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Design of non-flammable mixed-refrigerants Joule-Thomson refrigerator below -100℃

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Abstract

Refrigeration below -100℃ (170 K) is often demanded in various industrial applications such as biomedicine, food stocks, and semi-conductor processing. It is difficult to pump heat from 170 K to room temperature by a single pure refrigerant in Joule-Thomson (JT) refrigerator due to the insufficient thermodynamic properties. Mixed-refrigerants (MR) possess some attractive merit as an alternative for that temperature range. We select the non-flammable refrigerants to avoid the operation safety issues such as flammability and explosiveness of hydrocarbon refrigerants. This paper validates a possibility for obtaining 170 K by using a non-flammable mixture refrigerant and determines its maximum COP. A two-stage cascade cycle is selected for design simulation in order to achieve a high efficiency. In the main cycle, R14, R23, and R218 are used after we consider the characteristics of the iso-thermal enthalpy difference. In addition, R410A, which is broadly used in commercial refrigerators, is utilized in the precooling cycle. The optimal design and the operating condition are evaluated with several parameters in the main and the precooling cycles, such as the suction and discharge pressures of the compressors, the mass flow rate, the precooling temperature, and the MR compositions. The simulation assumes the ideal conditions to analyze the performance of the cycle. Consequently, the maximum COP is calculated at 0.78 when the mole composition of the ternary refrigerants (R14:R23:R218) is 0.7:0.1:0.2.

Keywords: mixed-refrigerant; non-flammable refrigerants; MR-JT refrigerator; SMR cycle; cascade cycle;

1. Introduction

With the 4th industrial revolution, the need for treating the amount and time of data is explosively increasing. As this tendency is accelerated, the demand of higher density semi-conductor is inevitable. In the previous semi-conductor manufacturing process such as an etching process, the required temperature of manufacturing chamber ranged from -20℃ to -30℃. Recently, as a new method for fabricating the advanced high-density semi-conductor, cryogenic-etching process where the lowest temperature is below -100℃ (170 K) is emerging as a novel technology for efficient production and precise manufacturing of the semi-conductor [1]. To obtain the low temperature below 170 K, the Joule-Thomson (JT) refrigeration could be utilized because of the several advantages such as high reliability due to no moving parts, low capital cost, simple structure, and adjustability of the cooling capacity. On the other hand, JT refrigerator has also several disadvantages such as clogging problem in the lowest temperature parts, large pressure ratio, which results in low efficiency. The substitution of a pure refrigerant with a mixed-refrigerant (MR) as the working fluid can be a solution to these problems in the JT refrigeration cycle. Recently, the global environmental issue is to cope with the global warming and the destruction of ozone layer. Many researches have focused on the investigation of the MR-JT refrigerator using flammable refrigerants, which could reduce the emission of the CO2 and increase the efficiency [2]. However, it has critical disadvantages such as the flammability and explosiveness when the system size grows. In the manufacturing process of semi-conductor, it is essential to facilitate a cleanroom which is designed to maintain extremely low levels of pollutant. When the flammable refrigerants are utilized as the working fluid of the

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refrigerator, it has a critical fire hazard, which is the single greatest risk among the cleanroom accidents. The damage from a fire can generate tremendous loss of the cost and time-consumption within several minutes. Due to these peculiar issues in the manufacturing process of semi-conductor, the concern of the safety is an essential factor. Therefore, in specific industrial applications, which need highest safety concerns like semi-conductor process, it is justifiable to construct a refrigeration system by using non-flammable refrigerants even though they have relatively high GWPs.

Over the past years, numerous investigations of the MR-JT refrigerator are concentrated on the flammable refrigerants as the working fluids due to their advantages such as high efficiency and lower global warming potential. On the other hand, few researches have addressed the non-flammable refrigerants in the past years. The cycle efficiency is affected by not only the composition of the MR but also the configuration of the cycle. The investigation by using non-flammable refrigerants for below 170 K needs more attention for various inevitable applications. Zhili Sun et al. (2019) explore the alternatives of refrigerant substitution in three cascade refrigeration system (TCRS) [2]. In the Zhili paper, the maximum COP is about 0.59 when the lowest temperature is about 170 K by using flammable refrigerants. In 2017, Cheonkyu Lee et al. presented a high-performance mixed-refrigerants JT refrigerator cycle by using non-flammable refrigerants for obtaining about 100 K [3]. The applied refrigerants for main and precooling cycle consist of Ar (Argon), R14, R23, and R218 in the main cycle and R410A in precooling cycle, respectively. In this research, the optimum operating condition is discussed and presented. In the research by Jisung Lee et al. (2011), three-stage cascade cycle was proposed for cooling HTS cables at the refrigeration temperature of about 70 K [4]. For reaching the temperature about 70 K, the non-flammable mixture of neon-nitrogen was selected as the working fluid of the main cycle. However, the flammable mixture of nitrogen, methane, ethane, and propane have been used as the components of MR to improve the cycle's efficiency. Since then, Jisung Lee et al. (2017) conducted the experimental investigation for validating the results of the previous numerical simulation [5].

The objective of this paper is to design a high efficiency MR-JT refrigerator for 170 K by using non-flammable refrigerants. The concepts of phase-liquid diagram and iso-thermal enthalpy difference are exploited to select the appropriate working fluid. Also, the comparison between the single-stage mixed-refrigerant and the cascade mixed-refrigerant cycle is performed in order to examine what configuration of cycle has a higher efficiency [6, 7].

2. Methodology

2.1. Selection of proper refrigerants and optimal compositions of MR

Cryogenic refrigerators were to be operated over wide temperature ranges from below 1 K to higher than 100 K usually up to 120 K. The traditional target temperature is below 170 K, which specifically dictates heat pumping from 170 K to 300 K. To cope with this wide temperature range (nearly 130 K), the mixed-refrigerants are preferred. One of the methods for selecting proper mixed-refrigerants as the working fluid is to utilize the liquid-phase diagram, which indicates the available range of liquid-phase between triple point and critical point. Fig. 1. shows the liquid-phase range diagram for several refrigerants with various temperature. Whenever the refrigerator is operating below 170 K, it is imperative to avoid any freezing problem of the working fluid.

According to Fig.1, Tetra-fluoro-methane (R14,CF_4), Tri-fluoro-methane (R23,C_2F_6), and Octa-fluoro-propane (R218,C_3F_8) can be selected as the non-flammable refrigerants. The total number of the divided cases per 0.1 mole with respect to their molar compositions of the ternary mixed-refrigerant is about 36 cases. Before we conduct the simulations for all cases, it is useful to sift out several cases for the analysis by considering their iso-thermal enthalpy differences. The iso-thermal enthalpy differences of the selected refrigerants (R14, R23, and R218) are presented in Fig. 2 both for the pure and the mixture refrigerants. The precooling refrigerant in the case of cascade configuration, is chosen as R410A which is one of the frequently used refrigerants in commercial refrigerators. R410A is the well-known near-zeotropic mixture of difluoromethane (R32,$CH2F_2$) and pentafluoroethane (R125,CHF_2CF_3).

From Fig. 2, it is possible to determine proper compositions of the mixture and estimate its ideal cooling capacity. To lift heat from 170 K to the ambient temperature (300 K), each of the ternary refrigerants of R14, R23, and R218 plays its role at the lowest, middle, and highest temperature ranges, respectively. It is important to recognize that the minimum iso-thermal enthalpy difference for the whole temperature range actually determines the cooling capacity of the cycle and its COP. This fact justifies the use of precooling cycle in a cascade configuration to narrow down the required temperature range, for example from 170 K to 240 K instead of 170 K to 300 K. Since the iso-thermal enthalpy difference of R14 is relatively smaller than the others, the composition ratio of R14 should be larger than that of the other refrigerants for approaching below 170 K. The candidates of the mixture for the analysis is summarized in Table. 1.

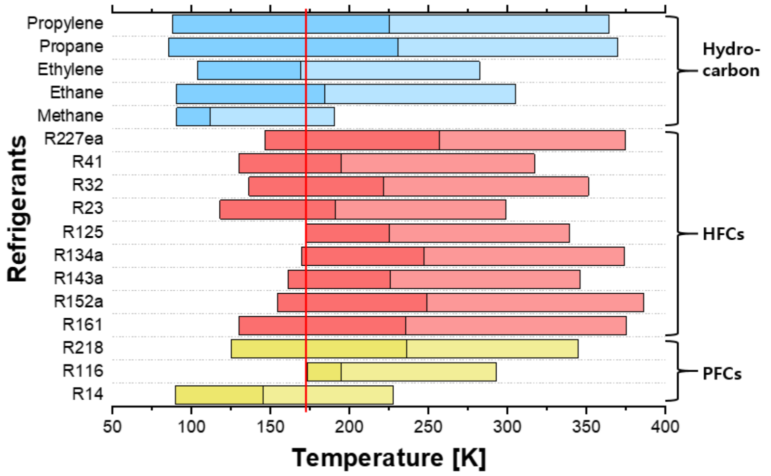
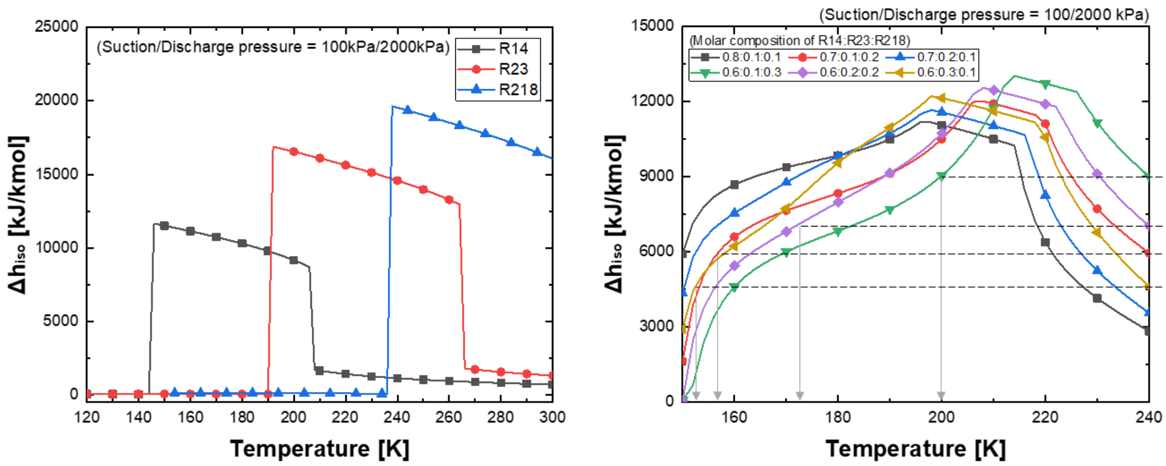


Fig. 1 Liquid-phase range diagram for various refrigerants



(a) Iso-thermal enthalpy difference for pure refrigerants (b) Iso-thermal enthalpy difference for various mixture

Fig. 2 Iso-thermal enthalpy difference for non-flammable refrigerants (R14, R23, R218)

Table 1. Details of molar compositions for the non-flammable mixed-refrigerant

Case	Composition		
	R14	R23	R218
(1)	0.8	0.1	0.1
(2)	0.7	0.1	0.2
(3)	0.7	0.2	0.1
(4)	0.6	0.1	0.3
(5)	0.6	0.2	0.2
(6)	0.6	0.3	0.1

2.2. Cycle description

2.2.1. Single-stage mixed-refrigerant cycle (SMR)

SMR cycle, which is referred to as Linde-Hampson cycle and illustrated in Fig.3., comprises a compression unit, which includes compressor and after-cooler, a heat exchanger, an expansion valve, and an evaporator. By using two-stage compression system, the compression work and the compression ratio can be reduced effectively. Also, the operational soundness of the compressor is improved.

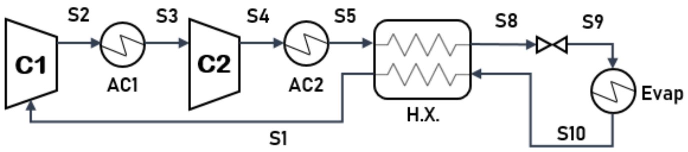


Fig. 3. Schematic of single-stage mixed-refrigerant cycle (SMR)

2.2.2. Cascade mixed-refrigerant cycle

Cascade cycle mainly consists of two cycles; the main (red-line) and precooling cycle (blue-line) in Fig.4. The configuration of the main cycle is derived from the basic Linde-Hampson cycle by adding the precooling cycle for the reduction of irreversibility inside H.X.2. In the previous research of C. Lee et al. and J. Lee et al., the two-stage cascade cycle used was proposed to enhance the cooling capacity [3, 4]. For the simplicity and ideal analysis, the minimum temperature approach in all heat exchangers is set to 3 K except for the low temperature side of H.X.1 between the temperature of Main6 and Main11. Generally, after the heat exchanger (H.X.1), the magnitude of the temperature difference inside the H.X.1 increases along the high-pressure stream. The increasing temperature difference inside the heat exchanger causes the area of heat exchange to be extended or the irreversibility in the heat exchanger to be increased. By deploying the precooling cycle inside the main cycle, these problems can be mitigated.

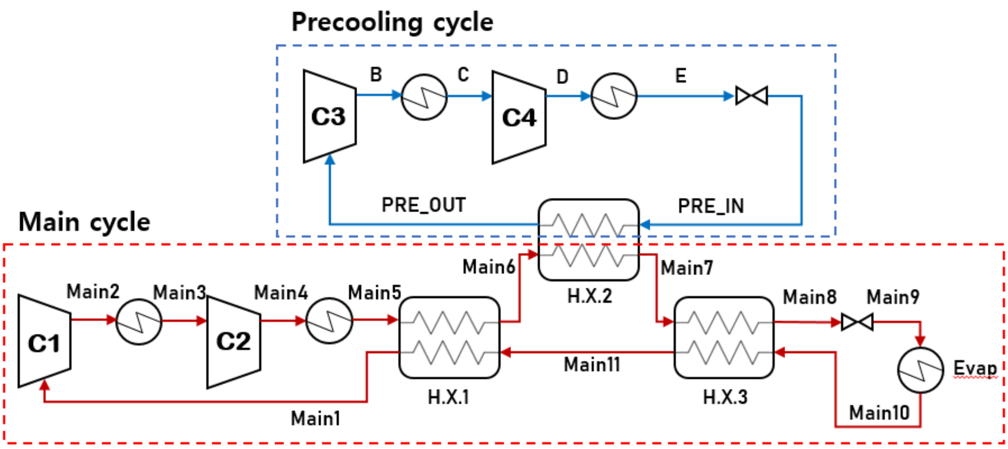


Fig. 4. Schematic of cascade mixed-refrigerant cycle (Cascade-MR cycle)

2.3. Simulation conditions and constraints

SMR and Cascade-MR are analyzed and compared to investigate the effect of precooling-cycle on the efficiency of the MR-JT refrigerator. For analyzing both refrigeration cycles, a commercial simulator, ASPEN HYSY V8.0 is utilized. In this paper, EOS is chosen Peng-Robinson equation in order to calculate the mixed refrigerant properties and the cycle efficiency. This EOS, which is presented below, has been commonly used for evaluating mixture properties in many previous researches [3-5]. P, R, T, v, a and b are pressure, universal gas constant, temperature, specific volume, fluid specific constants. P_c, T_c and w are critical pressure, critical temperature and acentric factor.

$$P = \frac{RT}{v-b} - \frac{a}{v^2+2bv-b^2} \quad (1)$$

$$a = \left(0.45724\frac{R^2T_C^2}{P_C}\right)\left[1+(0.37464+1.54226\omega-0.26992\omega^2)\left(1-\sqrt{\frac{T}{T_C}}\right)\right]^2 \quad (2)$$

$$b = 0.07780\frac{RT_C}{P_C} \quad (3)$$

For simplifying the cycle analysis, we apply the following conditions and assumptions into the refrigeration cycle.

2.3.1. Compression part

- Two stage compression in the main and precooling cycle is implemented to reduce the compression work.
- It is assumed that the compression occurs with the isentropic efficiency of 80%.
- Each compressor in the main and precooling cycle has the same compression ratio.

2.3.2. Heat exchanger parts including after-coolers

- It is assumed that the pressure drops in both hot and cold streams are negligible except for the Joule-Thomson valve.
- Minimum temperature approach is 3 K inside heat exchangers.
- The type of heat exchangers is counter-flow.

2.3.3. Expansion part

- The expansion process is an isenthalpic process.

2.3.4. Simulation constraints

In general, the maximum pressure (discharge pressure) of MR-JT refrigerator is set to 3500 kPa for efficient operation. The minimum limitation of the suction pressure is nearly 100 kPa (1atm) due to the operational safety issue. The summary of the simulation constraints is presented in Table. 2.

Table 2. Summary of the simulation constraints

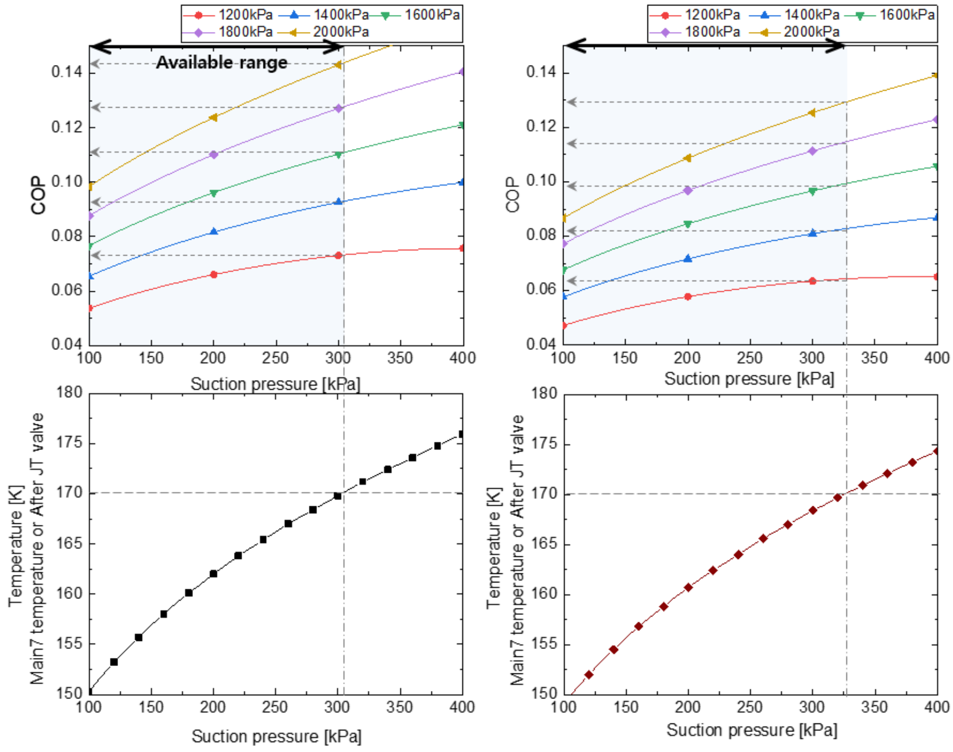
	Specification	Min	Max	Variation
Main cycle	Lower(suction) pressure [kPa]	100	500	40
	Higher(discharge) pressure [kPa]	1800	3400	200
	Mass flow rate [kg/s]	1	1	-
Precooling cycle	Higher(discharge) pressure [kPa]	1750	1750	-
	Temperature [K]	230	250	5

The mass flow rate of the main cycle is set as 1kg/s for the simplicity of the analysis. On the other hand, that of the precooling cycle is determined automatically in order to satisfy the minimum temperature approach 3 K in H.X.2. The discharge pressure of the precooling cycle is 1750 kPa, which means the subcooled or compressed state of R410A at ambient temperature (300 K).

3. Results

3.1. SMR cycle

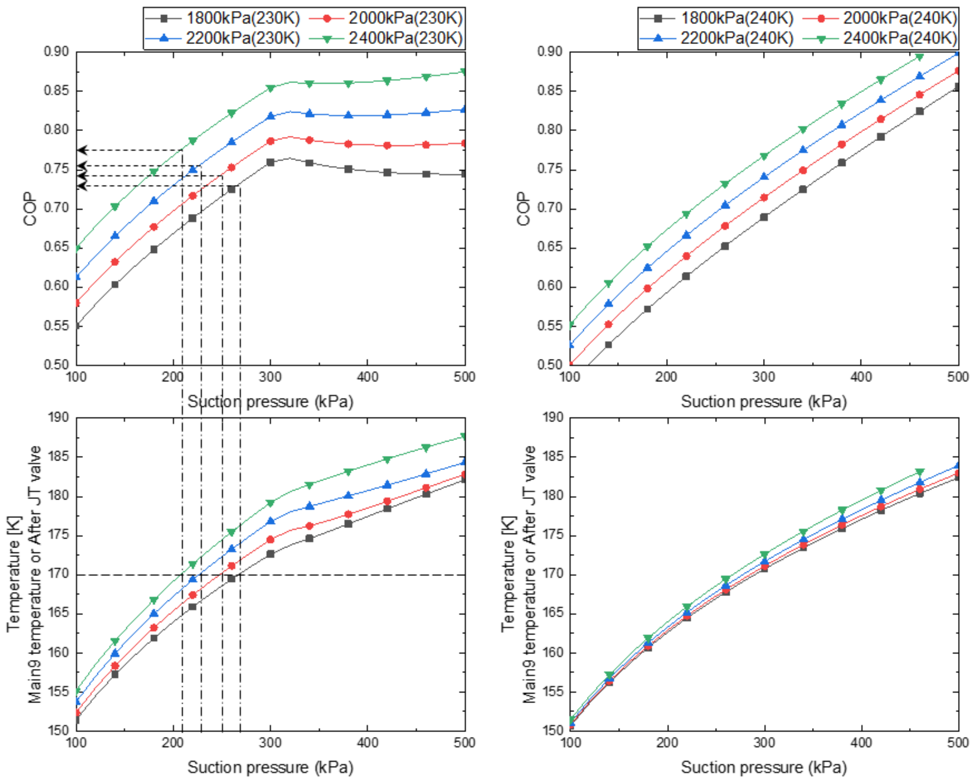
Fig. 5. describes the variation of COP and the temperature of after-JT valve with the suction pressure of the SMR cycle for two cases of ternary MR compositions of R14, R23, and R218 (0.7:0.1:0.2 and 0.75:0.1:0.15). The longitudinal scales of the upper and the lower graphs are fitted equally for the convenience. Both (a) and (b) in Fig. 5. have the similar tendency. As the suction pressure increases from the 100 kPa, the cycle efficiency and the temperature of after-JT valve also increase gradually. The available suction pressure to achieve the target temperature of 170 K are up to 300 kPa and 330 kPa as indicated in Fig.5. (a) and (b), respectively. The COP of the case (a) is larger than that of the case (b) with more molar composition of R218.



(a) R14:R23:R218 = 0.7:0.1:0.2

(b) R14:R23:R218 = 0.75:0.1:0.15

Fig. 5. COP and after-JT temperature with respect to the molar compositions in SMR cycle



(a) Precooling temperature 230 K

(b) Precooling temperature 240 K

Fig. 6. COP and after-JT temperature with respect to precooling temperature in cascade cycle

3.2. Cascade cycle

Fig. 6. (a) and (b) illustrate the variation of the achievable COP and the lowest temperature with the suction pressure and the discharge pressure in accordance with the precooling temperature in the cascade cycle. The overall tendency for the COP and the temperature of after-JT valve is similar with the SMR cycle's results as mentioned in the previous section. In the cascade cycle, the efficiency is primarily influenced by three main parameters, that are the suction, the discharge pressure, and the precooling temperature of Main7 which is the precooled temperature through H.X.2. From Fig. 6, it is evident that the lower precooling temperature leads to the higher efficiency of the cycle. Although the precooling temperature is controlled by the suction pressure in the precooling cycle, the temperature is limited by the suction pressure in the precooling cycle which isn't allowed below 100 kPa for the stable operation.

For more precise analyses in cascade cycles with different molar compositions, we considered several cases of 0.05 mole variations as presented in Table. 3. Also, in order to find the optimal operating conditions, the constraint range of discharge pressure in the main cycle extends from 2400 kPa to 3200 kPa with the variation of 200 kPa.

Table 3. Subdivided cases for several molar compositions

Case	Composition		
	R14	R23	R218
(1-1)	0.7	0.1	0.2
(2-1)	0.75	0.1	0.15
(3-1)	0.75	0.05	0.2
(4-1)	0.75	0.15	0.1

The sub-divided four cases are simulated and the results are plotted in Fig. 7. As a result, the maximum COP is obtained as 0.785 in the case of (1-1) with the compositions of R14, R23, and R218 (0.7:0.1:0.2). In that case, the suction and the discharge pressures are about 200 kPa and 2600 kPa for 170 K, respectively. The mass flow rate of the precooling cycle is estimated at 0.476 kg/s. Another case also has similar tendencies and the estimated maximum COP for 170 K is about 0.78. Table. 4 summarizes the simulation results in terms of the suction and the discharge pressures with the parameters of the precooling cycle.

Furthermore, the second law efficiencies of the sub-divided four cases in Table 3 are calculated to compare their realistic efficiencies with other cycles. The Carnot COP and the second law efficiencies can be calculated by eq.(4) and eq.(5), respectively. with the Carnot COP of 1.31. T_e and COP_{Carnot} stand for the evaporator temperature and the Carnot COP, respectively.

$$COP = \frac{T_e}{300-T_e} \tag{4}$$

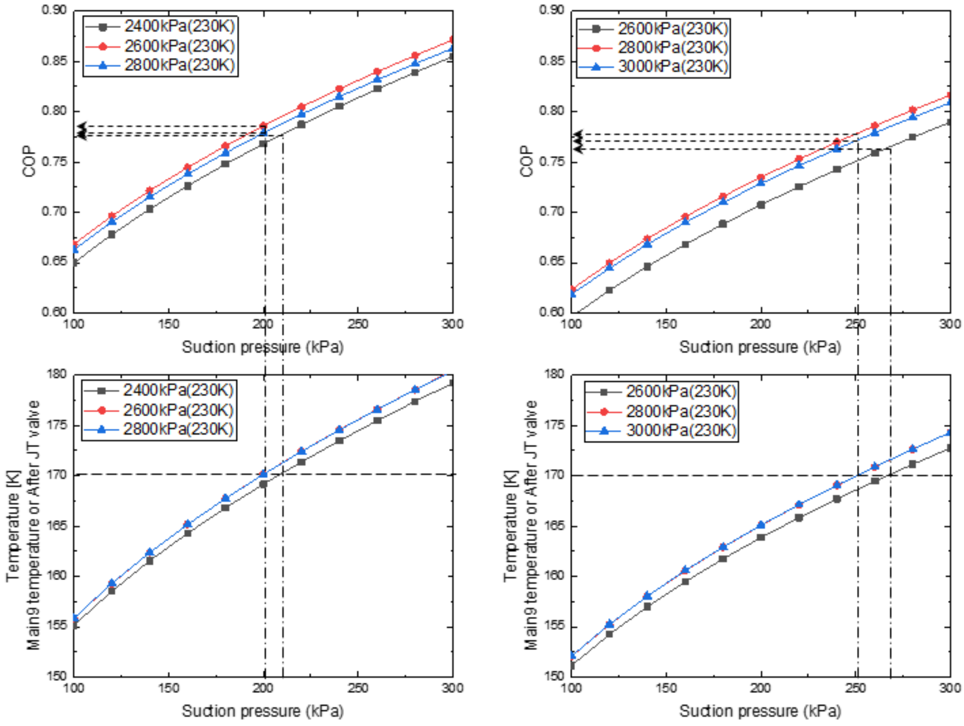
$$\eta_{II} = \frac{COP}{COP_{Carnot}} \tag{5}$$

The calculated results are depicted in Fig.8.

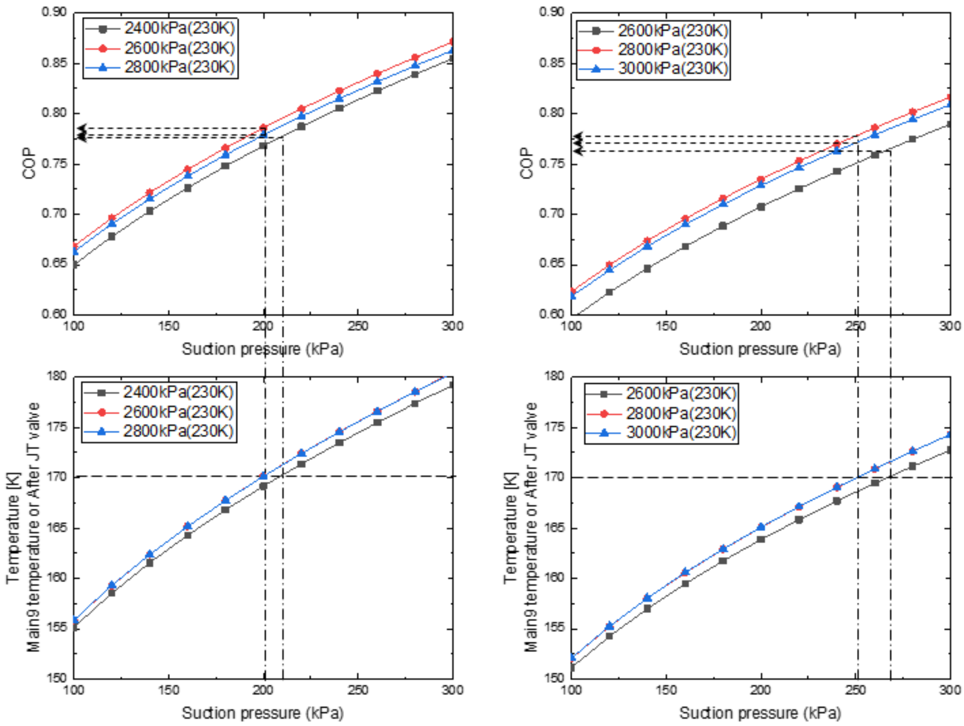
From the previous section, we deduce that the higher efficiency can be achieved when the precooling temperature decreases. In this numerical analysis, the suction pressure in the precooling cycle with R410A is primarily determined by the precooling temperature, 230 K.

Table 4. Summary of simulated results in cascade cycle

CASE	Main cycle Suction pressure [kPa]	Discharge pressure [kPa]	Precooling cycle Mass flow rate [kg/s]	Suction pressure [kPa]	Temperature [K]	COP
(1-1)	198.67	2600	0.476	134.4	230	0.7847
(2-1)	249.57	2800	0.479	134.4	230	0.7784
(3-1)	220.00	2600	0.458	134.4	230	0.7787
(4-1)	284.28	2800	0.501	134.4	230	0.7767



(a) R14:R23:R218 = 0.7:0.1:0.2 (CASE 1-1)   (b) R14:R23:R218 = 0.75:0.1:0.15 (CASE 2-1)



(c) R14:R23:R218 = 0.75:0.05:0.2 (CASE 3-1)   (d) R14:R23:R218 = 0.75:0.15:0.1 CASE(4-1)

Fig. 7. COP and after-JT temperature for four molar compositions

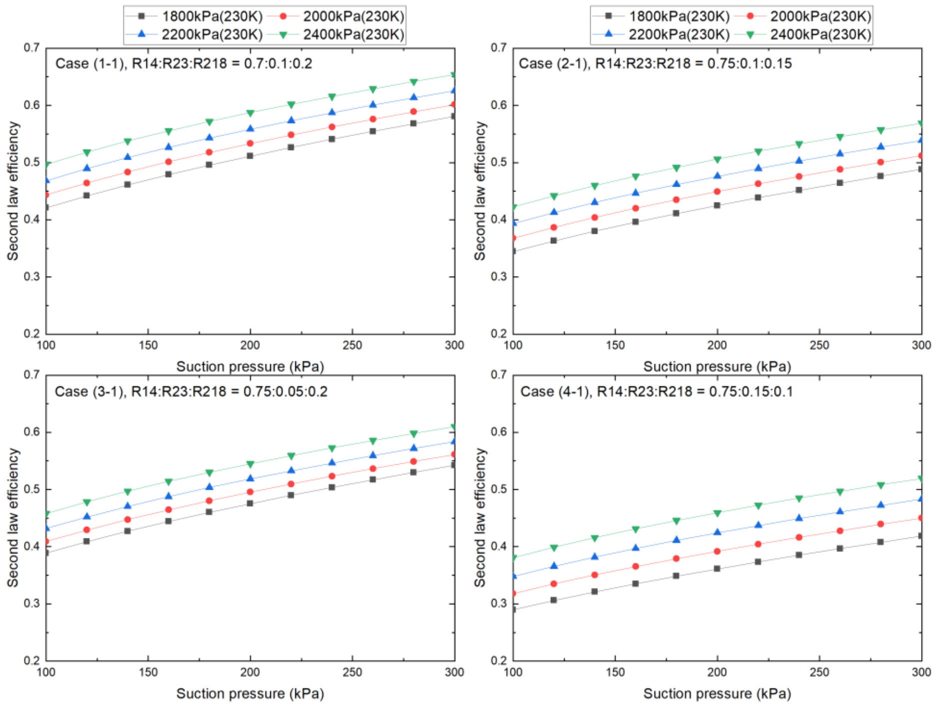


Fig. 8. The calculated second law efficiencies for four molar compositions

4. Discussion

Both SMR and cascade cycles with non-flammable refrigerants are analyzed by using commercial software ASPEN HYSYS V8.0. Both results of SMR and cascade cycles represent a similar tendency that the COP and the temperature of after-JT increase in accordance with the increase of the suction pressure. The reason for these characteristics is related to the pressure ratio between the suction (lower) and the discharge (higher) pressures. In condition with the same discharge pressure and the precooling temperature, as the suction pressure increases, the pressure ratio is reduced. As a result, the compression work is reduced by the decreased pressure ratio. By the definition of COP, a ratio of compression work and cooling capacity, the COP increases gradually to some extent. For example, the consumption of work and the cooling capacity in the case of (1-1) is illustrated in Fig. 9.

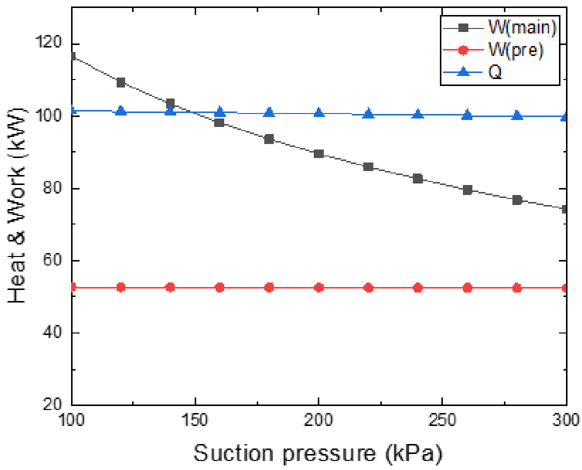


Fig. 9. Comparison between compression work and cooling capacity in the case of (1-1)

As the suction pressure increases, the temperature of after-JT also increases. It can be explained by the Joule-Thomson effect, where the difference between the lower and the higher pressures is a major factor in determining the temperature drop. In addition, as shown in the Fig.10, the precooling stage in the cascade cycle can decrease the temperature difference of hot and cold streams at the low temperature side of the heat exchanger. Therefore, the cascade cycle can result in higher efficiency with less entropy generation associated with the finite-temperature heat exchange in the counterflow heat exchangers.

This study has taken several ideal assumptions such as zero-pressure drop except for the expansion valve, higher compressor efficiency of 80%, and the minimum temperature difference of 3 K. For the realistic results, the effect of minimum temperature in the heat exchangers and the pressure drop in the cycle on COP should be considered as a future work. Furthermore, the predicted results should be validated by experiments.

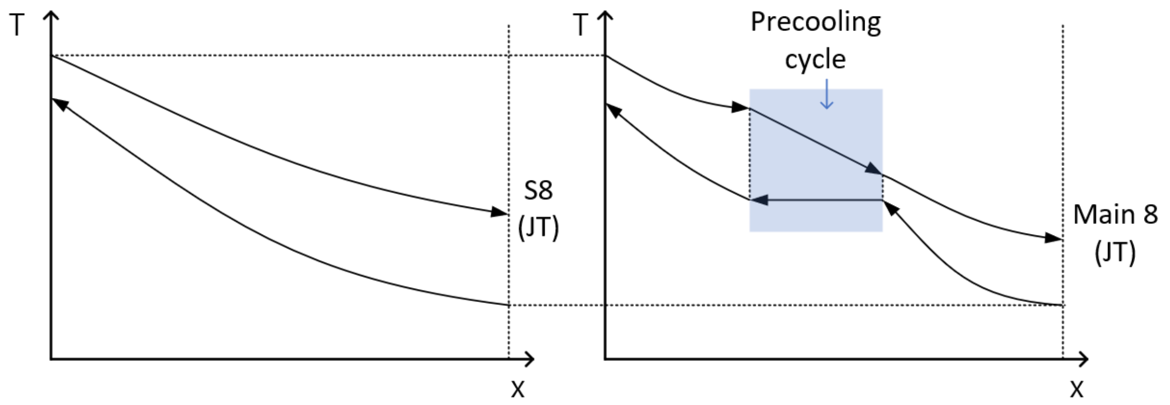


Fig. 10 Temperature distribution in the heat exchanger for SMR cycle (left) and cascade cycle (right)

5. Conclusion

The purpose of this paper is to show the possibility of efficient MR-JT refrigerator for 170 K by using non-flammable refrigerants only. At first, R14, R23, and R218 are sifted out and selected as the working fluids for the simulation. To achieve the target temperature, 170 K, the molar ratio of R14 should be larger than those of the other refrigerants. In this paper, the mixture composition is R14:R23:R218 = 0.7:0.1:0.2 for maximum COP. The analyzed configuration of the cycles is two-types; SMR and cascade-MR cycle. The comparison between the SMR and the cascade cycle clearly reveals that the efficiency of the low-temperature MR cycle is greatly enhanced by the implementation of precooling cycle. Deploying the precooling cycle in the appropriate location in the main cycle effectively reduces the generation of irreversibility in the recuperative heat exchanger of the refrigeration cycle.

Acknowledgements

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