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Refrigeration oils for low GWP refrigerants in various applications

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Abstract. The practical use of the refrigeration systems is considered as a methods to suppress global warming. The replacement of a refrigerant with a new one that has lower global warming potential (GWP) has been underway for several years. For the application fields of refrigerators, domestic air conditioners, automotive air conditioners and hot water dispensers, the investigation has almost finished. It is still underway for the application fields of commercial air conditioners and chillers, refrigeration facilities for cold storage, etc. And now, the refrigeration system is being applied in various ways to decrease global warming above the generation of electric power with organic Rankine cycle, the binary electric generation with ground source heat pump, and so on. In these situations, various refrigerants are developed and several kinds of suitable refrigeration oils are selected. This paper presents the consideration of suitable refrigeration oil for the various low GWP refrigerants.

1. Introduction

At present, the transition to the low-carbon society is pushed forward in various industries. Main issues considered are the reduction of fossil fuel through the methods of energy-saving and conversion from fossil fuel to natural energy. But the change of refrigerants and the effective utilization of refrigeration cycle are added to those issues in the field of refrigeration.

As the high global worming potentials (GWP) of the refrigerants are thousands of times against carbon dioxide, it seems to be expected the large effect of the carbon reduction by the change of refrigerants form high GWP to low GWP.

Studies had been groping the effective utilization of refrigeration cycle by using the unused thermal energy. One of such is the organic Rankine cycle using thermal deference between waste heat from factory and atmospheric temperature. Another is the high temperature heat pump, which represents a heat pump boiler that makes the high temperature based on the unused thermal energy.

Given such background, we introduce the results of the evaluation of the compatibility of the candidate refrigerants for several applications of various refrigeration cycles and refrigeration oils.

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2. Low GWP refrigerants for air conditioner and suitable refrigeration oil

In comparison with R-32 that is one of the low GWP mild flammable refrigerants adopted for the air conditioner for residential and store, various refrigerants are introduced for the purposes of GWP reduction, retrofit for the devises using R-22, change to nonflammable refrigerants and so on [1,2]. Most of them are the mixtures of HFO refrigerants which have C=C double bond and current HFC refrigerants. And the compatible refrigeration oils are the ester based synthetic refrigeration oil, polyol ester (POE), for current HFC refrigerants.

In Table 1, the solubility of refrigeration oils and low GWP refrigerants prepared from refrigerant suppliers is indicated.

Table 1. Comparison of Solubility of Low GWP Refrigerant with Current Refrigeration Oil

[CST*: Oil/Refrigerant = 1/4 Unit℃]

	Lower CST*	Upper CST*	GWP**	Flammability
POE VG 68 Oil for HFC				
R-410A (Reference)	+8	+39	1924	None
R-32	Insoluble	Insoluble	677	Mild
R-447A	-6	>+70	572	Mild
R-452B	-2	+50	676	Mild
R-454B	-4	+53	467	Mild
R-449C	-45	>+70	1146	None
R1123+R32	-35	+52	370	Mild
POE VG 68 Oil for R-32				
R-410A	-50	+60	1924	None
R-32	-6	+58	677	Mild
Naph VG56 Oil for R-22				
R-22	+12	>+70	1760	None

*: CST is critical solution temperature **: IPCC AR5

According to Table 1, because that R-32 has low solubility with “POE VG68 for HFC” (Current oil for HFC), the new POE refrigeration oil for R-32 has developed.

The refrigerant mixtures of HFO and HFC such as R-452B, R-454B, R-449C and HFO-1123 +R-32 have shown good solubility with same current POE VG68 refrigeration oil.

Table 2 shows the result of the compatibility test of the HFO+HFC refrigerant mixtures prepared from refrigerant supplier with current POE VG68 refrigeration oil for HFC.

Test method of the chemical stability test is almost same as the Ashrae 97. To obtain the acid number of tested oil, using larger glass tube (18 mm OD, 12 mm ID, 200 mm long), changing the amount of oil and refrigerant.

Table 2. Comparison of Chemical Stability of Refrigeration Oil with HFO mixture Refrigerant

Condition: Sealed Tube Tests, Oil / Ref =5g/1g, 175deg.C, 14days

Refrigeration Oil	POE VG68 for HFC				
Refrigerant	447A	452B	454B	449C	1123+32
Colour, ASTM	L0.5	L0.5	L0.5	L0.5	L0.5
Catalyst					
Fe	Good*	Good*	Good*	Good*	Good*
Cu	Good*	Good*	Good*	Good*	Good*
Al	Good*	Good*	Good*	Good*	Good*
Acid Number, mgKOH/g	0.01	0.01	0.01	0.01	0.01
Deposit	None	None	None	None	None

*: "Good" indicate that the surface of catalyst was almost unchanged.

According to Table 2, HFO refrigerant mixtures evaluated with this test had indicated excellent compatibility with current POE VG68 refrigeration oil.

3. Low GWP refrigerants for refrigerated facilities and suitable refrigeration oil

As the next refrigerant of HCFC refrigerant R-22, HFC refrigerant R-404A has been used in low temperature equipment such as the showcases for cold foods in supermarket, drug store, refrigerating devices for refrigeration vehicle, and so on. However, because this refrigerant has high GWP (3943 from IPCC 5th report), it is studied to be changed to the low GWP refrigerant in some countries. First, R-407F and R-407H developed from the change of formulation of current HFC refrigerant R-407 series are introduced as the refrigerant of GWP reduction to half of R-404A [1]. Next, HFO+HFC refrigerant mixtures are developed and announced. As the mild flammability of HFO refrigerant, these refrigerant mixtures have variety of flammability and GWP.

The result of HFC refrigerants and HFO + HFC mixture refrigerant solubility test with current refrigeration oil POE VG32 for HFC is shown in Table 3.

Table 3. Comparison of Solubility of Low GWPRefrigerant with Current Refrigeration Oil VG32

[CST: Oil/Refrigerant = 1/4 Unit℃]

	Lower CST*	Upper CST*	GWP**	Flammability
POE VG 32 Oil for HFC				
R-404A	<-60	+45	3943	None
R-32	+36	+42	677	Mild
R-448A	-53	>+70	1273	None
R-449A	-53	>+70	1282	None
R-454A	<-60	>+70	237	Mild
R-407F	-38	>+70	1674	None
R-407H	-16	>+70	1378	None
Naph VG32 Oil for R-22				
R-22	-8	>+70	1760	None

*: CST is critical solution temperature **: IPCC AR5

According to Table 3, R-32 can solve only a little with “POE VG32 for HFC” (Current oil for HFC).The refrigerant mixtures of HFO and HFC, such as R-448A, R-449A, R-454A, and HFC refrigerant R-407F and R-407H had shown good solubility with same current POE VG32 refrigeration oil.

Table 4 shows the result of the compatibility test of the HFO + HFC refrigerant mixtures and HFC refrigerant prepared from refrigerant supplier with current POE VG32 refrigeration oil for HFC.

Table 4. Comparison of Chemical Stability of Refrigeration Oil with HFO Refrigerant Mixtures

Condition: Sealed Tube Tests, Oil / Ref =5g/1g, 175deg.C, 14days

Refrigeration Oil	POE VG32 for HFC				
Refrigerant	448A	449A	454A	407F	407H
Colour, ASTM	L0.5	L0.5	L0.5	L0.5	L0.5
Catalyst					
Fe	Good*	Good*	Good*	Good*	Good*
Cu	Good*	Good*	Good*	Good*	Good*
Al	Good*	Good*	Good*	Good*	Good*
Acid Number, mgKOH/g	0.01	0.01	0.01	0.01	0.01
Deposit	None	None	None	None	None

*: “Good” indicate that the surface of catalyst was almost unchanged.

According to Table 4, HFO + HFC refrigerant mixtures evaluated with this test are indicating relatively good compatibility with current POE VG32 refrigeration oil.

On the other hand, Chlorine contained HFO refrigerants HCFO-1233zd (E) and HCFO-1224yd (Z) are proposed for substitute of R-245fa for water cooled chiller [3,4]. These HCFO refrigerants are not destructive to the ozone layer in spite of their chlorine content, because of the destruction of these refrigerants in the atmosphere by the C=C double bond of HFO’s feature.Therefore, the Ozone depletion Potential (ODP) of these HCFO refrigerants are nearly zero, and the non flammability is obtained from chlorine.

For the refrigeration oil point of view, with one chlorine in molecular structure of these refrigerants, the mineral oil is also soluble with them. The suitability of naphthenic mineral oil on the solubility is checked and indicated in Figure 1 as an example.

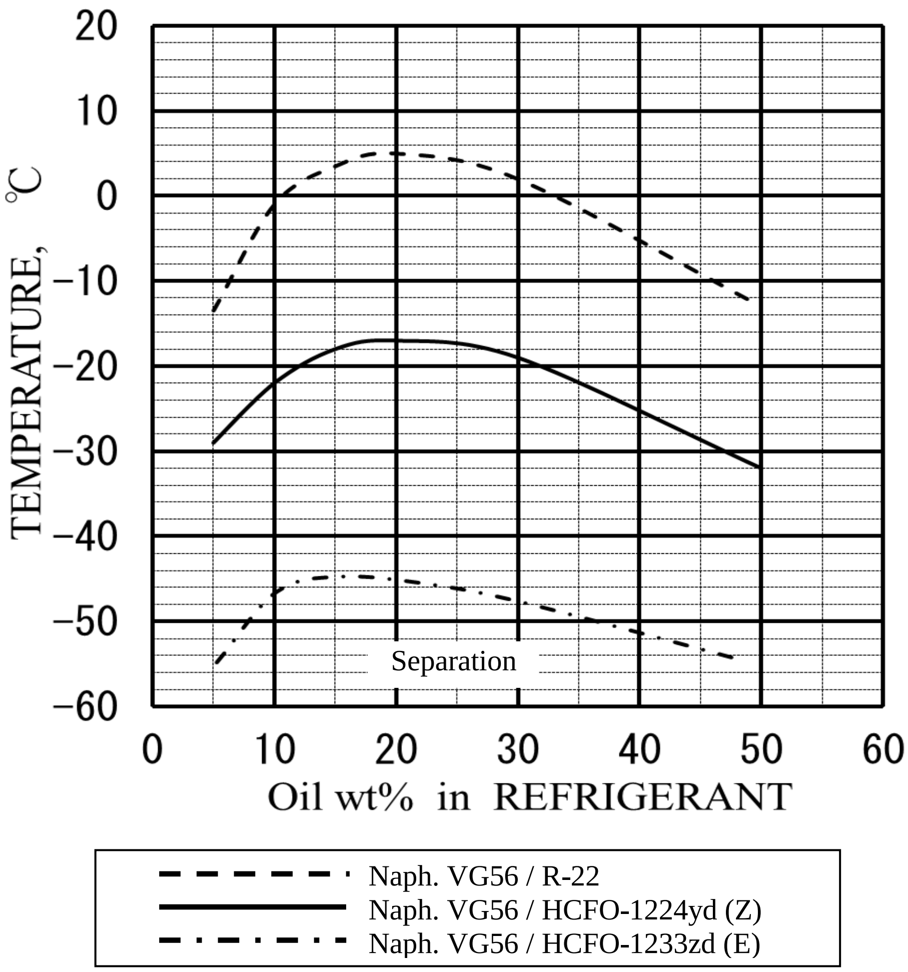

Figure 1. Separation Temperature of Naphthenic Mineral Oil VG56 in HCFO refrigerants

It is evaluated that this naphthenic mineral oil has good stability, with the result indicated in Table 5.

Table 5. Comparison of Chemical Stability of Refrigeration Oil with HCFO Refrigerants

Condition: Sealed Tube Tests, Oil / Ref =10g/2g, 175deg.C, 14days

Refrigeration Oil	NaphVG56for HCFC	NaphVG56for HCFC	POE VG68for HFC
Refrigerant	HCFO-1233zd(E)	HCFO-1224yd(Z)	HCFO-1233zd(E)
Colour, ASTM	L0.5	L0.5	L0.5
Catalyst			
Fe	Good*	Good*	Good*
Cu	Good*	Good*	Good*
Al	Good*	Good*	Good*
Acid Number,mgKOH/g	0.05	0.03	0.11
Deposit	None	None	None

*: “Good” indicate that the surface of catalyst was almost unchanged.

4. Low GWP refrigerant for high temperature application and suitable refrigeration oil

One of the methods of the progress to the low-carbon society is the effective utilization of refrigeration cycle by using the unused thermal energy of waste heat from factories, etc. The organic Rankine cycle and heat pump boiler have been studied with R-245fa for chiller and R-365mfc for precision cleaning as the refrigerant [5].

Furthermore, it is studied to change these refrigerants to low GWP ones such as the HCFO refrigerants written above as the R-245fa alternative, and HFO-1336mzz (Z) as the R-365mfc alternative.

For the refrigeration oil, it seems that viscosity and chemical stability needs to be improved, high solubility with refrigerant is not necessary. The compatibility of the combination of current naphthenic mineral oil for HCFC / HCFO refrigerant, and current POE oil for HFC / HFO-1336mzz (Z).

In Table 6, the solubility of refrigeration oils and low GWP refrigerants prepared from refrigerant suppliers is indicated.

Table 6. Comparison of Solubility of Low GWP Refrigerant with Current Refrigeration Oil

[CST: Oil/Refrigerant = 1/4 Unit℃]

	Lower CST*	Upper CST*	GWP**	Flammability
Naph.VG100 Oil for HCFC				
HCFO-1233zd(E)	-40	>+80	1	None
HCFO-1224yd(Z)	-7	>+80	<1***	None
POE VG 170 Oil for HFC				
HFO-1336mzz(Z)	<-60	>+80	2	None

*: CST is critical solution temperature **: IPCC AR5 ***: Data from Supplier (Asahi Glass)

The results of the compatibility test of the combination of current naphthenic mineral oil for HCFC / HCFO refrigerant, and current POE oil for HFC / HFO-1336mzz(Z), are shown in Table 7 and Table 8, respectively. Test conditions include the influences of the high temperature, air and water.

Table 7. Comparison of Chemical Stability of Refrigeration Oil for HCFC with HCFO Refrigerants

Condition: Sealed Tube Tests, Oil / Ref =5g/5g, 200deg.C, 14days

RefrigerationOil	NaphVG100 +Additive	NaphVG100 +Additive	NaphVG100	NaphVG100 +Additive
Refrigerant	HCFO-1233zd(E)	HCFO-1233zd(E)	HCFO-1224yd(Z)	HCFO-1224yd(Z)
Air, ppm	<0.1	100	<0.1	100
Water, ppm	<50	100	<50	100
Colour, ASTM	L3.5	L2.5	1.0	L2.5
Catalyst				
Fe	Cu P**	Cu P**	Good*	Good*
Cu	Good*	Good*	Good*	Good*
Al	Good*	Good*	Good*	Good*
Acid Number,mgKOH/g	0.19	0.43	0.05	0.01
Deposit	None	None	None	None

*: "Good" indicate that the surface of catalyst was almost unchanged.
**: "Cu P" indicate the copper plating occurred on the catalyst surface.

Table 8. Comparison of Chemical Stability of Refrigeration Oil for HFC with HFO-1336mzz(Z)

Condition: Sealed Tube Tests, Oil / Ref =5g/5g, 14days

Refrigeration Oil	POE VG220	POE VG220	POE VG220
Refrigerant	HFO-1336mzz(Z)	HFO-1336mzz(Z)	HFO-1336mzz(Z)
Temp. deg.C	200	200	250
Air, ppm	<0.1	100	<0.1
Water, ppm	<100	500	<100
Colour, ASTM	L0.5	0.5	L1.5
Catalyst			
Fe	Good*	Good*	Good*
Cu	Good*	Good*	Good*
Al	Good*	Good*	Good*
Acid Number,mgKOH/g	0.07	0.49	18.43
Deposit	None	None	None

*: “Good” indicate that the surface of catalyst was almost unchanged.

According to Table 7 and 8, bad influences occur under the situations of refrigerant, refrigeration oil, small amount of air and water coexist in the high temperature system. Therefore, the refrigerant have to be selected to match the temperature of the application, and contamination of air and water have to be controlled as little as possible.

5. Conclusion

On the transition to the low carbon society, we introduced the outline of studies of the compatibility of low GWP refrigerant and refrigeration oil from the standpoint of refrigeration oil.

Since the refrigeration cycle has high energy efficiency, it has a possibility to be applied for various purposes in the future. And, it seems to be adopted to control temperature and energy efficiency against the various climate conditions in the world. In addition, if the GWP of refrigerants for each application are reduced, the refrigeration field will be made a great contribution to transition to low carbon society.

References

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