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Research and Development of Next Generation Refrigerants and Refrigeration Systems

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ABSTRACT
After the innovative development of machine refrigeration in the nineteenth century, refrigerants used as working fluid in the refrigeration machine have changed in response to safety and environmental issues. And the refrigeration systems have also been designed to adapt the refrigerants. Currently used refrigerants called the third generation are facing regulations of production amount and usage methods because of global warming. In the Kigali amendment of the Montreal Protocol, the reduction of Hydrofluorocarbons which are the most widely used refrigerants is severely scheduled for developed countries, developing countries of groups 1 and 2, respectively. To satisfy the reduction schedule of the Kigali amendment is not so easy because there is very limited number of refrigerants that have low global warming potential (GWP) and safe properties such as no flammability and lower toxicity. And, each heat pump and refrigeration system demands suitable thermophysical properties for their operating conditions. Because the numerous number of operating conditions which are temperature, capacity and others exist, newly proposed pure refrigerants cannot cover all the systems. To fit the suitable thermophysical properties with acceptable GWP and safety properties, a lot of refrigerant mixtures with two to six components have been proposed and further searches are continuously carried out. Accurate estimation of thermophysical properties of new pure and mixture refrigerants is needed for the design and simulation of refrigeration systems. Therefore, measurements of the thermophysical properties are intensively being conducted. Drop-in tests of the new refrigerants are also being conducted. In this paper, the recent situation of next generation refrigerants and refrigeration systems are briefly reported.

Keywords: Refrigerant, Mixture refrigerant, Thermophysical property, HFO, GWP.

1. Introduction

In recent years, disasters due to abnormal weather occur all over the world. In Japan, especially, we suffer many disasters of heavy rain, floods, and typhoons almost every year. At COP25 held in Madrid in December 2019, an environmental think tank from Germany reported that Japan was the worst-hit by extreme weather in 2018. In 2019, there were a massive flood in August, and two strong typhoons in September and October. And, in 2020, we damaged by two massive floods caused by heavy rain in different areas in July. Not only typhoon and rain but also atmospheric temperatures are damaging us. Summer in recent years, the atmospheric temperature often reaches near or over 40 °C and we are threatened by heatstroke. Many people die every year. In 2018, more than 1500 people died from heatstroke in Japan. Atmospheric temperature is rising and such a high temperature is not normal.

It is considered that this abnormal weather is caused by Global Warming due to the increasing concentration of carbon dioxide in the atmosphere. Effects of refrigerants used in air-conditioners, refrigerators, and others on the Global Warming were first pointed out in the Kyoto protocol adopted in COP3 in 1997. Research on low Global Warming Potential (GWP) refrigerants was started against this background. Although researches and developments on low GWP refrigerants, fourth generation [1], were started, the effect of refrigerants on Global Warming was considered very small compared to carbon dioxide emitted by the combustion in power plants, manufacturing processes, cars, etc. After the decades of this, the situation was changed and the effect of the refrigerant became larger than before. And, in the Kigali Amendment of the Montreal Protocol, the regulation which is a phase down of refrigerants with high GWP has been adopted. McLinden [2] reported according to the analysis of Velders that the temperature increase will be around 0.3~0.5 K if the refrigerants are continuously used as the present conditions. Most of the refrigerants used in present air conditioners and refrigeration systems have high GWP from several thousand to over ten thousand. Even R32 which has relatively low GWP and is increasing its usage in air conditioners has a GWP value of 675.

In my previous paper [3], four ways of next generation refrigerants and heat pump/refrigeration systems were reported such as (1) natural refrigerants, (2) low GWP synthetic refrigerants, (3) refrigerant management, (4) refrigerant mixtures. Although the research and development on the next generation refrigerant and refrigeration systems are conducting intensively and some of them were solved, there are still issues remains. In this paper, a review and present situation of the research and development is reported.

2. History of refrigerant development

Here, a history of refrigerant development is briefly explained. A more detailed history is available in a report by McLinden and Huber [4]. An overview of refrigerant history is shown in Fig.1. At the first era when refrigerant machines were produced, many kinds of fluids were tried and used as refrigerants which are called the first generation. Some of them are toxic, some are flammable, and low efficiency. They were not suitable for the refrigerant. Only the ammonia NH_3 is continuously used so far though it is toxic and flammable. Carbon dioxide

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CO_2 started again to use as a refrigerant in Eco-cute which is a heat pump water heater. And, one of the hydrocarbons (HCs), isobutane, was used in domestic refrigerators.

The revolution of refrigeration was caused by the invention of Chlorofluorocarbons (CFCs) in 1920s and Hydrochlorofluorocarbons (HCFCs) in 1930s. Dichloro-difluoromethane (R12) which is non-toxic and non-flammable was commercially produced in 1931 and was used as a refrigerant in refrigerators. R22 which is one of the HCFCs was also commercialized in 1930s and it was used in air-conditioners which was widespread in 1950s. The evolution of refrigeration, air-conditioning and cold chain industries were brought about by non-toxic and non-flammable CFCs and HCFCs.

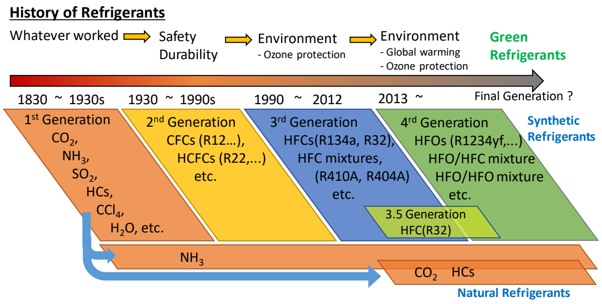

Fig.1 Overview of refrigerants history

However, as well known, the severe depletion of the ozone layer demanded strongly to phase out the CFCs and HCFCs. Currently, CFCs and HCFCs have almost phased out in most of the developed countries and are phasing down in developing countries. As alternative refrigerants of CFCs and HCFCs, Hydrofluorocarbons (HFCs) which do not deplete the ozone layer are developed and the usage of HFCs has been spread in 1990s. Representative HFCs are R23, R32, R125, R134a, R143a, R152a, etc. Because properties of these pure HFCs are limited in suitable pressure and non-flammability, mixtures of HFCs have also been developed. The representative mixtures are R404A (R125/R143a/R134a), R407C (R32/R125/R134a), R410A (R32/R125), etc. They are called the third generation refrigerants.

Although the usage of HFCs and their mixtures has been spread successfully and the crisis situation of ozone layer depletion seems to have been escaped, we are still facing the problem of Global Warming. After the Kyoto protocol, regulations on high GWP refrigerants were established and research and development are accelerated. For example, R134a used in most domestic refrigerators was replaced by isobutane. Eco-cute which is a heat pump water heater used CO_2 as a refrigerant was developed and spread the usage. Despite the efforts of researchers and engineers, the reduction of HFCs emission was not sufficient and the prevention of global warming was not enough. Therefore, further reduction and regulation were required. In accordance with the Kigali Amendment in 2016, the production and consumption of HFCs have to be reduced 85 % by 2036 in developed countries, 85 % by 2047 in developing countries of group 2, and 80 % by 2045 in developing countries of group 1, respectively. Reduction targets in the way are also scheduled. This reduction schedule is not easy to achieve because we have a limited number of new low GWP refrigerants and some of them have flammability and toxicity problems to be solved. Development time to achieve the reduction schedule is also limited. Currently, screening of promising pure refrigerants has almost been completed and many kinds of refrigerant mixtures with a variety of concentrations are being proposed [5].

3. Measures to prevent global warming caused by refrigerants

There are various factors affecting global warming. The emission of refrigerant to the atmosphere is one of the direct factors. Therefore, the replacement of high GWP refrigerants with low GWP refrigerants is the most important and urgent issue. Because the energy consumption of refrigeration systems also affects CO_2 emission and global warming as an indirect factor, the efficiency of the refrigerant is also important.

Hydrofluoroolefins (HFOs) are getting attention as alternative refrigerants because HFOs have zero-ODP and very low GWP. And, hydrochlorofluoroorefins (HCFOs) are also recently getting attention though they have non-zero-ODP in which the ODP values are very small. The reason for the attention to HCFOs is due to the limitation of proper thermophysical properties of proposed HFOs. Other low GWP refrigerants are hydrocarbons (HCs), carbon dioxide (CO_2, R744), and ammonia (NH_3, R717) which are called natural refrigerants. As well known, HCs have strong flammability and NH_3 is toxic and low flammable. CO_2 has low critical temperature, high pressure, and (in general) low cycle efficiency.

Promising refrigerant candidates to replace the current high GWP refrigerants are shown in Table 1 by ASHRAE designation number. Most of the current refrigerants are non-toxic, non-flammable and pure or behave as pure refrigerants which are azeotropic or quasi-azeotropic. In general, pure refrigerants have better performance and easier to handle than mixed refrigerants. Of course, non-toxic and non-flammable refrigerants are desirable. As shown in Table 1, non-flammable pure HFO and HCFO which are red-colored numbers are only for R123 which is mainly used in turbo chiller. R1234yf and R1234ze(E) are mildly flammable and both of them are alternate of R134a. Azeotropic mixtures which are R500 cerise are very limited, only R513A, R516, and R514A. The majority of the candidates are zeotropic mixtures which are R400 cerise. And, many other mixtures that are not listed are proposed. Although it seems that many candidates exist sufficiently for each current refrigerant, the actual situation is different. The mixtures listed in the non-flammable column have somewhat high GWP which cannot satisfy the Kigali amendment. Mixtures listed in mildly-flammable column can only be used for restricted systems because of safety problems mentioned in regulations, building codes, etc. Additionally, as explained above, zeotropic mixture refrigerants may have lower performance. And there is a lack of accurate thermophysical property data.

We need to find out the best alternative refrigerant for each current refrigerant. And reliable thermophysical property data are indispensable to design heat exchangers, compressors, systems, and other equipment. The thermophysical properties are also needed for refrigerant transportation, safe handling, and environmental treatment.

Table 1 Representative current refrigerants and promising alternative refrigerants.

Current (GWP)	Non-Flammable	Mildly Flammable	Flammable
R134a (1430)	R450A, R513A (HFC/HFO) R744 (CO_2)	R516 (HC/HFO) R1234yf (HFO) R1234ze(E) (HFO)	R290 (propane) R600a (iso-butane)
R404A (3920) R507 (3990)	R448A, R449A/B (HFC/HFO) R452A, R452C (HFC/HFO) R744 (CO_2)	R465A (HFC/HFO/HC) R457A, R454C (HFC/HFO) R455A (HFC/HFO/CO_2) R717 (ammonia)	N/A
R410A (2090)	R466A (HFC/CF3I)	R32 (HFC) R459A, R447A, R452B, R454C (HFC/HFO)	R443A (R1270/290/600a) (CO_2/HC) (R1270(propylene))
R123 (77)	R1233zd(E) (HCFO) R514A (R1336mzz(Z)/t-DCE) R1336mzz(Z) (HFO) R1224yd(Z) (HCFO)	N/A	N/A
R22 (1810)	R448A (HFC/HFO) R449A, R449B (HFC/HFO)	R457A, R454C (HFC/HFO)	R290 (propane) R443A (R1270/290/600a)
R23 (14800)	R469A(HFC/CO_2)	N/A	N/A

The usage of natural refrigerants is also expanding in some fields. As mentioned, isobutane is used in most domestic refrigerators. Because the charge amount limit of propane was increased from 150 g to 500 g, the usage of propane will expand. The usage of CO_2 is spreading not only to heat pump water heaters but also to showcases in supermarkets and convenience stores. NH_3 refrigeration system is increasing in cold storage warehouses.

Because current refrigerants are needed to use transiently until suitable alternative refrigerants have been established, refrigerant management is necessary. Reduce, recover, reuse, and destruction of refrigerants are also needed. The refrigerant management is conducted in accordance with rules determined in each country. We need to strengthen and expand the refrigerant management. The refrigerant managements prevent leakage of refrigerants to the atmosphere and can mitigate Global Warming caused by the current refrigerants.

4. Importance of accurate thermophysical properties of new refrigerants

To use the new refrigerants in various refrigeration systems, thermodynamic and transport properties are essential for designing heat exchangers, compressors, and entire systems. Based on accurate measurements of thermodynamic properties which are pressure-volume-temperature relation, vapor pressure in saturation condition, critical parameters, specific heat of ideal gas condition and sound speed, equation of state (EOS) of is built and other state quantities such as enthalpy and entropy are calculated by using the EOS. When the EOS installed in a software, the thermodynamic properties can be calculated arbitrarily. In REFPROP [6] which is a wildly used representative software, Helmholtz energy EOS is installed and all the thermodynamic properties can be calculated easily. However, the accuracy and reliability of the calculated values depend on the measured data which are used to build the EOS.

Transport properties which are thermal conductivity and viscosity can also be calculated by the REFPROP. When sufficient accurate data exist and a correlation is established for a refrigerant, the correlation is used and reliable values are obtained. When measured data do not exist for a refrigerant, the extended corresponding state model [7, 8] is used to estimate properties. However, the uncertainty of the estimation is somewhat large which is stated in REFPROP as 20%. In case there are some data though they are not sufficient numbers, fitting parameters are introduced in the ECS model and more reliable values can be calculated.

As an example, an effect of viscosity estimation is explained here. Fig.1 shows comparison of viscosity values of R1233zd(E) [9]. One group is experimentally measured values and another is estimated values by REFPROP ver.9.1 [10] which is a previous version. The measured viscosity has around 25 % to 37 % lower value than the estimated viscosity.

In Fig.3, measured condensation heat transfer coefficients of R1233zd(E) on a horizontal tube are compared with predicted heat transfer coefficients calculated by the Nusselt theory [11]. When this measurement was carried out, thermophysical properties of R1233zd(E) were not sufficiently clarified and the experimental data had around 25 % higher value than the Nusselt theory. On the other hand, the Nusselt theory calculated by using measured viscosity [9] shows better agreement with the experimental data. Although the results are not shown here, experimental heat transfer coefficients of R1234ze(E) and R1234ze(Z) agreed well with the Nusselt theory [11]. This result indicates that the reliability of measured viscosity and importance of accurate thermophysical properties.

When we evaluate new refrigerant performance, which are heat transfer, cycle simulation, drop-in test, etc., reliabilities of each property should be confirmed. Even widely used software such as REFPROP, calculated values are not fully reliable.

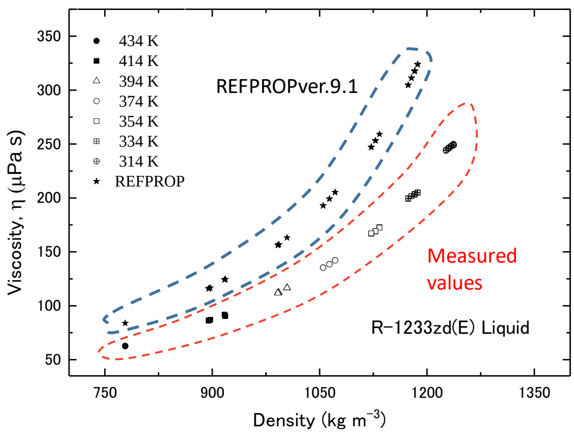

Fig.2 Measured viscosity of liquid R1233zd(E) and calculated value with REFPROP ver.9.1

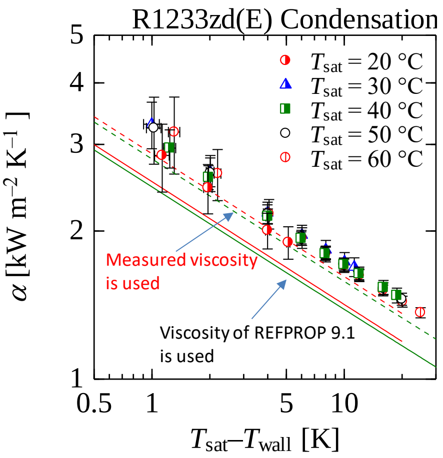

Fig.3 Measured condensation heat transfer coefficient and Nusselt theory of R1233zd(E) on a horizontal tube

5. Efficient use of new refrigerants

As shown in Table 1, most of the new refrigerants are zeotropic refrigerant mixtures in which temperature changes during condensation and evaporation processes in heat exchangers and heat transfer degraded. These characteristics have been previously revealed.

Figs.4 (a) and (b) show experimental values and simulation results on the temperature change of refrigerant and water in heat exchangers [12]. Although refrigerants used were R22 and R22+R114 mixture which have phased out because of ozone layer depletion problem, new refrigerant mixtures will also show similar behaviors. In this case, counter current type heat exchangers were used and quasi-parallel temperature differences between refrigerant and water were achieved for refrigerant mixture. The experiment was conducted under a condition of a heat pump system. The heat output was 1.98 kW, inlet and outlet temperatures of heated water in the condenser were around 30 °C and 50 °C and inlet temperature in the evaporator was around 20 °C. The heat pump system was operated to satisfy the above conditions and state points of refrigerants were measured. The cycle simulation was conducted by using correlations of heat transfer and pressure losses. The simulated cycles of both R22 and R22+R114 agree well with the experimental results.

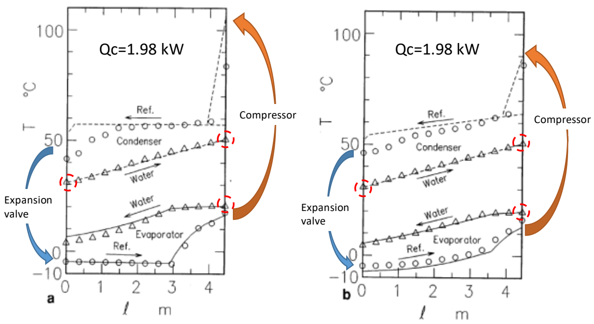

Fig.4 Temperature change of refrigerant and water in condenser and evaporator of a heat pump

The parallel temperature differences are expected to reduce irreversible losses in the heat exchangers and improve the coefficient of performance (COP) of the heat pump cycle. However, heat transfer degradation of the mixture prevents the improvement of COP. Fig.5 indicates the relation between COP and mass fraction of mixture with a parameter of heat transfer length. The solid lines are calculated results in which pressure loss is ignored. The dashed lines are results including the effect of pressure loss. Increasing the heat transfer length achieves improvement of COP. However, at the same time, the pressure loss also increases and the COP decreases. This is more remarkable in low pressure mixture with low R22 mass fraction. By using a multi-path heat exchanger, the increase of pressure loss and the decrease of COP might be avoided. Although the effect of mass fraction is weak, there are maximum peak in the long heat transfer tube and minimum peak in the short tube.

Appropriate design and simulation of refrigeration systems in which a new refrigerant mixture is used are expected.

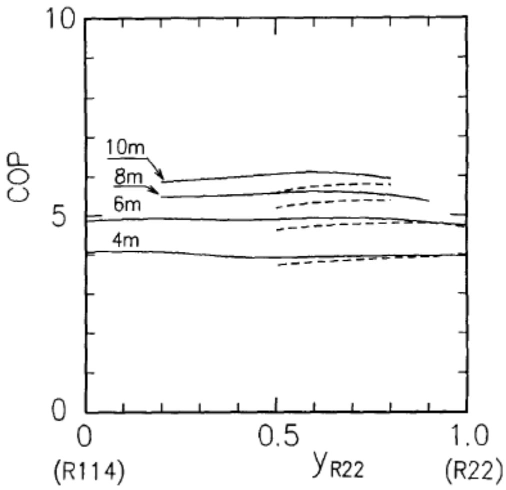

Fig.5 Effects of tube length on the change of COP with mass fraction

A series of comparative experimental studies on heat pump cycle using new refrigerants mixtures were conducted by Koyama et al. [13, 14]. Fig.6 shows the experimental apparatus which is a simple vapor compression heat pump system. Water cooled condenser and water heated evaporator were used and experiments were carried out by giving heating or cooling capacity as an operating condition of heat pump or refrigeration system, respectively. Degree of superheat at evaporator exit was kept as 3 K to 4.5 K.

Koyama et al. [13, 14] conducted the experiments on both heating mode and cooling mode. Heating or cooling output was varied as an operating parameter and temperatures of water inlet and outlet of condenser and evaporator were fixed as experimental conditions. Although they tested two conditions of heating mode and one condition of cooling mode, only the heating mode is explained here. The experimental result is shown in Fig.7. The condenser inlet and outlet temperatures were 20 °C and 45 °C. Evaporator inlet and outlet were 15 °C to 9 °C. Heating output was varied from 1.6 kW to 2.8 kW. Tested refrigerants are binary mixtures, R32+R1234ze(E), R32+R1234yf, ternary mixtures, R744+R32+R1234ze(E), R744+R32+R1234yf, and currently used refrigerants, R410A, R32. As shown in Fig.7, there are refrigerant mixtures which have higher COP than R410A. The 42mass%R32+58%mass%R1234ze(E) and the 4mass% R744+43mass%R32+53mass%R1234ze(E) have the highest COP though the COP of R32 is higher in the range of Q_{COND}>2.2 kW. This result indicates that there is a possibility finding a suitable refrigerant mixture under a given operation condition. Additionally, ODP, GWP, flammability and toxicity also need to be taken in to account for practical use.

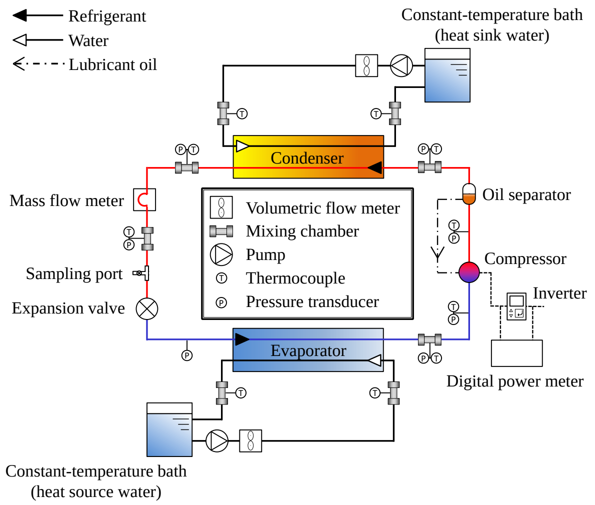

Fig.6 Experimental apparatus of heat pump cycle used by Koyama et al. [13, 14]

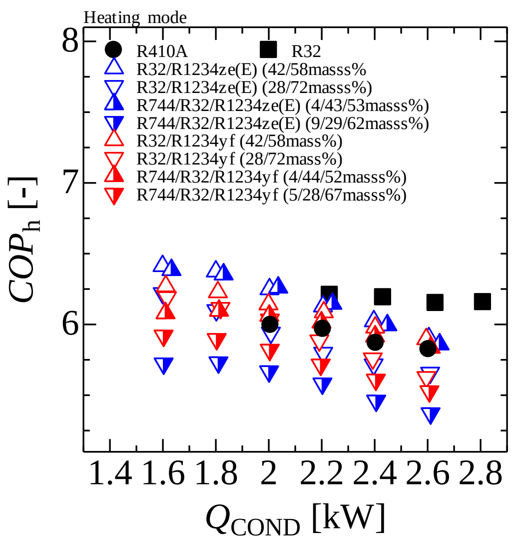

Fig.7 Relation between COP and heat output by Koyama et al. [13, 14]

Fig.8 shows ratios of irreversible loss and heat output of each component which are the condenser, evaporator, expansion valve, compressor, piping and pressure drop. Because the irreversible loss leads to the COP degradation and allows to compare the effects of each component with same scale, the comprehensive evaluation can be conducted. Irreversible losses of compressor and condenser are larger than other components. Therefore, improving the compressor and condenser is important. And it can be also understood that the lowest COP of 9mass%R744+29mass%R32 +62mass%R1234ze(E) is caused by larger irreversible losses of evaporator and expansion valve than other refrigerants.

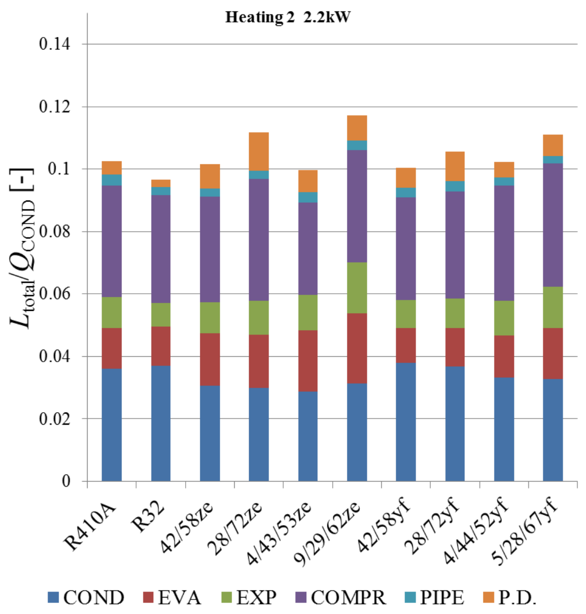

Fig.8 Irreversible losses of condenser, evaporator, expansion valve, compressor, piping, pressure drop in heat exchangers. [13, 14]

6. Refrigerant management

In midway of 3rd generation to 4th generation and even if the 4th generation refrigerants have been developed successfully, current refrigerants and drop-in refrigerants will be transiently used in current systems. Therefore, the refrigerant management is needed. In some countries, a law for refrigerant management is in place. However, the management ways which are not covered yet in the law should be considered for the smooth refrigerant transition. Regular inspection of refrigerant leakage and prompt repair when the leakage is detected are necessary. Although refrigerant recovery and recycle have been started, the recovery rate is not sufficient and many refrigerants are released in the atmosphere and some of recovered refrigerants are destroyed without recycle. Appropriate purification process of recovered refrigerants and quality assurance are needed.

7. Conclusions

In the history of refrigeration and air-conditioning, the transition to fourth-generation refrigerants is the biggest revolution to achieve the evolution of sustainable refrigeration and air-conditioning systems. Although some new refrigerants have been proposed, issues of GWP and flammability of the refrigerants have not been solved sufficiently yet. Further studies are required on thermophysical properties, heat transfer, and system evaluation. And, suitable refrigerants should be selected for each system with different temperature ranges, capacities, usage places/conditions.

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