13th IEA Heat Pump Conference
April 26-29, 2021 Jeju, Korea

Research and development for 200°C compressed water heat pump using exhaust heat with low GWP refrigerant for industrial use

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Abstract

According to the Paris Agreement (COP21), the increase in global average temperature should be less than 1.5°C. The industry demands to decrease CO_2 emissions; however, the demand for heat at high temperature “more than 100°C” is mostly met by fossil fuels. Therefore, we have studied the process of introducing heat pumps with heating water to 160°C or higher by utilizing exhaust heat. We filtered industrial processes that are highly effective for installing heat pumps and calculated the effect. The installation of heat pumps was confirmed to reduce the primary energy consumption by approximately 14% and running costs 32% compared with using only fossil fuels. Thus, we have been developing 160°C- and 200°C-type centrifugal heat pumps using a low GWP refrigerant and exhaust heat. By 2023, the performance is going to achieve more than a COP 3.5 by heating high temperature pressurized water to 200°C and using heat source water at 95°C with a heating capacity of 600kW. Furthermore, we have selected a refrigerant suitable for high temperature, and the refrigerant candidates have GWPs of 20 or less and stability.

Keywords: Low GWP refrigerant, Heat pump, Industrial use, High temperature, COP ;

1. Introduction

In December 2015, the 21st Session of the Conference of the Parties to the United Nations Framework Convention on Climate Change (COP21) adopted the Paris Agreement, requiring each country to update and submit its own CO_2 reduction goal every five years. For refrigeration and air conditioning equipment, fluorinated greenhouse gases (F-gases) regulations in Europe, and the Act for Rationalized Use and Proper Management of CFCs and HFCs in Japan were designed to reduce the environmental impacts of these gases.

HFC refrigerants that have a high global warming potential (GWP), such as R134a, have been replaced by new types of low GWP refrigerants. Several aspects of these low GWP refrigerants must be verified, including their physical properties, stability, toxicity and flammability. The choice of refrigerant depends on the capacity, compressor type, operating temperature, and conditions of the heat pump; thus, it is necessary to consider the following items when selecting alternative refrigerants [1].

- Environmental factors: GWP $\leq$ 100, not an Ozone Depleting Substance
- Low toxicity and non- or mild flammability
- Physical properties: Cycle efficiency equivalent to that of existing refrigerants. Design pressure not to be excessively high.

Several double bond olefin refrigerants are candidates. Table 1 shows a comparison of R-134a and olefin refrigerants. The GWPs of the olefin refrigerants are very low, and their cycle efficiencies are equivalent to that of existing refrigerants.

Heat pumps are increasingly being used for supplying of hot water and heating in the household sector,

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but their application in the industrial sector has been slower [6]. The adoption of exhaust heat recovery heat pumps offers great potential for improved energy efficiency and a reduction in CO_2 emission in the mechanical and chemical industries. So, investigation of in the mechanical and chemical industries in which high-temperature heat demand and unused exhaust heat exist, and high temperature heat pump systems capable of heating pressurized hot water to 160°C and 200°C with COPs of 3.5 or more, are part of the research and development program of the New Energy and Industrial Technology Development Organization (NEDO).

Table 1. Comparison of R-134a and olefin refrigerants

Refrigerant	HFC	Olefins				
	R-134a	R-1234yf	R-1234ze(E)	R-1234ze(Z)	R-1233zd(E)	R-1336mzz(Z)
Global Warming Potential (GWP)*1	1300	<1	<1	<1	1	2
Ozone-Depleting Substances*2	non	non	non	(non)*4	non	non
Flammability*3	non	mildly	mildly	(mildly)*4	non	non
Toxicity*3	low	low	low	low*5	low	low
Atmospheric lifetime*1	13.8 years	10.5 days	16.4 days	10.0 days	26.0 days	22.0 days
Allowable concentration [ppm] *3	1000	500	1000	-	800	500
Safety class*3	A1	A2L	A2L	(A2L)*4	A1	A1
Standard boiling point [°C] *6	−26.1	−29.5	−19.0	9.7	18.3	33.5
Critical point [°C] *6	101.1	94.7	109.4	150.1	166.5	171.4
Critical pressure [MPa (abs)] *6	4.06	3.38	3.63	3.53	3.62	2.90
Saturated pressure @ 91°C [MPa (abs)] *6	3.31	3.14	2.53	1.11	0.85	0.57
Saturated vapor specific volume @ 25°C [m^3/kg] *6	0.0309	0.0264	0.0380	0.1136	0.1388	0.1968
Theoretical heating COP *6 *7	1.55	1.31	1.56	1.90	1.91	1.77

*1: IPCC Fifth Assessment Report [2], *2: Montreal Protocol, *3: Refrigerant Safety Classification Standard ASHRAE 34 [3],
*4: Expected, *5: YUJICHEM MSDS [4], *6: Refprop Ver10.0 refrigerant thermal property database [5],
*7: Refrigeration cycle efficiency for a single stage cycle, evaporation temperature 25°C, condensation temperature 91°C, super heat 21°C, adiabatic efficiency 90%

2. Investigation and selection of the process of introducing heat pumps

The actual conditions of the heat process are not clear for the machinery and chemical industries, such as the existence of heat demand and exhaust heat, the balance between heat and energy, operating hours, and operating methods to introduce heat pumps. First, as shown in Fig. 1, we evaluated the effect of installing a heat pump from simple information, such as the process temperature, heat demand, and existence of exhaust heat. As shown in Table 2, the drying process and the chemical process were indicated to be particularly effective. As a result of the hearing investigation, it was clarified that the data on the heat demand is organized in detail, but only the supply temperature of the heating source is organized, and there is almost no data on the exhaust heat source. Therefore, we measured the actual conditions of the drying process [Company L] and the chemical process [Company B], which are highly effective when install, and we clarified the heat balance with respect to the measured temperature, flow rate, state, operating time, etc. in the system.

In addition, we examined an exhaust heat recovery system and pressurized water supply system, etc. for the existing facilities and studied the economic effect of installing a heat pump. As shown in Fig. 2, we found that the primary energy consumption and running costs could be reduced.

- Paint drying process [Company L]: As shown in Fig. 3, it is possible to reduce primary energy consumption by 14% and running costs by 32% by installing 160°C heat pump with a COP of 4 to a portion of existing burners into the current air circulation heating process, compared with only using burners.
- Chemical process [Company B]: As shown in Fig. 4, it is possible to reduce the primary energy consumption by 7% and the running costs by 23% by installing 200°C heat pump with a COP of 3 to a portion of the existing boilers heating process of the reactor, compared with only using boilers.

Therefore, we have been developing a 160°C heat pump and process system of air drying and thermostatic chamber and a 200°C heat pump for steam generation and chemical processes, by taking the two steps.

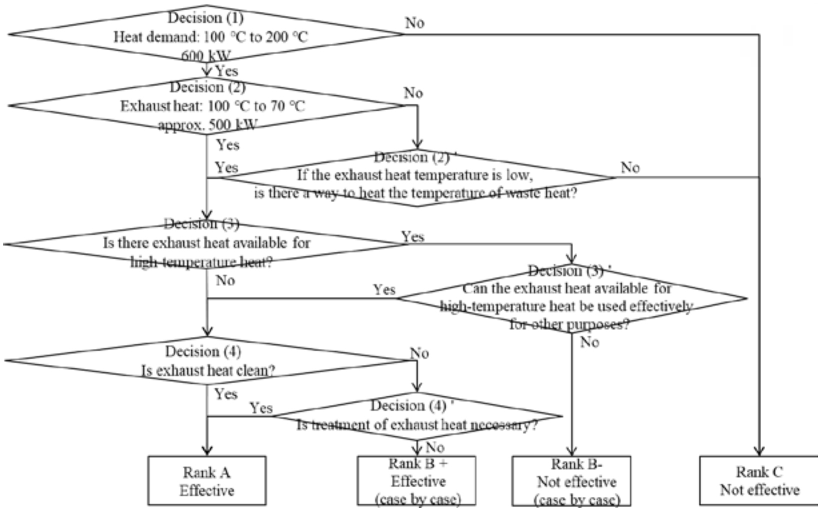

Fig. 1. Flow of assessment of introduction effect

Table 2. Survey results of the process introducing heat pumps

Business Type	Company	Process	Stability of temperature conditions/load		Rank	Remarks
			High temperature heat	Exhaust heat		
Ironmaking	A	Cleaning	200°C	200°C or higher	B -	Suitable heat demand, but too high temperature exhaust heat
Chemistry	B	Heating	135 ~ 190°C	100°C	A	Suitable heat demand and exhaust heat
Refuse incineration	C	Incineration	200°C	200°C or higher	B -	Suitable heat demand, but too high temperature exhaust heat
Sludge incineration	D	Incineration	200°C	200°C or higher	B -	Suitable heat demand, but too high temperature exhaust heat
Chemistry	E	Drying	120°C	35°C	C	Suitable heat demand, but too high temperature exhaust heat
Glass, earth and stone products	F	Drying	100°C or lower	-	C	Too low temperature heat demand
Rubber products	G	Mixing	100°C	40°C	C	Too low temperature heat demand
Chemistry	I	Distillation column	200°C	100°C	A	Suitable heat demand and exhaust heat
Chemistry	J	Rectification [distillation]	100~200°C	100°C	A	Suitable heat demand and exhaust heat
Chemistry	K	Sterilization, drying, distillation	100°C	40°C	C	Too low temperature heat demand
Machinery	L	Paint drying	120°C	100°C	A	Suitable heat demand and exhaust heat

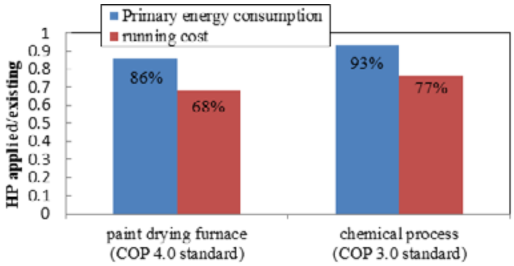

Fig. 2. Primary energy consumption and running costs compared with existing facilities

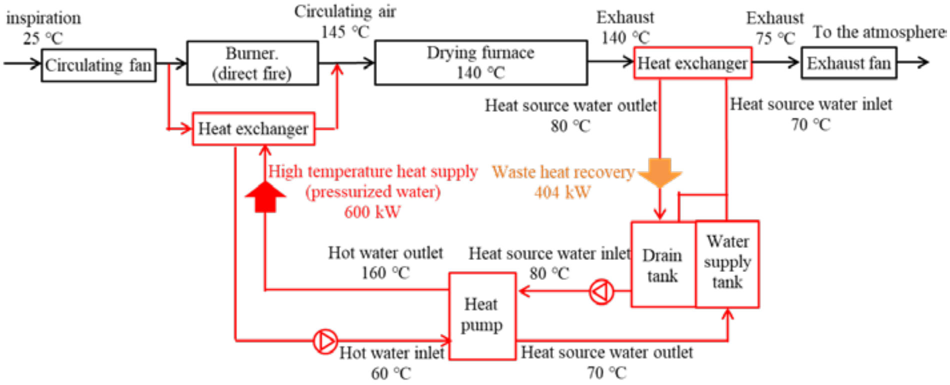

Fig. 3. Proposal for installation into the paint drying process

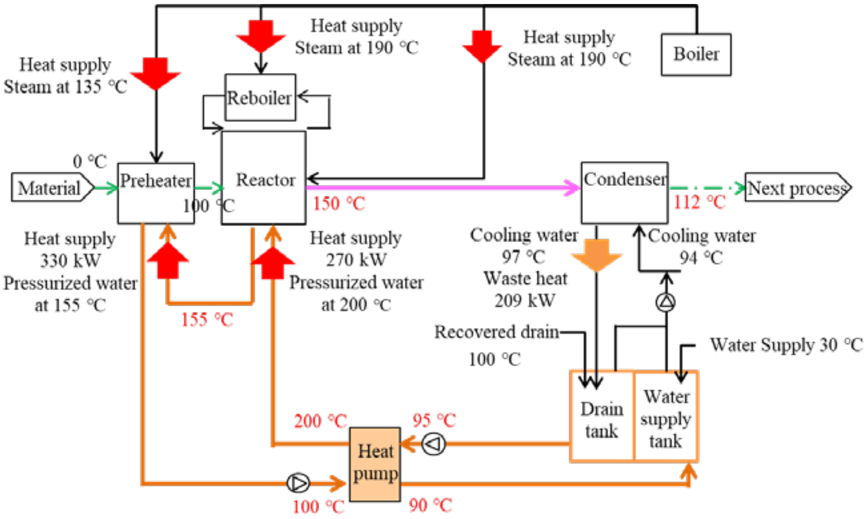

Fig. 4. Proposal for installation into the chemical process

3. Development of centrifugal heat pump heating pressurized water to 160°C

3.1. Selection of refrigerant

For the selection of a refrigerant, the operational temperature range of the heat pump must be considered, and physical properties suitable for the temperature range are required. This requires the following physical properties:

- Stability at high temperature: To prevent of isomerism and decomposition at the operating temperature of the heat pump.
- Standard boiling point: At the operating temperature, it is necessary that the design pressure of the equipment is not significantly high, and the compressor size is not too small to prevent a reduction in the adiabatic efficiency. Therefore, in high temperature, it is better to use a refrigerant which has a high standard boiling point.

R-134a is often used in existing centrifugal heat pumps, and Table 3 shows a comparison between R-134a and olefin refrigerants. If the olefin refrigerants is used for the 160°C heat pump, the refrigerant side pressure of the pressurized water in the heat exchanger can be reduced to approximately 3MPa(abs). It was confirmed that the thermal stability of R-1233zd(E) is poor at 175°C and 200°C. In addition, the internal pressure of the machine using R-1233zd(E) could be below atmospheric pressure when the heat pump is stopped; thus, the incoming air needs to be considered. However, as shown in Table 4, decomposition proceeds in a short period when air is added even at 150°C. Therefore, it is necessary to select R-1234ze(Z) or R-1336mzz(Z) to ensure the stability of the heat pump in the operating temperature range. The pressure on the refrigerant side of the high-pressure water heat exchanger of R-1336mzz(Z) is lower 37% (2.42MPa(abs)), the saturated vapor specific volume at 68°C is 54% higher, and the theoretical heating COP is 3.7% higher (3.61) than that of R-1234ze(Z). Therefore, the design pressure of the equipment is not too high, the compressor size is not too small, and the heat pump performance is expected to be improved. Thus, R-1336mzz(Z) is selected for the 160°C heat pump from the viewpoints of the thermal stability, design pressure, vapor specific volume, and theoretical heating COP.

Moreover, R-1336mzz(Z) is reported to have good stability up to 250°C and suitable for the 200°C heat pump [7].

Table 3. Comparison of R-134a and olefin refrigerants

Refrigerant	HFC	Olefins		
	R-134a	R-1234ze(Z)	R-1233zd(E)	R-1336mzz(Z)
Standard boiling point [°C] [*1]	-26.1	9.7	18.3	33.5
Critical point [°C] [*1]	101.1	150.1	166.5	171.4
Critical pressure [MPa (abs)] [*1]	4.06	3.53	3.62	2.90
Pressure of refrigerant side of pressurized water in heat exchanger [MPa (abs)] [*1]	10.87[*2]	3.87[*2]	3.30[*3]	2.42[*3]
Saturated vapor specific volume @ 68°C [m^3/kg] [*1]	0.0092	0.0323	0.0390	0.0496
Theoretical heating COP [*1]	3.18[*4]	3.48[*4]	3.39[*5]	3.61[*5]

*1: Refprop Ver 10.0 refractory thermal property database

*2: Superheated vapor pressure at 161°C and saturated gas entropy @ 68 °C, *3: Saturated pressure @ 161°C

*4: Refrigeration cycle efficiency for a single stage cycle, evaporation temperature 68°C, refrigerant temperature: inlet/outlet 161/71°C of pressurized water heat exchanger, adiabatic efficiency 90%

*5: Refrigeration cycle efficiency for a single stage cycle, evaporation temperature 68°C, condensation temperature 161°C, adiabatic efficiency 90%

Table 4. Thermal stability testing of R-1233zd(E)

Test condition[*1]		Result		
Air [ppm]	Moisture [ppm]	R-1233zd(E)[wt%]	F^- [ppm]	Cl^- [ppm]
<10	<10	0.0	0.6	0.5
<10	100	0.7	17.5	0.5
100	<10	0.4	0.3	0.4
100	100	0.4	14.3	3.4

*1: Temperature: 150°C, Duration: 168 h

3.2. Selection of lubricant oil and elastomer materials

As with the refrigerant, the lubricant oil must be stable in the high temperature range, and the solubility and viscosity of the lubricant oil with the refrigerant also need to been evaluated.

As a first step, we investigated lubricant oil for the 160°C heat pump using R-1336mzz(Z). The synthetic oil is commonly used with non-chlorine refrigerants, such as HFCs. The polyol ester (POE) oil was therefore selected because of the stability for R-1336mzz(Z). Therefore, as shown in Table 5, we carried out the accelerated thermal stability testing at 220°C and 200°C in consideration of a 200°C heat pump also, and the stability at 220°C was confirmed. Moreover, kinematic viscosity is 175%, compared with the requirements for the bearings of the 160°C heat pump. Thus, we selected the lubricant oil with sufficient high-temperature stability, lifetime, and lubricating performance for the 160°C heat pump.

The POE oil has a kinematic viscosity of 101%, compared with the requirements for the bearings of the 200°C heat pump.

Table 5. Thermal stability testing of POE oil

Test condition*1		Result
Temperature [°C]	Duration [h]	Acid Value [mg kOH/g]
200	168	0.01
220	168	0.01
220	336	0.23
220	672	0.45
250	168	2.25

*1: R-1336mzz(Z)/oil: 50/50, air/moisture [ppm]: 100/1000

We carried out autoclave testing for suitability of the elastomer material and R-1336mzz(Z)/POE oil. Table 6 shows the change in weight, volume, hardness, and refrigerant hue for the test specimens. Those (PTFE, PEEK, EPDM, FKM, FFKM, etc.) were compatible with the R-1336mzz(Z)/POE oil. Thus, we selected the suitable elastomer materials for the 160°C heat pump.

Table 6. Compatibility testing of elastomer material with R-1336mzz(Z)/POE oil

Test condition*1		Results			
Material	Temperature [°C]	Weight [%]	Volume [%]	Hardness [%]	Refrigerant hue
PTFE	175	+3	+4	-13	Transparent
	200	+3	+4	-14	Muddy
PEEK	200	+1	+1	+0	Transparent
POM	175	+0	+3	-6	Muddy
PPS	175	+0	+0	+1	Muddy
EPDM	200	+22	+21	-36	Transparent
NBR	175	+13	+10	-3	Muddy
HNBR	175	+18	+16	-8	Muddy
FKM	200	+17	+23	-20	Transparent
FFKM	200	+15	+24	-13	Transparent

*1: duration：336h

3.3. Drop-in verification test

To verify the component validity for the 160°C heat pump, we modified the verification machine with R-1336mzz(Z) from 90°C hot water heat pump with R-134a. In addition, we designed and manufactured the verification test equipment, so that it could operate with pressurized water up to 200°C, and we conducted a drop-in verification test. Table 7 shows the specifications of the verification machine, Fig. 5 shows the heat pump cycle, and Figs. 6 and 7 show the external appearance.

The evaluation items were as follows.

- Verification test equipment: The test equipment could be operated stably even at 160°C for a pressurized outlet water.
- Aerodynamic performance of the centrifugal compressor: The performance was equivalent to the estimated performance evaluated for the 90°C heat pump using R-134a, even if the refrigerant was replaced from R-134a to R-1336mzz(Z) and the centrifugal compressor was designed for high temperature.
- Heat exchanger performance: The performance was found to be equivalent to the estimated value, even if the refrigerant was replaced from R-134a to R-1336mzz(Z).
- Mechanical loss: The loss of bearings, motors, etc., was the estimated value.

Table 7. Specifications of the element verification test

Refrigerant [filling quantity]	R-1336mzz(Z) [106 kg]
Lubricating oils [filling quantity]	POE oil [20 L]
Heat pump cycle	Economizer cycle
Compressor	Centrifugal two-stage compressor
Evaporator/condenser/intermediate cooler/intercooler	Brazing plate heat exchanger
Size L × W × H	3.5 × 2.0 × 2.7 m
Power supply voltage	400 V
Starting method	Inverter

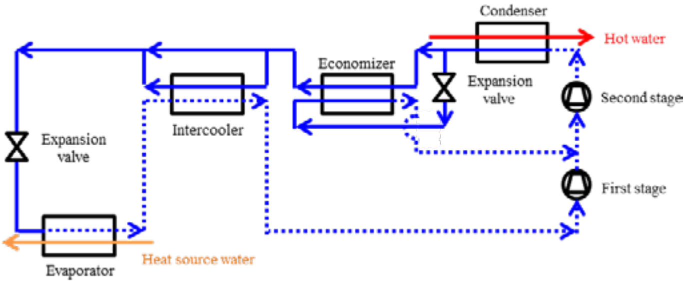

Fig. 5. Heat pump cycle of the verification machine

Fig. 6. External view of the verification machine

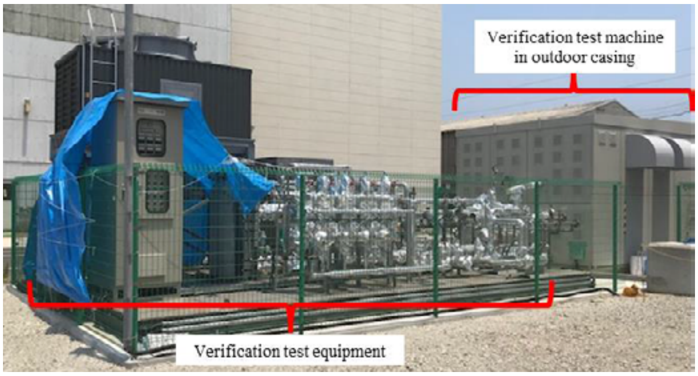

Fig. 7. External view of the verification test machine and equipment

Table 8 shows the result of the drop-in verification test. We confirmed that the verification equipment can be operated stably up to 160°C for pressurized water output, and that the performance of the heat exchanger is equivalent to the estimated value. However, there were discrepancies with regard to the estimated values for the compressor flow performance and the loss of motor. Therefore, after investigating the cause of the discrepancies, we has modified the verification machine as follows, and executed an additional drop-in verification test.

- Centrifugal compressor: To modify the shape, material and assembling method, in order to ensure a flow rate equivalent to the estimated value
- Motor: To modify the cooling system to control the motor temperature properly and the motor with high heat resistance to evaluate the characteristics of the deviation

Table 8. Results of element verification test

Items	Actual measurement value	Estimated value
Heating capacity	267.1 kW	
Hot pressurized water temperature	145.7 °C → 160.1 °C	
Hot pressurized water flow rate	16.9 m^3/h	
Heat source temperature	92.1 °C → 87.9 °C	92.5 °C → 87.9 °C
Heat source flow rate	34.1 m^3/h	
Centrifugal compressor: First stage flow rate ratio*1	0.94	1
Centrifugal compressor: Second stage flow rate ratio*1	0.89	1
Motor windage ratio*1	3.06	1
Motor efficiency ratio*1	0.97	1
Power consumption	117.0 kW	102.5 kW
Heating COP	2.28	2.61 (+ 14.5%)

*1: actual/estimated

3.4. Design of centrifugal heat pump

Heat pumps heating water to 90°C are applied for moderate high temperature, for example, for cleaning and food processes. However, there are thermal demands from 160°C to 200°C in industrial applications, for example, for chemical reactor and drying processes, etc.

160°C heat pumps need drain water as exhaust heat and we estimates exhaust heat (heat source water) temperature is less than 100°C. Therefore, two-stage compressors are planned to be arranged in series, so that one heat pump unit can operate even at the high differential pressure between the condenser and the evaporator.

The 90°C heat pump is adopted a two-stage compression economizer cycle. However, to obtain a higher COP, the two-stage compression bleeding cycle shown in Figs. 8 and 9 is adopted for a high temperature heat pump [8]. In the case of a process in which the inlet temperature of the hot water can be lowered to the temperature of the heat source water (For example, it is used to raise the temperature of a medium from ambient temperature to high temperature.), the bleeding cycle is highly efficient because it uses some of the refrigerant gas discharged from the low stage compressor for intermediate heating.

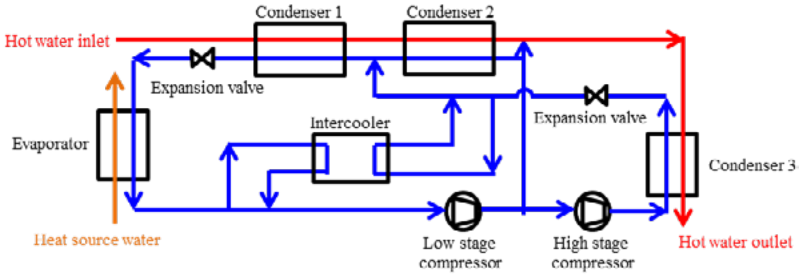

Fig. 8. Two-stage compression bleeding cycle

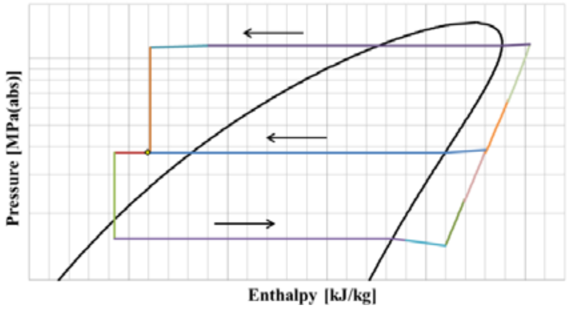

Fig. 9. P-h diagram of two-stage compression bleeding cycle

Table 9 shows the specifications of the 160°C heat pump. Under the conditions of a heating capacity of 600 kW, a hot water inlet/outlet temperature is 70°C/160°C, a heat source water inlet/outlet temperature is 80°C/70°C, and its COP is estimated to be 4.0.

Based on the results of the drop-in verification test, we are going to improve the accuracy of the estimated performance and expand the operational temperature range.

Table 9. Specifications for 160°C heat pump

Rated heating capacity	600 kW
Refrigerant,	R-1336mzz(Z)
Hot pressurized water temperature	70°C to 160°C
Hot pressurized water flow rate	6.0 m^3/h
Heat source water temperature	80°C to 70°C
Heat source water flow rate	40.5 m^3/h
Power consumption	146.7 kW
COP	4.0
Heat pump cycle	Two-stage compression bleeding cycle
Low and high stage compressors	Centrifugal two-stage compressor
Evaporator/condenser 1,2,3/intercooler	Brazing plate heat exchanger
Size L × W × H	3.6 × 2.0 × 2.5 m
Starting method	Inverter

4. Development of elements for centrifugal heat pump heating pressurized water to 200°C

We have been developing step by step 160°C and 200°C heat pumps with low GWP refrigerants. We will try to launch 200°C heat pump with pressurized hot water for practical applications by 2023.

As shown in Chapter 3, R-1336mzz(Z) may be a refrigerant candidate for 200°C heat pumps. A comparison of R-134a and R-1336mzz(Z) is shown in Table 10. The vapor specific volume @ 88°C of R-1336mzz(Z) is smaller at 94% than that of R-134a @25 °C. Under the condition of 200°C pressurized water and heat source water inlet/outlet temperature of 95/90°C, this may lead to be smaller compressor size and reduce in an adiabatic efficiency. Therefore, to prevent a reduction in an adiabatic efficiency, new refrigerant candidates that have a high standard boiling point and proper vapor specific volume for a 200°C heat pump must be selected. The candidates have GWPs of 20 or less and are stable at high temperature. We continue to examine toxicity, cycle characteristics, etc., and will evaluate whether or not to apply to a 200°C heat pump.

For the heat pump cycle of 200°C pressurized high-temperature water, we are going to adopt a two-stage compression bleeding cycle capable of achieving a COP of 3.5 or more, as with the 160°C heat pump.

Table 10. Comparison of R-134a and R-1336mzz(Z)

Refrigerant	Existing		New	
	R-134a	R-1336mzz(Z)	Candidate A	Candidate B
Standard boiling point [°C] [*1]	−26.1	33.5	During evaluation	
Saturated vapor specific volume @ 25 °C $[\text{m}^3/\text{kg}]$ [*1]	0.0309	-		
Saturated vapor specific volume @ 68 °C $[\text{m}^3/\text{kg}]$ [*1]	-	0.0496		
Saturated vapor specific volume @ 88 °C $[\text{m}^3/\text{kg}]$ [*1]	-	0.0291		

*1: Refprop Ver10.0 refrigerant thermal property database,

5. Conclusion

In response to the industry demands to decrease CO_2 emissions, we are developing 160°C and 200°C heat pumps with pressurized water at 100°C or higher and low GWP refrigerants.

As a result of investigation of the effective process to install the 160°C or 200°C heat pumps, we estimated that primary energy consumption could be reduced by 14%, running costs by 32% for painting drying process, and primary energy consumption by 7%, running costs by 23% for chemical process.

The 160°C heat pump with a heating capacity of 600kW is being developed with an existing refrigerant R-1336mzz(Z), which has a GWP of 2. R-1336mzz(Z) has low GWP, non- flammability and low toxicity, making it a suitable refrigerant for industrial heat pumps. In addition, under the conditions of hot water inlet/outlet temperature of 70°C/160°C and heat source water inlet/outlet temperature of 80°C/70°C, a two-stage compression bleeding cycle in which COP is improved was adopted, it is estimated to achieve COP is 4.0. Furthermore, a drop-in verification test has been started, and the additional drop-in verification test will be executed after modification of the verification machine, and we are going to improve the accuracy of the estimated heat pump performance and expand the operational temperature range.

We are also considering the use of a new refrigerant with a high standard boiling point for the heat pump heating pressurized high-temperature water to 200°C. The refrigerant candidates have GWPs of 20 or less and are stable at high temperature. We are going to continue to examine the toxicity, cycle characteristics, etc. of the refrigerant candidates for the 200°C heat pump. In the future, we will select a suitable refrigerant for the 200°C heat pump. A two-stage compression bleeding cycle has been adopted with the target of COP 3.5 and over, and we will carry out the element design and drop-in test, and proceed with the development of the high temperature heat pump.

Acknowledgements

This work was supported the project of research and development of innovative practical use technologies for unutilized thermal energy by New Energy and Industrial Technology Development Organization.

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