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Thermodynamic analysis of refrigerant selection for high temperature heat pump cycles

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Abstract

Industrial heat pump is recognized as one of decarbonization technologies in industry by a couple of its high efficiency and electrification with low carbon electricity. For expanding applications of heat pumps into various industrial heating processes, it is necessary to increase the supply temperature of heat pumps. Recently, some new refrigerants have been developed, which allows to increase the choice of refrigerants expected to be applied to higher temperature heat pumps. The purpose of this study is to illustrate working domain maps which can determine the promising refrigerant and the upper limit of heat pumping temperature lift for each supply temperature. First, with thermodynamic analysis for simple heat pump cycle, refrigerant selection in the wide range of the heat pump supply temperature from 60°C to 200°C is analyzed comprehensively for 17 pure refrigerants currently available on the market. Then, the effect of a high efficiency improvement by two-stage cycle with economizer are examined on the refrigerant selection.

Keywords: Industrial heat pump ; High temperature heat pump ; Refrigerant selection ; Low GWP ; Thermodynamic analysis

1. Introduction

Industrial heat pump is recognized as one of decarbonization technologies in industry by a couple of its high efficiency and electrification with low carbon electricity. Figure 1 shows the distribution of heat demand by temperature in the Japanese industrial sector [1]. The high temperature heat demand above 200°C is limited to energy-intensive industries such as steal, metals, cement and petrochemicals, and most of the heat is used as combustion by burner. On the other hand, below 200°C, various industries exist, having various types of heat demands such as drying, washing, sterilization, distillation and concentration. Another feature is that it is used mainly as a form of steam. This heat demand area below 200°C accounts for 28% of the total industrial heat demand and is expected to be applied to heat pumps.

For expanding the heat pump application range, it is necessary to prepare heat pumps with various supply temperatures up to 200°C for use in various heating processes. In general, heat pump performance largely depends on the refrigerant selection, and thus it is desirable to select the appropriate refrigerant. Recently, some new refrigerants have been developed for corresponding to lowering the global warming potential (GWP), which allows to increase the choice of refrigerants expected to be applied to higher temperature heat pumps.

The purpose of this study is to provide working domain maps which can determine the promising refrigerant and the upper limit of heat pumping temperature lift for each supply temperature. Brunin et al. investigate the working domain of many refrigerants in the heat pump supply temperature range up to 200°C [2]. However, majority of the investigated refrigerants are banned today (CFCs, HCFCs) and will be restricted in near future use (HFCs). Ommen et al. investigate the working domains focusing on 4 natural refrigerants (R290, R600a, R744 and R717) [3]. They consider not only technical and thermodynamic constraints but also economic constraints, however the investigated heat pump supply temperature is limited up to 120°C.

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In this study, for 17 pure refrigerants currently available on the market including newly developed HFOs and HCFOs, refrigerant selection in the wide range of the heat pump supply temperature from 60°C to 200°C is analyzed comprehensively with thermodynamic analysis for simple heat pump cycle. In addition, the effect of a high efficiency improvement by two-stage cycle with economizer are examined on the refrigerant selection.

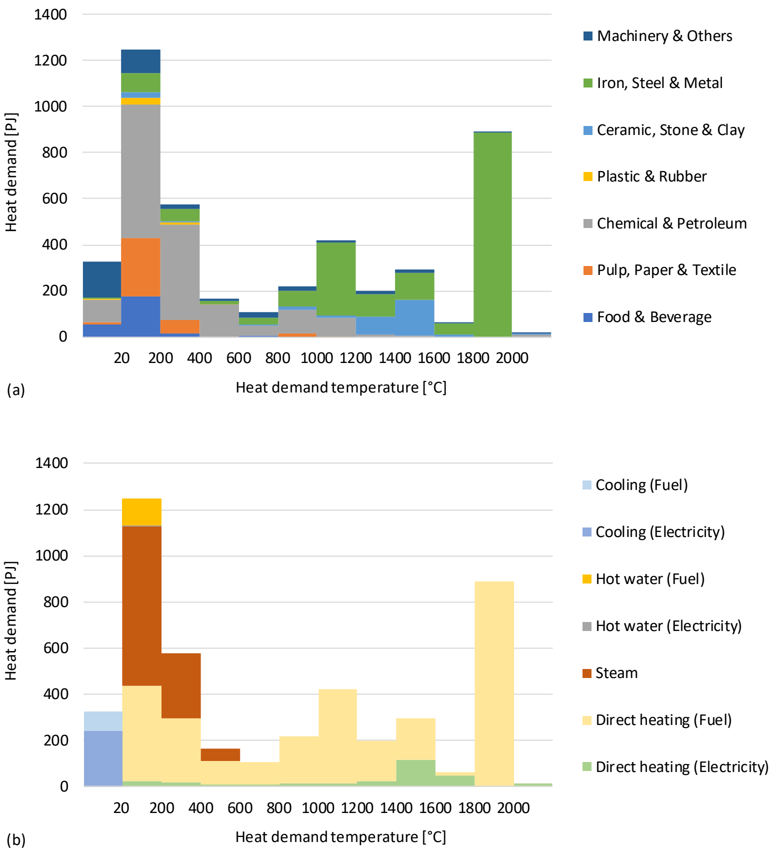

Fig. 1. Heat demand in the Japanese industry (a) by industry and (b) by heat use form

2. Refrigerants for high temperature heat pumps

Table 1 shows the basic properties of 17 refrigerants investigated in this study. Although 3 HFCs (R32, R134a and R245fa) have relatively high GWPs and will be restricted in near future use, they are included in this study for comparison. Other 14 refrigerants have very low GWPs. Among them, 2 HCFOs (R1224yd(Z) and R1233zd(E)), 1 HFO (R1336mzz(Z)) and 2 natural refrigerants (R718 and R744) are classified as A1 in ASHRAE Standard 34 safety group classification, which indicates low-toxicity and non-flammability. The ozone depletion potentials (ODPs) of the HCFOs are not zero but recognized negligible small. Thus, they are not listed as ozone depleting substances (ODSs) in the Montreal Protocol. 3 HFOs (R1234yf, R1234ze(E) and R1234ze(Z)) are classified as A2L of low-toxicity and mild-flammability. 5 HCs (R290, R600, R600a, R601 and R601a) are classified as A3 of low-toxicity and high-flammability. R717 is classified as B2L of high-toxicity and mild-flammability.

Table 1. Basic properties of 17 pure refrigerants

Type	Refrigerant	Chemical formula	Molar mass [g/mol]	ODP	GWP	Safety	Critical temperature [°C]	Critical pressure [MPa]
HFC	R32	CH_2F_2	52.0	0	677	A2L	78.1	5.78
	R134a	$C_2H_2F_2$	102.0	0	1300	A1	101.1	4.06
	R245fa	$C_3H_3F_5$	134.0	0	858	B1	153.9	3.65
HCFO	R1224yd(Z)	C_3HF_4Cl	148.5	0.00023	~1	A1	155.5	3.34
	R1233zd(E)	$C_3H_2F_3Cl$	130.5	0.00025	~1	A1	166.5	3.62
HFO	R1234yf	$C_3H_2F_4$	114.0	0	~1	A2L	94.7	3.38
	R1234ze(E)	$C_3H_2F_4$	114.0	0	~1	A2L	109.4	3.63
	R1234ze(Z)	$C_3H_2F_4$	114.0	0	~1	A2L	150.1	3.53
	R1336mzz(Z)	$C_4H_2F_6$	164.1	0	~2	A1	171.4	2.90
Natural	R290	C_3H_8	44.1	0	3	A3	96.7	4.25
(HC)	R600	C_4H_{10}	58.1	0	3	A3	152.0	3.80
	R600a	C_4H_{10}	58.1	0	3	A3	134.7	3.63
	R601	C_5H_{12}	72.1	0	4	A3	196.6	3.37
	R601a	C_5H_{12}	72.1	0	4	A3	187.2	3.38
Natural	R717	NH_3	17.0	0	0	B2L	132.4	11.4
(Others)	R718	H_2O	18.0	0	0	A1	373.9	22.1
	R744	CO_2	44.0	0	1	A1	31.0	7.38

Figure 2 shows the relation between the molar mass and the critical temperature for these refrigerants. Focusing on HCs, it can be seen that the critical temperature becomes higher as the molar mass becomes larger. However, some refrigerants have the same molar mass but the different critical temperatures, which is because of the isomers. The same tendency applies to HFCs, HCFOs and HFOs, however the molar mass is larger than that of HC when viewed at the same critical temperature. Therefore, because of its large molar mass and complicated molecular structure, the development possibility of new refrigerants for high temperature heat pumps is relatively high. On the other hand, it can be seen that R717, R718 and R744 show peculiar characteristics.

The relatively large molar mass is a characteristic of the refrigerant for high temperature heat pump. This characteristic affects the shape of saturated vapor curve. It is known that the slope of the saturated vapor curve on *T-s* diagram becomes positive from negative when the value of specific heat becomes relatively large. Morrison investigates the shape of saturation curves [4]. From general thermodynamic relation, the slope of the saturation curve on *T-s* diagram can be written as follows:

$$\left.\frac{dT}{ds}\right|_{sat} = \left[\frac{c_v}{T} + \left(\frac{\partial p}{\partial T}\right)_v \left.\frac{dv}{dT}\right|_{sat}\right]^{-1} \tag{1}$$

Here the value of c_v/T is always positive and the value of $(\partial p/\partial T)_v$ is generally positive. The value of $dv/dT|_{sat}$ is generally positive for liquid and negative for vapor. Therefore, the slope of the liquid saturation curve is generally positive, but the slope of the vapor saturation curve can be positive or negative mainly depending of the value of c_v. When the molar mass becomes relatively large and the specific heat c_v becomes relatively large, the slope of saturated vapor curve changes from negative to positive.

As an example, Figure 3 shows the comparison of the saturated curves of R134a and R1336mzz(Z) on *T-s* diagram. It can be seen that the slope of the saturated vapor curve of R134a (molar mass: 102.0 g/mol) is negative, but the slope of R1336mzz(Z) (molar mass: 164.1 g/mol) is positive. Therefore, when using R134a, there is no concern that liquid compression will occur even if the compressor suction superheating is zero, but when using R1336mzz(Z), liquid compression will occur unless the sufficient superheating is secured. Hence, it is necessary to secure the suction superheating when using some refrigerants for high temperature heat pumps, for example, by installing an internal heat exchanger.

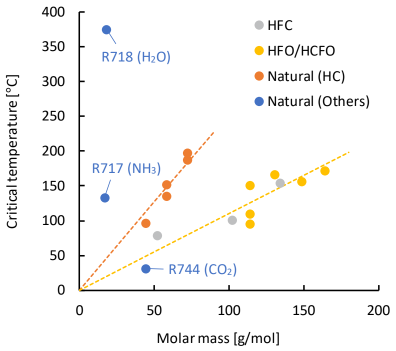

Figure 2. Relation between molar mass and critical temperature

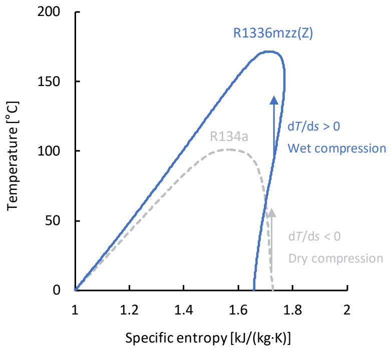

Figure 3. Slope of saturated vapor curve

3. Analysis for simple heat pump cycle

This study analyzes subcritical heat pump cycles using pure refrigerants, assuming that the temperature glides on both of heat source and heat sink are relatively small. Therefore, among the refrigerants shown in Table 1, 16 refrigerants were targeted, excluding R744, which has a lower critical temperature than 60°C.

3.1. Method

Figure 4 and Table 2 show the schematic diagram and calculation condition of the heat pump cycle, respectively. The temperature lift (ΔT_{lift}) is defined by the difference between the heat sink outlet temperature (T_{h2}, heat supply temperature) and the heat source inlet temperature (T_{c1}). The temperature glides on both of heat source (ΔT_{c}) and heat sink (ΔT_{h}) are fixed at 5 K. The pinch temperature differences on both of evaporator ($\Delta T_{\mathrm{pinch,evp}}$) and condenser ($\Delta T_{\mathrm{pinch,cnd}}$) are fixed at 2 K. Strictly speaking, the pinch point of the condenser occurs somewhere in the condenser, but in order to simplify the calculation, it is defined by the difference between the condensation temperature (T_{cnd}) and the heat sink outlet temperature (ΔT_{h2}). The evaporator superheating ($\Delta T_{\mathrm{sh,evp}}$) and the condenser subcooling (ΔT_{sc}) are fixed at 5 K. As mentioned above, depending on the type of refrigerant, the discharge superheating may be smaller than the suction superheating. Thus, the smaller superheating of them (ΔT_{sh}, minimum superheating) is fixed at 5 K. When the discharge superheating is smaller, the insufficient superheat amount covered with an internal heat exchanger. Compressor isentropic efficiency (η_{cmp}) generally depends on the pressure ratio of discharge pressure to suction pressure, but it is set to a constant value of 0.8 in this calculation. The thermophysical properties of each refrigerant are calculated using REFPROP Ver. 10.0 by NIST [5].

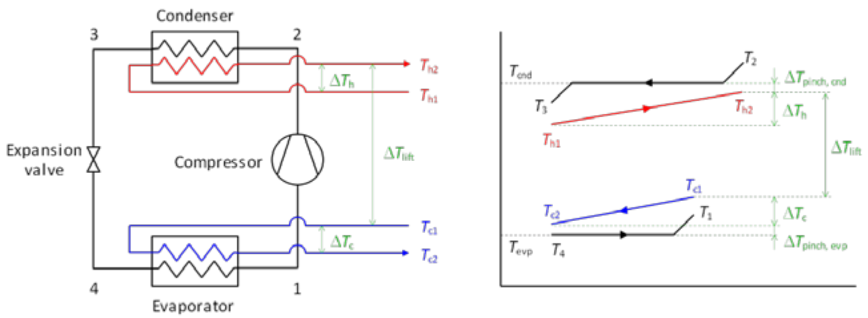

Figure 4. Schematic diagram of simple heat pump cycle and temperature profile

Table 2. Definition of temperature differences and calculation condition

Symbol	Value	Unit	Definition
ΔT_{lift}	Variable	K	$= T_{h2} - T_{c1}$
ΔT_c	5	K	$= T_{c1} - T_{c2}$
ΔT_h	5	K	$= T_{h2} - T_{h1}$
$\Delta T_{pinch,evp}$	2	K	$= T_{c2} - T_{evp}$
$\Delta T_{pinch,cnd}$	2	K	$= T_{cnd} - T_{h2}$
$\Delta T_{sh,evp}$	5	K	$= T_1 - T_{evp}$
ΔT_{sc}	5	K	$= T_{cnd} - T_3$
ΔT_{sh}	5	K	$= \min\{T_1 - T_{evp}, T_2 - T_{cnd}\}$
η_{cmp}	0.8	-	$= (h_{2,is} - h_1) / (h_2 - h_1)$

When selecting a refrigerant, it is necessary to take into consideration all of the following 5 items:

- Thermodynamic performance
- Safety
- Stability
- Economy
- Environmental friendliness

In this study, first, thermodynamic constraints are set from the viewpoint of energy and economic performances. Specifically, the constraints are placed on the coefficient of performance (COP) and the volumetric heating capacity (VHC). Assuming the current condition of industrial heat pump installation in Japan, the lower limits of COP and VHC are roughly set to 4 and 2 MJ/m^2, respectively. Next, it is conceivable to set a restriction on the discharge temperature from the viewpoints of thermal and chemical stabilities of refrigerant and lubricant and viscosity of lubricant, however in this study the restriction is not set because the limitation is not clear at this moment. For example, the upper limit temperature could be increased by newly development of addition agent. Then, considering the safety and environmental friendliness of refrigerant, this analysis divided into the following 3 cases; (1) the case of selecting from low GWP and A1 refrigerants, (2) the case of selecting from low GWP and A1 or A2 refrigerants, and (3) the case of selecting from natural refrigerants.

3.2. Results

As an example of the calculation result, Figure 5 shows the working domain in the case of R245fa. The maximum heat pump supply temperature is determined only by the critical temperature because there is no restriction set on the discharge temperature. This heat pump can operate competitively in the range of the temperature lift of about 50 K or less due to the constraint of COP of 4 or more. Then, it can be seen that there is a region where the VHC is less than 2 MJ/m^2, even when the COP is 4 or more.

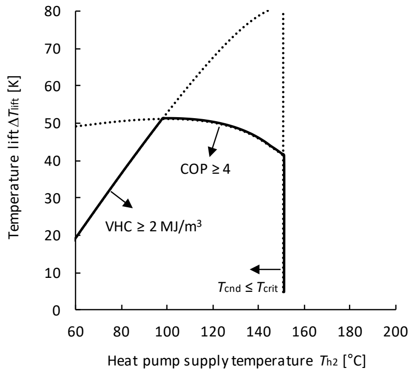

Figure 5. Constraints and working domain of simple heat pump cycle with R245fa

Figure 6 shows the working domains of each refrigerant. The left figure (a) illustrates HFC, HCFO and HFO refrigerants, and the right figure (b) illustrates natural refrigerants. It can be seen that the upper sides of the working domains of R1234yf and R1234ze(E) are close to R32 and R134a, respectively, and the right ends can be expanded. R1234ze(Z) and R1224yd(Z) have similar working domain to R245fa. R1233zd(E) and R1336mzz(Z) have the working domains on relatively higher temperature side.

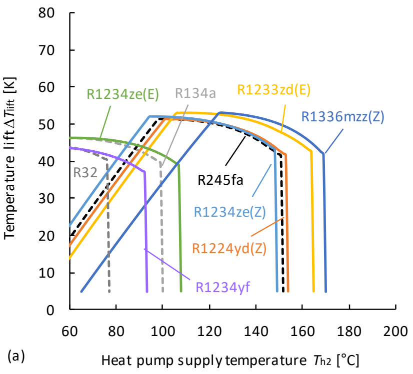

Figure 6. Working domains of simple heat pump cycles with 16 pure refrigerants

Figure 7 shows the composite diagrams so that the working domain is maximized when selecting refrigerants from each case of HFCs, HCFOs or HFOs, and natural refrigerants. It can be seen that the development of the new refrigerants (HCFOs and HFOs) has expanded the working domain and made it possible to construct competitive heat pumps under the conditions where the heat pump supply temperature is higher than before. On the other hand, natural refrigerant has the wide working domain. This indicates high temperature heat pumps can be constructed in a wide temperature range using only natural refrigerant in terms of thermodynamic performance.

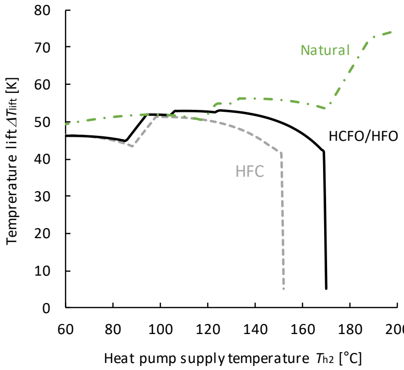

Figure 7. Maximum working domain of simple heat pump cycle

Next considers the safety and environmental friendliness of refrigerant. Figure 8 shows the maximum working domain in the following 3 cases; (1) the case of selecting from low GWP and A1 refrigerants, (2) the case of selecting from low GWP and A1 or A2L refrigerants, and (3) the case of selecting from natural refrigerants.

When selecting from low GWP and A1 refrigerants shown in the figure (a), R1224yd(Z) is promising in the heat pump supply temperature range below 105°C, R1233zd(E) from 105°C to 125°C, R1336mzz(Z) from 125°C to 165°C, and R718 over 165°C.

Then, when approving A2L refrigerants shown in the figure (b), R1234ze(E) becomes a candidate in the heat pump supply temperature range below 85°C, R1234ze(Z) from 85°C to 105°C, and then the working domain of R1224yd(Z) disappears.

On the other hand, when selecting from natural refrigerants shown in figure (c), R717 is promising below 120°C, R601a from 120°C to 130°C, R601 from 130°C to 170°C, and R718 over 170°C. However, it should be noted that the discharge temperature of R717 becomes relatively high. For example, the discharge temperature is 182°C when the heat pump supply temperature is 100°C. In the practical use, it would be necessary to cool the discharge vapor in some way.

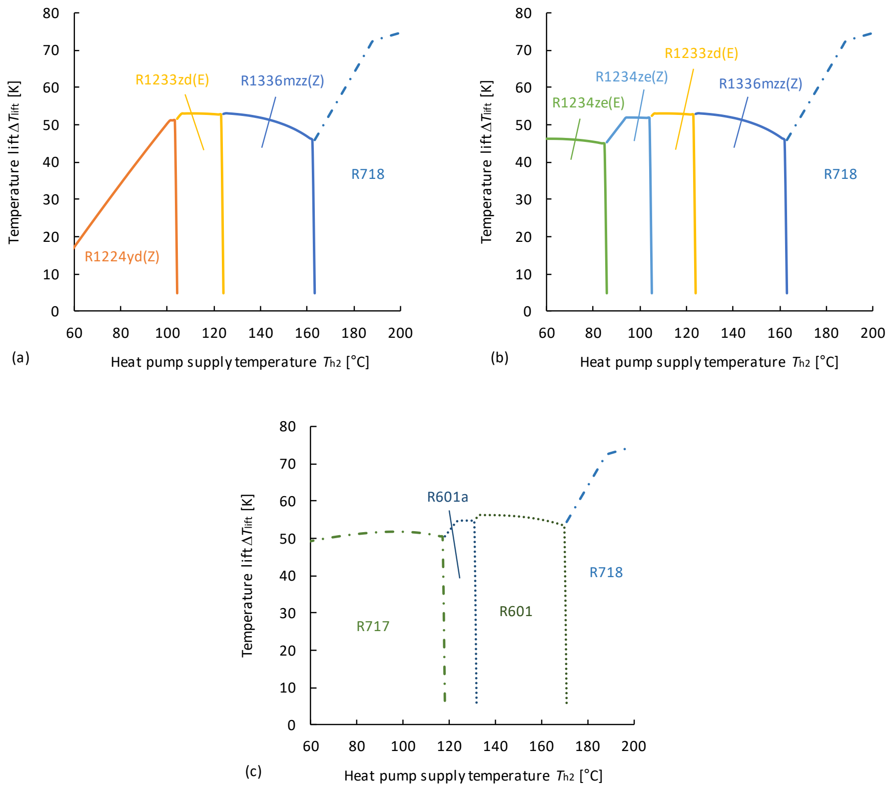

Figure 8. Maximum working domain of simple heat pump cycle (a) selecting from low GWP and A1 refrigerants (b) selecting from low GWP and A1 or A2L refrigerants (c) selecting from natural refrigerants

4. Analysis for two-stage heat pump cycle with economizer

Next, the effect of a high efficiency improvement by two-stage cycle with economizer are examined on the refrigerant selection.

4.1. Method

Each of the minimum superheating of the high-stage compressor and the low-stage compressor is fixed at 5 K. An internal heat exchanger is installed when the discharge superheating is smaller than the suction superheating. The compressor isentropic efficiency of each stage is set to a constant value of 0.8. The intermediate pressure is defined by the square root of the product of the discharge pressure and the suction pressure. The ratio of refrigerant mass flow rate in the high-stage and low-stage is fixed at 1.5.

4.2. Results

Figure 9 shows the maximum working domain in the following 3 case; (1) the case of selecting from low GWP and A1 refrigerants, (2) the case of selecting from low GWP and A1 or A2L refrigerants, and (3) the case of selecting from natural refrigerants.

When selecting from low GWP and A1 refrigerants shown in the figure (a), R1224yd(Z), R1233zd(E), R1336mzz(Z) and R718 are promising in ascending order of heat pump supply temperature like the case of simple heat pump cycle.

On the other hand, when approving A2L refrigerants shown in the figure (b), R1234yf in the heat pump supply temperature range below 70°C and R1224yd(Z) in a narrow range around 120°C become candidates unlike the case of simple heat pump cycle. This would be because R1234yf has a larger effect of improving COP by the two-stage compression with economizer than R1234ze(E) and R1224yd(Z) has the larger effect than R1234ze(Z).

When selecting from natural refrigerants shown in figure (c), the working domain of R717, which has a relatively small performance effect by the two-stage compression with economizer, becomes narrowed, and R600 becomes a candidate.

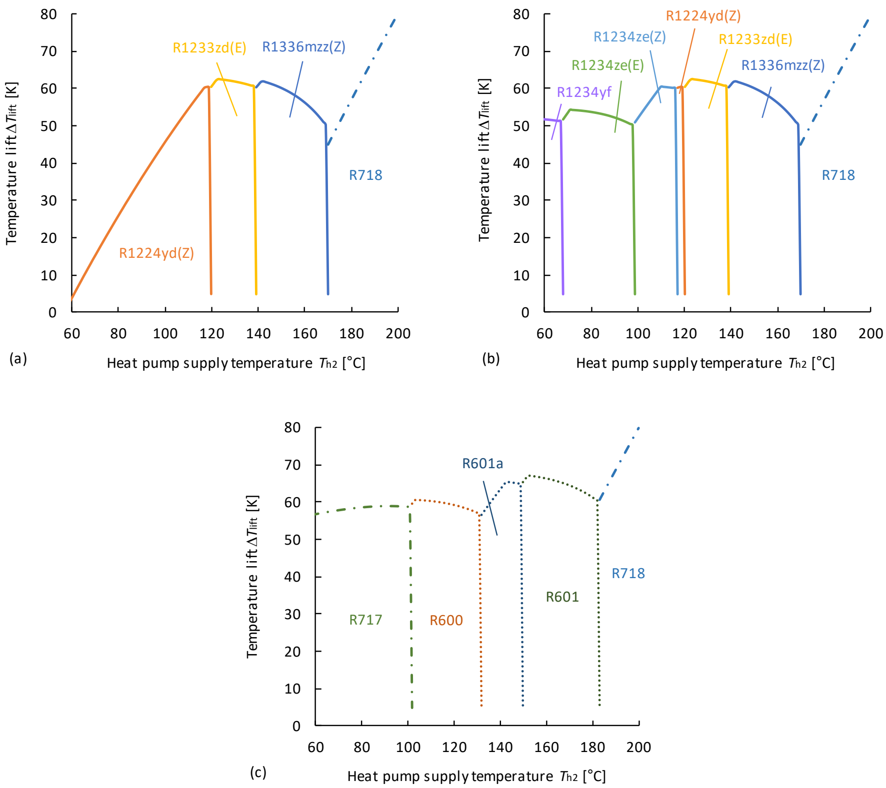

Figure 9. Maximum working domain of two-stage heat pump cycle with economizer (a) selecting from low GWP and A1 refrigerants (b) selecting from low GWP and A1 or A2L refrigerants (c) selecting from natural refrigerants

Figure 10 shows the comparison in maximum working domain between simple heat pump cycle and two-stage heat pump cycle with economizer. In any of the 3 cases, it can be seen that the temperature lifts expand by about 10 K thanks to the higher efficiency, although the improved ranges are limited; the range from 110°C to 160°C when selecting from low GWP and A1 refrigerants, the ranges below 85°C and from 110°C to 160°C when selecting from low GWP and A1 or A2L refrigerants, and the ranges below 115°C and from 140°C to 170°C when selecting from natural refrigerants. In other words, it means that the thermodynamic performance can be kept even when the heat source temperature become about 10 K lower than in the case of the simple heat pump cycle.

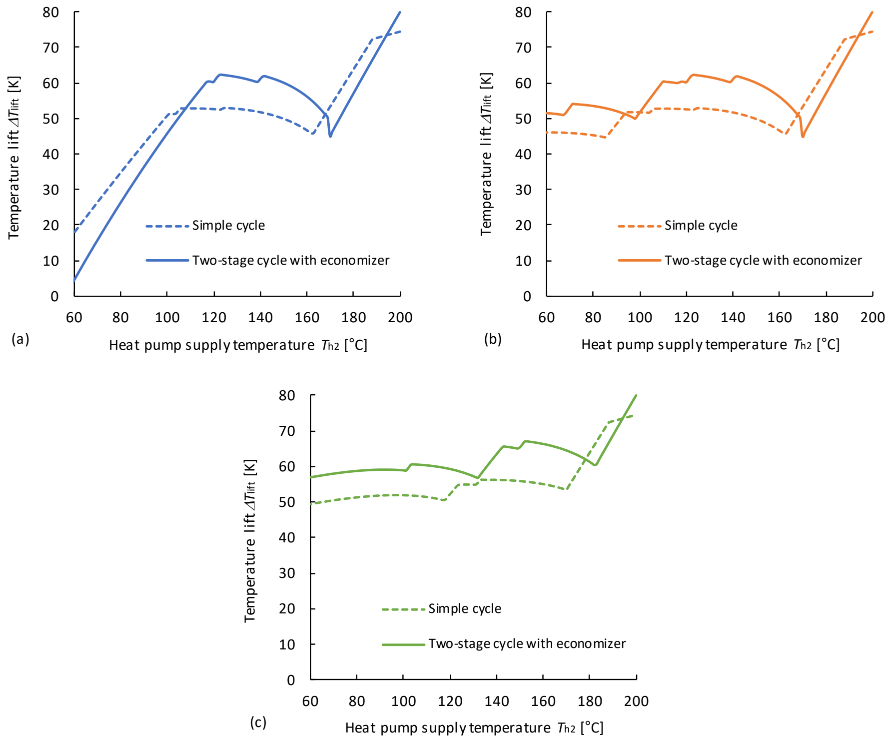

Figure 10. Comparison in maximum working domain between simple heat pump cycle and two-stage heat pump cycle with economizer (a) selecting from low GWP and A1 refrigerants (b) selecting from low GWP and A1 or A2L refrigerants (c) selecting from natural refrigerants

5. Conclusion

In this study, refrigerant selection for high temperature heat pump cycles is analyzed thermodynamically for the purpose of providing working domain maps which can determine the promising refrigerant and the upper limit of heat pumping temperature lift for each supply temperature. The following results are obtained:

- In terms of thermodynamic performance, high temperature heat pumps can be constructed in a wide temperature range from 60°C to 200°C using only natural refrigerant. R717, R601a, R601 and R718 are promising in ascending order of heat pump supply temperature. By improving the heat pump cycle with two-stage compression with economizer, R600 becomes a candidate and the working domain of R717 becomes narrowed.
- Considering the safety of the refrigerant, when selecting from low GWP and A1 refrigerants, R1224yd(Z), R1233zd(E), R1336mzz(Z) and R718 are promising. When approving A2L refrigerants, R1234ze(E) and R1234ze(Z) become candidates and the working domain of R1224yd(Z) disappears.

- By improving the heat pump cycle with two-stage compression with economizer, R600, R1234yf and R1224yd(Z), which have relatively larger effects, become candidates. And the temperature lift expands by about 10 K by the higher efficiency.

However, this study did not set the restriction on the discharge temperature. And this study focuses on the case where the temperature glides on both of heat source and heat sink are relatively small. Therefore, the following items are listed as the future issues:

- To set the restriction on the discharge temperature by considering the limitation of refrigerant stability and lubricant viscosity
- To analyze cases where the temperature glides on heat source and heat sink are relatively large by including transcritical heat pump cycle and other cycles with zeotropic mixed refrigerants

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