Applied Energy 213 (2018) 179–194

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Absorption refrigeration cycles based on ionic liquids: Refrigerant/absorbent selection by thermodynamic and process analysis

Daniel Moreno, Víctor R. Ferro, Juan de Riva, Rubén Santiago, Cristian Moya, Marcos Larriba, José Palomar*

Sección de Ingeniería Química, Universidad Autónoma de Madrid, 28049 Madrid, Spain

HIGHLIGHTS

- Absorption refrigeration based on ionic liquids is analyzed by process simulation.
- COSMO-based/Aspen Hysys methodology is applied to perform process calculations.
- COSMO-RS allows selecting best thermodynamic pairs among 8 refrigerants and 900 ILs.
- Selection of correct refrigerant/absorbent pair is revealed a key of cycle efficiency.
- Optimum operating ranges are proposed for different refrigerant/IL pairs.

ARTICLE INFO

Keywords:
Refrigeration
Absorption
Ionic liquids
COSMO-RS
Aspen HYSYS

ABSTRACT

A COSMO-based/Aspen HYSYS methodology has been used to perform an extensive thermodynamic evaluation of potential application of ionic liquids (ILs) to absorption refrigeration cycles. By applying this *a priori* methodology, 7200 systems, formed by 900 ILs and 8 refrigerants, representative of available commercial/cation and refrigerant, were evaluated, which would be otherwise unviable due to the lack of experimental data. Firstly, COSMO-RS analysis was carried out for the preliminary selection of suitable ILs as absorbents for each refrigerant, by means of predicted values of Henry's Law constants of refrigerants in ILs. Selected ILs were then introduced in Aspen HYSYS simulator database by using the molecular information by COSMO-RS method. The reliability of COSMO-based/Aspen HYSYS calculations was successfully validated by comparison to available experimental data (> 2700 points) of pure and mixture properties of absorbent-refrigerant systems. Then, the performance of selected ILs (and other proposed in the bibliography) in absorption refrigeration cycles was evaluated by process simulations (> 230 refrigerant/IL pairs studied at 60 different operating conditions) using COSMO-based/Aspen HYSYS methodology. Cycle efficiency was analyzed in terms of the coefficient of performance (COP), solution circulation ratio (*f* ratio) and the total mass flow pumped from the absorber to the generator, a new parameter proposed to compare the results obtained with different refrigerants. COSMO-based/Aspen HYSYS methodology allowed the selection of adequate refrigerant-absorbent pairs (refrigerant with high cooling capacities and IL with absorption capacity) competitive to conventional systems as H_2O/LiBr or NH_3/H_2O. Furthermore, the analysis of operating condition effects by COSMO-based/Aspen HYSYS methodology allows selecting refrigerant/IL pairs with maximum efficiency in the cycle for a fixed cooling temperature, revealing additional advantage of the applications of IL in absorption refrigeration technologies.

1. Introduction

Nowadays, cooling systems are an essential technology in the domestic and industrial sectors, such as food preservation, air conditioning, air separation, natural gas liquefaction, and ice production [1]. The two most common refrigeration systems used in domestic and industrial applications are compression and absorption refrigeration systems. In compression cycles, an electrical compressor is used to increase the pressure of the refrigerant. In contrast, in absorption refrigeration systems, the refrigerant is absorbed into another fluid (absorbent) and pumped to the condenser pressure [2]. In the generator (Fig. 1), a heating source provides the energy required to vaporize the refrigerant. Because of this, the main energy consumption of an absorption cycle is cheaper than the electric power used in compression

* Corresponding author.
E-mail address: pepe.palomar@uam.es (J. Palomar).

https://doi.org/10.1016/j.apenergy.2018.01.034
Received 6 November 2017; Received in revised form 10 January 2018; Accepted 11 January 2018

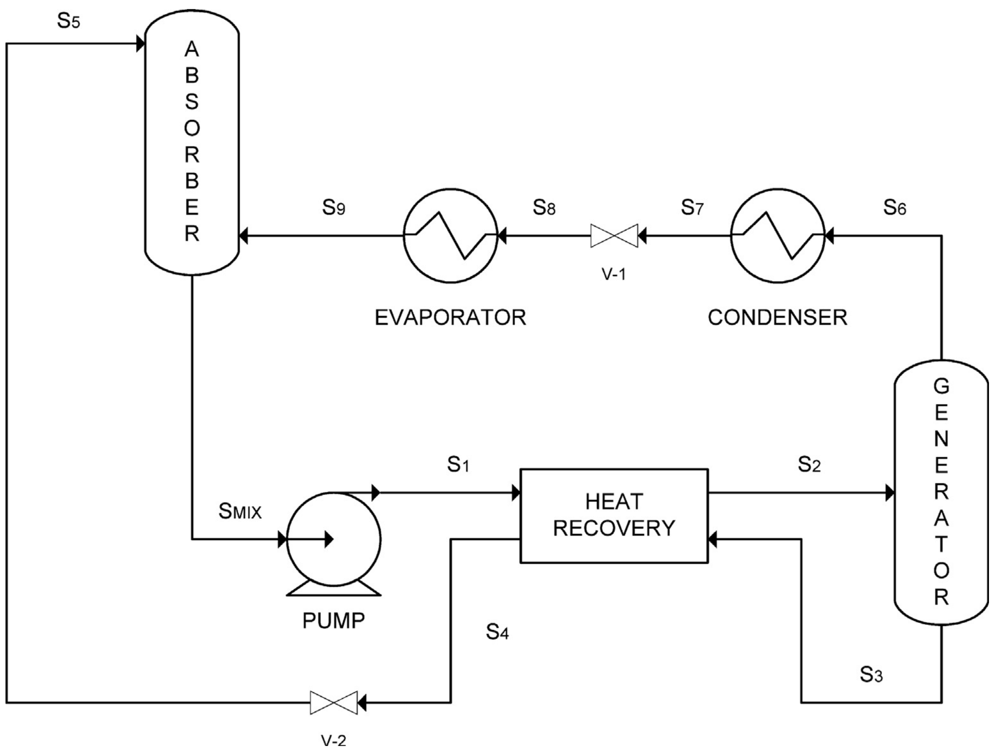

Fig. 1. Flowsheet of a single effect absorption refrigeration cycle.

cycles. In absorption refrigeration, the use of thermal energy to generate the refrigerant vapor allows the use of residual energy (e.g., combustion gases, low quality steam, etc.) and renewable energy (solar, geothermal) [3,4]. For this reason, absorption refrigeration cycles are becoming an attractive alternative to compression cycles.

Regarding the fluids involved in absorption refrigeration system, the refrigerant selection is crucial because it determines the operating conditions and cycle performance [5,6]. Water is a good refrigerant because it presents high enthalpy of vaporization and low molar mass, consequently water presents high cooling capacity per mass unit of refrigerant. Water is a nontoxic, nonflammable compound; however, it has a high triple point temperature (0 °C) and the requirement to operate at pressures below atmospheric due to its low vapor pressure are the main disadvantages of using water as refrigerant [5]. Absorption refrigeration cycles using H_2O as refrigerant and LiBr as absorbent present high performance, due to the high solubility of H_2O in the LiBr mixture and the high-water mass cooling capacity (high vaporization enthalpy). The main disadvantages of H_2O-LiBr systems are the crystallization of the mixture in the rich-absorbent solution at low temperatures, the low-pressure of the system and the impossibility to work at temperatures below 0 °C. As alternative refrigerant/absorbent pair, NH_3/H_2O system can work at temperatures below 0 °C. In fact, NH_3/H_2O absorption system is used in refrigeration applications at −77 °C and NH_3 as refrigerant allows working at pressures near 4–20 bar [7]. The main problem with this mixture is the small difference in volatility between the compounds, which may imply the use of a rectifier to prevent the presence of absorbent into the evaporator [8]. Other compounds evaluated as refrigerant in absorption cycles are alcohols with short alkyl chains (methanol, ethanol) and fluoroalcohols, which work at low pressures. Examples of fluoroalcohols used as refrigerants are 2,2,2-trifluoroethanol (TFE), 2,2,3,3-tetrafluoropronanol and hexafluoroisopropanol, which are non-corrosive and non-combustible and have appropriate thermal characteristics [6]. On the other hand, hydrofluorocarbons (HFCs) are widely used in compression refrigeration systems since they have good technical properties allowing moderate operating pressures but these compounds contribute to global warming. The selection of the refrigerant can also influence the required operations involved the refrigeration cycle. In fact, using water as refrigerant involves working at temperatures above 0 °C and negative system pressure; in addition, water/LiBr crystallization must be prevented. If the selected refrigerant is ammonia, depending on the chosen absorbent a rectifier may be necessary. Regarding the properties of the absorbent, it should be a fluid with a low vapor pressure to prevent its evaporation in the generator, thermally and chemically stable with a low freezing temperature and low viscosity to reduce the transport energy expenses and improve the mass and energy transfer. In addition, the refrigerant must present high solubility in the selected absorbent to minimize the operating and investment costs. In sum, it is well stated that the adequate selection of both the refrigerant and the absorbent are crucial for the suitable performance of the absorption refrigeration system [2,5,6,9].

Consequently, the research in this field is focused on finding more efficient and environmentally friendly absorption refrigeration compounds, searching for alternative refrigerant/absorbent pairs with improved properties [8,10,11]. Ionic liquids (ILs) are potential candidates to replace traditional absorbents, due to their high absorption capacity of common refrigerants, very low vapor pressure and good thermal stability [10,12–14]. The low volatility of ILs allows for a good refrigerant/absorbent separation in the generator, consequently advanced separation equipment is not necessary to achieve the separation of the pure refrigerant [15]. In this regard, Shiflett and Yokozeki patented the application of ILs as absorbents in absorption refrigeration systems [11]. They proposed using Freon, H_2O, NH_3 or CO_2 as refrigerants and ILs, such as H_2O/[emim][BF_4] [16], NH_3/[N_{11H}(EtOH)][MeCOO], as absorbents (see Table S1 for IL nomenclature) [15]. These studies included the evaluation of the thermodynamic performance of the absorption refrigeration cycles in terms of the solution circulation ratio (*f* ratio) and the coefficient of performance (COP) as common thermodynamic efficiency parameters of the cycle usually used. The results revealed that the selection of the IL had a significant influence on the performance of the system. Finally, they compared their results with a conventional system and found that the COP was slightly lower that the H_2O/LiBr system, concluding than ILs may be good absorbents for refrigeration systems. Kim et al. [17] evaluated additional refrigerant/IL