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# The Entropy Analysis on NH<sub>3</sub>/CO<sub>2</sub> Cascade Refrigeration Cycle

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#### ABSTRACT

This paper introduces a cascade refrigeration cycle that uses natural refrigerants of CO<sub>2</sub> and NH<sub>3</sub> at low temperature. It introduces the character of CO<sub>2</sub> and NH<sub>3</sub>, besides analyzes the cascade refrigeration cycle. The optimal intermediate temperature of NH<sub>3</sub>/CO<sub>2</sub> cascade refrigeration cycle is determined by the entropy production minimization method. We analyze the four processes entropy production in both CO<sub>2</sub> cycle (LT side) and NH<sub>3</sub> cycle (HT side) and research how the total entropy production changes in the conditions of different T<sub>0</sub>, different T<sub>CL</sub> and different  $\triangle$ T. We also find that in order to enhance the efficiency of NH<sub>3</sub>/CO<sub>2</sub> cascade refrigeration cycle, it is necessary to reduce  $\triangle$ T. It can be concluded that NH<sub>3</sub>/CO<sub>2</sub> cascade refrigeration cycle has a good future.

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# INTRODUCTION

Global environmental problems, such as global warming and depletion of the ozone layer, have become more and more severe by the use of synthetic refrigerants (CFC, HCFC and HFC). In order to keep sustainable development of environment, searching efficient, green and friendly refrigerants has become a common concern of the international community. Natural working fluid was regarded as the final plan to solve environmental problems by G. Lorentzen the former president of the International Institute of Refrigeration [1]. When the required  $T_{CL}$  is very low, we can use cascade refrigeration system. The cascade refrigeration system consisted by two single-stage compression refrigeration system usually uses R22 and R13 as refrigerant in most regions of the world. However R22 and

# Nomenclature

S	specific entropy (kJ kg <sup>-1</sup> )	1-5 points of refrigerant (LT side)
∆s	entropy production (kJ kg <sup>1</sup> )	6-10 points of refrigerant (HT side)
h	specific enthalpy (kJ kg <sup>1</sup> )	L lowtemperature circuit
Q	heat transfer rate (kW)	H high – temperature circuit
Q <sub>0</sub>	cooling capacity (KW)	Y compression process
m	mass flow rate (kg s $^{-1}$ )	C cooling process
T <sub>3</sub>	CO <sub>2</sub> condensing temperature	J throttling process
Т	temperature (T or $^{\circ}\mathrm{C}$ )	Z evaporation process
T <sub>0</sub>	condensing medium temperature	G the whole NH3/ CO2 cascade refrigeration cycle
T <sub>CL</sub>	refrigerated space temperature	GL the whole low -temperature cycle
Δт	temperature difference in cascade condenser	GH the whole high – temperature cycle
Subs	cripts	

R13 not only destroy atmospheric ozone layer, but also have serious greenhouse effect. Under the "Montreal Protocol", R13 has been forbidden currently, and R22 only can be used before 2030 in some countries.

Therefore, refrigerant friendly to environment is needed to meet the requirement of low-temperature refrigeration. W. R. Kitzmiller once promoted the program of NH<sub>3</sub>/CO<sub>2</sub> cascade refrigeration cycle in 1932, high pressure level with NH<sub>3</sub> as refrigerant, low-level with CO<sub>2</sub> as refrigerant. CO<sub>2</sub> has good heat transfer performance, rather large cooling capacity by using latent heat and small viscosity at low temperature compared with other low-pressure refrigerant [2]. The research of Pettersen A. and Jakobsen shows that when using CO<sub>2</sub> instead of NH<sub>3</sub> at low-level, the size of compressor will reduce to the original 1 / 10 compared with NH<sub>3</sub>/NH<sub>3</sub> system, and  $T_{CL}$  can reach to - 50°C—- 45°C, even reach to - 80°C through the dry ice for powder effect. At present, Europe has established a few of cascade refrigeration system with low-temperature using CO<sub>2</sub> as refrigerant in the supermarkets. Operation conditions indicate that it is technically feasible. This system can also be applied to low-temperature freeze-drying process.

# THE PHYSICAL PROPERTIES OF CO<sub>2</sub> AND NH<sub>3</sub>

As a refrigerant, CO<sub>2</sub> has some special advantages.

Mainly in: (1) CO<sub>2</sub> is harmless to environment and a substance naturally existing in nature (ODP = 0, GWP = 1). (2)  $CO_2$  has excellent economy. (3)  $CO_2$  has good security, and chemical stability. It is safe, non-toxic and non-combustible, adapting to mechanical parts materials using a variety of oil. Even at high temperature, it does not decompose to produce harmful gases. (4) CO<sub>2</sub> has good thermal physical properties, suiting to the refrigeration cycle and equipment. It has larger latent heat of evaporation and has greater cooling capacity(0  $^{\circ}$ C, the cooling capacity per unit volume of CO<sub>2</sub> is 1.58 times of NH<sub>3</sub>, 5.12 times of R22 and 8.25 times of R12) [3]. At the same time, its dynamic viscosity is low. 0°C, the dynamic viscosity of CO<sub>2</sub> saturated liquid is only 5.2% of NH<sub>3</sub> and 23.8% of R12. CO<sub>2</sub> has high thermal conductivity and small ratio of liquid density and vapor density; refrigerant between circuits is more easily distributed after throttling. CO<sub>2</sub> has excellent flow and heat transfer characteristics, so the size of the compressor and the system can be significantly reduced to make the whole system compact.

NH<sub>3</sub> has been used for 120 years and still applies to large-scale industrial systems in many countries. The advantage is ODP=0, GWP=0, with excellent thermodynamic properties, cheap price and convenient leak detection. It is the most vital refrigerant used in standard refrigeration equipment with reciprocating or rotary compressor and cooling capacity

higher than 25KW. And in the appropriate equipment, even more small-capacity NH<sub>3</sub> refrigerator has gradually appeared in the market. Most consideration about NH<sub>3</sub> is its safety, mainly about its toxicity and flammability, followed by pungent smell. In fact, its toxicity is only 1/10-1/50 of the toxicity of chlorine; its ignition limit is 15.5% (volume ratio), 3-7 times of the usual hydrocarbon and natural gas, while the heat of combustion is less than half of them. About 100 years historical experience shows that NH<sub>3</sub> has low accident rate. NH<sub>3</sub> has a strong pungent smell. Therefore, we can easily identify the leak. In addition, NH<sub>3</sub> is lighter than air, so it is easy to escape from the roof to outside. When NH<sub>3</sub> and water is contacted, NH<sub>3</sub> can be quickly absorbed by water. This performance can be used to eliminate the NH<sub>3</sub> vapor in the air, greatly reducing the accident.

# THE ENTROPY ANALYSIS OF NH<sub>3</sub>/CO<sub>2</sub> CASCADE REFRIGERATION CYCLE

# **Theoretical analysis**

NH<sub>3</sub>/CO<sub>2</sub> cascade refrigeration cycle is composed of NH<sub>3</sub> high-temperature cycle and CO<sub>2</sub> low-temperature cycle [4]. Fig. 1 schematically depicts the cascade refrigeration cycle. Fig.2 is the corresponding temperature-entropy diagram. In Fig. 2, 1-2-3-4-5-1 is cycle of low-temperature part (CO<sub>2</sub>), and 6-7-8-9-10-6 is the cycle of the high temperature part (NH<sub>3</sub>) .The evaporation of NH3 and the condensation of CO<sub>2</sub> complete in a "cascade condenser"; and this equipment insulates environment using insulation materials. Therefore, evaporation heat of NH3 is equal to the condensation heat of CO<sub>2</sub>, and temperature difference in cascade condenser( $\Delta$ T) is 5-8°C.

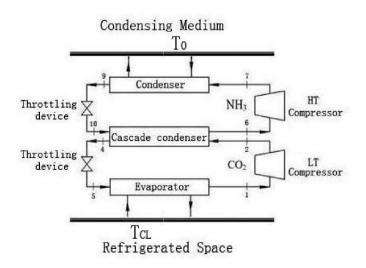


Fig.1 Schematic diagram of CO<sub>2</sub>/NH<sub>3</sub> cascade refrigeration cycle

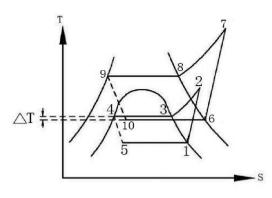


Fig.2 The temperature-entropy diagram of CO<sub>2</sub>/ NH<sub>3</sub> cascade refrigeration cycle

Theoretical cycle is calculated as follows The relation of the mass flow between HT circuit and LT circuit:

If the mass flow of LT part of  $CO_2$  is  $m_1$  and cooling capacity

is Q<sub>0</sub>, then

$$m_{L} = \frac{Q_{0}}{h_{1} - h_{5}}$$
(1)

Heat transfer rate of cascade condenser is,

$$Q_{KL} = Q_0 \frac{h_2 - h_4}{h_1 - h_5}$$
(2)

The mass flow of HT circuit is,

$$m_{\rm H} = \frac{Q_{\rm KL}}{h_6 - h_{10}} = \frac{Q_0^{(\rm h_2 - h_4)}}{(h_6 - h_{10}) \quad (h_1^{-\rm h_5})} \tag{3}$$

The entropy production [5] of LT circuit:

The compression process: 
$$\Delta S_{YL} = m_L (s_2 - s_1)$$
 (4)

The cooling process: 
$$\Delta S_{CL} = m_L(s_4 - s_2) + \frac{Q_{LZ}}{T_6}$$
 (5)

Where, 
$$Q_{LZ} = m_L(h_2 - h_4)$$

The throttling process: 
$$\Delta S_{JL} = m_L(s_5 - s_4)$$
 (6)

The evaporation process: 
$$\Delta S_{ZL} = m_L (s_1 - s_5) - \frac{Q_0}{T_{CL}}$$
 (7)

The entropy production of HT circuit:

The compression process: 
$$\Delta S_{VH} = m_H(s_7 - s_6)$$
 (8)

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The cooling process:  $\Delta S_{LH} = m_H (s_9 - s_7) + \frac{Q_{LH}}{T_0}$  (9)

where,  $Q_{LH} = m_H (h_7 - h_9)$ ,

The throttling process: 
$$\Delta S_{JH} = m_{H}(s_{10} - s_{9})$$
 (10)

The evaporation process:  $\Delta S_{ZH} = m_H (s_6 - s_{10}) - \frac{Q_{LZ}}{T_3}$  (11)

where,  $Q_{LZ} = m_H (h_6 - h_{10})$ 

#### Analysis of the calculating results

As the part of the HT cycle is cooled under ambient temperature conditions. So the condensing medium temperature(T<sub>0</sub>) is 25 °C.Condensing temperature can be taken as 40 °C .The temperature difference [7] in cascade condenser( $\Delta T$ ) is 5 °C. Evaporation temperature is -55 °C, and cooling capacity(Q<sub>0</sub>) is 3.5kw. The isentropic efficiency of compressing process is 0.8;the refrigerated space temperature(T<sub>CL</sub>) is - 45 °C, and CO<sub>2</sub> condensing temperature(T<sub>3</sub>) is a known constant.

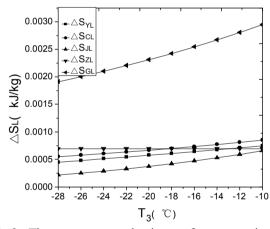


Fig.3 The entropy productions of compressing process, condensing process, throttling process, evaporating process and total entropy production ( $\triangle S_{YL}$ ,  $\triangle S_{CL}$ ,  $\triangle S_{JL}$ ,  $\triangle S_{ZL}$ ,  $\triangle S_{GL}$ ) in LT circuit change with T<sub>3</sub>

Fig.3 shows how the entropy productions of compressing process, condensing process, throttling process, evaporating process and total entropy production in LT circuit change with  $T_3$ . It can be seen from the figure that the entropy productions of compressing process, condensing process, throttling process increase as  $T_3$  rising. The entropy production of condensing process is the largest, followed is the compressing process. And the change of evaporating process is very small.

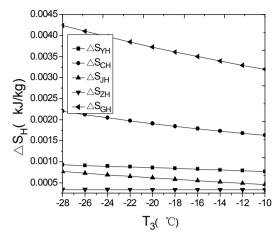


Fig.4 The entropy production of compressing process, condensing process, throttling process, evaporating process and total entropy production ( $\triangle S_{YH}$ ,  $\triangle S_{CH}$ ,  $\triangle S_{JH}$ ,  $\triangle S_{ZH}$ ,  $\triangle S_{GH}$ ) in HT circuit change with T<sub>3</sub>

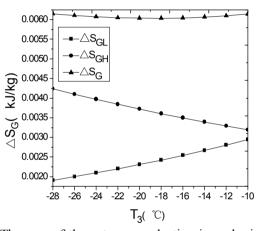


Fig.5 The sum of the entropy production in each circuit and total entropy production( $\triangle S_{GL}$ ,  $\triangle S_{GH}$ ,  $\triangle S_{G}$ ) change with  $T_3$ 

Fig.4 shows how the entropy productions of compressing process, condensing process, throttling process, evaporating process and total entropy production in HT circuit change with  $T_3$ . It can be seen from the figure that the entropy production of condensing process, throttling process decrease as  $T_3$  rising. The entropy production of condensing process is the largest, followed is the throttling process; the changes of compressing process and evaporating process are nearly constant.

Fig.5 shows how the sum of the entropy production in each circuit and total entropy production change with  $T_3$ . It can be seen from the figure that with the raise of  $T_3$ , the sum of the entropy production in LT circuit increases, while the sum in HT circuit decreases and the total entropy production first decreases, then increases. So there exists a minimum entropy production. The corresponding temperature of

minimum entropy production is called optimum intermediate temperature [6]. The optimum intermediate temperature of the calculating condition is  $-18^{\circ}$ C.

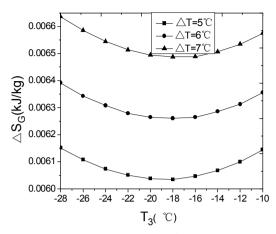


Fig.6 The total entropy production( $\triangle S_G$ ) changes with  $T_3$  in different  $\triangle T$ 

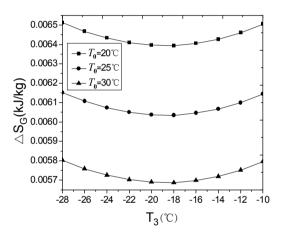


Fig.7 The total entropy production( $\triangle S_G$ ) changes with  $T_3$  in different  $T_0$ 

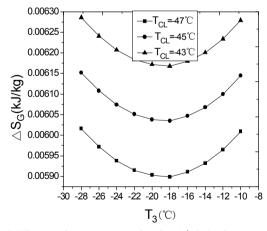


Fig.8 The total entropy production( $\bigtriangleup S_G)$  changes with  $T_3$  in different  $T_{CL}$ 

Figure 6, Figure 7, and Figure 8 separately shows how the total entropy production of  $NH_3/CO_2$  cascade refrigeration cycle changes with  $T_3$  under the conditions of different  $\triangle T$ ,

 $T_0$  and  $T_{CL}$ . It can be seen from the three figures, with the increase of  $T_3$ , the total entropy production decreases at first and then increases, so there exists a minimum entropy production. As for different  $\triangle T$ , the smaller the  $\triangle T$  is, the smaller the corresponding total entropy production is. That is, the irreversible loss is smaller. So we should reduce  $\triangle T$ .

#### CONCLUSIONS

The total entropy production of  $NH_3/CO_2$  cascade refrigeration cycle decreases at first and then increases with  $T_3$  increasing, and there is a minimum entropy production. The minimum entropy production can determine the optimal intermediate temperature of  $NH_3/CO_2$  cascade refrigeration cycle. In this paper, the optimal intermediate temperature is about -18°C.

(1) As  $T_3$  increases, the sum of entropy production in LT circuit increases while the sum of entropy production in HT circuit decreases, and the entropy production of condensing process is maximum.

(2) The minimum entropy production increases with  $\triangle T$  and  $T_{CL}$  increasing, and decreases with  $T_0$  increasing. Among them, the minimum entropy production changes greatest with  $\triangle T$ . In order to reduce irreversible loss of NH<sub>3</sub>/CO<sub>2</sub> cascade refrigeration cycle, we should first reduce  $\triangle T$ .

(3) This paper only analyzes the irreversible loss of  $NH_3/CO_2$  cascade refrigeration system by using entropy , but we need to do further research to optimize the system performance (COP).

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