Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Energy Conversion and Management 47 (2006) 2974–2982
ENERGY CONVERSION & MANAGEMENT
www.elsevier.com/locate/enconman

Influences of additives on the gas hydrate cool storage process in a new gas hydrate cool storage system

Yuehong Bi [a,b], Tingwei Guo [c], Tingying Zhu [c], Liang Zhang [c], Lingen Chen [b,*]

[a] *Institute of Civil and Architectural Engineering, Beijing University of Technology, Beijing 100022, PR China*
[b] *Postgraduate School, Naval University of Engineering, Wuhan 430033, PR China*
[c] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China*

Received 24 August 2005; received in revised form 1 March 2006; accepted 22 March 2006
Available online 22 May 2006

Abstract

Experimental research on the crystallization process of the gas hydrate HCFC141b is performed for this paper. The influences of different proportions of calcium hypochlorite or benzenesulfonic acid sodium salt on the crystallization process are studied. The results show that the degree of subcooling of formation is obviously decreased, and the formation rate of the gas hydrate is greatly accelerated by adding reasonable proportions of the additives. The degree of subcooling of formation decreases 0.78 °C by adding benzenesulfonic acid sodium salt of 0.03%, and the formation rate of the gas hydrate increases 0.2 g/s by adding calcium hypochlorite of 0.08%. In the cool storage system, clathrate hydrates can be formed effectively, and thermal energy can be stored efficiently. When adding benzenesulfonic acid sodium salt of 0.03%, the cold energy stored is 4.74 MJ, and the cool storage density is 206.07 MJ/m^3. The performance of this cool storage system can meet the needs of practical air conditioning engineering.

Keywords: Gas hydrate; Additive; Crystallization process; Cool storage; Cool storage materials; Experimental study

1. Introduction

Cool storage technology gradually developed with the appearance of air conditioning systems using mechanical refrigeration, and the development history of cool storage air conditioning technology is the development history of cool storage materials [1–6]. The cool storage materials in common use include water, ice, eutectic salt etc. Water as a cool storage medium utilizes sensible heat, whereas ice and eutectic salt utilize the latent heat of phase change. The phase change temperature of ice is lower, the latent heat of phase change of the eutectic salt is smaller, and the latter causes serious corrosion. These shortcomings urge research and development of new types of high temperature phase change cool storage materials. In 1982, American scientists suggested taking freon and forming a hydrate as a cool storage medium in air conditioning systems, and

* Corresponding author. Tel.: +86 27 83615046; fax: +86 27 83638709.
E-mail addresses: lgchenna@yahoo.com, lingenchen@hotmail.com (L. Chen).

0196-8904/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.enconman.2006.03.027

thereafter, the so called "gas hydrate warm ice" technology has been rapidly developed in the USA and Japan [7].

A gas hydrate, also called clathrate, is an ice like crystalline compound that occur when water molecules form a cage like structure around smaller "guest molecules" of gas or easily volatile liquid at certain temperature and pressure [8]. Hydrate crystals can form from the interaction between most refrigerants and water under a hydrate formable temperature (5–12 °C) condition. The phase change latent heat of the gas hydrate is similar to that of ice [9]. Therefore, most refrigerants are considered as the most ideal cool storage medium in air conditioning systems. Chatti et al. [10] reviewed the benefits and drawbacks of clathrate hydrates in their areas of interest in detail.

The ideal critical decomposition temperature and pressure of alternative refrigerant R141b are 8.44 °C and 43.0 kPa, respectively, and the latent heat of phase change is 344 kJ/kg. It is adapted to engineering applications because of its low saturated vapor pressure and low cost, and its negative pressure character avoids the difficulty of a pressure vessel. However, the degree of subcooling of the gas hydrate R141b formation is relatively large, and the rate of crystallization is slow. In recent years, a new type of gas hydrate cool storage system has been built by Guo et al. [11] and Lv et al. [12]. In the system, the inner heat exchange/outer crystallization technology and the integrated condenser/evaporator structure design were adopted. By experimental research with this system, one has found that the outer crystallizer can provide a larger cool storage density and higher efficiency of the charge and discharge processes only in a certain range of volume flow rate of the crystallizer, and the influence of additives and surfactants is one of the most important research works in the field of gas hydrate cool storage [13–16]. In this paper, the influences of different proportions of calcium hypochlorite or benzenesulfonic acid sodium salt on the crystallization process of the gas hydrate HCFC141b are experimentally studied.

2. Experimental system and experimental process

Gas hydrate R141b cool storage experiments are performed using an efficient gas hydrate cool storage experimental system, which is illustrated in Fig. 1. This experimental system includes cold/hot reservoirs, a gas hydrate cool storage tank and a data acquisition system.

The cold/hot reservoirs are composed of a chiller and cold/hot water tanks. A 30% glycol solution is used as the secondary refrigerant. Its volume flow rate is measured through a LZB-15 rotameter (range ability: 40–400 L/h, precision degree: 2.5). It supplies the cooling solution at the charge stage or the warm solution at the discharge stage for the cool storage tank.

The cool storage tank is a flat cube of net volume 23.52 L. The inner and outer shells of the tank are stainless steel. The interval between the inner and outer shell is 50 mm and is filled with polyurethane as the insulation material. Two double layer glass observation windows of 50 mm width and 600 mm height at the

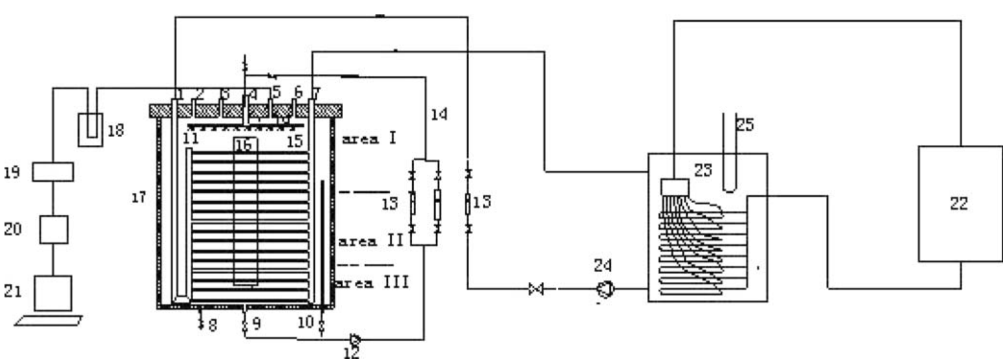

Fig. 1. Schematic of gas hydrate cool storage experimental system. (1) Inlet of second refrigerant; (2) vacuumizing joint; (3) sealed pins for connecting thermocouples; (4) sprinkler vertical pipe; (5) sealed pins for connecting thermocouples; (6) joint of vacuum pressure gauge; (7) outlet of second refrigerant; (8) liquid ejection pipe; (9)/(10) drop pipe; (11) sprinkler pipe; (12) crystallizer; (13) flow meter; (14) circumfluence pipe; (15) cool storage coil; (16) window; (17) cool storage tank; (18) ice bottle; (19) scan card; (20) digital voltmeter; (21) computer; (22) chiller; (23) cold/hot water tank; (24) second refrigerant pump and (25) electric heater.