

Article

Investigation on the Performances of Vuilleumier Cycle Heat Pump Adopting Mixture Refrigerants

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Abstract: The performances of thermodynamics cycles are dependent on the properties of refrigerants. The performances of Vuilleumier (VM) cycle heat pump adopting mixture refrigerants are analyzed by MATLAB software using REFPROP programming. At given operating parameters and configuration, performances of the VM cycle adopting pure refrigerant, H_2 , He or N_2 are compared. Thermodynamic properties of the four type mixtures, namely, He- H_2 , He- N_2 , H_2 - N_2 and He- H_2 - N_2 , are obtained with total 16 mixing ratio, and the coefficient of performance and the exergy efficiency of these four mixture types in VM cycle heat pump are calculated. The results indicate that within the temperature of heat source 400–1000 K, helium is the best choice of pure refrigerant for VM cycle heat pump. The He- H_2 mixture is the best among all binary refrigerant mixtures; the recommended proportion is 1:2. For trinary refrigerant mixture, suggested proportion of helium, hydrogen and nitrogen is 2:2:1. For these recommended mixtures, system COPs (coefficient of performances) are close to 3.3 and exergy efficiencies are about 0.2, which are close to pure refrigerant helium.

Keywords: VM cycle heat pump; coefficient of performance; exergy efficiency; pure refrigerant; mixture refrigerants

1. Introduction

Vuilleumier (VM) cycle is a thermally driven reversible Stirling gas cycle [1,2]. Selection of heat sources is of great flexibility [3]; it can be fossil fuels such as natural gas, or renewable energy such as solar energy or even waste heat. The advantages of using VM cycle heat pump are small output, low noise, long life span, high efficiency, etc. [4,5]. It can provide cold or hot production, even with power product. The cyclic efficiency of the ideal VM cycle is the same as that of the Carnot cycle [6].

However, the actual coefficient of performance of the VM cycle is only about 30~40% of the ideal cycle, due to the reciprocating flow of refrigerant in the VM cycle heat pump. The inevitable heat transfer and flow losses caused by the flowing of refrigerant account for more than half of the total losses [7], which has great influence on the performances of the VM cycle heat pump. Undoubtedly, different refrigerants have different characteristics in heat transfer and fluid flow. Therefore, the performances of the system vary under different working conditions with different working fluid [8].

Mixture refrigerants are good examples. Chakravarthy et al. obtained mixing criteria with a number of cycles within 4 K to 300 K, including the Stirling gas cycle [9]. Narasimhan and Venkatarathnam experimentally determined the mixture fraction that had the highest exergy efficiency of single-stage refrigeration [10]. Asadnia and Mehrpooya [11] studied the application of mixture refrigerants, namely, nitrogen, helium and hydrogen in Joule Brayton refrigeration cycle. Results showed that the coefficient of performance using the new mixture refrigerants was 0.1710 and the exergy efficiency was 39.5%, both of them were higher than the existing refrigerant. Lee et al. [12] carried out optimum research of a cryogenic refrigeration cycle adopted nitrogen and argon mixture

as refrigerant, from the distribution of temperature and the working pressure of compressor. He got the maximum coefficient of performance and the corresponding Carnot cycle efficiency. Lee et al. [13] researched the feasibility and effectiveness of helium-nitrogen mixture as refrigerant in the refrigeration cycle by Peng-Robinson equation of state.

There are more literatures on the mixture refrigeration cycles. Zhejiang University, which owns the National Key Laboratory [14], used the operation pressure ratio method to optimize the cyclic performance for single-stage compression by adopting binary mixture. They also obtained that constituent and the concentration of mixture, the low side pressure of cycle, and the pressure ratio were factors that had an influence on the coefficient of cycle performance. Literature [15] tested a small capacity pre-cooled mixture cycle system, and established a chromatographic analysis method for mixture concentration optimization.

REFPROP is used in these mixture properties investigations. Yin et al. [16] investigated mixtures of $\text{SF}_6\text{-CO}_2$ as working fluids for geothermal power plants by obtaining the thermophysical properties of the mixtures from National Institute of Standards and Technology (NIST) REFPROP software (Version 8.0). Seneviratne et al. [17] extended critical point literature data for methane and propane mixtures in a beta-version of REDPROP 9.2. Rivas et al. [18] measured a suitable doping agent in two CO_2 -rich, $\text{CO}_2 + \text{SO}_2$ mixtures with the same SO_2 composition from 263.15 to 373.19 K and up to 190.10 MPa, and validated the modeling with the REFPROP 9 software.

For VM cycle heat pump, gas hydrogen, helium or nitrogen are common working fluids, but all applications are single-refrigerant, few on the mixture. To know the performances of mixture, we set the given working condition and determine the configuration of all system parts. Using MATLAB and REFPROP software (Version 9.1) to simulate the variation of properties of pure refrigerant hydrogen, helium and nitrogen, calculate the coefficient of performance and exergy efficiency of the system. Then investigate the properties of four type mixtures, He-H_2 , He-N_2 , $\text{H}_2\text{-N}_2$ and $\text{He-H}_2\text{-N}_2$, separately. Finally, compare the system performances of mixture cycles at different mixture ratio with that of the pure refrigerant cycle.

2. Working Principle and Performances Calculation for VM Cycle Heat Pump

2.1. Working Principle

Figure 1 shows the schematic of VM cycle heat pump. The heat pump mainly contains two cylinders, a cold and a hot cylinder, two passing pistons, two regenerators and three heat exchangers. The two passing pistons are connected to the crankshaft by the driven connecting rod, and the pistons are moved following the rotation of the crankshaft. Between the hot passing piston and the top of hot cylinder is the hot space; while between the cold passing piston and the top of cold cylinder is the cold space. The volume between cold and hot cylinder which varies with the movement of the piston is called warm space.

When the VM cycle heat pump is in heating condition, it absorbs the heat from both heat source and cold source via hot and cold cylinder, then supplies the heat to the user by the warm heat exchanger. While in refrigeration condition, it absorbs the heat of the user, lowers the temperature of the subject, and rejects the heat to the environment at room temperature. Theoretically, in heating or refrigeration mode, the total heat absorbed by the hot space and the cold space is equal to the heat released at the warm space.

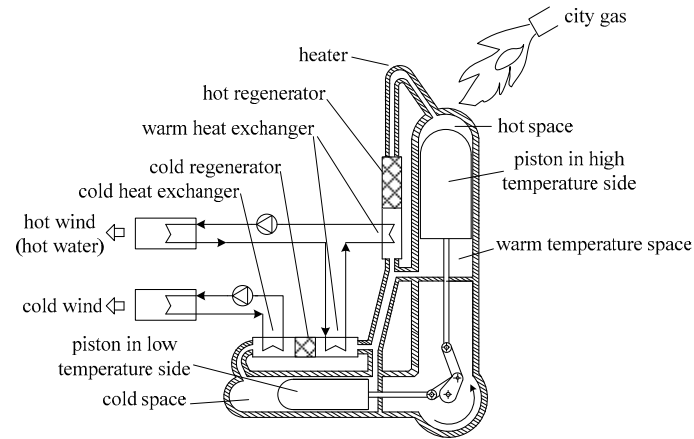


Figure 1. Schematic of Vuilleumier (VM) cycle heat pump.

2.2. Performances Calculation Method

Formulas used to calculate the performances of VM cycle heat pump are as follows [19,20]:

(1) Travel volume of the cold cylinder:

$$V_{co} = \frac{1}{4} \pi D_{co}^2 Z \quad (1)$$

(2) Temperature ratio of the hot and cold space:

$$\tau = T_h / T_{co} \quad (2)$$

(3) Pressure phase angle:

$$\theta = \arctan \frac{\omega(1 - \tau_h) \sin \varphi}{(\tau_{co} - 1) - \omega(1 - \tau_h) \cos \varphi} \quad (3)$$

(4) Temperature ratio of the cold side:

$$\tau_{co} = T_a / T_{co} \quad (4)$$

(5) Temperature ratio of hot side:

$$\tau_h = T_a / T_h \quad (5)$$

(6) Pressure parameter:

$$\delta = \frac{\sqrt{(\tau_{co} - 1)^2 + \omega^2(1 - \tau_h)^2 - 2\omega(\tau_{co} - 1)(1 - \tau_h) \cos \varphi}}{(1 + \tau_{co}) + \omega(1 + \tau_h)} \quad (6)$$

(7) Pressure ratio:

$$\frac{P_{\max}}{P_{\min}} = \frac{1 + \delta}{1 - \delta} \quad (7)$$

(8) Maximum pressure:

$$P_{\max} = P_{av} \sqrt{\frac{1 + \delta}{1 - \delta}} \quad (8)$$

(9) Minimum pressure:

$$P_{\min} = P_{av} \sqrt{\frac{1 - \delta}{1 + \delta}} \quad (9)$$

(10) Theoretical cooling capacity of cold cylinder:

$$Q_{co} = P_{av} V_{co} \frac{\pi n \delta \sin \theta}{60(1 + \sqrt{1 - \delta^2})} \quad (10)$$

(11) Theoretical heating absorption of hot cylinder:

$$Q_h = Q_{co} \frac{\tau_{co} - 1}{1 - \tau_h} \quad (11)$$

(12) Theoretical heating release of warm cylinder:

$$Q_a = Q_{co} + Q_h \quad (12)$$

(13) Theoretical coefficient of performance of heat pump:

$$COP = \frac{Q_a}{Q_h} \quad (13)$$

(14) Theoretical exergy efficiency of heat pump:

$$\eta_e = \frac{E_{x,out} - E_{x,in}}{E_{x,h} + E_{x,co}} = \frac{Q_a \left(\left(1 - \frac{T_0}{T_{out}} \right) - \left(1 - \frac{T_0}{T_{in}} \right) \right)}{Q_h \left(1 - \frac{T_0}{T_h} \right) + Q_{co} \left(\frac{T_0}{T_{co}} - 1 \right)} \quad (14)$$

3. Performances of Pure Refrigerants in VM Cycle

3.1. Properties of Pure Refrigerants

In order to get close to the ideal cycle, the actual VM cycle heat pump should choose the actual gas which is more similar to the ideal gas. Therefore, helium, hydrogen and nitrogen are the most common pure refrigerant to be used in the VM cycle. Here are some of their physical properties:

(1) Helium

Helium is a colorless, odorless gas. Its chemical nature is pretty stable; it could not normally combine with any other element. What is more, helium is the most difficult gas to liquefy in nature owing to the extremely low critical temperature. And the conversion temperature of it is also very low; helium has the lowest boiling point among all gases. In terms of high specific heat capacity, high thermal conductivity and low density, helium is only inferior to hydrogen.

(2) Hydrogen

Generally, hydrogen is also a colorless, odorless gas. It is extremely insoluble in water. It is also a gas with the lightest quality, the largest specific heat, the highest thermal conductivity, and the lowest viscosity of all gases. The conversion temperature of hydrogen is much lower than room temperature, for example, the maximum conversion temperature is only about 204 K. Therefore, in order to produce cold effect, hydrogen must be pre-cooled to 204 K firstly, and then throttled. It is noted that hydrogen belongs to flammable and explosive substances, there is a need for special attention to operate liquid hydrogen, and a need for rigorous control and gauging the purity of liquid hydrogen.

(3) Nitrogen

Similar to helium and hydrogen, nitrogen is also a colorless, odorless gas, it is slightly lighter than air and insoluble in water. The chemical nature of it is also stable, so it is frequently used as a protective gas. Furthermore, because it is non-toxic and has a lower boiling point than air, liquid nitrogen is the safest refrigerant in low-temperature research fields, but should be avoided of asphyxia.

Liquid nitrogen is also used as pre-cooling equipment in hydrogen or helium liquefaction installations. To prevent explosions, storage of liquid nitrogen should be careful, avoiding long-time contacting with hydrocarbons.

3.2. Properties Variation of Pure Refrigerants

The physical properties of three refrigerants, helium, hydrogen and nitrogen, are shown from Figures 2–4. The temperature range is 400–1000 K.

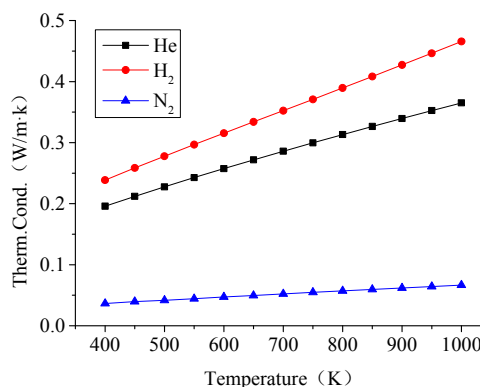


Figure 2. The thermal conductivity of three refrigerants.

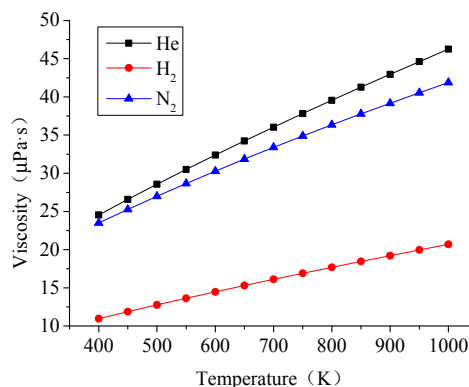


Figure 3. The viscosity of three refrigerants.

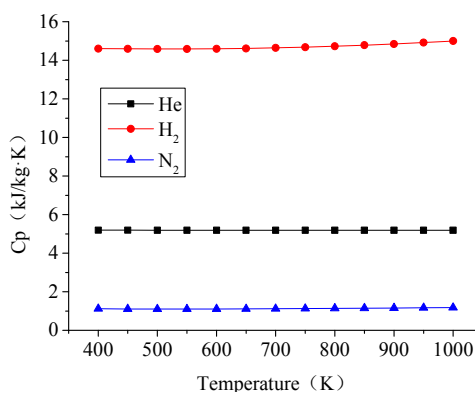


Figure 4. The constant pressure specific heat of three refrigerants.

As illustrated in Figures 2–4:

(1) The constant pressure specific heat and thermal conductivity of helium and hydrogen are greater than that of nitrogen, which indicates that helium and hydrogen have advantages over nitrogen in absorbing heat from heat source. However, the loss of heat conduction and heat dissipation is also greater than that of nitrogen.

(2) The viscosity of nitrogen is greater than hydrogen, so nitrogen has larger friction loss, further increasing the pressure loss. It has effect on the pressure ratio, and lower the refrigeration output than hydrogen. However, the viscosity of nitrogen is less than that of the helium.

As a result, each refrigerant has different characteristics in terms of heat transfer and flow resistance. Hydrogen shows the best performance overall. When comparing helium with nitrogen, both of them have advantages in heat transfer and flow, respectively. For example, the flow resistance of nitrogen is smaller, but the heat transfer performance of helium is better.

3.3. Performances of Pure Refrigerants

To make a clear comparison, the configuration and some operating parameters of the VM heat pump are given in Tables 1 and 2.

Table 1. Structure parameters of VM cycle heat pump [19–21].

Parameter	Symbol, Formula, Basis, Introduction	Value
Cylinder bore	D_{co}	0.0699 m
Distance of run	Z	0.0312 m
Phase angle of volume	φ	90°
The length of passing piston	L	0.04359 m
Radial clearance of passing piston	σ	0.00015 m
Diameter of regenerator	D_R	0.0226 m
Length of regenerator	L_R	0.0226 m
Filler of regenerator	Mesh of stainless steel	—
Pressure parameter	δ	0.3
Mode of driving	Piston driving of single handle, dual power	—
Proportion of volume	ω	10
Rotation rate	n	600 rpm = 10 Hz

Table 2. Calculation parameters of VM cycle heat pump.

Parameter	Symbol, Formula, Basis, Introduction	Value
Temperature of hot space	T_h	500 K
Temperature of warm space	T_a	340 K
Temperature of cold space	T_{co}	300 K
Ambient temperature	T_0	273 K
Average temperature	$T_{av} = \frac{T_h + T_{co}}{2}$	400 K
Average pressure	P_{av}	10.0×10^6 Pa
Theoretical exergy efficiency	η_e	—
Theoretical coefficient of performance	COP	—

As shown in Figure 5, the COPs (coefficient of performances) of three working fluids increase with the elevation of the heat source temperature. It trends to go gentle at higher temperature. The COPs of heat pump adopting hydrogen and helium are very close, which are higher than that of the nitrogen.

Figure 6 shows the exergy efficiency to temperature of heat source of these three working fluids. Exergy efficiency of the VM cycle heat pump adopting hydrogen and helium decrease as the temperature of the heat source increases. The trends are opposite to that of the COP. While for nitrogen, the exergy efficiency variation trend is the same as that of the COP. They both increase as the temperature of heat source increases.

Therefore, according to the system performances of the three pure refrigerants, helium and hydrogen are similar to each other, better than that of the nitrogen. Considering the liable explosion problem of hydrogen, helium is the best choice of working fluid for VM cycle heat pump. For economic concern, nitrogen should be introduced to lower the cost of the whole facility.

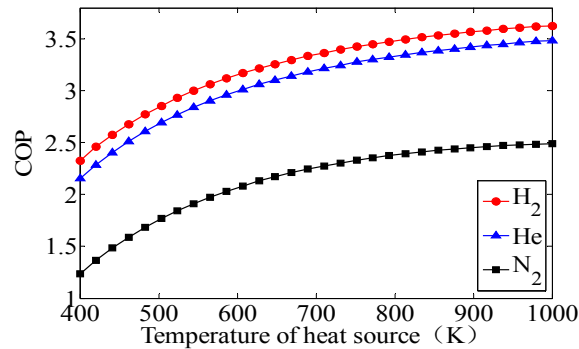


Figure 5. The COP (coefficient of performance) for the three pure refrigerants.

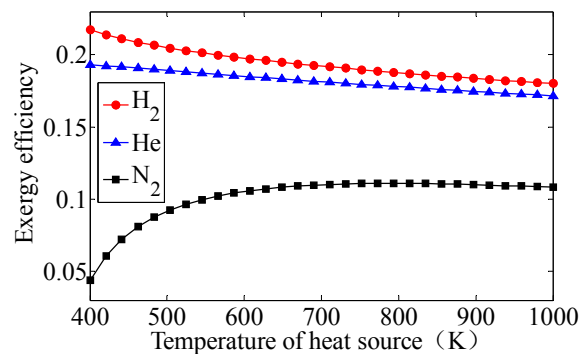


Figure 6. The exergy efficiency of three refrigerants.

4. Performances for Mixture Refrigerant in VM Cycle

Giacobbe analyzed the heat transfer properties of helium, hydrogen and other inert gases [22]. Hosseinnnejad et al. carried out numerical calculations of transport properties on the mixture of hydrogen and inert gas [23]. For security and economy reasons, four kinds of mixture refrigerants were discussed in this paper, namely, helium and hydrogen, helium and nitrogen, hydrogen and nitrogen, helium, hydrogen and nitrogen.

4.1. Properties of Mixture

In Figures 7 and 8, the thermal conductivity and viscosity of helium and hydrogen mixture increase as the elevation of heat source temperature. When at mixing proportion of 1:2, it has the maximum value of the thermal conductivity and the minimum value of viscosity. This could be explained by Figures 2 and 3, in which the thermal conductivity of hydrogen is the highest, but the viscosity is the lowest. Figure 7 also indicates that there are a cross point of mixture proportion 2:1 and 1:1 when the heat source temperature is about 550 K.

Figures 9 and 10 indicate that the thermal conductivity and viscosity of helium and nitrogen mixture also increase with the heat source temperature rise. In addition, the bigger the number of mole fractions of helium, the higher the value of thermal conductivity and viscosity. The curves for viscosity have the same variation, but the difference of viscosity values for the three mixing proportions is relatively small.

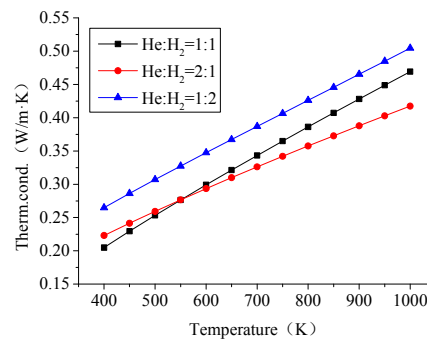


Figure 7. Thermal conductivity for He-H₂ mixture.

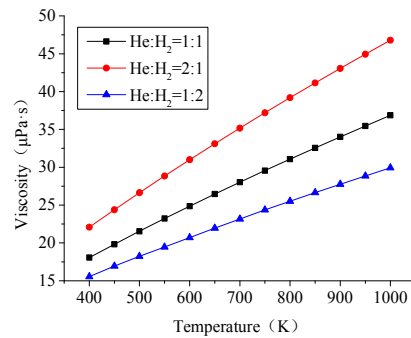


Figure 8. Viscosity for He-H₂ mixture.

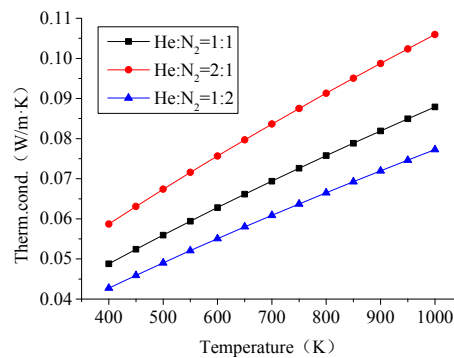


Figure 9. Thermal conductivity for He-N₂ mixture.

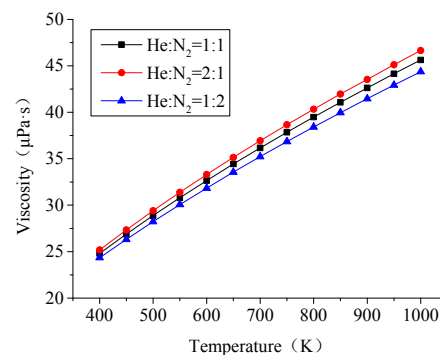


Figure 10. Viscosity for He-N₂ mixture.

Comparing Figures 11 and 12 to Figures 9 and 10, we can find that the change regulations of He-N₂ and H₂-N₂ are similar. The difference is the divergence between each value of each mixing proportion. For the H₂-N₂ mixture, the difference of the thermal conductivity is smaller.

For the helium, hydrogen and nitrogen mixture, the thermal conductivity and viscosity increase as well as the heat source temperature, as shown in Figures 13 and 14. The change of viscosity is obsolete. Furthermore, for thermal conductivity, at mixing ratio of 1:2:1, 1:2:2, and 2:1:2, the values are relatively small; at ratio of 2:1:1, it has the smallest value.

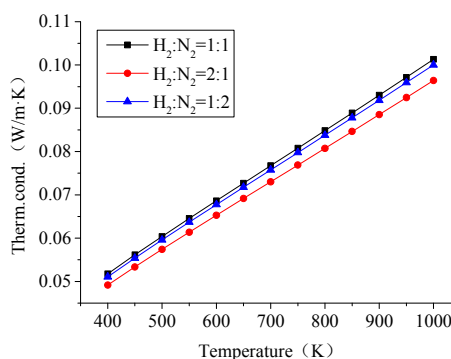


Figure 11. Thermal conductivity for H₂-N₂ mixture.

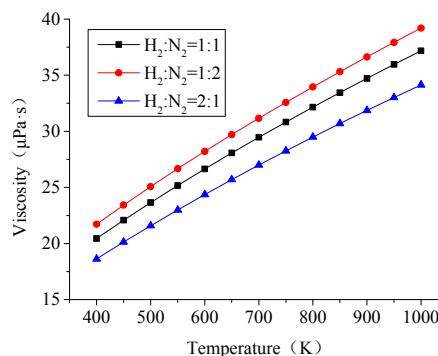


Figure 12. Viscosity for H₂-N₂ mixture.

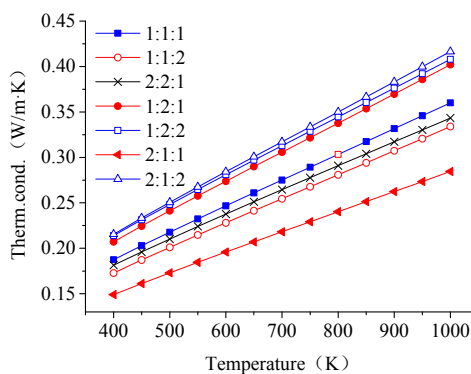


Figure 13. Thermal conductivity for He-H₂-N₂ mixture.

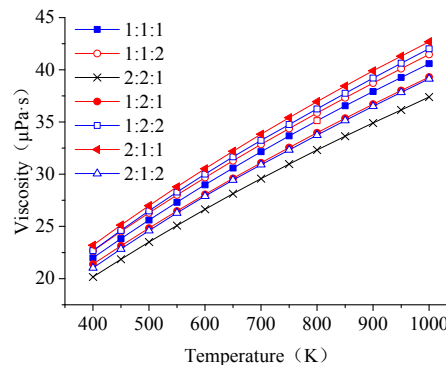


Figure 14. Viscosity for He-H₂-N₂ mixture.

4.2. Result Analysis

Figures 15 and 16 are the COP and exergy efficiency for VM cycle heat pump adopting He-H₂ mixture. There is a small difference of COP in different proportions of mixture. The COP increases at elevated temperature, reaches maximum value of 3.5 at calculating range. Mixing ratio of 1:2 has the highest values of exergy efficiency but when temperature approaches 1000 K, the values of exergy efficiency for the three He-H₂ mixtures are very close.

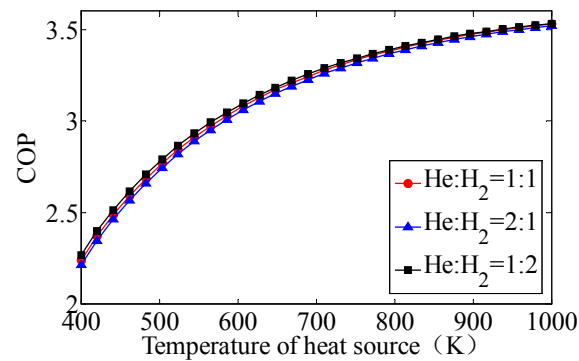


Figure 15. The COP for He-H₂ mixture.

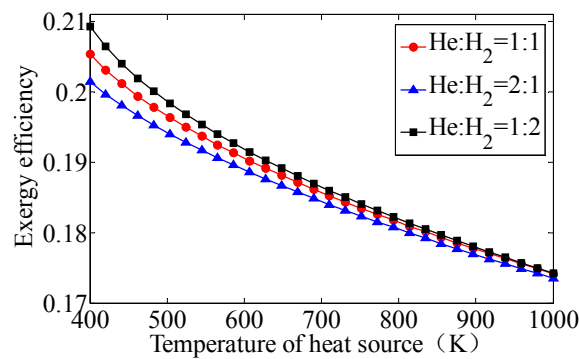


Figure 16. The exergy efficiency for He-H₂ mixture.

Figures 17–20 are the COP and exergy efficiency for VM cycle heat pump adopting He-N₂ and H₂-N₂ mixture. The tendency of the two kinds of binary mixtures with different ratio is similar. That is, the higher the heat source temperature, the bigger the value of COP; exergy efficiency goes up then down; the 2:1 proportion of mixture has the largest value of COP and exergy efficiency. Overall, H₂-N₂ mixture shows better performance than that of the He-N₂ mixture.

The COPs of VM cycle heat pump using He-H₂-N₂ mixture as refrigerant are shown in Figure 21. The COP increases as well as the temperature of heat source. Among the seven mixture ratios, proportion 2:2:1 has the largest COP, it reaches about 3.5 at 1000 K. The difference of COP is relatively small at lower temperature, and becomes bigger at higher temperature.

Figure 22 is the exergy efficiency of VM cycle heat pump adopting the three refrigerant mixtures. At lower temperature, the tendency is not clear. Exergy efficiency for some proportion mixture goes up, while some goes down. There are crossover points between mixing ratio 1:2:1 to 2:1:1 and mixing ratio 1:2:2 to 2:1:2. At higher temperature, the exergy efficiency declines. Mixing ratio 1:1:2 has the worst curve of exergy efficiency.

To sum up, there are 16 mixing ratios and four kinds of mixture refrigerants investigated in this paper. For binary He-H₂ mixture, the difference of COP is not significant; ratio 1:2 has higher exergy efficiency. For binary He-N₂ or H₂-N₂, ratio 2:1 has both higher COP and exergy efficiency. Basically, the overall system performances of mixture H₂-N₂ are better than mixture He-N₂. For ternary He-H₂-N₂ mixture, at the proportion of 2:2:1, the system has the best COP and exergy efficiency.

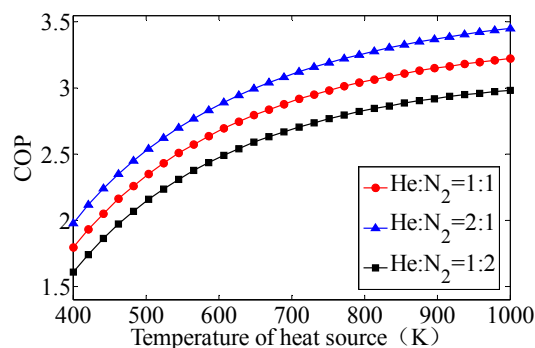


Figure 17. The COP for He-N₂ mixture.

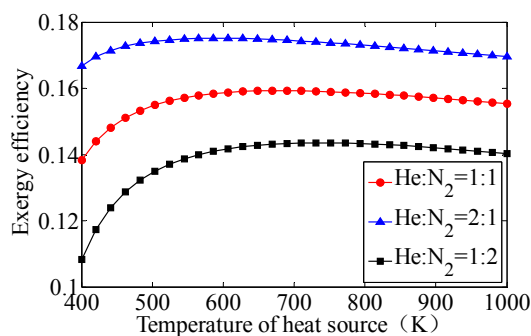


Figure 18. The exergy efficiency for He-N₂ mixture.

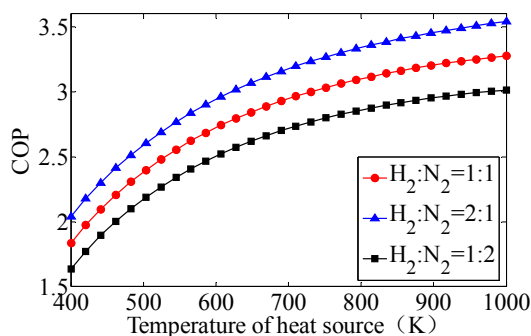


Figure 19. The COP for H₂-N₂ mixture.

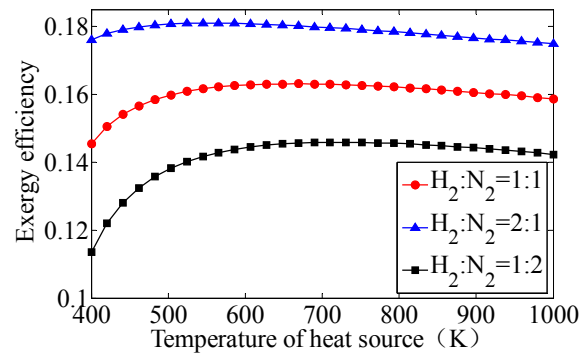


Figure 20. The exergy efficiency for H₂-N₂ mixture.

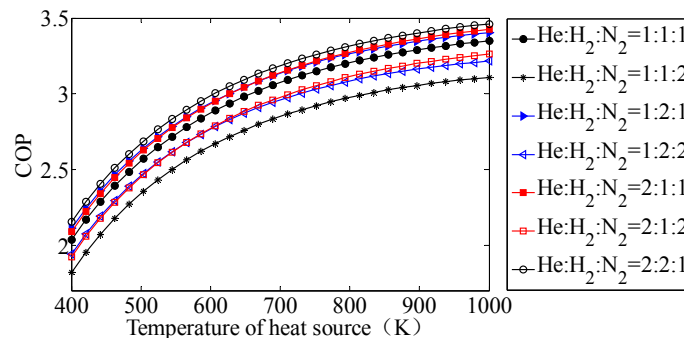


Figure 21. The COP for He-H₂-N₂ mixture.

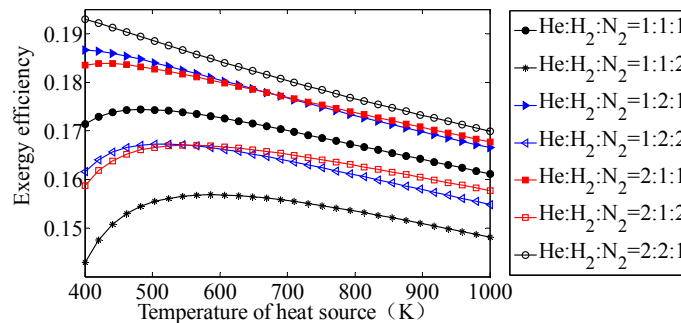


Figure 22. The exergy efficiency for He-H₂-N₂ mixture

5. Conclusions

Mixture refrigerants may have effects on the cycle performances. In this paper, at the temperature of heat source within 400–1000 K and at given system configuration parameters, the COP and exergy efficiency of VM cycle heat pump adopting mixture as refrigerants are calculated, and compared with each other or pure refrigerants. We can draw conclusions as follows:

- (1) For pure refrigerants, helium and hydrogen are similar to each other, better than that of nitrogen. Considering the liable explosion problem of hydrogen, helium is the best choice of pure refrigerant for VM cycle heat pump.
- (2) For binary mixture, He-H₂ mixture has optimum thermodynamic performance, the recommended ratio is 1:2. The other binary mixture is also an optimum proportion of mixture.
- (3) For ternary mixture, at the proportion of He-H₂-N₂ mixture is 2:2:1, the system has the best COP and exergy efficiency. Furthermore, all the system performances of recommended binary and ternary mixture are close to pure refrigerant helium. For these recommended binary and ternary

mixtures, system COPs are close to 3.3 and exergy efficiencies are about 0.2, which are close to pure refrigerant helium.

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Author Contributions: Yingbai Xie proposed and designed the research; Kai Zhong performed the calculation. Both authors jointly worked on deriving the results and wrote the paper. Both authors have read and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

Symbol	Implication
COP	Coefficient of performance
D_{co}	Diameter of cold cylinder
$E_{x,co}$	Exergy of cold space
$E_{x,h}$	Exergy of heat space
$E_{x,in}$	Exergy of fluid inlet
$E_{x,out}$	Exergy of fluid outlet
P_{av}	Average pressure
P_{max}	Maximum pressure
P_{min}	Minimum pressure
Q_a	Theoretical heating release of warm cylinder
Q_{co}	Theoretical heat capacity absorbed by cold cylinder
Q_h	Theoretical heating absorption of hot cylinder
T_a	Temperature of warm space
T_{co}	Temperature of cold space
T_h	Temperature of hot space
T_{in}	Inlet temperature
T_o	Ambient temperature
T_{out}	Outlet temperature
V_{co}	Travel volume of the cold cylinder
Z	Distance of the stroke
τ	Temperature ratio
τ_{co}	Temperature ratio of the cold side
τ_h	Temperature ratio of the hot side
ϕ	Phase angle of volume
θ	Pressure phase angle
δ	Pressure parameter
n	Rotation rate
ω	Proportion of volume
η_e	Theoretical exergy efficiency

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