Application of Low Global Warming Potential Refrigerants for Room Air Conditioner

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Abstract: An application of the low Global Warming Potential (GWP) refrigerants, HFO-1234yf (2,3,3,3-tetrafluoropropene) and R-32/HFO-1234yf mixtures, for the room air conditioner was performed.
Acid number of polyolester refrigeration oil for R-410A has greatly increased after aging with HFO-1234yf containing air. HFO-1234yf breakdown products such as hydrogen fluoride may cause this phenomenon. However, other materials compatibility has been almost identical to R-410A.
Using R-410A room air conditioner, the drop-in tests of HFO-1234yf and R-32/HFO-1234yf mixtures were carried out. The performance of HFO-1234yf is significantly lower than that of R-410A as a result of the pressure drop increasing. The performance of R-32/HFO-1234yf improves as the R-32 concentration becomes richer. The COPs of R-32/HFO-1234yf (50/50 wt%) under cooling and heating conditions are 95% and 94% of those of R-410A respectively.

Key Words: Refrigerants, Evaluation, Quantum Chemistry, Reaction, Room Air Conditioner, Drop-in Test, Performance, HFO-1234yf, R-32/HFO-1234yf Mixtures

1 INTRODUCTION

R-410A, used in room air conditioners, is one of the HFCs which has to be controlled to reduce the emission in accordance with the Kyoto Protocol because of high GWP. Under F-gas regulations set by the Europe Committee, R-134a will be banned from 2011 for use in automobile air conditioners. HFO-1234yf (2,3,3,3-tetrafluoropropene) is expected to be used as an alternative refrigerant of R-134a [1].

This paper shows the application of the low GWP refrigerants, HFO-1234yf and R-32/HFO-1234yf mixtures, in room air conditioners.

2 THERMODYNAMIC PROPERTIES AND IDEAL CYCLE PERFORMANCE

Using thermodynamic properties furnished by Daikin Industries, Ltd., Japan and REFPROP 8.0 [2], the ideal cycle performances of the HFO-1234yf and R-32/HFO-1234yf mixtures are calculated and compared with that of R-410A.

2.1 Comparison of Characteristics of Refrigerants

Table 1 shows the comparison of characteristics of R-410A, HFO-1234yf, R-32/HFO-1234yf mixtures and R-32.
HFO-1234yf has low GWP and high boiling temperature but is mildly flammable, A2L. R-32 has one third of R-410A's GWP and almost same boiling temperature as that of R-410A but is mildly flammable, too. R-32/HFO-1234yf mixtures have intermediate characteristics between HFO-1234yf and R-32 but are zeotropic mixtures and temperature glide is large.

Table 1 : Comparison of Characteristics of Refrigerants

Refrigerant		GWP	Flammability	Boiling Point (Dew) ℃	Temperature Glide K
R-410A		2088	A1	-51.4	0.1
HFO-1234yf		4	A2L	-29.4	0
R-32/1234yf Mixtures	20/80wt%	128	A2L	-36.9	7 .1
	50/50wt%	340	A2L	-45.6	3.5
R-32		675	A2L	-51.7	0

2.2 Comparison of Ideal Refrigeration Cycle Performance

Table 2 shows the conditions of the ideal cycle and the calculated performances of the HFO-1234yf and R-32/HFO-1234yf mixtures compared with that of R-410A.
HFO-1234yf has lower pressure, lower discharge temperature and lower volumetric capacity but 5% higher COP (Coefficient of Performance) than those of R-410A. R-32 has higher pressure, higher discharge temperature and higher volumetric capacity and higher COP than those of R-410A. R-32/HFO-1234yf mixtures have intermediate characteristics between HFO-1234yf and R-32. As R-32 concentration becomes richer, R-32/HFO-1234yf mixtures develop the same characteristics as those of R-410A.

Table 2 : Theoretical Refrigeration cycle Condition and Calculation Results

Condition	Condensing Temperature ℃	Evaporating Temperature ℃	Superheat at Evaporator Outlet K	Subcooling at Condenser Outlet K
Cooling	45	10	5	5

Refrigerant		Condensing Pressure MPa	Evaporating Pressure MPa	Discharge Temperature ℃	Volumetric Capacity kJ/m3	COP
R-410A		2730	1086	64.7	6629 (100%)	6.420 (100%)
HFO-1234yf		1153	438	48.0	2855 (43.1%)	6.777 (105.6%)
R-32/1234yf Mixtures	20/80	1710	656	58.1	4227 (63.8%)	6.690 (104.2%)
	50/50	2259	888	65.2	5621 (84.8%)	6.580 (102.5%)
R-32		2795	1107	75.8	7228 (109.1%)	6.561 (102.2%)

3 MATERIALS COMPATIBILITY TEST RESULTS

Installation of split-type room air conditioners may cause air contamination of the refrigeration cycle. Low GWP refrigerants like HFO-1234yf would easily break down in contact air. Compatibility tests for HFO-1234yf in the presence of air have been performed for refrigeration oil, plastics, and rubber samples. We have shown them to be similarly compatible with HFO-1234yf as they are with R-410A.

3.1 Reaction of HFO-1234yf with Air

We have evaluated reactivity of HFO-1234yf with air contamination. All experiments were performed in 150cc pressure tight reactive containers made of stainless steel. Refrigerant and air were introduced into these containers with copper, steel, and aluminum coupons. Air-refrigerant ratio was controlled in the same proportion as actual room air conditioners at worst installation operation; indoor unit and connecting pipes were not evacuated. In addition, a little amount of water was introduced as moisture vapor in the air.
After aging at 448K for 336h inner gas were analyzed using GC-MS (QP-2010Plus/ Shimadzu Corp.) with HP-PLOT Q column (Agilent Technologies). Table 3 is a summary of detected materials and area ppm in GC-MS total ion chromatograms. In the presence of oxygen, many bi-products have been detected. However, without air, very small amounts of those products can be detected.

Breakdown products as alcohol, aldehyde, ketone, and ester were oxidation products of the refrigerant. Difluorodimethylsilane and fluorotrimethylsilane are reacted products from hydrogen fluoride and column surface of GC-MS (Figure 1).

Table 3 : The aging test results of HFO-1234yf with air (1) and without air (2)

Sample	1	2
Aging temperature [K] and time [h]	448K 336h	
1234yf (g)	22.5	22.5
Air (ml)	67.5	(no)[a)]
Products	Relative intensity (area ppm)	
$CH_2{=}CH_2$	7.12	-[b)]
1234yf	(base peak)	(base peak)
CH_3OH	4.29	-
CH_3CHO	43.99	4.05
$HCOOCH_3$	2.20	-
$SiF_2(CH_3)_2$	8.32	-
CF_3COCH_3	15.57	3.43
CH_3CH_2OH	8.31	-
CF_3COOCH_3	4.01	-
$SiF(CH_3)_3$	4.32	-
CH_3COCH_3	2.55	-
$HCOOCH_2CH_3$	0.80	-
$CF_3COOCH_2CH_3$	4.32	-
$CH_3COOCH_2CH_3$	0.32	0.10
$CF_3COOCH_2CH(CH_3)_2$	-	0.17

a)No air injection in the reaction vessel. b)Not detected (<0.1ppm).

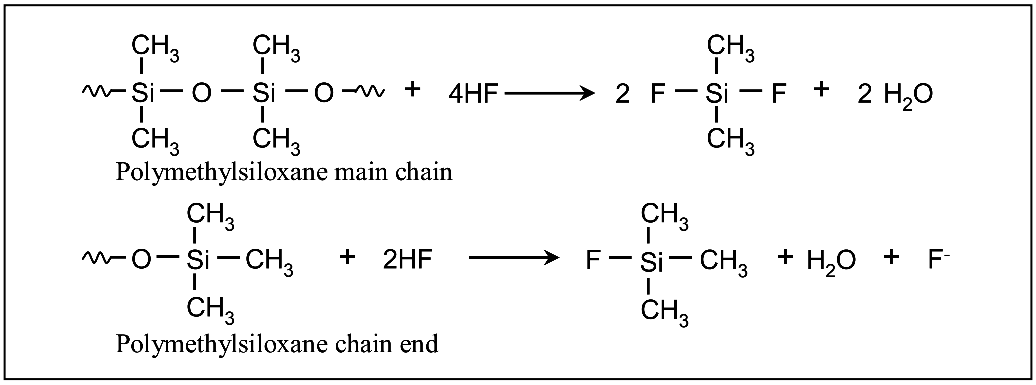

Figure 1. The formation of difluorodimethylsilane and fluorotrimethylsilane on the GC-MS fused silica capillary column

3.2 Laboratory Evaluation of HFO-1234yf with Polyolester Refrigeration Oil

Polyolester (POE) refrigeration oil for R-410A (Nippon Oil Corporation) is miscible with HFO-1234yf in all proportions. We have evaluated the stability of the POE refrigeration oil under HFO-1234yf conditions with steel, copper and aluminum coupons in 200cc containers. These results are summarized in the Table 4.
At the standard test conditions of 448K for 336h acid number increased to 1.39mgKOH/g (No.3) and 2.13mgKOH/g (No.4). As acid number of the sample with air and water (No.4) is larger than that without air (No.2), acids are believed to come from HFO-1234yf and air reacting with each other. Fluorine ion in POE refrigeration oil was detected at No.3 and No.4, and high acid number may cause sludge.

Table 4 : POE Refrigeration Oil Stability Test Result

	1	2	3	4	5	6
Refrigerant/weight(g)	HFO-1234yf / 30g				R410A / 30g	
Oil/weight(g)	POE (Polyol ester oil) / 30g					
Air(ml)	(no)	(no)	90	90	90	90
Moisture in oil [ppm]	<10	1000	<10	1000	<10	1000
Condition	448K/336h					
Acid Number [mgKOH/g]	0.01	0.06	1.39	2.13	0.08	0.35
Color [ASTM]	L0.5	L0.5	L2.0	L4.0	L4.0	L6.0
Sludge	Not collect	Collect	Collect	Collect	Collect	Collect
Ion in oil F^- [ppm]	<1	<1	6	4	-	-
Residual ratio of additives: Acid catcher [%]	30	<10	<10	<10	10	10
Residual ratio of additives: Antioxidant [%]	100	90	60	40	10	10
Oil appearance						

3.3 Laboratory Evaluation of HFO-1234yf with Refrigeration Materials

Material compatibility of typical plastics and rubber materials with HFO-1234yf was performed. The test was carried out at temperature 413K for 2000h with these materials, POE refrigeration oil and air in 300cc containers. Tensile strength was measured after aging. Despite significant drops in some materials, tensile strengths make a little difference in between HFO-1234yf and R-410A (Table 5). Increasing acid may not influence the strength. And HFO-1234yf molecule is larger than R-32 or R125 relatively; it cannot penetrate into polymer chains.

Table 5 : Comparison of HFO-1234yf and R-410A with Selected Plastics and Elastomer

Aging temperature [K] and time[h]	Initial	413K 2000h	
Refrigerant	-	HFO-1234yf	R-410A
Materials	Tensile Strength (relative to initial)		
PPS	1	0.94	1.03
PA66	1	0.70	0.93
PTFE	1	1.09	0.94
PET	1	0.42	0.50
PBT	1	0.41	0.39
LCP	1	0.99	0.92
HNBR	1	0.95	0.86

4 REACTION SCHEME IN AIR CONDITIONERS

POE refrigeration oil causes auto oxidation reaction in the presence of air [6], so it usually contains antioxidants. However acid number increased more with HFO-1234yf than with R-410A, the antioxidant in the refrigeration oil consumed much less with HFO-1234yf than with R-410A. It implies that HFO-1234yf reacts more quickly with air than with antioxidants in POE refrigeration oil. Scheme A in Figure 2 shows that HFO-1234yf is decomposed via OH additive into formaldehyde and trifluoroacetylfluoride [3-5]. Furthermore formaldehyde is oxidized to formic acid and trifluoroacetylfluoride is decomposed with water into trifluoroacetic acid.

However, we observed acetaldehyde, trifluoroacetone, and other products which are not observed in breakdown products of HFO-1234yf in atmosphere. These breakdown products are from other reaction path (Scheme B). OH radical and HFO-1234yf can react rapidly to additive, and the additive eliminates fluoride to trifluoroacetone in a row under low oxygen concentration compared to in the atmosphere. Fluoride radical can abstract hydrogen into hydrogen fluoride. Acetone, acetaldehyde, and acetic acid were produced from trifluoroacetone.

Furthermore we considered the HFO-1234yf/OH addition reaction to which side of double bond in HFO-1234yf can react with OH radical using computational chemistry. In this work, the Gaussian 03 software package was used to perform all computational chemistry calculations [7]. We used the B3LYP method combined with the 6-311G (d,p) basis set. According to energy calculation including zero point energies, α-adduct is more stable than β-adduct. Energy difference between α-adduct and β-adduct is 9kcal/mol.

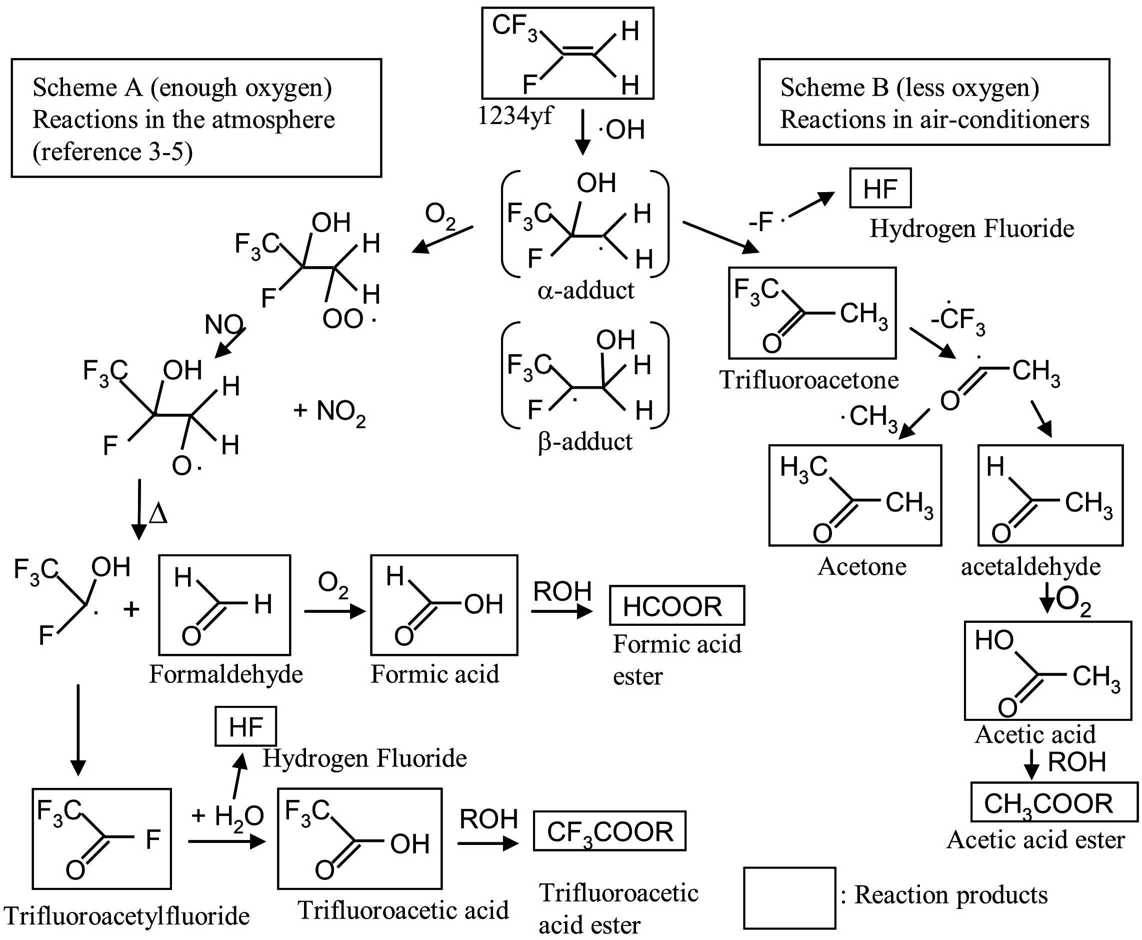

Figure 2. 2 ways of Reactions from HFO-1234yf and OH radical

5 PERFORMANCE EVALUATION OF REFRIGERANTS USING ROOM AIR CONDITIONER

The drop-in tests of HFO-1234yf and R-32/HFO-1234yf mixtures were carried out using R-410A room air conditioner (RAC).

5.1 Experimental Procedure

The R-410A RAC, of which cooling rated capacity is 4kW and the heating rated capacity is 5kw, is used for the test. The R-410A RAC is not modified for other refrigerants. It is called the drop-in test. Figure 3 shows the schematic of the experiment and Table 6 shows the test conditions. The indoor and outdoor air temperature conditions of the test are the cooling and heating conditions according to JIS B8615-1.The indoor fan and outdoor fan speeds are the same as those of the R-410A RAC under each condition. For each refrigerant, the charge amount of the refrigerant in the RAC and the opening of the expansion valve are adjusted to maximize the COP under cooling and heating condition respectively. The capacities of RAC are measured by air enthalpy method testing apparatus (psychometric type).

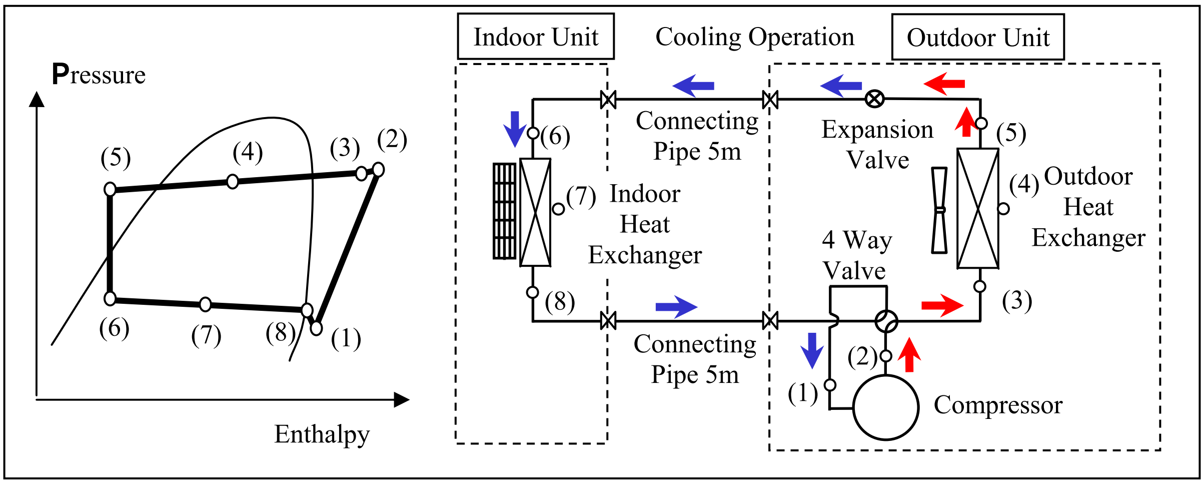

Figure 3. Refrigeration Cycle and Experimental Apparatus

Table 6 : Specifications of the Room Air Conditioner and Test Conditions

Rated Capacity	Cooling / Heating (kW)	4 / 5
Compressor	Type	Inverter Driven Scroll Compressor
	Refrigeration Oil	Polyol Ester Oil
Indoor Heat Exchanger	Pipe Diameter (mm)	6.35 - 5 - 7 - 7.94
	Row	3 – 2
	Number of Paths	1 - 5 - 2
Outdoor Heat Exchanger	Pipe Diameter (mm)	7
	Row	2
	Number of Paths	4 - 2 - 1
Expansion Devices		Electronic control l Expansion Valve
Connecting Pipes	Pipe Diameter Gas / Liquid (mm)	9.52 / 6.35
	Length (m)	5

Test Conditions		Cooling	Heating
Indoor Air Temperature	Dry Bulb (℃)	27	20
	Wet Bulb (℃)	19	—
Outdoor Air Temperature	Dry Bulb (℃)	35	7
	Wet Bulb (℃)	—	6

5.2 Experimental Results of HFO-1234yf

Figure 4 shows the drop-in tests results of HFO-1234yf compared with R-410A. The cooling rated capacity of R-410A RAC is 4kW and the heating rated capacity is 5kw. Though the compressor speed is increased to adjust the capacity to the same as that of R-410A, the cooling capacity and heating capacity of HFO-1234yf don't reach the rated capacities under the maximum compressor speed, 110 rps. The cooling capacity and heating capacity are 70% and 83% and the cooling COP and heating COP are 58% and 79% of those of R-410A respectively.

At half of the rated capacity, the compressor speeds increase 2.4 times of R-410A under cooling condition and 2.3 times under heating condition. The cooling COP decreases 91% of that of R-410A and heating COP decreases 85%.

Though the ideal cycle COP of HFO-1234yf is 5% higher than that of R-410A, the COP of HFO-1234yf, in the drop-in tests, decreased. The reason for this is the increase of the pressure drop in the pipe and compressor loss. In order to improve the performance of HFO-1234yf, decreasing the pressure drop in the pipes, especially evaporator and connecting pipe of gas phase, is necessary.

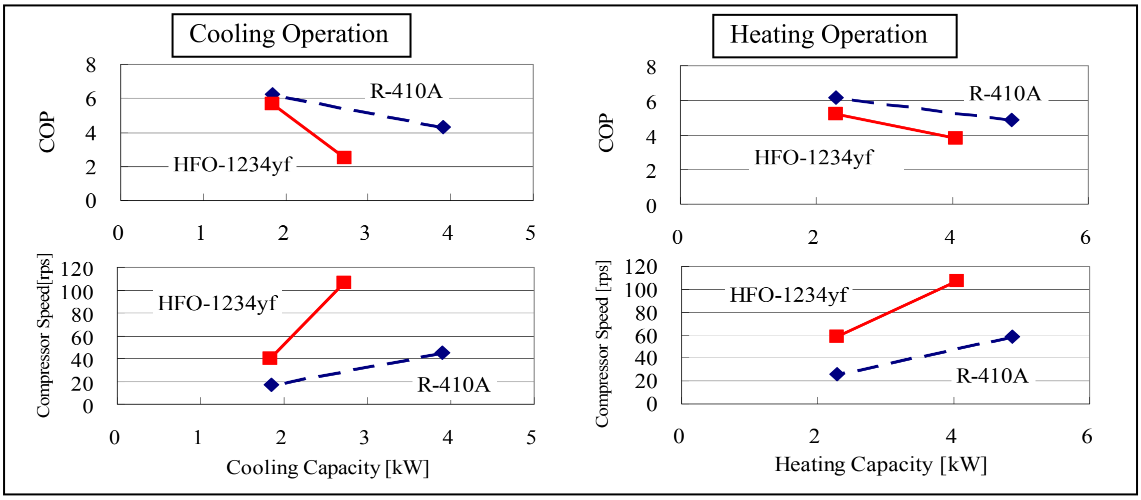

Figure 4. Experimental Results of HFO-1234yf

5.3 Experimental Results of R-32/HFO-1234yf Mixtures

Figure 5 shows the drop-in tests results of HFO-1234yf and R-32/HFO-1234yf mixtures. The compressor speed is increased to adjust the capacity to the same as that of R-410A. The cooling capacity and heating capacity of R-32/HFO-1234yf 20/80 wt%become the rated capacities ,which are the same as those of R-410A, under the maximum compressor speed, and the cooling COP and heating COP are 57% and 78% of those of R-410A respectively. As the concentration of R-32 becomes richer, the compressor speed decreases and COP increases. The cooling COP and heating COP of R-32/HFO-1234yf 50/50 wt% become 95% and 94% of those of R-410A respectively.

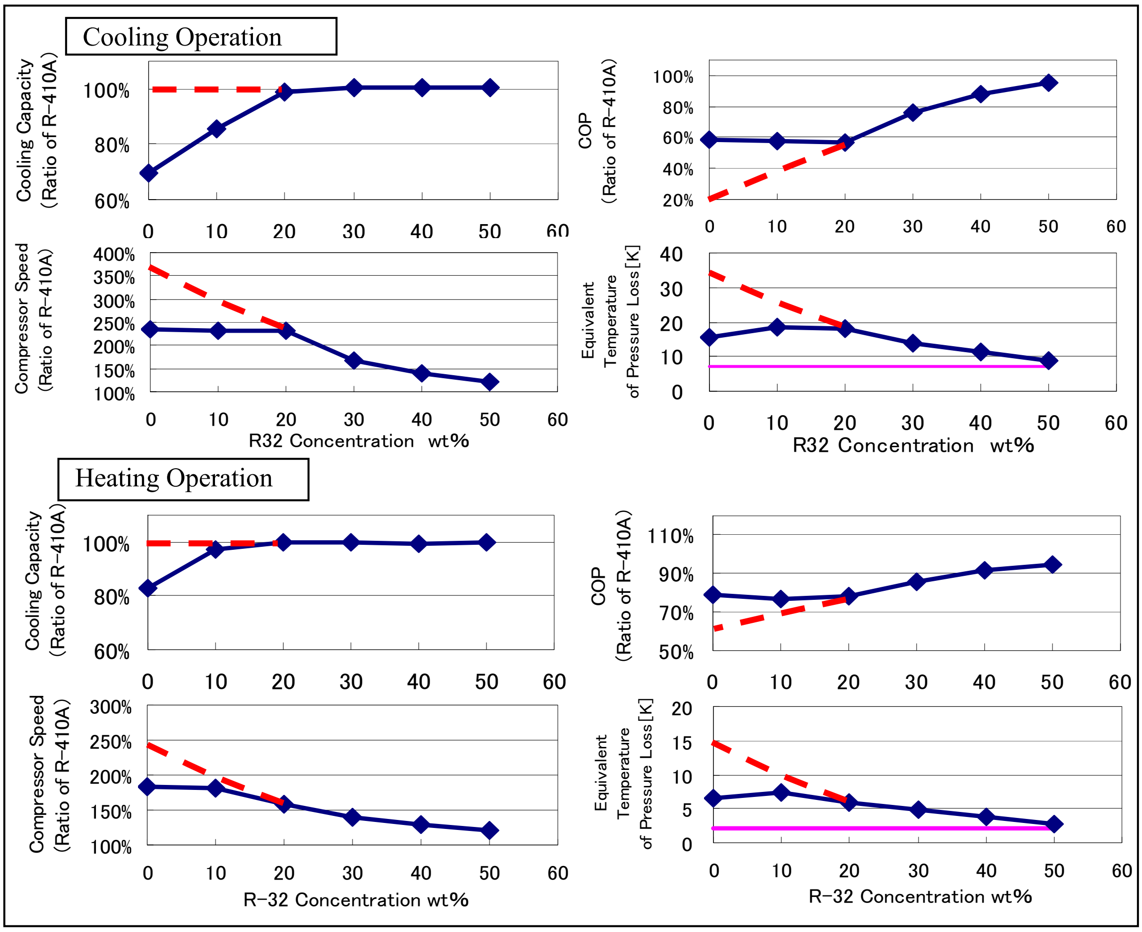

Figure 5. Experimental Result of R-32/HFO-1234yf Mixtures

6 CONCLUSIONS

The material compatibility test of HFO-1234yf and the drop-in tests of HFO-1234yf and R-32/HFO-1234yf mixtures were carried out.
(1) After the compatibility test of HFO-1234yf and POE refrigeration oil under air containing conditions, the acid number of the POE refrigeration oil increases. It suggests the decomposition of HFO-1234yf and the formation of HF.
(2) The materials used in R-410A room air conditioner can be used for HFO-1234yf under the air containing conditions.
(3) The performance of HFO-1234yf is significantly lower than that of R-410A as a result of the pressure drop increasing. Cooling capacity of HFO-1234yf is only 70% of the rated capacity under maximum compressor speed and the COP is 58% of that of R-410A.
(4) The performance of R-32/HFO-1234yf improves as the R-32 concentration becomes richer. The COPs of R-32/HFO-1234yf (50/50 wt%) under the cooling and heating condition are 95% and 94% of those of R-410A respectively.

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