International Journal of Air-Conditioning and Refrigeration Vol. 15, No. 4 (2007) 182~190

Current State and Future of Refrigerants for Refrigeration and Air Conditioning

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(Received August 24, 2007; Revision received December 14, 2007)

Abstract

Refrigeration and air-conditioning equipments are indispensable products in this civilized society. However, discharged refrigerants used in the equipments and exhausted carbon dioxide to drive the refrigeration and air-conditioning equipments are related to serious environmental problems and energy problems. Especially, the destroyed ozonosphere by the discharged refrigerants and the increased normal temperature by carbon dioxide and fluorocarbon refrigerants (green house gases) are sounded as serious global problems. For alleviating these problems, environmental-friendly refrigeration and air-conditioning equipments must be developed and will spread soon. To develop new equipment, a suitable refrigerant for each usage must be presented. In this paper, the current state of refrigerants was introduced. And, thermophysical properties of the refrigerants were introduced briefly. From the properties, the refrigerants and refrigeration cycles are promising to be used in the future, were proposed

Key words: Alternative refrigerant; Natural refrigerant; Thermophysical property; Refrigerant mixture; Refrigeration cycle; Cycle performance

1. Introduction

Refrigeration and air-conditioning equipments are indispensable products in the current civilized society that had dramatically advanced since the Industrial Revolution. In Japan, the amount of consumed energy by refrigeration and air conditioning including supplying hot water, reaches about 15% (2400×10^{15} J) of the domestic energy consumption. However, discharged refrigerants used in the equipments and exhausted carbon dioxide to drive the equipments are related to serious environmental problems and energy problems. Especially, the destroyed ozonosphere by the refrigerants discharged from the equipments into the atmosphere (depletion of ozone layer) and the normal temperature increase by green house gases such as carbon dioxide and fluorocarbon refrigerants (global warming) are sounded as serious global problems.

Therefore, environmental-friendly refrigeration and air-conditioning equipments must be developed quickly and then will spread widely. To develop new equipment, a suitable refrigerant for each usage must be selected, and the cycle and its elements should be designed optimally. There is an important relation between refrigeration cycle (vapor compression cycle) and refrigerant, so the cycle performance changes depending on thermophysical properties of the refrigerant.

In this paper, the current state of the refrigerants used for refrigeration and air-conditioning equipments is described. And, the thermophysical properties of refrigerants are briefly introduced. Then, the future of refrigeration and air-conditioning equipments is considered from the viewpoint of thermophysical properties of the refrigerants.

2. Thermophysical properties of refrigerants

It is necessary to understand the thermophysical properties of refrigerants when selecting one for the equipment. This chapter outlines the thermophysical properties of refrigerants.

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2.1 Thermodynamics of refrigerants

Cooling capacity is obtained by using the state (phase) change of refrigerant at vapor pressure compression cycle (Rankine cycle). As concerns of refrigeration machine, important processes of the cycle are evaporating process and compression process. During the former process that obtains low temperature, the refrigerant is mainly in a two-phase region consisting of vapor and liquid, and the latter is in a superheated vapor region (vapor phase). However, those processes become different in each refrigerant so the thermodynamic state surface changes by the refrigerant. The shape of thermodynamic state surface of refrigerant mixtures is significantly different from single (pure) refrigerant. The shape of the mixtures is more complicated so that it becomes inconvenience for usage. As known well, attention to refrigerant mixtures are paid as alternative refrigerants in recent years, because there is no suitable pure refrigerant used as alternative refrigerant.

As an example, vapor pressure curves of two pure materials and a mixture are shown in pressure-temperature (*P-T*) diagram of Fig. 1. On the vapor pressure curve, the maximum temperature and pressure point calls the critical point. The vapor pressure curve of the pure material becomes one curve (saturated vapor pressure curve), and two appear in case of the mixture (dew- and bubble-point curves). The temperature changes on the saturated liquid side (bubble point) and the superheating vapor side (dew point) even along an isobaric process of evaporation or condensation. It causes a temperature gradient (temperature glide) of isobar in the two-phase region.

In the two-phase region, the refrigerant mixture is

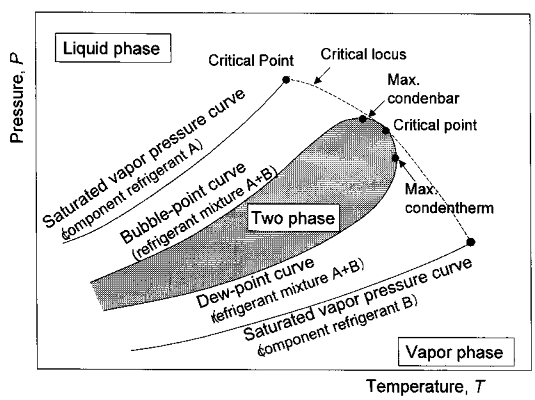


Fig. 1. Dew- and bubble-point curve of mixture on *P-T* diagram

separated to vapor and liquid, and the composition changes with temperature and pressure, respectively. The state change is presented as vapor-liquid equilibrium curves in phase diagram which can show the relation between the temperature (or the pressure) and the composition at each dew point and bubble point at a certain pressure (or temperature).

In the phase diagram, the refrigerant mixtures show the complex behavior, and are classified as azeotropic, pseudoazeotropic, and nonazeotropic refrigerant mixtures. Their refrigerant numbers by ASHRAE are 400, and 500 series. The dew- and bubble-point curves becomes a single point for each azeotropic mixtures, such as R 502, R 507A, and itself behaves like a pure refrigerant. There are pseudoazeotropic refrigerant mixtures such as R 404A, R 410A though the dew- and bubble- point curves are not exactly on the same line. However, the differences are little on practical use so that the azeotropic and pseudoazeotropic mixtures can be treated as pure refrigerant.

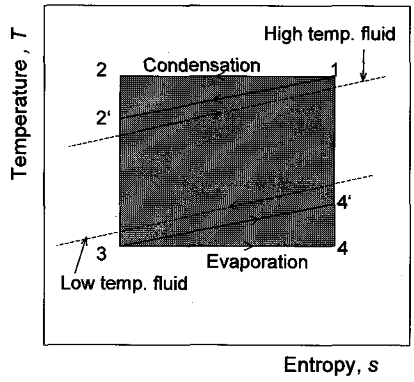
Most of the refrigerant mixtures including R 407C are nonazeotropic whose thermodynamic state surface becomes complex, and accompanies the composition change in the two-phase region. As for the nonazeotropic mixtures, there are some technical problems for usage related to decreased performance of heat transfer in the two-phase region and total composition change in the cycle when leaking.

If the temperature gradient of isobar is applied, the Lorenz cycle can be realized (Fig. 2). By adopting a counter flow heat exchanger, the required compression work is decreased (Fig. 2(d)), and the loss during the expansion process is decreased. As a result, the coefficient of performance (COP) of the cycle will be increased.

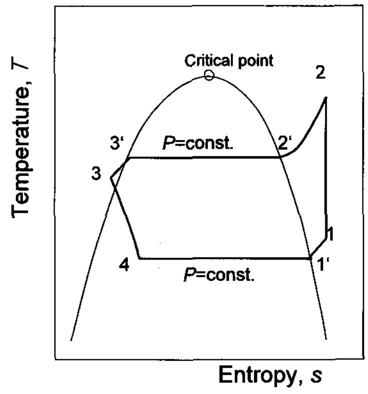
2.2 Thermodynamic state surfaces of refrigerants

Tables 1 and 2 show the cycle performance of R 22[2], R 23[3], R 32[3], R 134a[3], R 404A[4], R407C[5], R 410A[5], R 502[6], R507A[4], propane[7], iso-butane[7], ammonia[8], and carbon dioxide[9]. Generally, the thermodynamic state surface means pressure-volume-temperature (*PvT*) surface, and other three-dimensional thermodynamic property surfaces. Instead of complicated 3-D diagrams, saturated vapor pressure curves and dew- and bubble-point curves on the *P-T* diagram are shown in this paper.

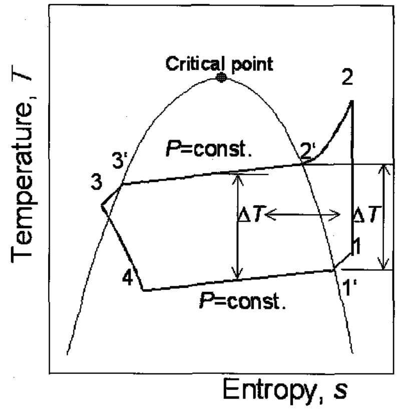
The saturated vapor pressure curves of the pure refrigerants are shown in Fig. 3, and the dew- and bubble-point curves of the mixtures are also shown in Fig.



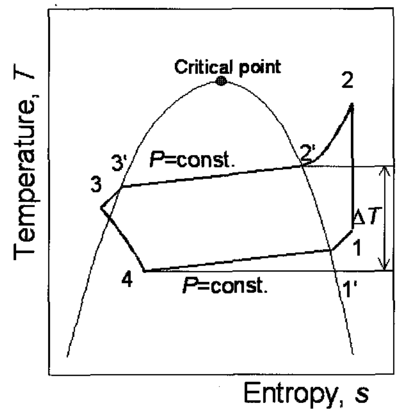
(a) Theoretical Carnot Cycle (1-2-3-4-1) and Theoretical Lorentz Cycle(1-2'-3-4'-1)



(b) Pure refrigerant



(c) Nonazeotropic mixtures (set T_1', T_2')



(d) Nonazeotropic mixtures (set T_2', T_4)

Fig. 2. Refrigeration cycles in temperature-entropy (T-s) diagram.

Table 1. Characteristics of pure refrigerant and cycle conditions.

Refrigerant	R 22	R 23	R 32	R 134a	R 290	R 600a	R 717	R 744
Chemical formula	$CHClF_2$	CHF_3	CH_2F_2	CH_2FCF_3	C_3H_8	i-C_4H_{10}	NH_3	CO_2
Molar mass	86.468	70.014	52.023	102.031	44.096	58.122	17.030	44.010
Boiling point (℃)	-40.810	-82.15	-51.65	-26.07	-42.090	-11.670	-33.327	-78.400
Critical temp., T_C (℃)	96.15	25.85	78.105	100.933	96.675	134.67	132.25	30.978
Condensing Temp. for max. COP (℃) (T_CX0.9)[10]	59	-4	43	64	60	94	92	0
Max. condensing temp. (℃) (Condensing Press.<3 MPa)	70.042	6.772	48.028	86.194	77.720	123.19	65.725	-5.552
Min. evaporating temp.(℃) (Evaporating press.>0.1 MPa)	-41.019	-82.376	-51.913	-26.355	-42.387	-12.003	-33.588	-

4. If the evaporating and condensing temperatures, which corresponds to target cycle temperatures, are decided as understood from Figs. 3 and 4, the highest and lowest pressure values, so-called evaporating and the condensing pressures, are obtained. Generally, the refrigerant is selected from cycle operating conditions; the evaporating pressure should not be set below the atmospheric pressure, the compression ratio is not higher than 8, and the condensing pressure is not higher than 3 MPa. These operating conditions and typical thermodynamic cycle information are arranged in Tables 1 and 2.

Table 2. Characteristics of refrigerant mixtures and cycle conditions.

Refrigerant	R 404A	R 407C	R 410A	R 502	R 507A
Composition	R125/R143a/R134a (44/52/4 mass%)	R32/R125/R134a (23/25/52 mass%)	R32/R125 (50/50 mass%)	R22/R115 (48.8/51.2 mass%)	R125/R143a (50/50mass%)
Molar mass	97.604	86.204	72.585	111.63	98.859
Boiling point (℃)	-46.13	-43.57	-51.65	-45.55	-47.10
Critical temp., T_C (℃)	72.05	86.03	71.36	80.15	70.617
Condensing Temp. for max. COP (℃) (T_C X0.9)[11]	37	51	36	45	36
Max. condensing temp. (℃) (Dew-point Press.<3 MPa)	62.014	68.84	49.10	66.84	60.83
Min. evaporating temp.(℃) (Dew-point press.>0.1 MPa)	-45.743	-36.90	-51.70	-45.23	-47.01

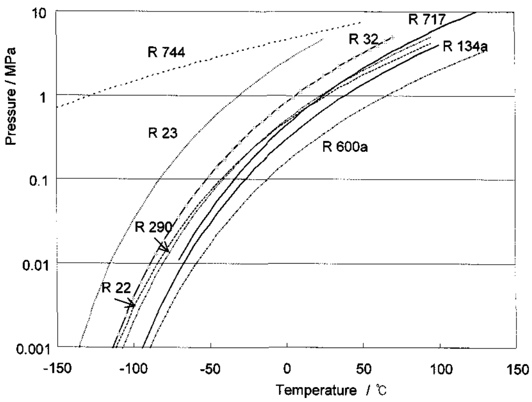
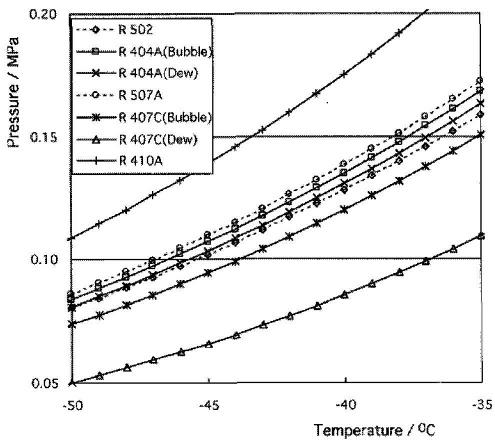
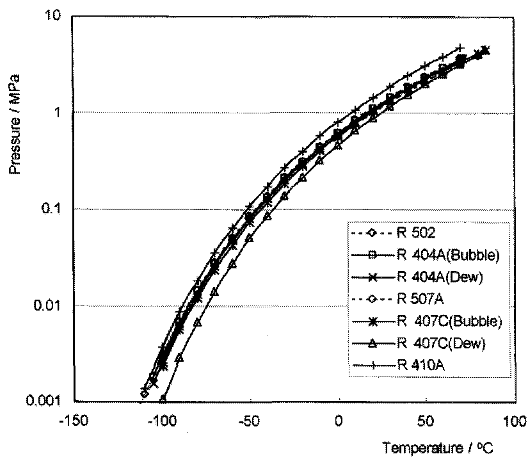


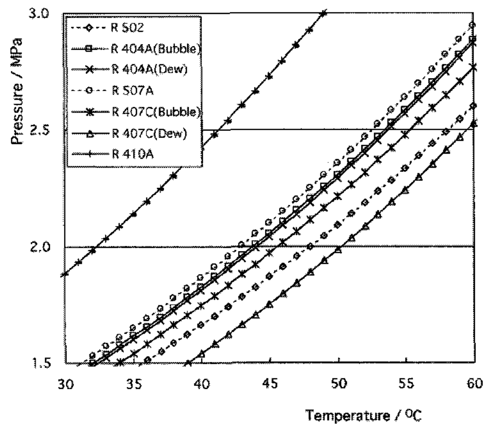
Fig. 3. Saturated vapor pressure curve of pure refrigerants.



(b) -50 ~ -35 °C



(a) -150 ~ 100 °C



(c) 30 ~ 60 °C

Fig. 4. Dew- and bubble-point curve of refrigerant mixtures.

Moreover, when specifications of the compressor are decided, the value of suction specific volume becomes important. When the suction specific volume is large, the refrigerant doesn't flow sufficiently. In this case, the refrigerant mass flowing into the compressor decreases. As becoming low temperature, the suction specific volume increases.

There are other thermodynamic properties such as isobaric heat capacity, isochoric heat capacity, specific heat ratio, speed of sound, entropy, and enthalpy. For the equipment design, enthalpy difference in the evaporation process becomes very important. The curves of latent heat which relate to this enthalpy difference divided by the suction specific volume, are shown in Figs. 5 and 6. If the value is large, even a smaller compressor swept volume obtains a bigger cooling capacity per unit mass.

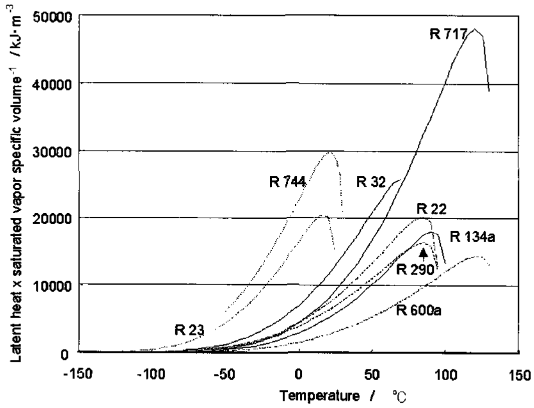


Fig. 5. Latent head divided by saturated vapor specific volume of refrigerant mixtures.

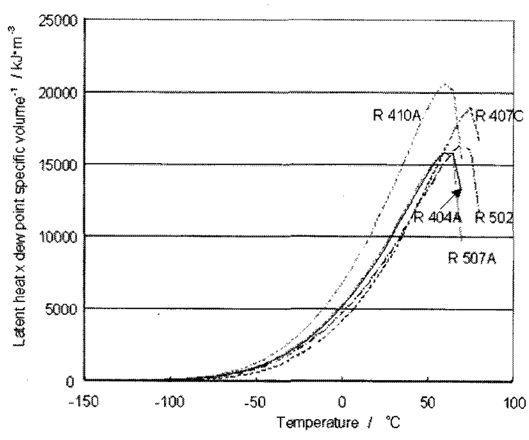


Fig. 6. Latent head divided by dew-point specific volume of pure refrigerants.

A reliability of the compressor improves with lower specific heat ratio, because the specific heat ratio controls the compressor discharging temperature. The discharging temperature becomes low with a small specific heat ratio. As for the specific heat ratio and the specific heat capacities, these values are significantly different depending on the refrigerant and the cycle conditions. Thus, it is necessary to select an appropriate refrigerant considering the cycle conditions and the specifications of equipment.

2.3 Transport properties of refrigerants

When a refrigeration or air-conditioning equipment is designed, it is necessary to clarify pressure loss, heat transfer, and heat conduction phenomenon. In this case, these transport properties become important. However, the measurement with high accuracy is very limited because it is difficult to measure transport properties such as viscosity and thermal conductivity of the refrigerants, especially for the mixtures.

The coefficient of liquid viscosity decreases as the temperature rises; however, the coefficient of vapor viscosity increases with the temperature rise. The liquid thermal conductivity decreases and the vapor thermal conductivity increases with the temperature rise.

As in Fig. 7, the coefficient of viscosity for the saturated liquid R 134a shows the highest value among the refrigerants, but the coefficient of viscosities for the saturated liquid R 23, carbon dioxide, and propane are small. R 32 and R 143a show little small values. These refrigerants with smaller values are expected to have higher COP in an actual machine by considering the influence of pressure losses in the heat exchanger and the expansion valve. As for the coefficient of viscosity for the saturated vapor, R 23

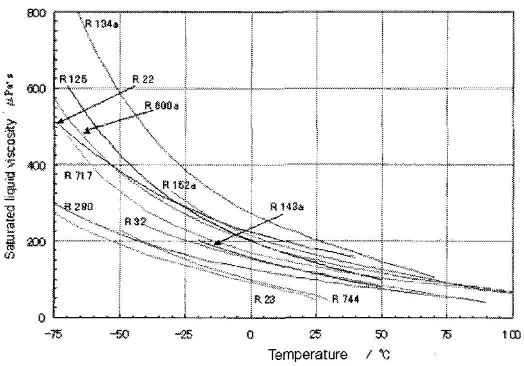


Fig. 7. Saturated liquid viscosity of pure refrigerants.

and carbon dioxide show higher values, and isobutane, propane, and ammonia show smaller ones. It would be better to use a refrigerant with smaller coefficient of viscosity considering the pressure losses in the compressor and the valve system.

As shown in Fig. 8 thermal conductivity data for the saturated liquid refrigerants, R 32 and carbon dioxide show higher values. Especially, for ammonia it is from 300 to 800 $mW \cdot m^{-1} \cdot K^{-1}$, outside of the diagram temperature range. A refrigerant with the highest thermal conductivity is approximately twice as high as one with the lowest value. The selection of the refrigerant that has a higher thermal conductivity is preferable to improve the heat transfer coefficient at the heat exchanger. When designing, it is also necessary to note that the value might be tripled by refrigerant with the high and with low for the thermal conductivity of the saturated vapor.

As for the coefficient of viscosity for R 407C, in Fig. 9 which shows the bubble-point curves of the

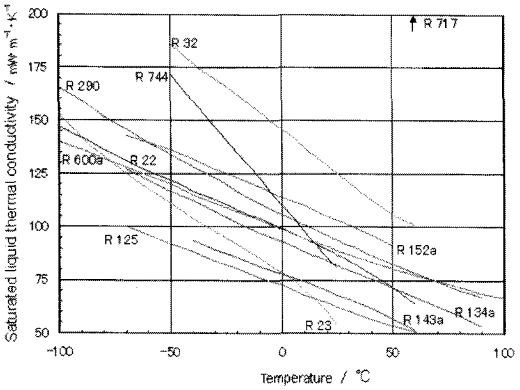


Fig. 8. Saturated liquid thermal conductivity of pure refrigerants.

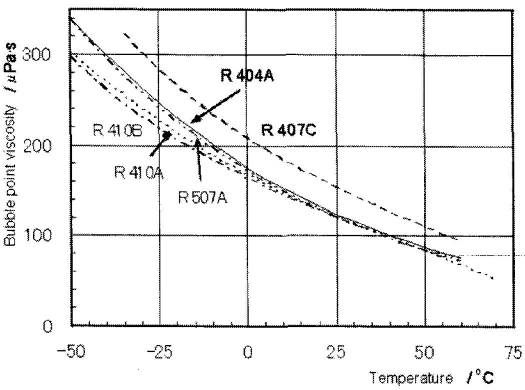


Fig. 9. Bubble-point viscosity of refrigerant mixtures.

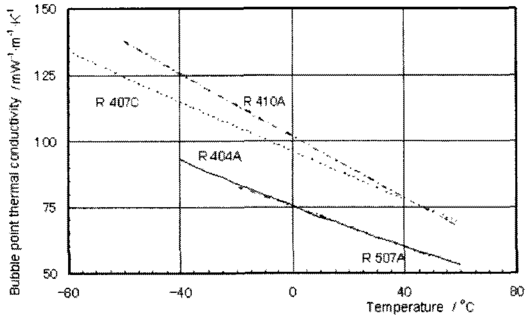


Fig. 10. Bubble-point thermal conductivity of refrigerant mixtures.

mixtures, the coefficient of viscosity is larger than that of other mixtures, because R 407C is composed of more R 134a. As shown in Fig. 7, R 134a has higher values. R 410 mixtures have smaller R 134a ratio oppositely. As for the coefficient of viscosity on the dew-point curves, notable difference is not observed between the listed mixtures.

The thermal conductivity on the bubble point curves is shown in Fig. 10. As for R 407C and R 410A, the thermal conductivity of the saturated liquid is larger than that of other mixtures because both have a lot of ratio of R 32 with higher values that is one of each element composition. R 32 has higher values as shown in Fig. 8. Among the dew-point curves, R 407C shows slightly lower ones.

3. Consideration concerning refrigerants in the future

The gross mass of the refrigerants used in the world shows the tendency to increase even though the circumstances of the refrigerants become severe. The refrigerants that had been mainly used are arranged in Table 3. Alternative refrigerants such as HFC (hydrofluorocarbon) refrigerants, R 134a, R 407C, R 410A, R 404A, and R 507A are being used now instead of CFC (chlorofluorocarbon) refrigerants with higher ozone depletion potential, ODP, such as R 11, R 12, R 13B1, R 114, and R 502. CFCs had been used before the restriction by the Montreal Protocol in 1995. However, HCFC (hyrochlorofluorocarbon) refrigerants have ODP. Therefore, the production and use of HCFCs in some European countries were already restricted. At latest, other countries will restrict HCFCs by 2025. However, the group of the restricted refrigerants is still being used in a part of old equipments. Drop-in and retrofit refrigerants are prepared for old equipments. Most of them are non-azeotropic

Table 3. Major Refrigerants currently used.

Refrigerant	Composition (mass fraction)	Pure subst./Mixture	Application
R 11		Pure (CFC)	Refrigeration, air cond. (restricted in 1995)
R 12		Pure (CFC)	Refrigeration, air cond. (restricted in 1995)
R 22		Pure (HCFC)	Refrigeration, air cond. (new charge. available until 2010)
R 123		Pure (HCFC)	Air cond. (new charge. available until 2010)
R 134a		Pure (HFC)	Refrigeration, air-cond.
R 290	propane	Pure (natural)	Freezing, Refrigeration
R 404A	R 125/143a/134a (44.0/52.0/4.0)	Pseudoazeotrope	Freezing, Refrigeration
R 407C	R 32/125/134a (23.0/25.0/52.0)	Nonazeotrope	Refrigeration, air cond.
R 410A	R 32/125 (50.0/50.0)	Pseudoazeotrope	Refrigeration, air cond.
R 413A	R 218/134a/600a (9.1/88.0/3.9)	Nonazeotrope	Refrigeration, air cond. (drop-in mixture for R 12)
R 417A	R 125/134a/600 (46.6/50.0/3.4)	Nonazeotrope	Refrigeration, air cond. (drop-in mixture for R 22)
R 422A	R 125/134a/600a (85.1/11.5/3.4)	Nonazeotrope	Refrigeration, air cond. (drop-in mixture for R 22)
R 423A	R 134a/227ea (52.5/47.5)	Nonazeotrope	Refrigeration, air cond. (drop-in mixture for R 12)
R 502A	R 22/115 (48.8/51.2)	Azeotrope	Freezing, Refrigeration
R 507A	R 125/143a (50.0/50.0)	Azeotrope	Freezing, Refrigeration
R 600a	Iso-butane	Pure (natural)	Refrigeration
R 717	ammonia	Pure (natural)	Freezing, Refrigeration
R 744	carbon dioxide	Pure (natural)	Hot water

CFCc(chlorofluorocarbons) : R 11, R 12, R 115
HCFCs(hydrochlorofluorocarbon) : R 22, R 123
HFCs(hydrofluorocarbon) : R 23, R 32, R 125, R 134a, R 143a, R 152a, R 227ea
PFCs(perfluorocarbon) : R 218
Natural refrigerants : R 290 (propane),R 600 (butane),R 600a (isobutane),R 717(ammonia), R744 (carbon dioxide)

refrigerants including HFC refrigerants and hydrocarbons.

Fluorocarbons of the alternative refrigerants used widely at present are obligated to be recovered for the global environment protection by the reason of their higher global warming potential, GWP. However, it is quite difficult to increase the recovery amount of refrigerants. Hereafter, it is necessary to set a strong mechanism that the amount of refrigerant leakage should be decreased, or to convert from the HFC refrigerants to less environmental impact materials with no ODP, and with less GWP, like as natural refrigerants.

Many applications receive the restrictions for alleviating global environmental concerns though fluorocarbon refrigerants have been used up to the present time. Because the global warming potential of hydrofluorocarbons is high, the use and production of hydrofluorocarbons will be strictly limited in the near future. Currently, it pays attention to use hydrocarbon refrigerants as refrigerant for home-appliance frozen refrigerators, e.g., iso-butane and propane. Electric heat pump type boilers in which carbon dioxide is used as a refrigerant begin to spread. Moreover, there are equipments that use ammonia as a refrigerant for large-scale freezers. For usage, it should be noted that ammonia has toxicity though flammability is less. Iso-butane and propane have strong flammability.

The future is expected that a lot of refrigerant mixtures be proposed. Then, it is a current state that there is no appropriate one in pure refrigerants used in refrigeration cycle though it is necessary to develop environmental-friendly refrigerants. There is a possibility of less flammability by mixing with a hydrocarbon and a HFC refrigerant, or with a hydrocarbon and carbon dioxide. It leaks from the lower boiling-point refrigerant with a lot of compositions of the vapor phase when leakages occur in case of the non-azeotropic mixture. For instance, it is desirable on safety because it leaks from carbon dioxide when carbon dioxide is mixed with propane. This refrigerant mixture will be available for a refrigerant separate cycle with preferable characteristics, which is introduced in the next chapter.

4. Cycle for new refrigerants

In the development of refrigeration and air-conditioning equipments, the cycle design is important because there is a suitable cycle for each refrigerant. Advanced practical use of the cycle is possible with technological improvements of each cycle element.

As the cycle for low temperature application, multistage compression cycles are available. Among

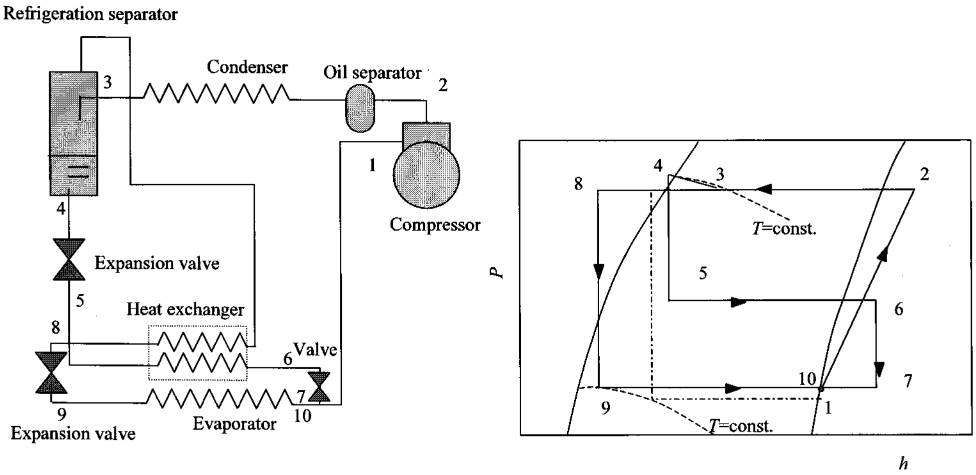


Fig. 11. Refrigerant separation cycle.

them, two-stage compression cycle is common. There is an advantage used besides the low temperature application; the two-stage compression improves the compressor efficiency. Moreover, there are one- and two-expansion systems for the two-stage compression cycle.

A dual cycle uses two kinds of refrigerants, and the compressor efficiency is improved. Because this cycle uses a pure refrigerant at each separate cycle, problems related to the refrigerant mixtures, e.g., complexity of the design and the maintenance can be avoided.

There is a refrigerant separation cycle, which is a comparatively new cycle for non-azeotropic refrigerant mixtures and to makes the best use of their characteristics (Fig. 11). When it is compared with the basic cycle, the refrigerant separation cycle has a weak point of the complication of cycle design and an increase of the number of elements. However, the cycle seems not to be difficult to develop if it is developed with the state of art of refrigeration and air conditioning.

5. Conclusions

By the aggravation of environmental problems, the refrigerants used for the equipments in the refrigeration and air-conditioning field have changed bewilderingly. Refrigerant mixtures including R 32 and carbon dioxide are promising to be used, because the substances have the favorable thermodynamic and transport properties as shown in Sections 2.2 and 2.3. However, these substances have some problems to use as pure refrigerant. For example, R 32 has moderate flammability and a GWP[1], and carbon dioxide has the low critical temperature, which restricts cycle operating conditions. R 23 is suitable to be used for lower temperature application. However, it has a lager GWP[1]. Therefore, adequate refrigerant mixtures including R 32 and/or carbon dioxide will have a possibility to be used widely. When a new refrigerant that eases environmental problems is used, a series of thermophysical property information of the refrigerant is indispensable. However, it takes time until the information being reported because the measurements are complex. The information is necessary for developing equations of state and correlations which are required as designing the equipments.

From such a viewpoint, the thermodynamic tables including transport property information and various pressure-enthalpy (*P-h*) charts and software have been issued by the Refrigerant Technological Subcommittee (JARef) of Japan Society of Refrigerating and Air Conditioning Engineers (JSRAE) and the former committees of JAR (Japanese Association of Refrigeration). Some of them are listed in References.

References

[1] I.I.R., 1995, 11th Informatory Note on CFCs, HCFCs and Refrigeration –Refrigeration and Greenhouse Effect: GWP, TEWI, or COP?, I.I.R.

[2] Japanese Association of Refrigeration (JAR), 2006, Thermophysical Properties of Refrigerants, Chlorodifluoromethane (R22), JAR (1975), or JSRAE, Re-

[1] R23 and R 32 of GWP values relative to carbon dioxide (contribution in 100 years) are 12000 and 550, respectively.

frigeration Cycle Calculation Program Software, JSRAE.

[3] JSRAE, 2005, JSRAE Thermodynamic Tables Vol.1,'JARef HFCs and HCFCs', Ver. 2, JSRAE.

[4] Lemmon, E. W., McLinden, M. O., Huber, M. L., 2002, NIST Standard Reference Database 23, NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP): Version 7.0, NIST.

[5] Tillner-Roth, R., Li, J., Yokozeki, A., Sato, H., and Watanabe, K., 1998, Thermodynamic Properties of Pure and Blended Hydrofluorocarbon (HFC) Refrigerants, JSRAE.

[6] Japanese Association of Refrigeration (JAR), 1986, Thermophysical Properties of Refrigerants, Azeotrope of R22 and R115 (R502), JAR.

[7] JSRAE, 2006, *p-h* Diagrams of Iso-butane and Propane, JSRAE, or JSRAE, 2006, Natural Refrigerant Program Software, JSRAE.

[8] JSRAE, 2003, *p-h* Diagram of Ammonia, JSRAE, or ref. 4), or JSRAE, 2006, Natural Refrigerant Program Software, JSRAE.

[9] JSRAE, 2006, *p-h* Diagram of Carbon dioxide, JSRAE, or JSRAE, 2006, Natural Refrigerant Program Software, JSRAE.

[10] Kagawa, N., Uematsu, M, Watanabe, K., 1990, Trans. of JAR, Vol.7, pp.43 (in Japanese).

[11] Kagawa, N., Uematsu, M, Watanabe, K.: Trans. of JAR, Vol. 8, pp.43 (1991) (in Japanese).

[12] JSRAE, Reito-Kucho-Binran (Handbook of Refrigeration and Air Conditioning) Fundamentals, JSRAE (to be published in 2007).

[13] Kagawa N., Higashi, Y., Okada, M., Murakami, K., Ichikawa, H., Tanaka, N., Kayukawa, Y., 2005, Reito, Vol.80, pp.31-, JSRAE (in Japanese).