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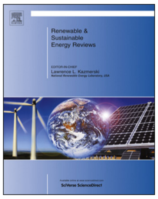

Clathrate hydrate technology for cold storage in air conditioning systems

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ABSTRACT

Clathrate hydrate is an attractive technology for cold storage applications. It offers a high cold storage density and elevates the phase change temperature compared to water. It offers better heat transfer properties and improved cyclic stability compared to eutectic salts. This paper reviews previous work on clathrate hydrates as phase change materials (PCMs) for cold storage air conditioning applications. Three aspects have been focused on: the characteristics of clathrate hydrates, modification of clathrate hydrate properties, and practical utilization of clathrate hydrates as cold storage media. Specifically, refrigerant clathrate hydrates, CO_2 hydrates, hydrocarbon clathrate hydrates and multi-component clathrate hydrates are introduced. Technologies to decrease equilibrium pressure, increase dissociation enthalpy, accelerate formation process, decrease supercooling extent and enhance gas solubility are summarized. Clathrate hydrates based cold storage air conditioning systems that transport cooling in a manner of fixed container as well as in hydrate slurry are reviewed, and optimizing methods of system performance are studied. Finally, four features of clathrate hydrates, namely the self-preservation effect, memory effect, gas conversion and hydrate structure transformation are discussed.

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1. Introduction

Air conditioners equipped with cold storage offers a means to alleviate peak loading on electricity grids and to utilize power in off peak periods. Water and ice are the most commonly used cold storage media, for their low price and safety. However, liquid water has an intrinsic low cold storage density, thus a large storage volume is needed to achieve the required cold storage capacity. Ice melts and freezes at 0 °C, therefore the chiller has to work at low evaporating temperatures, resulting in an inferior Coefficient of Performance (CoP). By contrast, clathrate hydrates commonly have a latent heat of phase change close to that of ice, and a phase change temperature of 5–12 °C that matches well with the operating conditions of conventional air conditioning systems. Moreover, clathrate hydrate could enable direct contact charging and discharging, thus dramatically improving the heat transfer efficiency to and from a cold store. Clathrate hydrate manifests obvious advantages over conventional cold storage media (Table 1), thus is considered to be a promising candidate for cold storage and has sprouted numerous investigations [1].

Clathrate hydrates are crystalline solid compounds formed from water and gas molecules. The gas molecules (guest) are trapped in cages that are composed of hydrogen-bounded water molecules (host) [2]. The guest gas is usually a refrigerant gas, natural gas or other small gas molecule. The former is specified in this work as the gas of conventional refrigerant, namely chloro-fluoro-carbons (CFCs), hydro-chloro-fluoro-carbons (HCFCs) or hydro-fluoro-carbons (HFCs); the latter refers to terrestrial gases and mineral gases, typically including CO_2, N_2 and hydrocarbon gases [3]. Molecular properties of some featured guest gases are listed in Table 2 [4].

The aim of this work is to present a review of research progress on clathrate hydrates as PCMs in cold storage air conditioning systems, concerning the formation/dissociation conditions, optimizations and applications of various clathrate hydrates. Refrigerant clathrate hydrates, CO_2 clathrate hydrates, hydrocarbon clathrate hydrates, and multi-component clathrate hydrates are introduced in detail. Technologies to decrease the equilibrium pressure, increase dissociation enthalpy, accelerate formation process, decrease super-cooling effect and enhance gas solubility are analyzed. Moreover, clathrate hydrate based cold storage air conditioning systems that transport cooling in a manner of fixed container as well as clathrate hydrate slurry are studied for practical system design and optimization.

2. Clathrate hydrates

Fundamental studies of clathrate hydrates generally concerns the following properties:

- the phase equilibrium conditions, for the compatibility with the operating conditions of cold storage systems;
- the phase change enthalpy, for evaluating the cold storage capacity;
- the hydrate nucleation and growth rate, for predicting the cold storage rate.

Van der Waals–Platteeuw solid solution theory is commonly used for theoretical studies of phase equilibrium behavior of clathrate hydrates [5]; while for experimental measurements, an apparatus including of a high-pressure cell was usually employed [6,7]. The dissociation enthalpy can be calculated by Clapeyron equation based on experimental data, or directly measured by an insulated boil-off chamber in a constant temperature bath [8].

2.1. Refrigerant clathrate hydrates

Most refrigerant gases can form clathrate hydrates under supportive conditions. However, CFCs and HCFCs have been gradually prohibited due to their ozone depletion potential and greenhouse impact. In contrast, HFCs clathrate hydrates have been widely studied since 1992 when CFCs phase out began to be implemented [9]. Equilibrium data of HFC-134a, HFC-125 and HFC-143a hydrate were measured by Hashimoto et al. [7], showing that HFC-134a hydrate had the lowest equilibrium pressure. The dissociation enthalpies of the three HFCs hydrates were all about

Table 1
Performance and economical features of different cold storage media.

Cold storage medium	Water	Ice	Eutectic salt	Clathrate hydrates
Phase change temperature	0–10	0	8–12	5–12
CoP of refrigerator	1	0.6–0.7	0.92–0.95	0.89–1
Heat transfer performance	Superior	Medium	Inferior	Superior
Investment	< 0.6	1	1.3–2	1.2–1.5

Table 2
Molecular properties of guest gases.

Guest	Structure	Hydrate dissociation pressure at 273 K (MPa)	Melting temperature (K)	Boiling temperature (K)	V (A^3)	Max length (A)
CH_3F	sI	0.2	131	195	33.5	4.7
CH_2F_2	sI	0.2	137	221	38.9	5.2
CHF_3	sI	0.3	118	191	42.9	5.2
CF_4	sI	4.2	89	145	49.4	5.3
CH_4	sI	2.5	91	112	28.6	4.3
C_2H_6	sI	0.5	90	185	45.6	5.6
C_3H_8	sII	0.2	85	231	62.4	6.7
CO_2	sI	1.2	195	\	33.3	5.4
H_2S	sI	0.1	188	213	25.2	3.8
O_2	sII	11.9	55	90	20.6	3.9
N_2	sII	15.9	63	77	21.7	3.9
Ar	sII	10.5	84	87	27.8	1.9
Kr	sII	1.5	116	120	34.5	2.0
Xe	sI	0.2	161	165	42.2	2.2