

Progress in the field of heat pumps has been steadily increasing over the last decade, driven primarily by a growing market demand, which in turn has being “fueled” by volatile oil and gas prices. Moreover, stricter international climate protection and safety regulations have been methodically pushing the industry towards new research areas, in pursuit of better performing and environmentally-friendlier substances. Thermally driven heat pumps on the other hand, belonged for many decades to a niche market, focused primarily on industrial or commercial applications, mainly due to the fact that such systems were bulky, capital intensive and often deemed unsafe for a domestic environment. Today however, this picture is slowly changing as breakthroughs in manufacturing processes are opening new possibilities for small scale efficient residential units.

Commercially available absorption systems have traditionally been dominated by ammonia/water and water/lithium bromide (LiBr) working pairs. Although very efficient systems in terms of thermodynamic performance, significant disadvantages or flaws have slowed their adoption and commercialization. More specifically, ammonia/water heat pumps present considerable hazards due to ammonia's toxicity, corrosiveness and high system pressure whereas water/LiBr systems are considered safer but also plagued by severe temperature limitations and even higher corrosion problems [8].

Alternative absorption heat pump working pairs have already been extensively reviewed by Donnellan et al. (2015), Shrikirin et al. (2001), and Sun et al. (2012) [5,17,18] with main focus on replacements for water, as the absorbent, in the case of ammonia, and LiBr in the case of water. A smaller part of the studies concerns refrigerant replacement with organic substances like alcohols, amines and hydrocarbons. Additionally, over the last few years organic ionic liquids have been gaining momentum as potential absorbent candidates. Nevertheless, despite all efforts there is still no recognized alternative working pair with the potential to exceed the success of the two conventional pairs [8]. For this reason, a number of researchers have worked on pinpointing the fundamental working pair criteria that influence thermodynamic efficiency in order to facilitate the identification of alternative working pairs.

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Nomenclature

COP	coefficient of performance
c_p	average mass specific heat capacity [J/kg K]
CR	circulation ratio
f	function
H	mass specific enthalpy [J/kg]
K_1-K_5	dimensionless parameters
M_i	molecular weight of component i (i = 1–2)
$\dot{m}_j$	mass flow of stream j (j = 1–10) [kg/s]
p	vapor pressure [Pa]
$\dot{Q}$	heat flow [W]
RV	relative volatility [-]
SSC	specific solution circulation [l/s kW]
T	temperature [K]
$X_{i,j}$	liquid molar fraction of component i in stream j
$Y_{i,j}$	vapor molar fraction of component i in stream j

Greek letters

$\gamma_{i,j}$	activity coefficient of component i in stream j
$\zeta_{i,j}$	vapor mass fraction of component i in stream j
$\xi_{i,j}$	liquid mass fraction of component i in stream j
ρ	mass density
ω	acentric factor

Subscripts

1	component 1, refrigerant
2	component 2, absorbent
1–10	state points in Fig. 1
abs	absorber conditions
c	critical point
ce	condenser-evaporator average conditions
cool	cooling
con	condenser conditions
des	desorption
eva	evaporator conditions
gen	generator conditions
genin	generator inlet conditions
genout	generator outlet conditions
HP	heat pump
shex	solution heat exchanger conditions
sol	solution
tot	total
v	vaporization
xs	excess mixing property

Iedema (1982) [10] performed a quasi-quantitative analysis of an idealized single and double stage absorption heat pump. Among some of the major assumptions for the working pair were that specific heat capacities, vaporization enthalpies and excess mixing enthalpies were all independent from temperature. The conclusions concerning the thermodynamic performance pointed towards a low ratio of excess mixing enthalpy to vaporization enthalpy, a high vaporization enthalpy, a strong negative deviation from Raoult's law and low solution specific heat capacities. Hodgett (1982) [9] presented a simplified approach for the coefficient of performance (COP) that depended on three dimensionless parameters, the ratio of excess mixing enthalpy to vaporization enthalpy, the ratio of pump work to vaporization enthalpy and the generator sensible heat duty to vaporization enthalpy. The final requirements for an efficient working pair included, a high solution density, a large concentration difference between rich and poor solution, high concentrations for both rich and poor solution and a low solution specific heat capacity.

Perez-Blanco (1984) [15] investigated the influence of non-ideal solutions' negative deviation from Raoult's law on the COP and the circulation ratio (CR) of ammonia single stage absorption heat pumps. The conclusions were that there is an optimum temperature and concentration dependence of the activity coefficients and that too strong negative deviations are undesirable. Furthermore, it is stated that the absorbent specific heat capacity must be as low as possible. Eisa & Holland (1987) [6] reviewed previous literature works and collected a list of desirable properties for the working pair. Specifically, the refrigerant should exhibit a high vaporization enthalpy, a low heat capacity per unit mass and low boiling point. The absorbent should have as low a vapor pressure as possible, a low heat capacity per unit mass and create solutions with the refrigerant with high negative deviations from Raoult's law, low viscosity and density. Furthermore, they also investigated the influence of various ions in water–salt solutions on the heat of solution, vapor pressure lowering and solubility.

Narodoslawsky et al. (1988) [13] followed an analytical method based partly on semi-empirical relations and concluded that high performance working pairs should show high refrigerant vaporization enthalpies at normal boiling point and an extremum of excess mixing Gibbs free energy between −1000 and −2000 J/mol preferably located at high refrigerant concentrations. Additionally, it is argued that the absorbent should also have a high boiling point vaporization enthalpy, a low acentric factor (definition can be found in the appendix Eq. (48)), a low reduced boiling point, a high critical temperature and low critical pressure. On the other hand, the refrigerant should have a high acentric factor, a high reduced boiling point, a low critical temperature and a high critical pressure.

Nowaczyk (1991) [14] carried out a literature review summarizing that, the refrigerant should have a high specific vaporization enthalpy, a high critical temperature, a flat vapor pressure curve. In addition, the solution with the absorbent should have a high negative deviation from Raoult's law, a low excess mixing enthalpy, low specific heat capacity, a low viscosity, a high density and a high difference in boiling points.

Alefeld, Radermacher and Hwang (1994) [1] pointed out that the refrigerant should exhibit a low heat capacity to vaporization enthalpy (per unit mass) ratio in order to obtain a high efficiency. Additionally, the resulting pressure ratios between the high pressure and low pressure sides should be low and the refrigerant volumetric heat capacity should be as high as possible.

However, the lack of success of these partially qualitative screening processes signifies the need for an alternative quantitative approach. Accordingly, this study gives a hand towards improving the quantitative understanding of the multitude of parameters that influence the performance of absorption heat pumps/chillers. An AHP model that made very few assumptions for the working pair properties, but did consider a perfect mechanical apparatus is introduced. This entailed no external heat losses, no friction or pressure losses. The system, a simple single-effect absorption heat pump, comprised an evaporator, an absorber, a solution pump, a solution heat exchanger, a generator with an optional rectifier column, a condenser, an expansion and a solution valve (Fig. 1). All components were assumed to contain infinite heat and mass transfer surfaces and therefore were always able to

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