Evaluate the possibility of adsorption heat pump application using Activate Carbon and Freon refrigerant pairs

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https://doi.org/10.5109/5909083

出版情報：Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES). 8, pp.141-146, 2022-10-20. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University
バージョン：

Evaluate the possibility of adsorption heat pump application using Activate Carbon and Freon refrigerant pairs

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Abstract: *In order to utilize the adsorption chiller or heat pump as a next-generation air conditioning system, several issues still remain, such as performance improvement, miniaturization, and cost reduction. It is known that the activated carbon-freon refrigerant pair has a relatively lower coefficient of performance (COP) than the silica gel-water or freon refrigerant pair and zeolite-water pair. However, there is a possibility to contribute minimize the adsorption heat pump system utilizing Freon refrigerant since it works in high-pressure regions and has a high saturation vapor density. Therefore, evaluating and improving the performance of Freon refrigerant is an important future task.*

Keywords: Activated Carbon; Freon refrigerant; Adsorption isotherm; Adsorption heat pump

1. INTRODUCTION

Various environmental problems such as global warming and depletion of fossil energy have become serious problems. In order to solve these kinds of problems, various types of research are being conducted all over the world toward the realization of a carbon-neutral society. The Japanese government declared that greenhouse gas emissions would be reduced to net zero by 2050. The adsorption heat pump system can utilize renewable energy which is 100 degrees or less such as solar energy or exhaust heat. Therefore, It is expected as one of the next-generation refrigerant systems. However, there are some tasks to solve for the further application of the adsorption heat pump. The performance of adsorption heat pump is relatively lower than the conventional vapor compression system driven by electric energy, and the initial installation cost is higher than the conventional system as well.

The performance of adsorption heat pumps system is drastically affected by the physical properties of adsorbents and adsorbates (refrigerants). Basically, the adsorption and desorption phenomenon is the interaction of adsorbent and adsorbate(refrigerant). When the adsorption process is proceeding, heat is released. During the desorption process, heat is absorbed. The heat of adsorption or adsorbed quantity which are crucial factors in utilizing adsorption and desorption phenomenon, significantly depend on the physical properties of adsorbent and adsorbate. Therefore, it is a critical factor that is evaluating and selecting suitable materials for the adsorption system. Fig. 1. shows the adsorption and desorption phenomenon and heat transfer of adsorption and desorption processes.

Activated carbon is one of the promising adsorbents which can be obtained from nature. Activated carbon and ethanol pair has a lot of previous study cases since it has suitable suitability. It is expected as a dehumidification material as well, Charunnisa et al. [1] presented that activated carbon showed a better performance than silica-gel at a lower desorption temperature. The primary method to produce the activated carbon is well known as the carbonization and activation processes at a higher temperature region. Typically, the temperature for the carbonization process can be considered 500-700 ℃, and the activation process can be considered around 900-1000℃. One of the main characteristics of activated carbon is that the adsorption capacity of activated carbon has been dramatically improved, and it is expected to show a higher adsorption performance due to its high specific surface area. Therefore, it is used as a representative adsorbent and promising material for the future as well. At the same time, it can be obtained from natural materials such as pine cones and acorns which is excellent in reducing the environmental load. Table 1. shows the characteristic of some activated carbon and other adsorbents that were applied to the previous study.

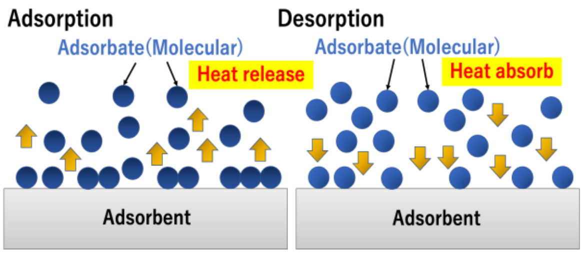

Fig. 1. Adsorption and Desorption phenomenon.

Table 1. Characteristics of activated carbon and other adsorbent

Adsorbent	Surface Area(m^2/g)	Pore Volume (cm^3/g)
MSC-30[2]	3203	1.721
SAC-2[3]	2910	2.53
ACF A-20[4]	2206	1.01
RD silica-gel[5]	780	0.44
RD-2060 silica-gel [5]	707	0.34

Freon refrigerant is expected to contribute a wide utilization to adsorption heat pump systems in the future due to their high saturation pressure and density. These characteristics are expected to contribute to minimizing the equipment of adsorption systems.

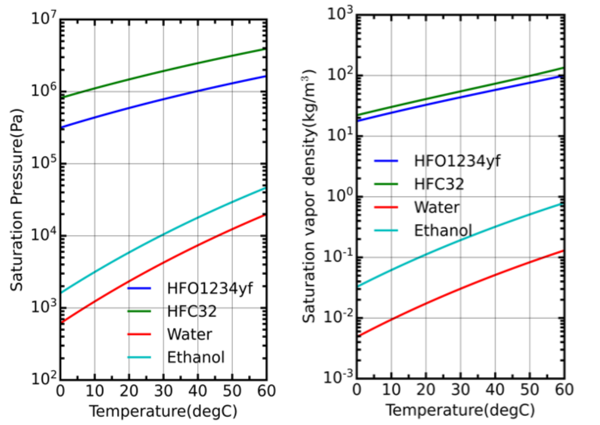

Fig. 2. Saturation Pressure and Saturation vapor density of several refrigerant (Referred from CoolProp 6.4.1).

Fig. 2. shows the saturation pressure and saturation vapor density at the temperature range 0-60℃. As shown in the figure, Water and ethanol which are classified as natural refrigerants have lower saturation vapor density and saturation pressure. On the other hand, Freon refrigerants such as HFC32 or HFO1234yf show a higher saturation vapor density and saturation pressure. Table 2. summarizes the saturation vapor density, saturation pressure, and volumetric capacity of several refrigerants.

Table 2. Saturation vapor density, saturation pressure, and volumetric capacity of several refrigerants.(at 5℃) (Referred from CoolProp 6.4.1).

Refrigerant	Saturation vapor density (kg/m^3)	Heat of vaporization (kJ/kg)	Volumetric capacity (kJ/m^3)
R32 (HFC)	25.89	307.31	7956.26
R245fa (HFC)	3.98	202.13	804.48
R134a (HFC)	17.13	194.74	3335.9
R1234yf (HFO)	20.74	160.02	3318.81
Ethanol	0.04514	941.15	42.48
Water	0.006802	2489.04	16.93

The volumetric cooling capacity of the adsorption system can be calculated by Saturation vapor density by multiplying the Heat of evaporation of refrigerant which is applied to the system. As shown in Table 2. Freon refrigerants show a higher saturation vapor density. Therefore, it is expected that Freon refrigerant can contribute the minimizing the size of the adsorption system due to their higher volumetric capacity than ethanol and water. However, there is a huge difference in the heat of vaporization. The performance of the adsorption heat pump system highly depends on the heat of vaporization of refrigerant. Therefore, still, there is a limitation to applying the actual utilization of Freon refrigerant to the adsorption heat pump system. Fig. 3. shows the heat of evaporation of several refrigerants.

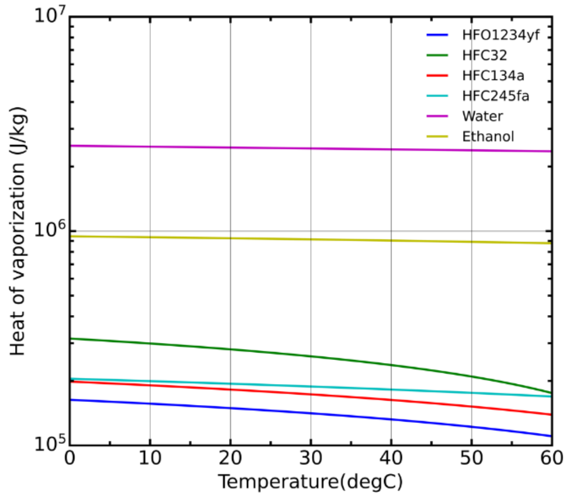

Fig. 3. Heat of evaporation of several adsorbent. (Referred from CoolProp 6.4.1)

Currently, to prevent global warming, it is limited or regulated using Freon refrigerants. Therefore, it is a crucial issue to replace conventional refrigerants. HFC refrigerant has a higher global warming potential (GWP). Therefore, it is planning to limit the usage of HFC refrigerant in many countries. However, still, most countries are using it mainly for the conventional vapor compression system. In Japan, HFC32 is the most popular refrigerant for the household air-conditioning system. It shows a relatively lower GWP than HFC134a or HFC245fa. However, it is still significantly higher than natural refrigerants such as water or carbon dioxide.

Table 3. Properties of Freon refrigerant

Refrigerant	R32 (HFC)	R245fa (HFC)	R134a (HFC)	R1234yf (HFO)
Chemical Formula	CH_2F_2	CHH_2 CH_2 CH_3	CH_2 FCF_3	$C_3H_2F_4$
Molecular Weight [g/mol]	52	134	102	114
ODP*1	0	0	0	0
GWP*1	677	858	1300	<1
Toxicity*2	A (Non)	B (Toxicity)	A (Non)	A (Non)
Flammability*2	2L (Lower Flammability)	1(No Flame Propagation)	1(No Flame Propagation)	2L (Lower Flammability)

Recently, HFO refrigerant was developed as an alternative refrigerant to HFC refrigerant. It has an extremely lower GWP value, almost close to 0. HFO1234yf has already started to replace R134a which was mainly used for the car air-conditioning system. Due to their extremely lower GWP, HFO refrigerant is expected as a next-generation refrigerant. However, there are some tasks that should be solved in the future. The main problem is their lower performance than HFC refrigerant if it is applied to vapor compression systems. To improve this problem, utilizing a binary mixture(HFC+HFO) of refrigerant or a ternary mixture(HFC+HFO+Carbon dioxide) of refrigerant is considered. Kyaw Thu et al. [6] evaluated the performance of a vapor compression air-conditioning system using HFC32 and HFO1234yf binary mixture, and a target GWP was below 150. The properties of Freon refrigerant and natural refrigerant have been summarized in Table 3. and Table 4.

Table 4. Properties of Natural refrigerant

Refrigerant	Water	Carbon dioxide
Chemical Formula	H_2O	CO_2
Molecular Weight [g/mol]	18.0	44.01
ODP*1	0	0
GWP*1	<1	1
Toxicity*2	A(Non)	-
Flammability*2	1(No Flame Propagation)	-

*1 IPCC Fifth Assessment Report, 2014 (AR5)
*2 ASHRAE34-2013

GWP : Carbon Dioxide is the reference(GWP=1) / 100-year global warming potential.
ODP : Ozone Depletion Potential

2. ADSORPTION ISOTHERM ANALYSIS

The fundamental characteristics of working pairs(adsorbent + adsorbate) are normally expressed by adsorption isotherm analysis. Therefore, analyzing the adsorption isotherm is a crucial task due to it shows various characteristics of adsorbent and adsorbate working pairs. One example is understanding the water vapor uptake behavior of the adsorbents. Currently, water scarcity is a global issue due to that affects a large portion of the world's population. Therefore, it is a crucial process to understating water vapor uptake behavior to utilize water harvesting using the adsorption phenomenon. Muhammad Aleem et al. [7] presented the adsorption isotherm analysis using water, zeolite, and MOFs(Metal Organic Forms) by several adsorption isotherm models.

In 1985, the International Union of Pure and Applied Chemistry(IUPAC) suggested six types of adsorption isotherm models. During the past 30 years, various new characteristics of material have been defined and presented. It was necessary to suggest a new classification of the adsorption model. In 2015, a new classification was suggested which has been modified as eight types of isotherm models[8]. The new adsorption isotherm model of I and IV are split into two models I(a), I(b), and IV(a), IV(b). Md. Matiar Rahman et al. [9] presented simulation-based optimum Models for Type-I(a) and Type-I(b) of the new IUPAC classification. Activated carbon is typically classified as Type-I of IUPAC. Type I isotherm model is applied to microporous solids. It has a relatively small pore width of *nm*. One of the leading materials is activated carbon. Type I(a) is applied to the material which has below 1*nm* pore width. Type I(b) is applied to a slightly bigger pore width that is below 2.5*nm*. Fig. 4. shows the shape of adsorption isotherm model Type I(a) and I(b).

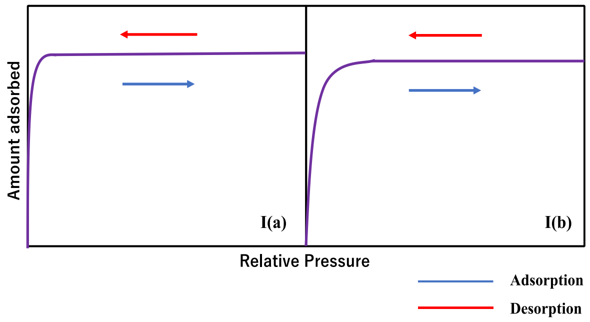

Fig. 4. Adsorption isotherm model of Type I [8,9].

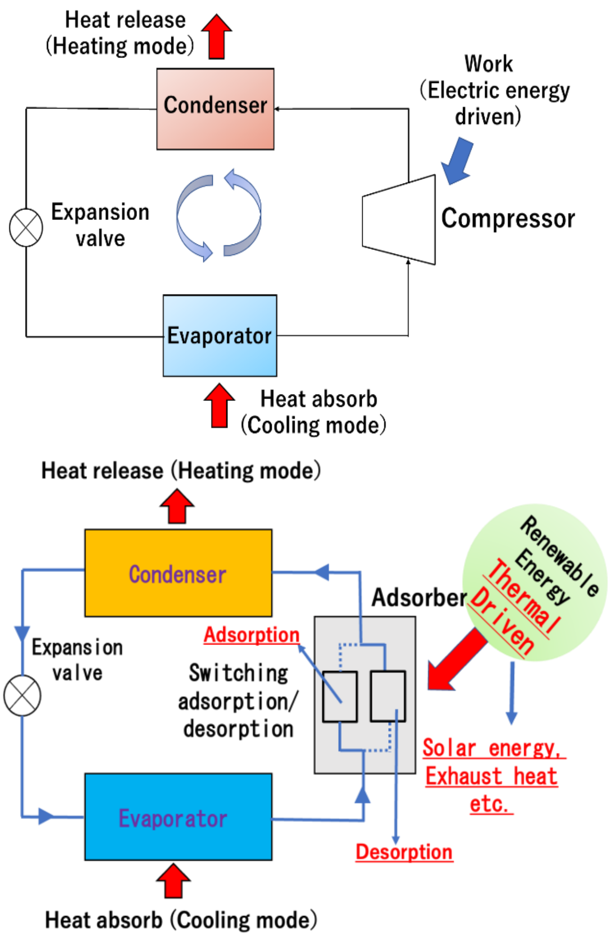

Fig. 5. Schematic diagram of vapor compressor system(upper) and adsorption system(lower).

3. HEAT PUMP APPLICATION

A heat pump system is usually used for the air conditioner, chiller, refrigerator, etc. Until now, in most cases, the conventional vapor compression system is used due to its superior performance than other systems such as absorption or adsorption heat pumps. Nevertheless, it is a necessary and crucial task to develop an alternative system for the next generation. As one of the alternative systems, the adsorption heat pump system is getting significant attention due to its significantly lower environmental load than the conventional system.

3.1 Adsorption heat pump system

Fig. 5. shows the conventional vapor compression system and adsorption system, respectively. The main difference between the two systems is that one is electric energy driven, another one is thermal energy driven. It has the merit of using thermal energy(low-temperature heat source below 100℃)which is usually hard to utilize. Therefore, to solve the environmental problem by using renewable energy, using an adsorption system has a high expectation as the next generation system.

Fig .6. shows the shape of a typical adsorption isotherm line by the CVVP(constant volume various pressure) method experiment. Drawing the adsorption isotherm line is an essential procedure to analyze the characteristic of adsorption working pairs. As shown in Fig. 6. the adsorbed quantity increases at lower temperatures and higher pressure. Furthermore, it is important that the performance of the adsorption cycle can be predicted draw the cycle on the isotherm line. It is useful to expect superior adsorption working pairs.

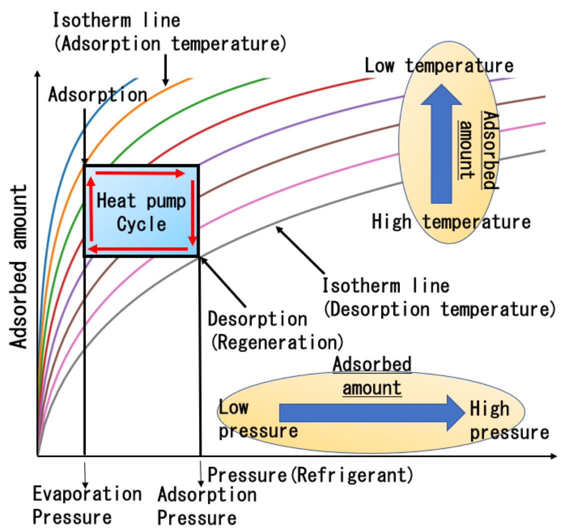

Fig. 6. Adsorption heat pump cycle(blue square) on the adsorption heat pump cycle.

3.2 Concept of heat and mass recovery cycle

Fatin et al.[10] presented the improved model for the isosteric heat of adsorption, and they presented the performance analysis of the adsorption heat pump system using the new model. Some working pairs of them have been summarized in Table 5. As shown in Table 5., Freon refrigerant (HFC134a) shows significantly lower performance than ethanol under the same temperature condition. One of the main reasons for that is considered a lower evaporation heat of Freon refrigerant than ethanol which is mentioned and shown in Fig. 3. B.B Saha et al.[11] reviewed emerging sorption pairs for heat pump applications. Various pairs were selected for the analysis. Ethanol and water showed a higher performance than others with activated carbon, silica gel, and zeolite. The Coefficient Of Performance(COP) of water and ethanol was around 0.7 to 0.8 with various adsorbents. However, Freon refrigerant(HFC410a) with activated carbon(ACF A-20) showed a lower COP value which was below 0.3 under the same temperature condition(Heat source temperature 85℃ / Adsorption, condensation temperature 30℃ / Evaporation temperature 10℃). Seo et al.[12] presented thermodynamic analysis and impact of thermal masses on the adsorption cycle, MSC-30 and SAC-2 are selected as an adsorbent, and HFC245fa is selected as a refrigerant of the system. MSC-30/HFC245fa and SAC-2/HFC245fa showed a COP of around 0.3 to 0.35 under the heat source temperature of 80℃, adsorption and condensation temperature of 30℃, and evaporation temperature of 5℃, respectively. This result showed significantly lower performance than using ethanol as well.

Due to this, there is still a limitation to applying to the actual utilization using activated carbon and Freon refrigerant working pairs, even though they have a high possibility of contributing to minimizing the size of the adsorption system.

Table 5. Coefficient Of Performance(COP) of adsorption working pairs using activated carbon [10]

Adsorbent (Activated Carbon)	Adsorbate (Refrigerant)	COP
MSC-30	Ethanol	0.731
SAC-2	Ethanol	0.742
MSC-30	HFC134a	0.230
MSC-30	Propane	0.198

*Cooling application
Heat source temperature : 80℃
Condensation, adsorption temperature : 30℃
Evaporation temperature : 7℃

Various modified cycle theories and experimental results have been studied to improve the performance and use lower heat source temperatures effectively. Heat recovery cycle and mass recovery cycle have often been applied to the adsorption working pair using ethanol or water for a few decades before. However, there are almost no study cases using activated carbon and Freon refrigerant. COP of the adsorption heat pump cycle can be expressed as follows:

$$SCP = (w_{max} - w_{min})\left\{h_{fg}(T_{Evap}) + \int_{Cond}^{Evap} dh_f\right\} \quad (1)$$

$$COP = \frac{SCP}{Q_{IN}}, \quad Q_{IN} = Q_{Latent} + Q_{Sensible} \quad (2)$$

Here, SCP is Specific Cooling Power, Q is Specific thermal energy, w is equilibrium uptake in mass ratio, *hfg* is specific enthalpy of evaporation, *hf* is enthalpy of saturated liquid, *Cond* is condensation, *Evap* is Evaporation, and *T* is Temperature.

The heat recovery cycle uses the temperature difference between two absorbers. At the end of each half cycle, one adsorber is a lower temperature side, and another adsorber is a higher temperature side. Heat is recovered between the two adsorbers due to this temperature difference. There for total Q_{IN} of the adsorption cycle with heat recovery cycle can be considered as $Q_{IN} = Q_{Latent} + Q_{Sensible} - Q_{Recovered}$. S. Szarzynski et al.[13] presented the internal vapor transport for adsorption cycles with heat regeneration. Is it shown that COP improvement suing zeolite-Nax and water pair. The zeolite requires a relatively higher desorption temperature than activated carbon. However, it is shown that COP was higher than one at the temperature range above 200℃ with a double effect cycle. The schematic diagram of the mass recovery cycle is shown in Fig. 7. (b).

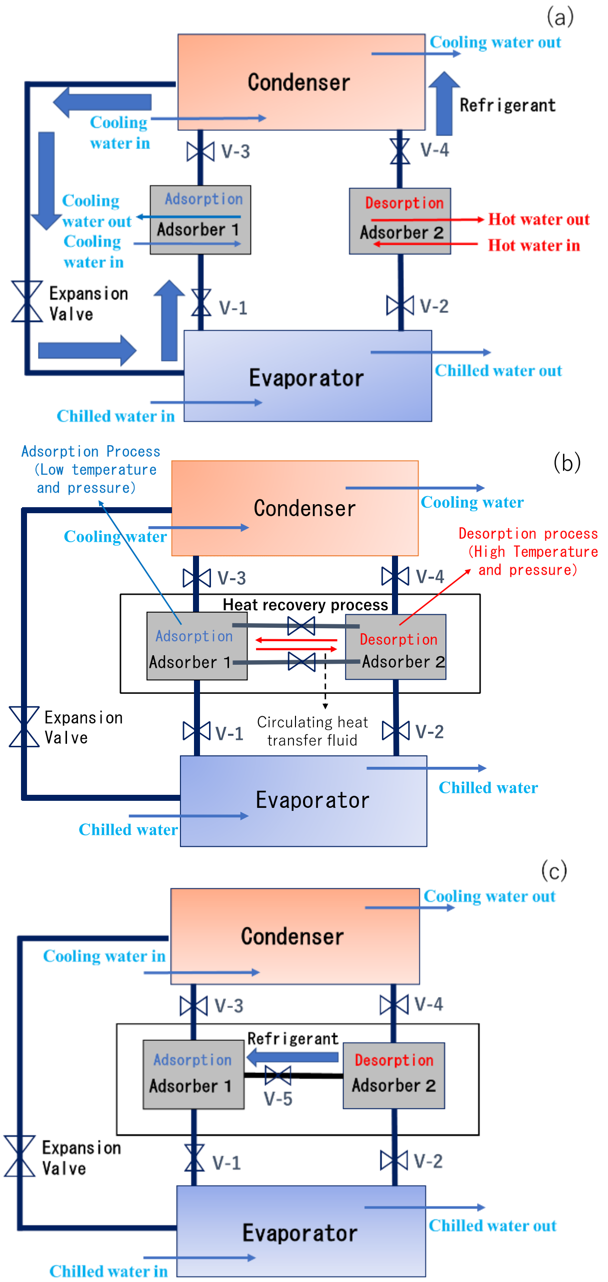

Fig. 7. Adsorption process and Desorption process of adsorption heat pump(a), Heat recovery cycle(b), Mass recovery cycle(c).

The mass recovery cycle is a cycle that incorporates a mass recovery process using the pressure difference in the two adsorbers. When the valve connecting the two adsorbers is opened after the adsorption/desorption process, the refrigerant moves from the high-pressure side (desorption process) to the low-pressure side (adsorption process). The mass recovery cycle increases the amount of refrigerant circulating, it makes a bigger difference between the adsorbed quantity on the adsorption side and the desorption side, and it is expected that the SCP can be improved. AKAHIRA et al.[14] presented the equilibrium analysis result with mass recovery cycle using silica-gel/water working pair. It is present that the mass recovery cycle shows more performance improvement in the low-temperature heat source region from 60°C to 70°C. The COP is improved from around 0.72 to 0.765 at 60°C and around 0.74 to 0.77 at 70°C, respectively(Adsorption and condensation temperature 30°C, Evaporation temperature 14°C). The schematic diagram of the mass recovery cycle is shown in Fig. 7. (c).

4. SUMMARY

In this study, the potential of Freon refrigerant and activated carbon as an adsorption material is evaluated. Activated carbon is a promising material as an adsorbent since its high adsorption ability. Freon refrigerant is expected to contribute to minimizing the size of the adsorption system due to its higher density and volumetric capacity shown in Fig. 2. and Table 2. At the same time, it has a higher saturation pressure, and it works above the atmospheric pressure in the adsorption system. This characteristic of Freon refrigerant is expected to increase adsorption speed. However, the performance of the activated carbon-Freon working pair is significantly lower than ethanol or water. For the actual usage of activated carbon-Freon working pair, performance improvement is necessary. Many previous studies presented ethanol's performance analysis of heat recovery and mass recovery cycle. However, it is almost not applied to the activated carbon and Freon refrigerant pairs. Freon refrigerant is one of the promising materials to solve the current problem of adsorption systems. Especially, HFO refrigerant has extremely low GWP, and it has a high expectation for the next generation system. To utilize activated carbon and Freon refrigerant, especially HFO refrigerant, applying the modified adsorption cycle such as heat recovery and mass recovery cycle to improve the performance and analyze the merit is a necessary future task.

ACKNOWLEDGMENT

This work was supported by JST SPRING, Grant Number JPMJSP2136.

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