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Energy analysis of two-phase secondary refrigeration in steady-state operation, part 1: Global optimization and leading parameter

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ABSTRACT

A great deal of attention is paid to secondary refrigeration as a means of reducing excessively high emissions of refrigerants (most of which have a potent greenhouse effect) due to leaks in large cooling units. Among the environmentally friendly fluids that can be used in secondary circuits for transporting and storing cold, hydrate slurries offer the advantage of significant latent heats of fusion associated with good fluidity. Research programs have focused attention on hydrate systems, including CO₂, TBPB (tetra*n*-butyl-phosphonium-bromide), and mixed CO₂-TBPB hydrates. In addition to feasibility concerns, energy efficiency is also a crucial concern requiring an objective analysis of the improvements likely to result from these new materials. An impartial framework was thus constructed based on the principles of optimization methods. This approach was applied to these three hydrate slurries as well as to the well-known ice slurry for comparison purposes. A numerical model of secondary refrigeration system is teady state was built, on the basis of which optimized systems subjected to common external constraints can be designed for each slurry according to its thermophysical properties. Global performance can then be compared on a sound basis, which also makes it possible to identify the hydrate property that is most influential on energetic performance. Part 2 of this study is dedicated to exergy analysis and phase change kinetics.

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1. Introduction

One of the challenges facing the refrigeration industry is the need for drastic reduction of its contribution to global warming. The Global Warming Potential (GWP) of current refrigerant fluids is on the order of several thousand [1,2], yet large cooling units unfortunately experience significant leakage rates. After adding in the indirect effects due to energy consumption, this industry contributes as much as 8% of all greenhouse gas emissions. Research on new refrigerants with low GWP is underway, but secondary refrigeration is an already existing solution: when distributing cold via a loop containing an environmentally friendly fluid, the volume of refrigerant as well as leaks can be severely limited. Until recently, the choice of a secondary fluid was essentially limited to chilled water and ice slurry. Chilled water transports sensible heat, which requires significant flow rates, while the latent heat transported by

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https://doi.org/10.1016/j.energy.2018.07.055 0360-5442/© 2018 Elsevier Ltd. All rights reserved. ice slurries is delivered at temperatures below 0 °C. However, a new class of phase-change materials is emerging for refrigeration applications: hydrate slurries. Well-known in the petroleum industry, semi-clathrate hydrates are ice-like crystals where H₂O molecules form cages around host molecules. These molecules can be a gas (CH₄, CO₂, alkanes, SO₂, etc.) or salts like tetra-*n*-butyl-ammonium-, or phosphonium-bromide (respectively TBAB and TBPB). Mixed hydrates may also form, e.g. with CO₂-TBPB [3]. These two-phase solid-liquid materials offer several advantages: the transport of latent heat [4,5], good fluidity [6], and such a wide variety that the phase-change temperature can be adapted to the design application [7]. Hydrate slurries are thus good options for secondary refrigeration [8–10] or cold storage [7,11]. Their rheology [12,13], thermal properties [14,15], and phase-change kinetics [11,16,17] have been studied extensively. Apart from these characterization studies, performance analyses of secondary refrigeration systems using hydrate slurries are still scarce [18–21]. They may invoke various features as efficiency arguments, including significant latent heat of fusion, fusion temperature, low viscosity, rapid

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Nomenclature		$\eta \ \sigma$	efficiency (isentropic) [–] carbon dioxide solubility in aqueous phase [kg.kg ⁻¹]
Usual notations (T for temperature, P for pressure, \dot{Q} for heat		Indexes	
fluxes, Re for Reynolds number, etc.) are not recalled here		0	initial liquid solution $(W + A)$
Α	heat-transfer area [m ²]	1-7	refer to points in Fig. 1
СОР	Coefficient Of Performance of the primary cooling	Α	additive
	unit	С	condenser
D	hydraulic diameter [m]	CD	carbon dioxide
f	Fanning friction factor [-]	Ε	evaporator
L	distance between the primary cooling unit and the	eq	equilibrium
	end-user [m]	f	fusion
К, п	rheology parameter for non-Newtonian fluids	G	gas phase
и	flow velocity [m.s ⁻¹]	HX∙	referred to the corresponding heat exchanger, C, E or
U	overall heat transfer coefficient [W.m ⁻² .K ⁻¹]		U
x	additive concentration in its aqueous solution	Ι	insulation
	[kg.kg ⁻¹]	in	inlet of a HX section
Χ	solid mass fraction in the slurry $[kg.kg^{-1}]$	L	liquid phase
у	axial position [m]	Р	slurry pump
Y	component fraction in the solid phase $[kg.kg^{-1}]$	PC	primary compressor
		S	solid phase (crystals)
Greek symbols		Т	total
χ	mass fraction in the total flow $[kg.kg^{-1}]$	U	user
ϕ	crystal volume fraction in the slurry $[m^3.m^{-3}]$	W	Water (H ₂ O)

kinetics, etc. This makes it difficult to compare the various slurries on common criteria.

The purpose of this article is to build a thermodynamic framework for evaluating the energy efficiency of secondary fluids and comparing them on a sound and impartial basis. The approach adopts the fundamental principle of optimization, i.e. minimization of an objective function under given constraints equally applied to each system under comparison. Four slurries were considered, three with either CO₂-hydrate, TBPB-hydrate, or CO₂-TBPB mixed hydrate, as well as the ice slurry for comparison purposes. These four slurries were chosen for their variety of thermodynamic properties, enthalpy of fusion, viscosity and rheological behavior, melting temperature, and presence or absence of gaseous CO₂. Rather than simply ranking these slurries, one purpose of this study is to ascertain which slurry property has the leading influence on energy efficiency by using thermodynamics-based arguments. A numerical model of secondary refrigeration system in steady-state was built. For each of the four slurries, this model was used for designing the system that minimizes the energy consumption and fulfills the prescribed constraints. The four systems can then be compared on a fair basis.

2. Thermodynamic framework

In thermodynamic terms, a secondary refrigeration loop simply transports heat from the *user*, e.g. an air-conditioned room or food needing to be preserved, to the *primary cooling* unit, or more precisely to its evaporator. The loop itself is merely a dissipative process, while the primary unit converts electricity into cold production. As the notion of energy efficiency only makes sense for energy conversion processes, energy analysis of secondary refrigeration can be relevant only when it considers the whole system, secondary loop plus primary unit, as presented in Fig. 1. This framework contains all the basic components of secondary refrigeration. The loop (123451) transports cold to the user over the distance *L*. Ice- or hydrate-crystals are generated in the *HXE* heat exchanger, which also is the evaporator of the cooling unit. The



Fig. 1. Sketch of a secondary refrigeration process. 123451: slurry loop; *P*: slurry circulation-pump; *HXU, HXE* and *HXC*: heat exchangers on the user's side, at the evaporator and at the condenser of the primary cooling unit, respectively; *PC*: primary compressor; *V*: throttling valve; 67: return line for gaseous CO_2 and *CG*: gas compressor (when involved). *L* = distance between user and primary cooling unit.

slurry circulates in the loop via the pump *P* and receives the heat flux \dot{Q}_I from ambient air through the thermal insulation of the secondary circuit. Most of these crystals melt in the user's heat exchanger *HXU*. The cooling unit consumes mechanical power for its primary compressor (*PC*) and rejects heat outdoors through its condenser (*HXC*). When the hydrate contains CO₂, crystal fusion produces gaseous CO₂. This gas is separated from the slurry at the outlet of *HXU*; it is re-pressurized in the gas-compressor *C_G* and circulated via the line (67) toward the *HXE*, where it contributes to formation of new hydrates.

When applied to this global system, the First Law in steady state gives the following balances:

$$\dot{Q}_E = \dot{Q}_U + \dot{Q}_I + \dot{W}_P + \dot{W}_G \tag{1}$$

$$\dot{Q}_{C} = \dot{Q}_{E} + \dot{W}_{PC} = \dot{Q}_{E} \cdot \left(1 + COP^{-1}\right)$$
(2)

The COP of the primary cooling unit (\dot{Q}_E/\dot{W}_{PC}) is related to the

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