

Performance analysis of hydrate-based refrigeration system



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ABSTRACT

A novel refrigeration system called hydrate-based refrigeration system was proposed, and its performance was analyzed by using Aspen Plus. The system consisted of five parts, compressor/pump, hydrate formation tank, hydrate dissociation tank, expander and gas/liquid separator. Compared with conventional compression refrigeration cycle, hydrate-based refrigeration system uses hydrate formation tank to replace condenser to achieve heat release; hydrate dissociation tank for evaporator to achieve refrigeration. There were three types of the hydrate-based refrigeration system, which refrigeration cycles were analyzed through using Aspen Plus. Methyl fluoride, cyclopentane/monofluoro cyclopentane and water were used to form hydrate as the working fluids. For the system of methyl fluoride, cyclopentane and water, the highest coefficient of performance was 8.01–8.97. For the system of methyl fluoride, monofluoro cyclopentane and water, the best coefficient of performance was 7.58–8.49. Based on it, the relation of temperature and entropy during refrigeration process for hydrate-based refrigeration system was analyzed. Its coefficient of performance was 2–4 times of the conventional compression refrigeration.

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1. Introduction

The economic growth and technology development of every country depended on the energy [1]. The available energy reflected the living quality [2]. With the energy crisis, the energy-efficient technology was extremely urgent. At present, heating, ventilation, and air-conditioning had consumed a large amount of energy [3]. Chinese total electricity consumption was 5.55 trillion kW h in 2015, rising 0.5% year-to-year, and the air conditioning accounted for above 30% of total electricity consumption [4]. Air conditioning system had a great energy-saving potential.

The main commercial air conditioning in society includes vapor compression refrigeration system, absorption refrigeration and ejector refrigeration currently. In air-conditioning system, energy-saving technology includes heat exchanger design [5], refrigerants selecting, and so on. There were three generations of refrigerants. The earliest refrigerants were ethyl ether, carbon dioxide, ammonia and sulfur dioxide. The second generation was Freon, such as CFCs, HCFCs, and HFCs. Sag and Ersoy [6] reported the COP of an ejector expansion refrigeration system of tetrafluoroethane (R134a) worked as refrigerants was 2.6–3.0. Liu et al. [7] reported the coefficient of performance (COP) of the refrigera-

tion system of difluoromethane/hexafluoropropane (R32/R236fa) worked as refrigerants was 2.42–4.14. Jafari et al. [8] reported the COP of the refrigeration system of R134a worked as refrigerants was 2.6–4.1. The third generation was working pairs, such as lithium bromide-water, lithium chloride-water, ammonia-water, whose COP was still low [9]. For the working pair of the lithium chloride-water, its COP was just 0.589–0.891 [10]. And for the working pair of the ammonia-water, Singh et al. reported its COP was just 0.707–0.776 [11], while Gogoi and Konwar reported its COP was 0.697–0.877 [12]. The newest refrigerant was the materials of 0 ODP, low GWP. COP of the refrigeration system was improved little through the above methods. The cycle was the key of the improvement of the COP. There were few researches on the change of the cycle. And the COP of the new cycle of absorption refrigeration was low.

In recent years some researchers begun to utilize hydrate to change the cooling cycle. Hydrate was mainly applied on cool storage air conditionings design, flow performance, thermodynamic and capability of cold storage. Douzet et al. [13] designed a real size air-conditioning system using a tetrabutyl ammonium bromide (TBAB) semiclathrate hydrate slurry as secondary two-phase refrigerant. Delahaye et al. [14,15] studied the rheological properties of tetra-n-butyl phosphonium bromide (TBPB) and carbon dioxide (CO₂) worked as the cold storage media. Lin et al. [16] made research on the thermodynamic properties of semiclathrate

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hydrate, and Youssef et al. [17] studied the thermodynamic properties of CO₂ hydrate and TBPB semiclathrate hydrate. Zhang et al. [18] calculated the COP of cold storage by TBAB hydrate slurry was 1.95–2.50 for homogeneous storage, and 2.00–2.95 for heterogeneous storage. Hydrate refrigeration systems reduced the energy loss caused by cool supplied indirectly. Kim et al. [19] made the LCC analysis of CO₂ hydrate cooling system. Fournaison et al. [20,21] reported some gas hydrates have a high dissociation enthalpy around 500 kJ kg_{water}⁻¹, and additives (such as sodium dodecyl sulfate) could significantly improve the flow properties of the slurry. The research found that COP of hydrate cool storage air conditioner was small, and it was not applicable for cooling at the high ambient temperature above 303 K.

Nowadays a novel hydrate refrigeration system was proposed [22]. Cool supply was achieved through hydrate dissociation at 278–298 K. Heat release was achieved by hydrate formation above 303 K. Ohmura et al. [23] found that R32, cyclopentane (CP) and TBAB mixture hydrate could form at 0.027–1.544 MPa and at temperatures from 280.4 K to 289.7 K, which meant CP can be used as efficient additive to moderate hydrate formation condition. Imai et al. [24] reported CP could moderate formation and dissociation condition of clathrate hydrate, which meant clathrate hydrate formation temperature achieved higher than 303 K under the pressure of lower than 5 MPa. Satoshi et al. [25,26] verified that the methyl fluoride (R41) and CP mixture hydrate can form at 293.7 K/305.9 K, 0.336 MPa/2.988 MPa. Hydrate can be used as hydrate-based refrigeration system (HBRS), which means R41 and CP or monofluoro cyclopentane (FCP) mixture can used as the working medium of hydrate refrigeration system. However, present HBRS can only achieve heat release at about 298 K, which COP is of 1–7. The COP is difficult to satisfy with the commercial

demand under the condition of clean medium working as the refrigerants. At present work, based on the reported concept of hydrate refrigeration, the paper proposed a novel cycle of hydrate cooling. Gas and liquids in working fluids were pressurized.6(h0.02eressu7 the rematicomperandemproyP) and c(efficies)1220(t)259pe(fA-t)TJTAnkred81

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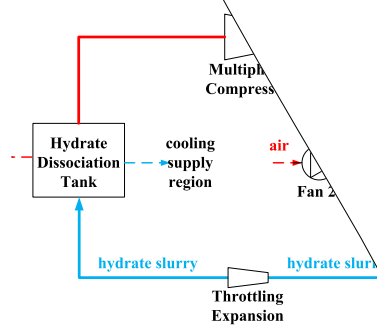
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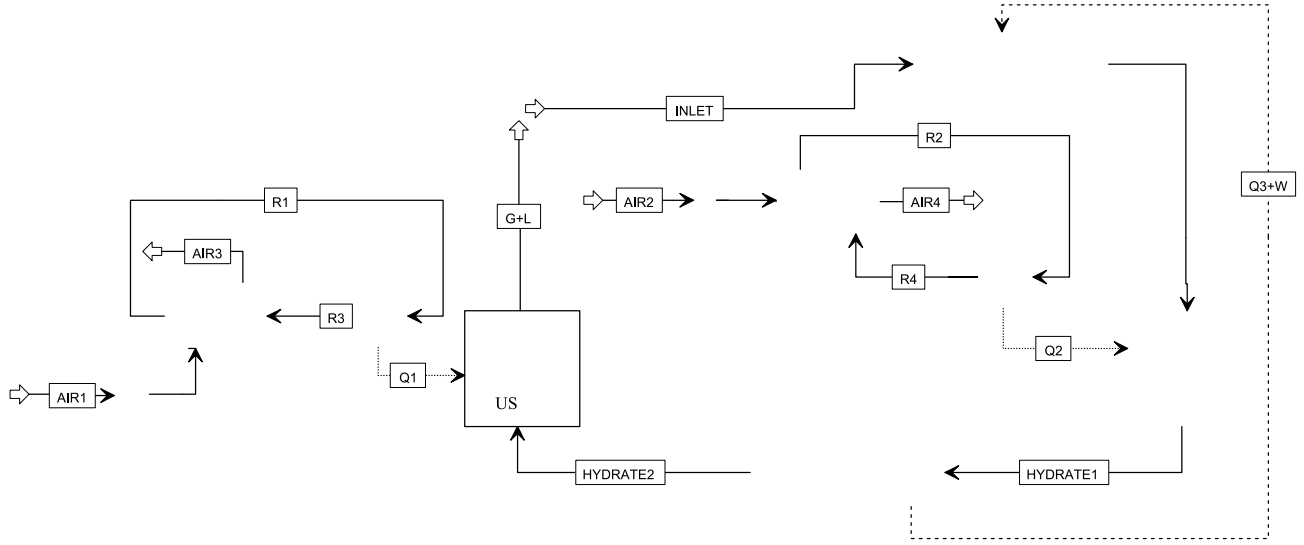
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3. Working m

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MPa) for the system



1. Flow sheet of HBRS-A.



ties of materials simulated by using Aspen Plus was shown in Table 1.

$$Q_{cc} = \frac{\alpha c_a \rho_a Sh (T_{am} - T_{in})}{3600} \quad (1)$$

$$G_{hydrate,n} = \frac{3600 Q_{cc}}{\Delta H_{diss}} \quad (2)$$

$$G_{R41} = \frac{G_{hydrate,n} M_{R41} n_{R41}}{M_{hydrate}} \quad (3)$$

$$G_{H_2O,n} = \frac{G_{hydrate,n} M_{H_2O} n_{H_2O}}{M_{hydrate}} \quad (4)$$

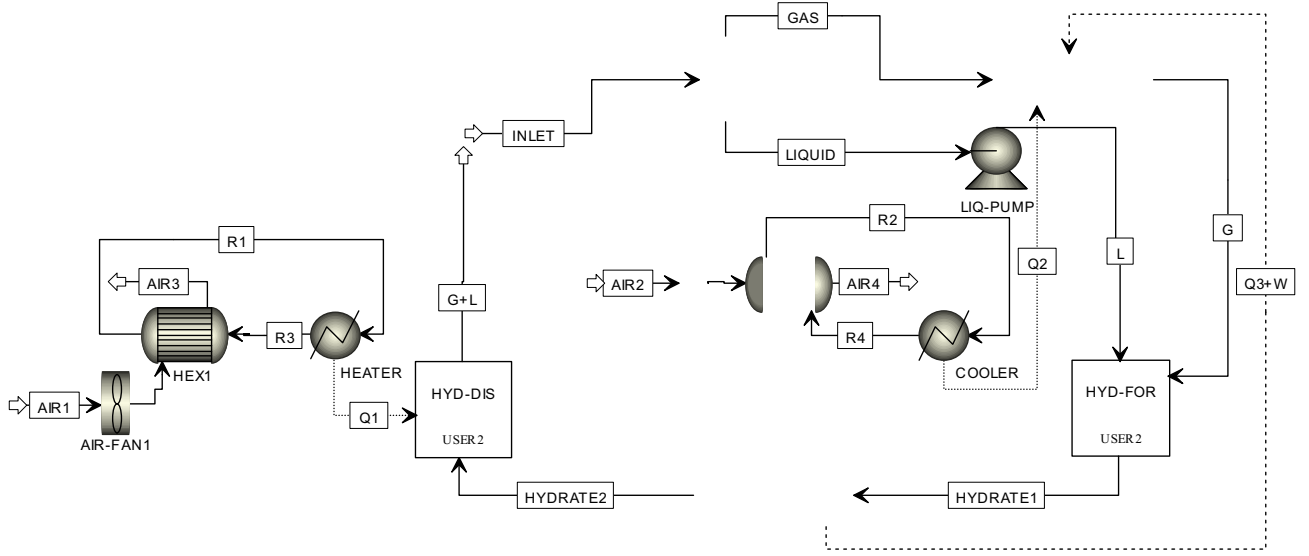
$$G_{H_2O} = G_{H_2O,n} + \frac{G_{hydrate,n} (1 - \eta_{hydrate})}{\eta_{hydrate}} \quad (5)$$

$$G_{CP} = G_{H_2O} W_{CP} \quad (6)$$

$$G_{FCP} = G_{H_2O} W_{FCP} \quad (7)$$

2.5. Coefficient of performance calculation

In general, the efficiency of any cooling system was measured by the coefficient of performance (COP), which was a measure of how efficiently the input energy was transformed to a useful output cooling effect [29]. It was defined as the ratio of cooling capacity to the energy supplied to the system [30]. In the HBRS, power-consuming units included the compressor, the pump, multiphase compressor and the air fan. COP of the HBRS was determined as Eqs. (8)–(10). For HBRS-A and HBRS-B, power consuming parts included gas compressor, liquid pump, air fan and separator. For HBRS-C, power consuming parts were consists of multiphase compressor and air fan. The paper used Aspen Plus to simulate cool



$$COP = \frac{Q_{cc}}{W} \quad (8)$$

$$COP = \frac{Q_{cc}}{W_c + W_p + W_{af} + W_s} \quad (9)$$

$$COP = \frac{Q_{cc}}{W_{mc} + W_{af}} \quad (10)$$

3. Results and discussion

The paper discussed the COP of the HBRs-A, HBRs-B and HBRs-C, which was up to 8. And this paper also analysis the changes of temperature and entropy (T-S) during the cooling process.

3.1. Coefficient of performance results

COP was the main index to reflect the capacity of refrigeration systems. The effect of temperature and unit on the COP of HBRs was as follow.

3.1.1. Temperature factors

COP of different types of HBRs was changed with the ambient temperature. Table 2 showed the COP of the simulation of HBRs-A, B, C under the different temperatures with various refrigerants.

supply process in HBRs, and attained power consumption of each units. And then calculate the COP of different types of HBRs.

Table 2
COP of the simulation under the different conditions.

Temperature/K	COP					
	R41 + CP + H ₂ O			R41 + FCP + H ₂ O		
	HBRS-A	HBRS-B	HBRS-C	HBRS-A	HBRS-B	HBRS-C
298	4.6	7.81	8.32	6.56	7.34	7.58
299	5.64	7.77	8.01	7.06	7.52	7.75
300	6.98	7.99	8.23	7.16	7.7	7.93
301	7.5	8	8.23	7.24	7.71	7.92
302	8.05	8.24	8.47	7.25	7.9	8.11
303	5.95	8.48	8.7	7.35	8.1	8.3
304	7.01	8.74	8.97	7.42	8.29	8.5
305	7.66	8.61	8.42	7.58	8.13	8.13
306	7.57	8.16	8.35	7.33	7.85	8.03
307	7.36	8.15	8.31	6.78	7.65	7.79
308	7.3	8.14	8.29	6.45	7.61	7.74

For HBRS-C in the system of R41, CP and H₂O, it showed the best performance, whose COP was up to 8.01–8.97, while 7.77–8.74 for HBRS-B and 4.60–8.05 for HBRS-A. In R41 + CP + H₂O system, the maximum value of COP of the HBRS-B and HBRS-C occurred under the condition of 304 K, while 302 K for HBRS-A, it was 8.74, 8.97 and 8.05 respectively. Since the temperature of hydrate formation was set to 305.8 K, the corresponding pressure of hydrate formation matches the set ambient temperature.

In the case of system of R41, FCP and H₂O, HBRS-C also showed the best performance, whose COP was 7.58–8.50, and the maximum of COP showed at 304 K. For HBRS-B, the COP was 7.34–8.29, and the maximum of COP also showed at 304 K. For HBRS-A, the COP was 6.45–7.58, and the maximum of COP also showed at 305 K.

HBRS showed the excellent performance of cooling. The coefficient of performance of all types remained a high level. Under the setting of the simulation, HBRS showed the best performance when the ambient temperature is close to the temperature of hydrate formation.

3.1.2. Unit factors

For in the system of R41, CP and H₂O, energy consumption distribution and the cooling capacity were shown in Fig. 8. Energy consumption equipments of HBRS-B and HBRS-C include air fan,

gas compressor, liquid pump, gas/liquid separator. Energy consumption of gas/liquid separator, very close to zero, could be omitted here. HBRS-A includes air fan, multiphase compressor. The cooling capacity increases with the ambient temperature. Energy consumption of the gas compressor or multiphase compressor accounted for a large proportion of 54.5–62.2% in total consumption for HBRS-B while 53.3–64.2% for HBRS-C and 99.7–99.8% for HBRS-A. The proportion of the liquid pump was 34.4–38.8% for HBRS-B and 35.5–39.8% for HBRS-C. Air fan accounts for 2.1–7.3% for HBRS-B, 0.2–0.6% for HBRS-C, and 0.2–0.4% for HBRS-A.

For in the system of R41, FCP and H₂O, power consumption distribution and the cooling capacity were shown in Fig. 9. Similar to the above system, the cooling capacity increases with the ambient temperature. Energy consumption of the gas compressor or multiphase compressor accounts for the main content of 68.7–75.5% in total consumption for HBRS-B, 73.1–77.0% for HBRS-C and 99.6–99.8% for HBRS-A. The proportion of the liquid pump was 22.0–24.9% for HBRS-B and 22.7–25.5% for HBRS-C. Air fan accounted for 1.9–6.9% for HBRS-B, 0.2–0.4% for HBRS-C and HBRS-A.

Power consumption in the system went for flowing fluid. Gas compressor was used for flowing gas and compressing gas. Liquid pump was used for flowing water and compressing water. Air fan was used for flowing air indoor and outdoor. Multiphase compressor was used to press and flow the refrigerants which composed of

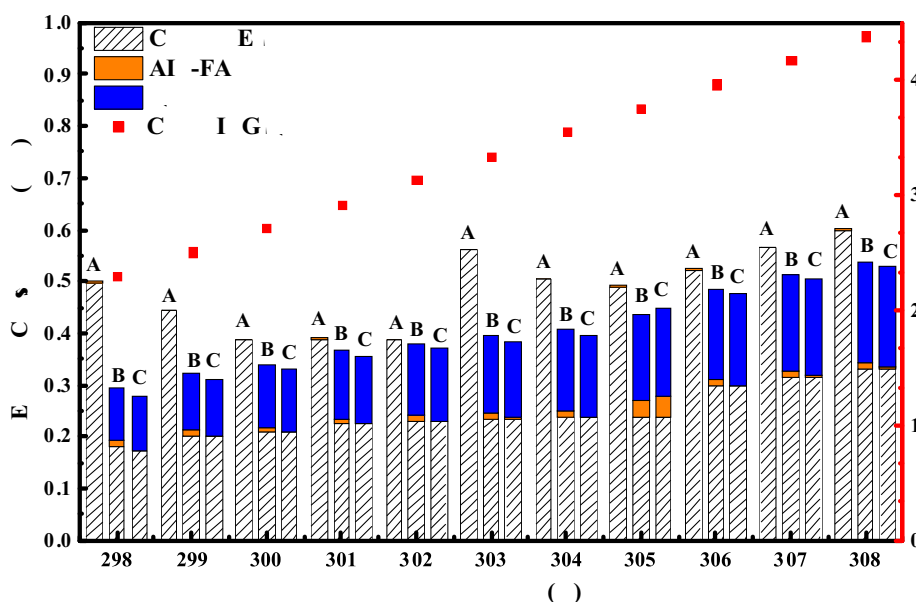


Fig. 8. Power consumption distribution and the cooling capacity in the system of R41, CP and H₂O.

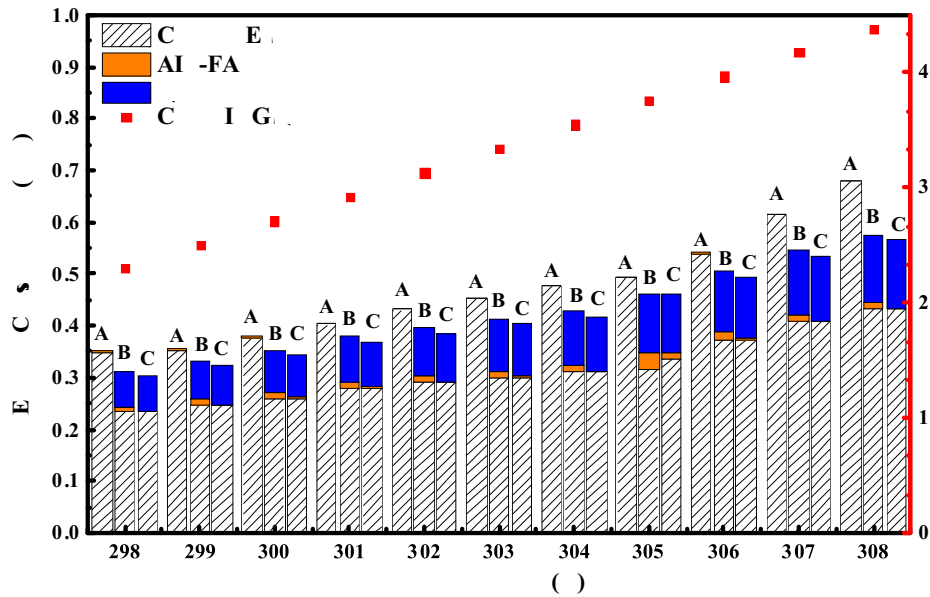


Fig. 9. Power consumption distribution and the cooling capacity in the system of R41, FCP and H₂O.

R41, CP/FCP and H₂O. The device which went for compressing fluids accounts for a very large proportion in total power consumption.

Since the compression ratio of the system of R41, CP with H₂O was 8.89 and the system of R41, FCP with H₂O was 9.96, the dissociation enthalpy of the hydrate for the different system was not the same. It results in the energy consumption for the system of R41, CP with H₂O was less than the other system of R41, FCP with H₂O.

3.2. Temperature and entropy diagram

In the HBRs-C system, evaporation and condensation were replaced with hydrate formation and dissociation. Gas and liquids formed hydrate to release heat and hydrate dissociated to gas and liquids to absorb heat, which supplied the cooling.

The relationship of temperature and entropy during cooling cycle was shown in Fig. 10. 1-2-3-4-5-1 meant the refrigeration process of vapor compression refrigeration system (VCRS). C1-C2-C3-C4-C5-C6-C1 meant HBRs-C cooling cycle. Both of the air

conditioners included heat absorption, heat release, vapor compression and throttling expansion.

In VCRS, 1-2 meant adiabatic compression process. Refrigerant vapor with high temperature and high pressure was attained at the point 2. 2-3-4 meant condensation of gas vapor. Liquid refrigerant with high temperature and high pressure was attained at the point 4. 4-5 meant throttling expansion process, liquid with low temperature and low pressure was attained at the point 5. 5-1 meant evaporation. Liquid refrigerant was evaporated to the initial state at the point 1. Cooling supply was achieved. It was returned to state 1, and so on.

In HBRs-C, C1-C2 meant compression and pumping process. Refrigerant vapor with high temperature and high pressure was gotten at the point C2. C2-C3 meant air cooling process. The temperature of refrigerant vapor was reduced. C3-C4-C5 meant hydrate formation. Refrigerant vapor with high pressure and the liquid solution flowed into hydrate formation tank to form hydrate. C5-C6 meant expansion throttle. The temperature and pressure of hydrate became low enough for cooling. C6-C1 meant hydrate dissociation. Hydrate with low temperature and low pressure absorbed the heat of the cooling region to dissociate. Cooling supply was achieved. It was returned to state 1, and so on.

Air cooling of refrigerant vapor and hydrate formation heat replaced traditional condensation to release the heat to the atmosphere. Hydrate dissociation replaced traditional evaporation to absorb the heat from the cooling region. With the same refrigerating capacity, the heat absorption $Q_{VCRS} = Q_{HBRs-C} = S1 = SC1$. Energy consumption of the HBRs-C was W_{HBRs-C} , $W_{HBRs-C} = SC2$. Power consumption of VCRS was W_{VCRS} , $W_{VCRS} = S2$.

It was derived $COP_{HBRs-C} > COP_{VCRS}$. And $COP_{HBRs-C} = 2-4 COP_{VCRS}$. HBRs-C consumed less power than VCRS. It possessed more energy-saving superiority.

For three types of HBRs, temperature and entropy state of working fluids during cooling process were shown in Fig. 11. For the points A1, A2, A3, A4, and A5, it meant the cooling process of the HBRs-A. It consumed the most power among the three types of HBRs. It was the earliest type of HBRs proposed by researchers. A1-B1 meant compression. Mixture of refrigerant vapor and liquid solution with high pressure and high temperature was attained at the point A2. A2-A3-A4 meant air cooling and hydrate formation. Heat exchange efficiency was enhanced by the existing liquid solu-

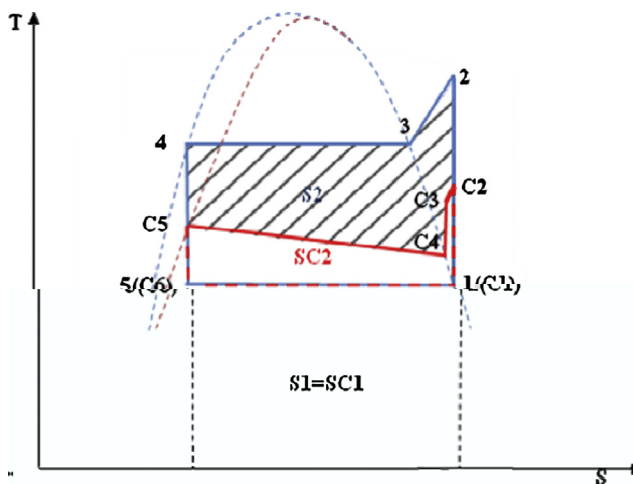


Fig. 10. T-S contrast of CCRC and HBRs-C.

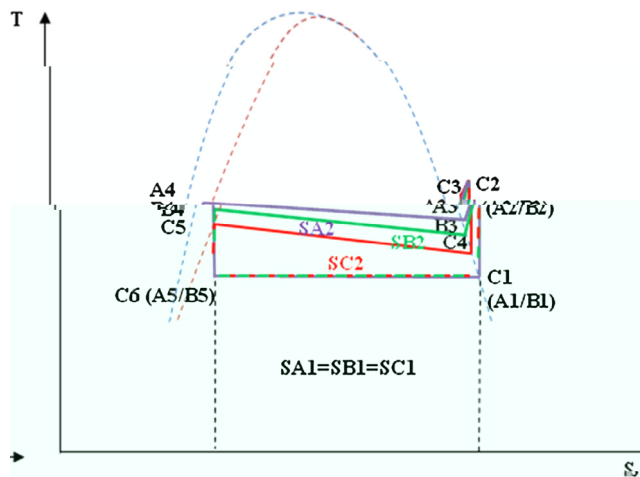


Fig. 11. T-S contrast of HBRS-A, HBRS-B and HBRS-C.

tion. Hydrate was attained at the point A4. A4–A5 meant expansion throttle. Hydrate with low temperature and low pressure was attained at the point A5. A5–A1 meant hydrate dissociation, cooling supply was achieved, and so on.

Based on it, the paper presented to flow the refrigerant vapor and liquid solution separately which was HBRS-B. For points B1, B2, B3, B4, and B5, it meant the cooling process of the HBRS-B which was similar to HBRS-A. The difference was to use individual pressurization for refrigerant vapor and liquid solution. In the system, refrigerant vapor accounted for a relatively small proportion which made pressurization separately better. It resulted in low power consumption under the condition of compression separately. Therefore HBRS-B consume less power than HBRS-A.

The temperature change of gas was much more than liquids after compression. The paper proposed the third HBRS, which was HBRS-C. For points C1, C2, C3, C4, C5 and C6, it meant the cooling state point analysis of the HBRS-C. At the point C2, refrigerant vapor with high temperature was gotten. Condense the pressurized refrigerant vapor separately and turned to the point C3. Then refrigerant vapor and liquid solution mixed in the hydrate formation tank at the point C4. Hydrate was attained at the point C5. After expansion throttle and hydrate dissociation, it come to the point C1. It consumed the least power.

Hydrate was used to be the refrigerant in hydrate-based refrigeration systems which made full use of the sensible heat and the latent heat of vapor-liquid and liquid-solid. It made the hydrate-based refrigeration system expressed better cooling capacity than other cooling medium [27,28].

4. Conclusions

Air conditioning power consumption occupied a large proportion nowadays. A novel refrigeration system is proposed which called hydrate-based refrigeration system. HBRS, instead of evaporation and condensation of conventional air conditioner, cooled space through hydrate formation and dissociation. There are three types of hydrate-based refrigeration systems. HBRS-A is a multi-phase compressor, HBRS-B is a single phase compressor with a single phase pump (mixed cooling), HBRS-C is a single phase compressor with a single phase pump (separated cooling). It is adopted methyl fluoride, cyclopentane, monofluoro cyclopentane and water to form hydrate as the refrigerant. Coefficient of performance is calculated.

The results show the highest coefficient of performance was 8.01–8.97, which is HBRS using methyl fluoride, monofluoro

cyclopentane and water. Coefficient of performances of different types of hydrate-based refrigeration systems are changed with the ambient temperature. Analyzing temperature and entropy during refrigeration process for hydrate-based refrigeration systems find that coefficient of performance was three or four times of the conventional compression refrigeration. In hydrate-based refrigeration systems, the large proportion in total power consumption is used in compressing fluids, which hinders the improvement of the coefficient of performance of the hydrate-based refrigeration system. In future work, it is urgent to make hydrate dissociation pressure higher, cut pressure ratio down and find the materials whose value of dP/dT is smaller in the hydrate phase equilibrium curve. It can diminish power consumption in the hydrate-based refrigeration system and improve the coefficient of performance of the hydrate-based refrigeration system.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.enconman.2017.04.091>.

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