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Performance implications of chemical absorption for the carbon-dioxide-cofluid refrigeration cycle

George Mozurkewich [a,*], Luke D. Simoni [b], Mark A. Stadtherr [b], William F. Schneider [b,c]

[a] Zelenidyne, 1161 Laurel Loop NE, Albuquerque, NM 87122, USA
[b] Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA
[c] Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

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ABSTRACT

In a CO_2-cofluid refrigeration cycle, CO_2 condensation and evaporation are replaced by absorption into and out of a non-volatile liquid ("cofluid"). This paper investigates whether the refrigeration performance of such a cycle can be improved in theory by using a cofluid that exhibits chemical affinity for CO_2. A Langmuir-like model is used to represent the thermodynamics of CO_2 absorption, and steady-state performance metrics are computed by solving a set of physically based equations. Chemically absorbing cofluids having sufficiently strong affinity for CO_2 are predicted to have higher specific cooling capacity and higher coefficient of performance (COP) than physical cofluids and also higher COP than transcritical CO_2. The useful range of chemical absorption strength is limited by practical considerations like desirable operating pressures.

Implications de la performance de l'absorption chimique pour le cycle frigorifique au dioxyde de carbone mélangé à un liquide non-volatile absorbant (*cofluid*)

Absorption chimique : Liquide ionique ; Dioxyde de carbone ; Compression de vapeur ; Compression humide ; Modéle thermodynamique

* *Corresponding author.*
E-mail address: gm@zelenidyne.com (G. Mozurkewich).
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Nomenclature

C	heat-capacity rate (W K^{-1})
C_p	heat capacity (J K^{-1})
h	enthalpy (J mol^{-1})
K	equilibrium constant
$\dot{m}$	molar flow rate (mol s^{-1})
N	number of moles
Q_c	cooling power (W)
q_c	specific cooling capacity (J mol^{-1})
P	pressure (bar)
s	entropy (J mol^{-1} K^{-1})
T	temperature (K)
v	molar volume (m^3 mol^{-1})
W	compressor work (W)
x	mole fraction
Δh°	standard enthalpy of absorption (J mol^{-1})
Δs°	standard entropy of absorption (J mol^{-1} K^{-1})
ε	heat-exchanger effectiveness
θ	mole ratio, chemical absorption
ξ	mole ratio, physical absorption
ϕ	fugacity coefficient

Subscripts

c	chemical
D	desorber
ihx	internal heat exchanger
p	physical
L	liquid phase
R	resorber
V	vapor phase

1. Introduction

Refrigeration technology is in flux because of environmental concerns, among them the high global warming impact of mainstream refrigerants. CO_2 is a natural, alternative refrigerant having low Global Warming Potential (Lorentzen and Pettersen, 1993). Although CO_2 can be used in a transcritical vapor-compression cycle, it has a lower coefficient of performance (COP) than established refrigerants and requires much higher operating pressures (McEnaney et al., 1999; Brown et al., 2002). Prior work has attempted to mitigate these deficiencies by circulating CO_2 in tandem with a low-volatility absorbing liquid. The resulting "cofluid" cycle replaces CO_2 condensation and evaporation with physical absorption of CO_2 into and desorption out of the cofluid:

$$CO_2(\text{vap}) \underset{des}{\overset{abs}{\rightleftharpoons}} CO_2(\text{phys}) \quad (1)$$

This concept was first adapted to CO_2 by Groll and Kruse (1992) using acetone as the absorbent, though the concept is considerably older (see Stokar and Trepp (1987) and references therein). Subsequent modeling attained very good agreement with the CO_2-acetone experiments (Groll, 1997). Additional candidate cofluids have included a range of organic liquids, for which CO_2-cofluid refrigeration systems have been shown to operate at pressures lower than pure CO_2 with satisfactory cooling capacity; measured COPs are however not competitive with COPs of mainstream refrigerants (Spauschus et al., 1999; Niu et al., 2007). The COP limitation can be traced to the limited affinity of organic solvents for CO_2. Previous analysis of this CO_2-cofluid cycle (Mozurkewich et al., 2002) found that cycle performance is closely tied to the partial molar enthalpy of CO_2 absorption and that, for common organic co-fluids, this enthalpy of physical absorption is exothermic (negative) and spans a rather narrow range around -12 kJ mol^{-1}.

Ionic liquids (ILs) constitute another class of absorbing liquids that could be used in a cofluid cycle. ILs have been widely proposed for use in heat-driven absorption refrigeration (and heat pump) cycles, as reviewed by Zheng et al. (2014), and a hybrid cycle combining heat-driven and mechanical compression has been patented (Shiflett and Yokozeki, 2014). The refrigerant member of proposed refrigerant–absorber pairs has included H_2O, NH_3, CO_2 (Sen and Paolucci, 2006), and conventional vapor-compression refrigerants. Absorption of CO_2 in the proposed pairs tends to occur via physical processes, with IL–CO_2 absorption enthalpies falling in the range -6 to -18 kJ mol^{-1} (Martín and Bermejo, 2010). These low enthalpies in combination with the relatively high molecular weights of typical ILs leads to high ratios of IL flow relative to refrigerant flow, contributing to low COP. Whether in the context of heat-driven absorption refrigeration or in the context of the CO_2 cofluid cycle of primary interest here, there seems to be a need for stronger absorbers.

One approach to increasing absorption strength and potentially improving the performance of the cofluid cycle would be to introduce a chemically reactive moiety into the cofluid:

$$CO_2(\text{vap}) + A(\text{l}) \underset{des}{\overset{abs}{\rightleftharpoons}} ACO_2(\text{chem}) \quad (2)$$

Absorbents that chemically react with CO_2 are well known; aqueous amine solutions, for instance, have been widely studied for use as reversible CO_2 capture solvents (Rochelle, 2009). Typically amine absorption enthalpies are on the order of -80 kJ mol^{-1}, implying desorption temperatures >100 °C, unsuitable for a cofluid cycle. Recently ionic liquid (IL) solvents have been discovered that chemically absorb CO_2 in one-to-one proportion with much more modest absorption enthalpies, -50 kJ mol^{-1} or less (Gurkan et al., 2010). These IL solvents have virtually no vapor pressure, have good lubrication properties, are thermally robust, and thus have the potential to be more satisfactory cofluids.

The choice of optimal cofluid involves a compromise. Stronger absorption increases the cooling effect per mole of CO_2 circulated, improving cooling capacity and lowering operating pressures, thereby increasing COP. For too strong an absorbent, however, desorption of CO_2 will require excessively high temperature, and operating pressures will become impractically low. The goal of this work is to systematically explore this trade-off. We take a theoretical approach,