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## DEVELOPMENT OF RECTIFYING CIRCUIT WITH MIXED REFRIGERANTS

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### Abstract

The use of mixed refrigerants for heat-pump cycles have attracted the attention of the International Energy Agency as an important subject of heat-pump technology and its research and developments have been promoted all over the world. We have tried to apply mixed refrigerants to air-conditioners and developed an epoch-making technology for efficiently separating and varying the mixing ratio of the refrigerants inside the refrigerating circuit.

Computing programs for evaluating the thermodynamic properties of mixed refrigerants from those of the pure components was developed in our laboratory and thermodynamic diagrams such as VLE diagram, pressure-enthalpy diagram, etc., became easily available for our work. The mixed fluorinated refrigerants of R22 - R13B1 were proved experimentally to be promising for heat-pump application in cold districts. The change of working fluid from pure R22 to the mixed refrigerants enhances the effects of an inverter-driven compressor. The technique of estimating the composition of mixed refrigerants operating in our rectifying circuit were developed too, and the calculated values almost coincide with the experimental values.

We also developed a small rectifier with new coiled packings. Effects of shapes of packings and diameters of column were examined by an experimental rectifier alone. The separation characteristics of the packed rectifier, 150 mm in diameter and 210 mm in height, cooled at the top by 60 kcal/h, was about six times as much as the equilibrium separation characteristics. In case of R13B1 - R22, this result corresponds to 70% versus 5% separation of R13B1.

In our original refrigerating circuit of air-to-air heat-pump, the bottom of the rectifier, which is in the middle-pressure, is connected with high-pressure (condenser) and low-pressure (evaporator) heat exchangers respectively by capillary tubes in parallel with the expansion device. When the expansion device is open, it operates with charged mixed refrigerants, resulting in larger heating capacity. When expansion device is shut off, mixed refrigerants flow into the rectifier and rectification starts by vapors generated in capillary tube without heating devices. The separated lower boiling-point refrigerant is cooled by its own refrigerating circuit and liquefied and stored in a reservoir connected to the top of the rectifier. Separation characteristics of the rectifier in the air-to-air heat-pump almost coincide with the results of the preliminary test of the rectifier alone. Then the heating capacity, the input wattage and the fluid pressure of the air-to-air heat-pump operating with the separated refrigerants are decreased to a lower level and its energy efficiency is improved.

We named our refrigerating circuit with the rectifier the "Auto Mixed Freon" method. The newly developed rectifier for commercial models is so small that it is easily installed in the conventional outdoor unit. "Auto Mixed Freon" air conditioner CS-223GR came into the market in Japan in 1986 November for the first time.

## MISE AU POINT D'UN CIRCUIT DE RECTIFICATION AVEC MELANGES DE FRIGORIGENES.

RESUME : L'utilisation de mélanges de frigorigènes pour les cycles de pompe à chaleur a attiré l'attention de l'Agence Internationale pour l'Energie en tant que sujet important de la technologie des pompes à chaleur et ses recherches-développements ont été favorisés à travers le monde. Les auteurs ont essayé d'appliquer les mélanges de frigorigènes aux conditionneurs d'air et ils ont mis au point une technologie qui fait date pour séparer efficacement et faire varier le taux de mélange des frigorigènes dans le circuit frigorifique.

Les programmes de calcul pour évaluer les propriétés thermodynamiques des mélanges de frigorigènes à partir de celles des composants purs ont été établis dans le laboratoire des auteurs et des diagrammes thermodynamiques tels que le diagramme d'équilibre vapeur-liquide, le diagramme pression-enthalpie, etc, devenus facilement disponibles. Les mélanges de frigorigènes fluorés, R22-R13B1, se sont révélés expérimentalement prometteurs pour l'application aux pompes à chaleur dans les régions froides. Le passage du fluide actif de R22 pur aux mélanges de frigorigènes renforce les effets d'un compresseur entraîné par inverseur. La technique d'estimation de la composition des mélanges de frigorigènes fonctionnant sur le circuit de rectification a été mise au point également et les valeurs calculées coïncident presque avec les valeurs expérimentales.

Les auteurs ont aussi développé un petit rectificateur avec nouveaux remplissages en serpentins. L'influence de la forme des remplissages et des diamètres de la colonne a été examinée avec un rectificateur expérimental seul. Les caractéristiques de séparation du rectificateur rempli, 150 mm de diamètre et 210 mm de haut, refroidi en haut avec une puissance de 60 kcal/h, étaient environ 6 fois celles de la séparation d'équilibre. Dans le cas de R13B1-R22, le résultat correspond à 70 % au lieu de 5 % de séparation de R13B1.

Dans le circuit frigorifique initial de la pompe à chaleur air-air, le fond du rectificateur qui est à une pression moyenne, est relié à des échangeurs de chaleur haute pression (condenseur) et basse pression (évaporateur), respectivement par des tubes capillaires en parallèle avec le détendeur. Lorsque le détendeur est ouvert, il fonctionne avec une charge de frigorigènes en mélange ce qui accroît la puissance thermique. Lorsque le détendeur est fermé, le flux du mélange de frigorigènes entre dans le rectificateur et la rectification commence avec les vapeurs produites dans le capillaire sans dispositifs de chauffage. Le frigorigène à point d'ébullition plus bas séparé est refroidi par son propre circuit frigorifique, liquéfié et stocké dans un réservoir relié au haut du rectificateur. Les caractéristiques de séparation du rectificateur de la pompe à chaleur air-air coïncident presque avec les résultats de l'essai préliminaire du rectificateur seul. Ensuite la puissance thermique, la puissance électrique d'entrée et la pression du fluide de la pompe à chaleur air-air fonctionnant avec les frigorigènes séparés diminuent jusqu'à un niveau inférieur et le rendement énergétique est amélioré.

Les auteurs ont appelé le circuit frigorigène à rectificateur la méthode à "halogènes auto-mélangés". Le rectificateur nouvellement mis au point pour les modèles commerciaux est si petit qu'il est facilement installé dans l'appareil extérieur usuel. Le conditionneur d'air à "halogènes auto-mélangés" CS-223 GR a été mis sur le marché japonais pour la première fois en novembre 1986.

## DEVELOPMENT OF RECTIFYING CIRCUIT WITH MIXED REFRIGERANTS

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### 1. INTRODUCTION

Technology concerning the use of mixed refrigerants has in recent years attracted attention from the viewpoint of energy-saving as well as expanded applications of heat pumps. The International Energy Agency (IEA) has also taken up mixed refrigerants technology as important for improvement of heat pumps, and related research and development are being conducted throughout the world.

An important requirement for the expansion of the variable width of the capacity, temperature, etc. by mixed refrigerants is rectification technology of great separation width. The authors have, in an attempt to increase heating capacity at low temperature and thereby realize efficient operation by the heat pump, experimented with applications to the air-conditioner of mixed refrigerants. The rectifying circuit that we have developed has superior rectification performance, and the mixing ratio of the mixed refrigerants can be varied within the refrigerating circuit. This report concerns the characteristics of mixed refrigerants, the principles of the rectifying circuit, and data obtained as the result of experiments concerning the rectifier only as well as for the refrigerating circuit, and also includes a comparison with the calculated results of rectification performance.

### 2. SELECTION OF THE MIXED REFRIGERANTS

In order to fully understand and evaluate the thermodynamic properties of mixed refrigerants from those of pure refrigerants, a computing program by utilizing a generalized equation of state was developed.<sup>1)</sup> The equation used was the Redlich-Kwong-Soave equation<sup>2)</sup>, and, in order to further improve the precision of the estimation, a dual-component system that introduces an interaction parameter obtained through correlation of vapour/liquid equilibrium data is formalized in the following equations.

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)}$$
$$a = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2 \quad (1)$$
$$b = b_1x_1 + b_2x_2$$
$$a_{12} = (1 - k_{12})\sqrt{a_{11}a_{22}}$$

In addition, as the result of experimental research and suppositions concerning characteristics obtained by circuit simulations, fluorinated R22-R13B1 was adopted as the mixed refrigerant for realization of increased capacity when the outside air temperature is low. A diagram showing pressures at various measured constant temperatures of R22-R13B1 is shown in Fig. 1<sup>3)</sup>. The interaction parameter correlated by utilizing eq. (1) is  $k_{12} = 0.0378$ . The pressure vs. enthalpy graph of R13B1 (30 wt %)/R22 (70 wt %) resulting from the use of this  $k_{12}$  is shown in Fig. 2.

Heating characteristics resulting from the use, in the refrigerating circuit of an inverter-driven compressor, of the R22 pure refrigerant and of the R22-R13B1 mixed refrigerant are shown in Fig. 3. As can be seen in Fig. 3, the heating capacity increases when the mixed refrigerant is used when the outside temperature is low, and the heat pump can operate to a low temperature. This is due to the fact that the condenser enthalpy difference decreases and because the flow rate of

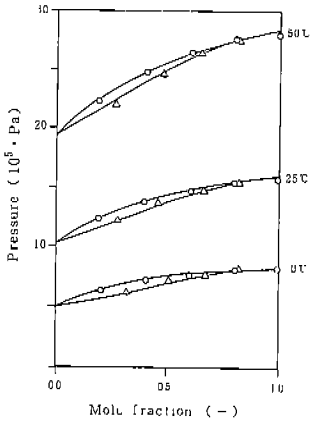


Fig. 1 PX-Diagram of R13B1/R22

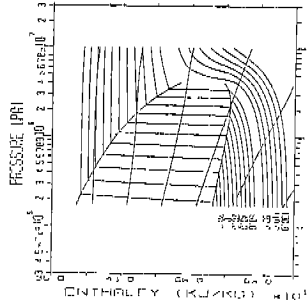


Fig. 2 P-H-Diagram of R13B1/R22 (R13B1 : 30 wt%)

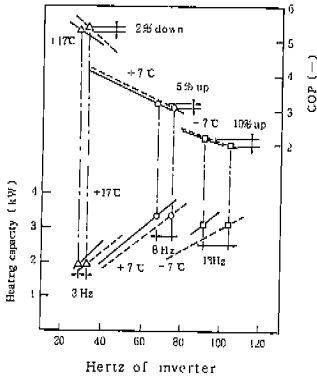


Fig. 3 Heating mode without rectifying  
 — : R13B1/R22 (30%/70%)  
 --- : R22

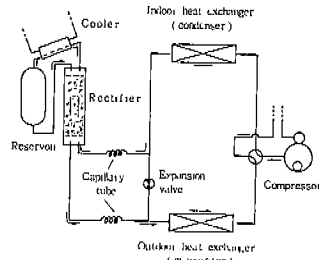


Fig. 4 Configuration of new rectifying circuit

refrigerant compensates for that, and increases even further. In addition, the ratio of decrease of the heating capacity due to a decrease of the outside temperature is lower than that for R22, and, when this is viewed as energy efficiency with relation to the same capacity, the R22-R13B1 mixed refrigerant is higher at low outside air temperature. Its disadvantages, on the other hand, are the fact that the energy efficiency decreases to lower than that of R22 as the outside air temperature increases, and that the pressure also becomes high. In order to overcome those disadvantages, therefore, a rectifying circuit that changes the composition of the refrigerant, thereby making it possible to use the mixed refrigerant when the outside air temperature is low, and the pure refrigerant when the outside air temperature is higher, was developed.

### 3. PRINCIPLES OF THE RECTIFYING CIRCUIT

An example of the rectifying circuit we developed is shown in Fig. 4. The features of the rectifying unit shown in Fig. 4 are as follows. The configuration consists of a circuit that connects the bottom of the rectifier (which is filled with a large amount of packings) with the bottom of the condenser outlet and the

low-pressure evaporator inlet (and the capillary tube for each), bypassing the expansion valve, and the top of the rectifier (via the cooler and the reservoir); the cooler is cooled at the compressor suction line. In other words, our rectifying circuit differs very much from the Schwind system<sup>4)</sup> in that the reservoir is located at the top of the rectifier.

As for the operation of this rectifying circuit, when the expansion is regulated so that a large amount of refrigerant is caused to flow to the rectifying unit, vapour is produced in the capillary tube and, even though there is no heat source, rises within the rectifier. At this time, the liquid refrigerant within the reservoir is caused to reflux to within the rectifier by the vapour pressure even though the position of the reservoir is at the low level. The lower boiling-point refrigerant included within the downcoming liquid is vapourized and rises, and, conversely, the higher boiling-point refrigerant included within the rising vapour is condensed and falls. In this way, the lower boiling-point refrigerant is concentrated at the top of the rectifier, and the higher boiling-point refrigerant is concentrated at the bottom of the rectifier, with the result that the main circuit connected to the bottom can be thereby made to be almost all higher boiling-point refrigerant only.

The operational principles of the circuit in this type of rectifying mode will be explained by using the temperature vs. composition graph shown in Fig. 5. Of the refrigerant flowing in the rectifier in the two phases, for the vapour the concentration of R13B1 becomes larger, and for the liquid it becomes smaller. When, at the next stage, the vapour is cooled and once again becomes a mixture, the R13B1 becomes even more largely concentrated at the vapour side, and the repetition of this process results in largely concentrated vapour of the R13B1. Further, when the heating of the liquid and mixing are repeated, a largely concentrated liquid of R22 is produced. A cooler is provided for vapour liquefaction at the top of the rectifier, and vapour/liquid direct contact causes mass transfer and thermal transfer. The packings function to make the distribution of the liquid smooth and accelerate the vapour/liquid contact, and, by one rectifier, to also perform continuous separation while doing so.

#### 4. DEVELOPMENT OF THE RECTIFIER

Using a prototype with the rectifier only in Fig. 6, we conducted experiments to determine the optimum packings and tower diameter. The prototype is composed of the packing tower (which is filled with the packings), the heater, the water cooler, the lower reservoir, and the upper reservoir. The vapour that is produced by the heater and the liquid that is condensed by the cooler come into contact on the packings, with the result that rectification occurs, and then the higher boiling-point refrigerant (R22) is stored in the lower reservoir and the lower

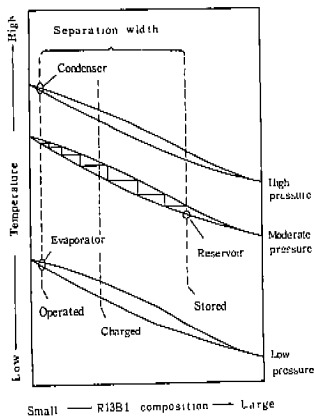


Fig. 5 Principle of rectifying mode

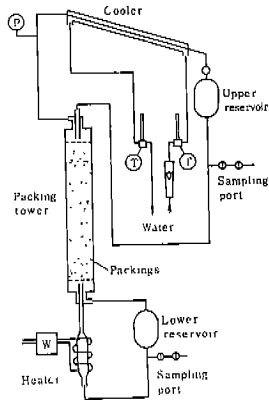


Fig. 6 Prototype of rectifier only

boiling-point refrigerant (R13B1) is stored in the upper reservoir. R13B1 (30 wt %)/R22 (70 wt %) refrigerant is used as the charged refrigerant. The heating calorification was adjusted by changing the heater input, and the cooling calorification was adjusted by changing the water temperature and flow rate. The diameter of the packing tower, as well as the height and the type of packings, were varied, and, after sampling of the refrigerant from both reservoirs, the composition was measured by gas chromatography, and thereafter the number of theoretical plates (NTP) was determined.

In order to make the rectifier of compact size, packings of superior rectification performance were required, and, in addition, there was the necessity to consider the stability and cost of the packings. Approximately 30 types of packings were therefore examined, with the result that the metal coiled packings, which feature low cost and good rectification performance, were developed. The relationship between these packings' NTP (number of theoretical plates) and the cooling calorification  $Q_c$  is shown in Fig. 7, with the packing heights as the parameters. The NTP increases in accordance with an increase of the cooling calorification, and the rectification performance improves in accordance with the packing height; for a packing height of 210 mm, and at a cooling calorification of approximately 70 watts, and adding the equilibrium separation at the lower reservoir, a high rectification performance of about 7 plates is obtained. For R22-R13B1, this rectification performance corresponds to separation of approximately 70 wt % for R13B1 at the top and approximately 5 wt % for R13B1 at the bottom.

### 5. CHARACTERISTICS OF AIR-TO-AIR RECTIFIED HEAT-PUMP

Experiments concerning the rectifying circuit were conducted by using the model experimental apparatus shown in Fig. 4. Based upon results of the prototype, the heater, rectifier, cooler, reservoirs, etc., which form the sub circuit, were connected to the main circuit. With this apparatus, the rectifier pressure could be further adjusted, and an inverter-driven compressor was used. In the same way as for the prototype, the mixed refrigerant composed of R13B1 (30 wt %)/R22 (70 wt %) was charged, and experiments were conducted varying the heating calorification (rate of vapour generation), cooling calorification and rate of branch flow. In addition, the characteristics of the main circuit were investigated under conditions of rectification and non-rectification. Note that, for the rectification performance, both compositions of the main circuit and the reservoir were measured by employing the same method as that for the prototype.

For the Japanese heating standards, the cycle characteristics at various compressor frequencies are shown in Fig. 8. The solid line represents a composition

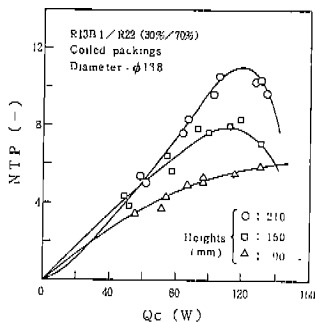


Fig. 7 Characteristics of developed packings

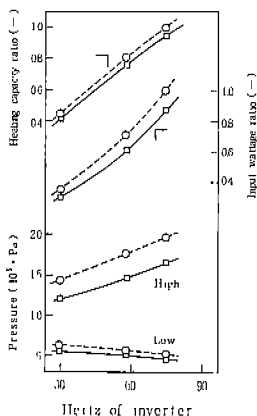


Fig. 8 Comparison of circuit  
 — : with rectifying  
 --- : without rectifying

of R13B1 of approximately 5 wt % (with rectification), and the broken line represents 30 wt % (without rectification). For heating capacity and compressor input, the figure "1" indicates the value at a frequency of 75 Hz and at 30 wt %. It can be seen that the capacity, input and pressure all decrease more under conditions of with rectification than for without rectification, and, furthermore, a high COP as a cycle is realized. From these results, it thus became possible to realize a cycle in which there is no rectification, and high capacity is exhibited, when the outside air temperature is low, and, when the outside air temperature is higher, to achieve a lower capacity and high COP operation by employing rectification. Note that it is also confirmed that heating calorification can be greatly reduced by causing an inflow to the heater at the moderate pressure, by reducing the pressure, even though the same degree of rectification performance is achieved.

## 6. SIMULATION OF RECTIFICATION

The rectification performance of the circuit is shown, as the relationship between cooling calorification  $Q_c$  and HETP (height equivalent to a theoretical plate = height of packings/NTP), by a comparison of the results using the same rectifier only, in Fig. 9. Both rectification performance of the rectifier only and the circuit, even though the heating method and the refrigerant circulation method are different for each, show comparatively good coincidence when HETP and NTP are compared; thus, if the cooling calorification  $Q_c$  is known, the rectification performance of the circuit can be deduced from that of the rectifier only.

Regarding coupling of the rectifier to the main circuit, even if the NTP for the rectifier only is known, the finally operated circuit composition is unclear, and there are also instances in which rectification is not possible as a result of an unbalance of the rate of vapour generated and cooling calorification. For this reason, therefore, in order to obtain the desirable rectification performance, there is a need for a simulation method that would determine such design conditions as the rectifier pressure, the rate of refrigerant inflow, the rate of vapour generated, the cooling calorification, the storage ratio, etc. In this regard, there follows, as one method of simulation, modeled upon the rectifying circuit shown in Fig. 4, an example of an enthalpy analysis method, presuming a plate-type of rectifier, and its results.

Excluding the vapour inflow conditions at the bottom of the rectifier and the subcooled conditions at the top of the rectifier, the following equations are established for general application at each  $j$  stage at the middle part (vertically) of the rectifier.

$$\begin{aligned}
 x_{j+1} &= y_j \\
 L_{j+1} &= V_j \\
 L_{j+1}h_{j+1} + V_{j-1}H_{j-1} &= L_jh_j + V_jH_j \\
 Q_c &= V_jH_j - L_{j+1}h_{j+1}
 \end{aligned}
 \tag{2}$$

where:

- x: equilibrium liquid composition
- y: equilibrium vapour composition
- h: liquid enthalpy
- H: vapour enthalpy
- L: descending liquid flow rate
- V: ascending vapour flow rate
- $Q_c$ : cooling calorification

In addition, by using the mass equation

$$Z_f = (T/F) \cdot Z_t + (1 - T/F) \cdot Z_b \tag{3}$$

where:

- $Z_f$ : charged composition
- $Z_t$ : stored composition
- $Z_b$ : operated composition
- T/F: storage ratio



and making a convergent calculation to each stage of eq. (4),

$$NTP = f(Q_c) \quad (4)$$

the equilibrium temperature profile, the rate of ascending vapour flow, and the rate of descending liquid flow, as well as the top stored composition and the circuit operated composition can be calculated.

Fig. 10 shows the calculated results of stored composition and the operated composition with the range of possible rectification when only the cooling calorification is varied while other conditions (such as the rectifier pressure P, the rate of refrigerant inflow  $G_R$ , the heating calorification  $Q_H$ , etc.) are held constant. For the experimental data in Fig. 9, other conditions were also varied, and excellent agreement was obtained. From this it can be considered that the cooling calorification exerts the greatest influence upon the performance of the rectifier, and that appropriate design conditions do exist.

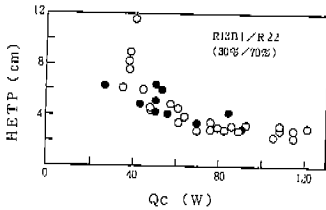


Fig. 9 Comparison of separation  
 ○ : rectifier only  
 ● : circuit

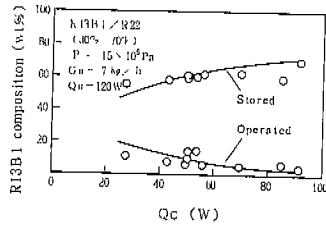


Fig. 10 Comparison of composition  
 — : calculated  
 ○ : experimental

## 7. CONCLUSIONS

- (1) A lower boiling-point storage type of rectifying circuit has been developed that has rectification performance equivalent to that of only the rectifier itself, and which can operate under high-COP conditions in accordance with the load.
- (2) A high-performance, compact rectifier has been developed that features cooling calorification of approximately 70 watts, a packing height of 210 mm, and a number of theoretical plates of about seven.
- (3) A rectification performance simulation method that agrees comparatively well with the experimental values has been developed.

We call the rectifying circuit that we developed the "Auto Mixed Fron" system, and because the size of the newly developed rectifier is compact, it can be installed within the outdoor unit of ordinary air-conditioners. The first air-conditioner to employ this "Auto Mixed Fron" system, the model CS-223GR, was introduced as the first in Japan in November, 1986.

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