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Assessing the Impact of Using Very Low GWP Alternatives to R-404A

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ABSTRACT

Global pressures on hydrofluorocarbon (HFC) refrigerants have reached new levels. With ongoing country ratifications of the Kigali Amendment to the Montreal Protocol and refrigerant shortages across Europe driven by the F-Gas regulations, equipment manufacturers are working hard to implement lower global warming potential (GWP) solutions. R-404A is one of the higher GWP refrigerants (GWP_{100 Year} = 3,922, per AR4) used widely in commercial refrigeration. Several very low GWP (LGWP) candidates have emerged as potential replacements. For many hermetic and split system applications, hydrofluoroolefin-based (HFO) blends represent lower flammability alternatives to hydrocarbon (HC) refrigerants, that also allow for significantly larger charge sizes.

Two mildly flammable, very LGWP blends, XL40 (R-454A) and XL20 (R-454C) were tested and compared to the R-404A baseline performance of a commercially available, double-door, upright reach-in freezer via soft-optimization testing. Refrigerant compatibility with lubricants and other system materials was also examined. Miscibility, water solubility, and dielectric properties were also characterized.

1. INTRODUCTION

Regulatory activities continue to drive the ACR industry to lower GWP refrigerants. Given the relatively high GWP of R-404A, many options are being developed to replace it. While nonflammable (A1 Safety Rating - ANSI / ASHRAE Standard 34-2016) solutions, such as XP40 (R-449A) (Minor, 2015) and XP44 (R-452A, previously referred to as DR-34) (Minor, 2014), are seeing wider spread acceptance, still even lower GWP options are required to meet upcoming regulatory requirements (e.g. EU F-Gas 2014). Mildly flammable (A2L Safety Rating) refrigerants provide very LGWP options for self-contained equipment and small split systems. Their more-favorable flammability parameters (e.g. LFL, MIE, etc.) help allow OEMs to develop larger charge systems using these products than with the highly flammable (A3 Safety Rating) hydrocarbons. Similar properties to R-404A also allow for limited levels of redesign to existing system architectures.

XL20 (R-454C) and XL40 (R-454A) are two mildly flammable binary mixtures of R-32 / R-1234yf that can serve as R-404A replacements. Basic information for these blends can be found in Table 1.

Refrigerant	Refrigerant Nominal Blend Composition (by weight %)		Safety
R-404A	44.0% R-125 / 52.0% R-143a / 4.0% R-134a	3,922 / 3,943	A1
XL40 (R-454A)	35.0% R-32 / 65.0% R-1234yf	239 / 238	A2L
XL20 (R-454C)	21.5% R-32 / 78.5% R-1234yf	148 / 146	A2L

Table 1: Refrigerant Blend Compositions, GWPs, & Safety Ratings

Soft-optimized system performance of the refrigerants was tested in a commercial freezer. Lubricant properties, water solubility, dielectric properties, and material compatibility were also examined for the replacements.

2. THERMODYNAMIC PROPERTIES & THEORETICAL PERFORMANCE

Similar operating characteristics are highly desirable for replacement refrigerants, as this allows OEMs to minimize equipment redesign. Thermophysical properties of all three refrigerants are shown in Table 2. Normal boiling points (NBPs) are similar for R-404A, XL20 and XL40. Critical points are higher for the alternatives, which may contribute to better higher ambient performance. XL40 has close saturation pressures to R-404A, while XL20's pressures are slightly lower. Liquid and vapor densities of both replacements are similar and lower overall than those of R-404A, which will likely result in lower mass flow rates for the alternatives.

	R-404A	XL40 (R-454A)	XL20 (R-454C)
Normal Boiling Point (°C)	-46	-48	-46
Critical Point Temperature (°C)	72	79	82
Liquid Pressure @ 25°C (kPa)	1255	1342	1169
Vapor Pressure @ 25°C (kPa)	1241	1145	963
Liquid Density @ 25°C (kg/m ³)	1044	977	980
Vapor Density @ 25°C (kg/m ³)	65.3	47.7	44.3

Table 2:	Refrigerant	Thermophysical	Properties
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Ideal thermodynamic cycle simulations were performed to estimate the relative performance of the refrigerants in a low temperature application at 35° C / -28° C Condenser / Evaporator temperatures, 13.3K / 3.9K Subcooling / Superheat, and 70% compressor isentropic efficiency (see Table 3). These conditions were selected to closely match the R-404A baseline freezer test runs during the last minute of pull-down. XL40 is shown as having higher capacity than R-404A, while XL20's capacity is slightly lower. Both replacements showed slightly higher efficiencies than R-404A. Overall, XL40 was a close pressure match to R-404A, while XL20 showed lower operating pressures. Discharge temperatures were higher for the replacements. For XL20, the differences are small enough that discharge temperature mitigation is unlikely to be required. However, for XL40, discharge temperature control may be required in certain applications under high ambient conditions. Glide levels are higher for both LGWP replacement options.

Table 3:	Thermodynamic	Cycle Performance	Comparison
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	R-404A	XL40 (R-454A)	XL20 (R-454C)
Capacity (Relative to R-404A - %)	100	106	89
COP (Relative to R-404A - %)	100	103	104
Mass Flow Rate (Relative to R-404A - %)	100	73	81
Suction Pressure (Relative to R-404A - %)	100	95	80
Discharge Pressure (Relative to R-404A - %)	100	101	87
Discharge Temperature ∆ (from R-404A – K)	N/A	19.5	10.1
Average HX Temperature Glide (K)	0.5	5.0	6.0

3. EQUIPMENT TEST SETUP

Relative cooling performance of the three refrigerants was determined using an instrumented R-404A double-door standalone upright reach-in freezer, with a top-mounted refrigeration skid, placed in a climate controlled constant temperature room. Internal volume of the freezer box compartment was 1.5 m³. The refrigeration circuit used a reciprocating compressor and two adjustable TXVs to feed a dual evaporator assembly. Factory system charge was 1.05 kg of R-404A and 1.15 kg of ISO 32 grade polyolester (POE) oil.

Instrumentation included thermocouples, pressure transducers, a Coriolis mass flow meter, and a digital power meter. Schematics and pictures of the experimental setup are shown in Figure 1. Seven thermocouples were used to measure condenser temperature while five were used on each evaporator.



Figure 1: Equipment Test Setup

4. EQUIPMENT TEST PROCEDURES

Baseline performance of the system was established for R-404A, using a target evaporator temperature of -30°C, per the OEMs instructions, and ambient temperatures of 23.9°C and 32.2°C in line with the temperature requirements of ANSI/AHRI Standard 1200 (2013 version) and AHAM HRF-1 (2016 version), respectively. Refrigerant system pressures, temperatures, and flow rates were recorded, as were compressor run times, system run cycles, defrost times and energy consumption. System tests were duplicated for repeatability.

Once baseline testing was completed, the existing refrigerant was recovered and the system was thoroughly evacuated (< 500 microns). The refrigerant was replaced with an alternative product, and tests were run to optimize the refrigerant charge for energy consumption at the 32.2°C ambient temperature. Superheats were matched by adjusting the TXVs for each fluid to that of R-404A (3.9K) using the dew point at the evaporator outlet. This process was repeated for each of the new refrigerant candidates. Results of the testing are shown in section 5.

5. EQUIPMENT EXPERIMENTAL RESULTS

Charge size and TXV positions were adjusted for each refrigerant, as part of the system soft-optimization. Results are shown in Table 4. XL40 had the highest system charge -9.1% higher than that of R-404A, while XL20 used 5.1% less charge weight than R-404A to obtain peak performance. The change in TXV positions shown in Table 4 is the average of both TXVs. TXV superheat setting screws were adjusted inward, relative to R-404A. This is expected, as the alternative refrigerants require significantly lower flow rates than R-404A to produce similar

cooling levels. XL40 required the least adjustment, overall.

	System Charge (g)	# Turns Adjusted
R-404A @ 23.9°C / 32.2°C	1,054	+0 / +0
XL40 (R-454A) @ 23.9°C / 32.2°C	1,150	-3/16 / -7/16
XL20 (R-454C) @ 23.9°C / 32.2°C	1,000	-11/2 / -11/2

 Table 4: System Charge & Thermostatic Expansion Valve (TXV) Adjustments

System operating properties for the different refrigerants were also captured, and are shown in Tables 5 and 6. When comparing operating pressures, XL20 had lower suction and discharge pressures. Differences in values at the 23.9°C ambient show good agreement with the simulated values shown in Table 3 for this blend. XL40 had close suction pressures. Both alternatives produced higher compression ratios than R-404A. Discharge temperatures were higher for the replacement blends, and were lower for XL20 than XL40. This again is consistent with the trends shown in Table 3. Mass flow rates were similar for both alternative fluids and noticeably lower than those of R-404A. The magnitude of the differences in mass flow rates are close to the magnitude of the differences in vapor densities of these products shown previously in Table 3.

Table 5: Refrigerant Operating Properties – 23.9°C Ambient

	R-404A	XL40 (R-454A)	XL20 (R-454C)
Suction Pressure (kPa)208.2		191.7	159.3
Discharge Pressure (kPa)	1662	1767	1403
Compression Ratio	7.98	9.23	8.82
Discharge Temperature (°C)	79.1	94.8	86.5
Mass Flow Rate (kg/min)	50.2	36.1	33.2

Table 6: Refrigerant Operating Properties - 32.2°C Ambient

	R-404A	XL40 (R-454A)	XL20 (R-454C)
Suction Pressure (kPa)	222.0	195.1	148.2
Discharge Pressure (kPa)	2072	2143	1648
Compression Ratio	9.33	10.98	11.12
Discharge Temperature (°C)	94.3	111.6	102.4
Mass Flow Rate (kg/min)	47.0	32.9	32.3

Freezer performance is shown in Table 7. From the data, XL40 shows similar pull-down times to R-404A. This is expected, as these two refrigerants are similar in capacity. However, XL20 produced longer pull-down times. This again is an expected result, as it is a slightly lower capacity blend. Energy consumption was lower than R-404A overall for XL40 (2.4% lower on average). XL20 consumed 4.1% more energy, on average, each day than R-404A. While pull-down times for XL20 were longer than those of R-404A and XL40, the freezer ran for fewer cycles each day. Figure 2 shows a comparison of daily energy consumption for these refrigerants.

	R-404A	XL40 (R-454A)	XL20 (R-454C)
Pull-Down Time @ 23.9°C (min)	2.0	2.2	4.3
Pull-Down Time @ 32.2°C (min)	5.1	5.0	11.0
Energy Consumption @ 23.9°C (kWhr/day)	<u>25.70</u>	<u>25.08</u>	27.03
Relative to R-404A (%)	100.0	97.6	105.2
Energy Consumption @ 32.2°C (kWhr/day)	<u>34.17</u>	<u>33.36</u>	<u>35.15</u>
Relative to R-404A (%)	100.0	97.6	102.9
Compressor Run Time Percent @ 23.9°C (%)	43.20	43.26	56.38
Compressor Run Time Percent @ 32.2°C (%)	65.44	64.99	83.36

 Table 7: Freezer Performance



Figure 2: Daily Energy Consumption vs. Ambient Temperature

While theoretically, both replacements are more energy efficient than R-404A, only XL40 showed lower energy consumption during testing. However, this does not consider testing of refrigerants in a system optimized only for R-404A. Modifying the system design to better match each individual refrigerant's properties and compensating for the higher glides of the replacements would likely lead to enhanced efficiencies for both alternatives, better matching the COP levels predicted in Table 3.

Overall impact of the alternatives on lubrication was also considered. Oil sump conditions were approximated using temperature and pressure measurements at the compressor inlet. Daniel plots were developed for the replacements with ISO 32 grade polyolester (POE) oil. Kinematic viscosities were then determined at compressor inlet or sump conditions. An example of these results can be found in Table 8. Results show similar working kinematic viscosities of R-404A and XL20. However, the viscosity of XL40 is 9.1% lower. These changes in viscosity may

impact compressor drag, potentially contributing to higher efficiencies for XL40.

	R-404A	XL40 (R-454A)	XL20 (R-454C)
Suction Pressure (kPa)	208.2	192.4	162.7
Suction Temperature (°C)	-6.1	-4.5	-4.4
Kinematic Viscosity (cSt)	<u>98.6</u>	<u>89.6</u>	<u>102.5</u>
Relative to R-404A (%)	100	90.9	104.0

Table 8: Lubricant Properties

6. LUBRICANT MISCIBILITY

Miscibility of XL20 and XL40 was also tested with a standard ISO 32 grade POE lubricant. A series of varying refrigerant-oil ratio compositions were prepared and tested in sealed glass tubes. The tubes were then heated to 75°C for XL20 and 60°C for XL40, and then cooled to -50°C. Observations of the tubes were made over 5K increments. Both XL20 and XL40 exhibited excellent miscibility with the POE oil. XL40 showed complete miscibility over the range tested. XL20 was also miscible at lower temperatures, but showed immiscibility at temperatures of \geq 65°C. The results of the XL20 miscibility testing are shown in Figure 3. Given these results, both replacement refrigerants are expected to be miscible with this grade of POE oil over the operating ranges used in commercial refrigeration systems.



Figure 3: Miscibility of XL20 with ISO 32 Grade POE Oil

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7. PLASTICS AND ELASTOMER COMPATIBILITY

Compatibility of all three refrigerants was tested and compared with a selection of plastic and elastomer materials commonly used in the ACR industry. Samples of the materials were prepared and measured for initial weights, dimensions, and hardness. These samples were then placed in sealed glass tubes (per ANSI/ASHRAE 97-2007) filled with either pure refrigerant or a 50/50 mixture of the refrigerants and POE oil. The loaded sealed tubes were then heated in an oven to 100°C for two weeks. Upon completion, the material samples were removed from the tubes. After 24 hours, the samples were once again measured for changes in physical properties.

An overall "Rating" value was given to the material samples based on the following rating system -

Rating

- $0 \leq 10\%$ weight gain/loss and $\leq 10\%$ linear swell and $\leq 10\%$ change in hardness
- 1 > 10% weight gain/loss or > 10% linear swell or > 10% change in hardness
- 2 > 10% weight gain/loss and > 10% linear swell and > 10% change in hardness

Testing results are shown in Table 9. Less reactivity was observed with the plastics than with the elastomers, which is typical behavior for most fluorocarbon based refrigerants. Overall compatibility is similar for R-404A and the replacements, indicating suitability with many types of plastics and elastomers. However, it is important to note that while sealed tube testing results are very useful, compatibility in real systems depends on many factors. These include operating conditions, grades/types of polymers, curing and vulcanization processes, as well as many more.

			R-404A			XL4	40 (R-454	4A)		XL2	20 (R-454	4C)
Material Tested	Rating	Weight <u> </u> <u> </u> (%)	Length <u> </u> <u> </u> (%)	Hardness A	Rating	Weight <u> </u> <u> </u> (%)	Length Δ (%)	Hardness A	Rating	Weight <u> </u> <u> </u> (%)	Length <u>A</u> (%)	Hardness A
				EI	AS	STOME	RS					
neoprene 1	0	3	1	1	0	2	1	0	0	2	2	3
epichlorohydrin	0	9	3	-9	0	6	2	-8	0	9	3	-6
butyl rubber	1	13	4	-8	1	8	3	-15	1	13	5	-10
EPDM	0	7	2	-8	1	10	4	-12	0	7	3	-9
fluorosilicone	1	6	3	-14	0	6	2	-7	0	6	3	-8
HNBR	1	16	5	-6	1	4	2	-11	1	16	4	-7
NBR	1	12	4	-10	1	14	4	-8	1	11	5	-9
fluorocarbon FKM	1	18	10	-12	1	11	3	-11	1	19	9	-11
neoprene 2	0	9	4	-6	1	18	9	-17	0	9	4	-4
Viton A	1	17	8	-12	1	17	8	-15	1	18	9	-10
Viton GF	0	10	5	-10	1	9	4	-12	1	9	4	-13
PLASTICS												
polyester	0	9	3	-3	0	9	2	2	0	9	2	-5
nylon resin	0	-1	1	-1	1	0	-11	-11	0	0	-1	0
polyamide-imide	0	0	0	0	0	0	0	0	0	0	0	-1
polyphenylene sulfide	0	0	0	-2	0	2	0	0	0	0	0	0
PEEK	0	0	0	-1	0	1	0	0	0	0	0	0
nylon 6.6 polymer	0	-1	0	0	0	1	0	0	0	0	0	0
PTFE	0	2	1	-1	0	2	1	1	0	2	2	-3

 Table 9: Plastics & Elastomers Compatibility for R-404A, XL40, & XL20 after 24 Hours

8. WATER SOLUBILITY

Solubility of XL20 and XL40 with water was determined using Vapor-Liquid-Liquid-Equilibrium (VLLE) calculations with the replacement blends and water. By measuring the vapor-liquid and liquid-liquid equilibria of the individual binary substituent systems, theoretically consistent thermodynamic models were fit to calculate the concentrations of refrigerant and water present in the vapor phase, liquid refrigerant-rich phase, and aqueous phase.

Results of these findings are shown in Figure 3. Saturated water solubility of XL20 and XL40 was found to be higher than with R-404A, meaning that more water can dissolve into these refrigerants before saturation occurs. Therefore, it is less likely to create a free water phase from water contamination in an ACR system with these products than with R-404A.



Figure 3: Saturated Solubility of Water in XL20, XL40, & R-404A

9. DIELECTRIC PROPERTIES

Determination of dielectric properties is essential for refrigeration systems using hermetic compressor motors. The static dielectric constants for both the saturated liquid and vapor phases of XL20 and XL40 were calculated based on experimental values of R-32 (Gbur, 2005) and R-1234yf (Sedrez and Barbosa, 2014). As the constituents of these blends have comparable volatility, Oster's Rule was applied, using an assumption of zero for excess volume of the mixture (Harvey and Lemmon, 2005). Kirkwood Theory for polar components was then used for the mixture calculations (Wang and Anderko, 2001) – results are given in Table 10. The calculated values of R-404A agree well with Gbur's experimental values. As such, a high degree of confidence can be assumed for the calculated values of XL20 and XL40.

Table 10:	Dielectric	Constants	(a)	25°C
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Refrigerant	Determination	Dielectric Constant	Dielectric Constant
	Method	(Saturated Liquid)	(Saturated Vapor)
R-404A	Experimental	8.06	1.18
R-404A	Calculated	8.10	1.19
XL20 (R-454C)	Calculated	10.25	1.18
XL40 (R-454A)	Calculated	10.69	1.19

6. CONCLUSIONS

Soft-optimized (e.g. refrigerant charge size and TXV adjustment) testing demonstrated that both XL40 and XL20 are viable replacement options for R-404A in new refrigeration applications. While mildly flammable, the similar operating characteristics of these products allow for limited system redesign. XL40 showed improved energy performance, while XL20 showed slightly higher energy consumption. Optimization of the equipment design (e.g. TXV, HXs) for the replacement products will likely lead to improved performance. Miscibility, compatibility, water solubility, and dielectric properties are similar to those of R-404A for the replacement products. This helps limit the level of system redesign required to implement the HFO-based blends.

Given the favorable performance and similarity in operating conditions, XL20 and XL40 both represent viable LGWP replacement options for equipment manufacturers looking to reduce the climate impact of their refrigerant emissions, as well their energy consumption.

NOMENCLATURE

A1	ASHRAE Safety Rating - Lower Toxicity, No Flame Propagation
A2L	ASHRAE Safety Rating - Lower Toxicity, Lower Flammability
	with Maximum Burning Velocity ≤ 10 cm/s
A3	ASHRAE Safety Rating - Lower Toxicity, Higher Flammability
ACR	Air-Conditioning / Refrigeration
АНАМ	Association of Home Appliance Manufacturers
ANSI	American National Standards Institute
AHRI	Air-Conditioning, Heating, & Refrigeration Institute
AR4	IPCC Fourth Assessment Report
AR5	IPCC Fifth Assessment Report
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers
СОР	coefficient of performance
GWP	global warming potential
HFC	hydrofluorocarbon
HFO	hydrofluoroolefin
ISO	International Organization for Standardization
LGWP	low global warming potential
POE	polyolester
TXV	thermostatic expansion valve

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