Energy & Store
Development Conference

E+SD 2015

New Generation of HFO Refrigerants

Chuck Allgood, PhD
The Chemours Company

Chemours

A Brief History of Refrigerants

1800 – 1920's

Ammonia (NH_3), Methyl Chloride (CH_3Cl), and Sulfur Dioxide

1920's

Fatal Accidents with CH_3Cl
People moved refrigerators to their backyards

Collaborative Search for Safer Refrigerants by
General Motors, Frigidaire, & DuPont

1928 Thomas Midgley and Charles Kettering invent a "miracle compound" called Freon®

The Freon® Age Begins

CFC's:

Freon-12

dichlorodifluoromethane

KINETIC CHEMICALS, INC.

Du Pont Building

Wilmington Delaware

Technical Paper No. 1March, 13, 1931

THE THERMODYNAMIC PROPERTIES FO DICHLORODIFLUOROMETHANE (F-12)

The Equation of State of Superheated Vapor

KINETIC

Safe Refrigerants

KINETIC CHEMICALS, INC.

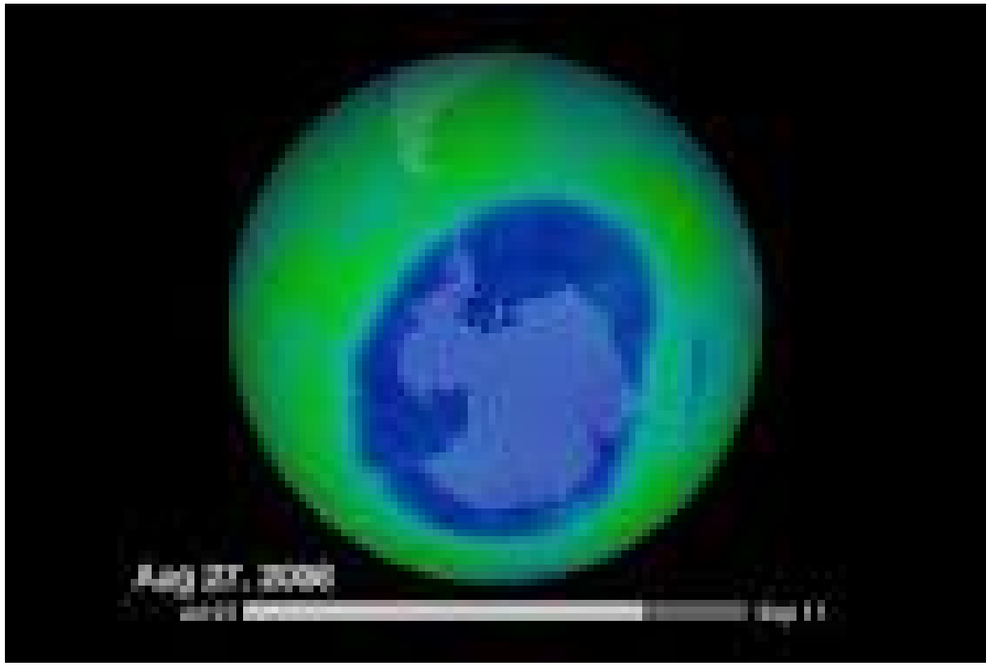
DuPONT BUILDING

WILMINGTON • DELAWARE

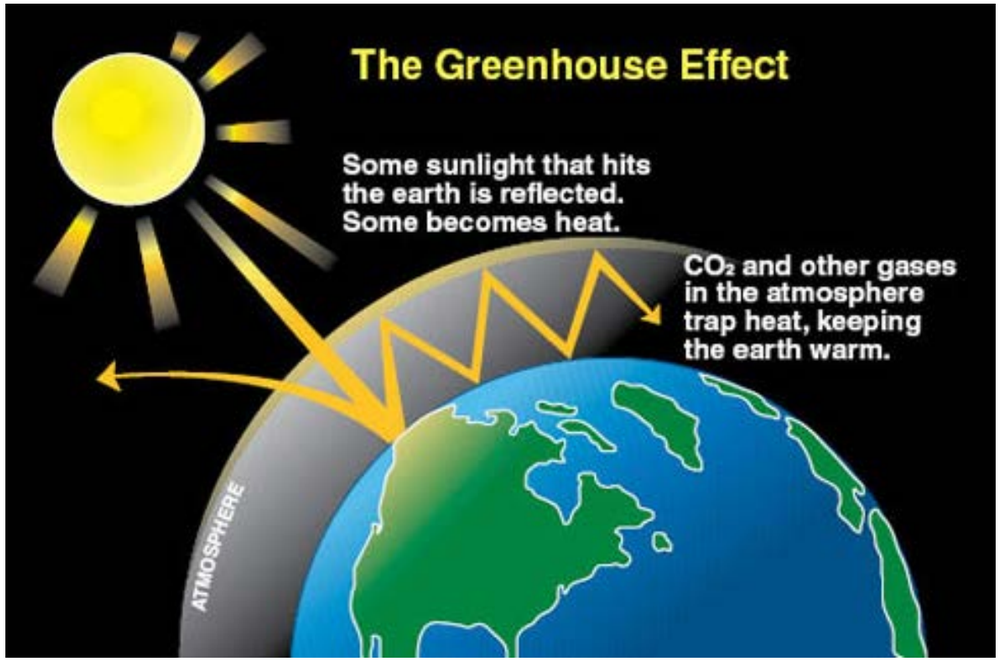
Why Do We Need New Refrigerants Now ?

Worldwide focus on:

“Ozone Depletion”



“Climate Change”

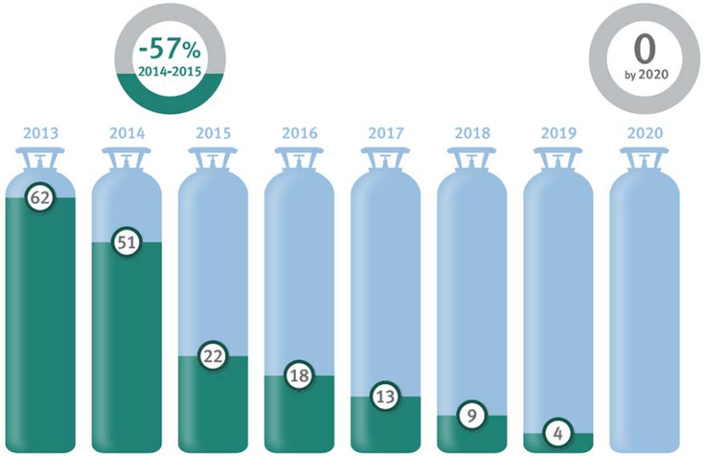


Regulations Driving Change

MONTREAL PROTOCOL
1987-2012

f-gas register
FGASREGISTER.COM

SNAP
SIGNIFICANT · NEW · ALTERNATIVES · POLICY



EPA Final Rule – R-22 Consumption Allowances

U.S. ENVIRONMENTAL PROTECTION AGENCY
GREENCHILL
ADVANCED REFRIGERATION PARTNERSHIP

CARB
California Air Resources Board

EPA
United States
Environmental Protection
Agency

Energy
Money Isn't All You're Saving

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

What exactly is a Global Warming Potential (GWP) Anyway ?

$$GWP = \text{Atmospheric Lifetime} \times \text{Infrared Absorbance}$$

Atmospheric Life → rates of destruction reactions (hydroxyl radical)

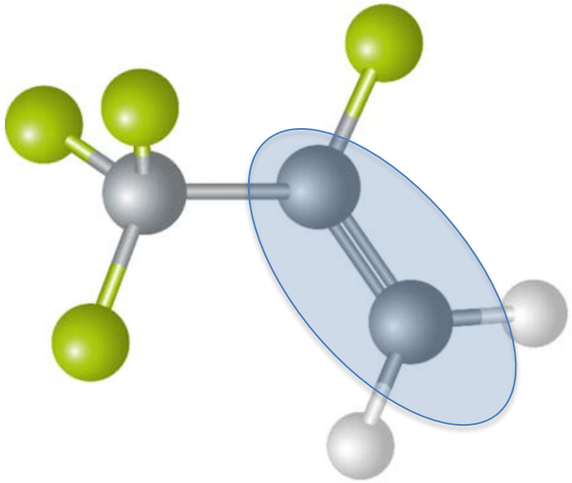
$$\text{HFC} \xrightarrow[k]{\cdot[OH^-]}$$

Designing a Low GWP Molecule

Molecule	Structure		Atmospheric Lifetime	GWP
PFC-116	*CF3-CF3*	*No hydrogen*	*10,000 years*	*11,100*
HFC-134a	*CH2F-CF3*	*2-H atoms*	*13 years*	*1300*
HFO-1234yf	*CH2=CF-CF3*	*“Olefin”*	*10 days*	*< 1*

How HFOs Work

HFC
Hydro fluorocarbon

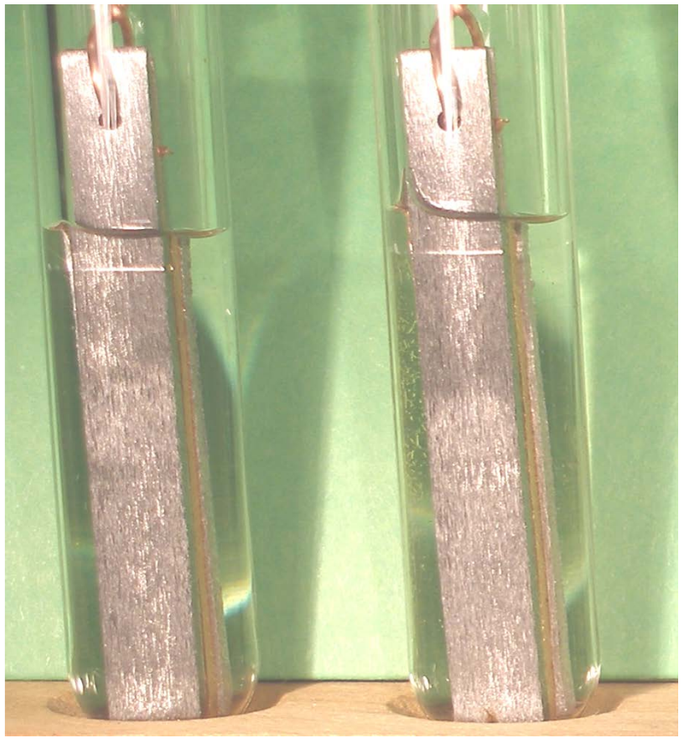


HFO
Hydro fluoro olefin

Double bond in HFOs
Quicker breakdown in the atmosphere,
yet stable in systems

HFO's have Good Thermal Stability and Materials Compatibility

HFO-1234yf + POE Lubricants, 175° C TWO WEEKS



HFO-1234yf + POE

R-134a + POE

HFO-1234yf + POE

R-134a + POE

No Breakdown, Fluoride or Acid Generation

Long Term Stability of HFO's

Long Term Viability of HFO-1234yf in Stationary Refrigeration Systems

Dr. Charles Allgood, Joshua Hughes, Dr. Bianca Hydutsky, and Dr. Thomas Leck

DuPont Chemicals and Fluoroproducts
Wilmington, DE, USA

15th International Refrigeration and Air Conditioning Conference Purdue University, West Lafayette, IN
July 2014

CSI Consulting Services International

Engineering Report

Subject:	Wear analysis of an Embraco compressor after 5 years of field operation in a domestic freezer using HFO-1234yf.
File Name:	DuPont - Wear Analysis of Embraco Compressor with HFO-1234yf
CSI File Number:	2013202
Prepared By:	Michael F. Callan, E.I.T.
Prepared For:	Thomas Leck DuPont Chemicals & Fluoroproducts 974 Centre Road Wilmington, DE 19805
Issue Date:	February 18, 2014

A Division of Anderson Engineering of New Prague, Inc.
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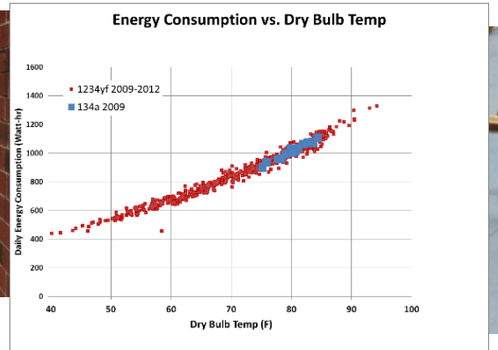


ICP Analysis for Trace Metals		
	RL10H Virgin Oil	Chest Freezer Oil Sample
Al	2 ug/g	3 ug/g
B	1	2
Ca	7	3
Cr	<1	<1
Cu	<1	<1
Fe	<1	2
Mg	<1	<1
Mn	<1	<1
Na	2	1
Ni	<1	<1
Si	26	11
Si	1	2
Zn	2	1

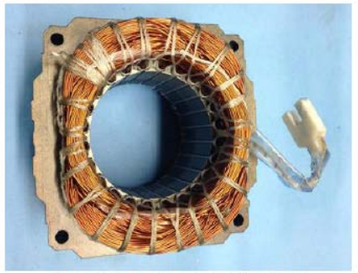


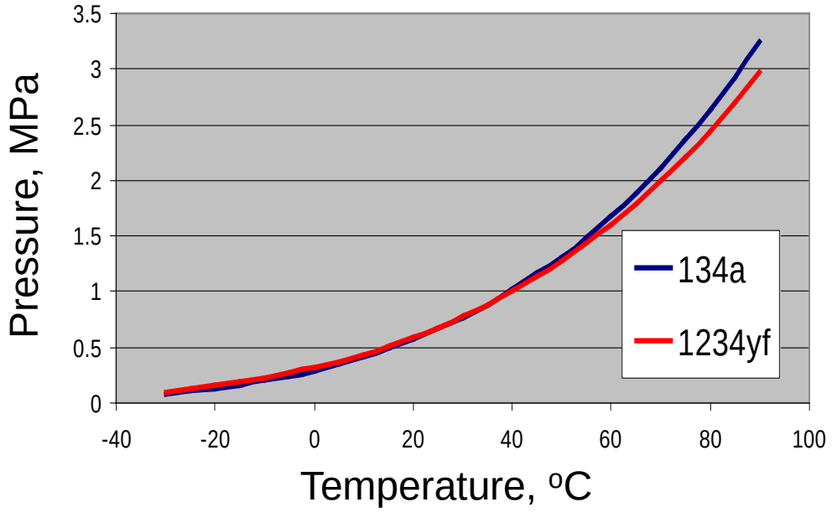
Photo 2.20a: Motor Stator & Electrical Components

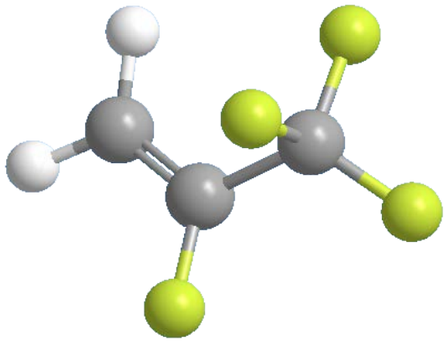
Visual Analysis:

Photo 2.18b: Reed Valves

HFO-1234yf Similar to HFC-134a
Very low GWP but Mildly Flammable

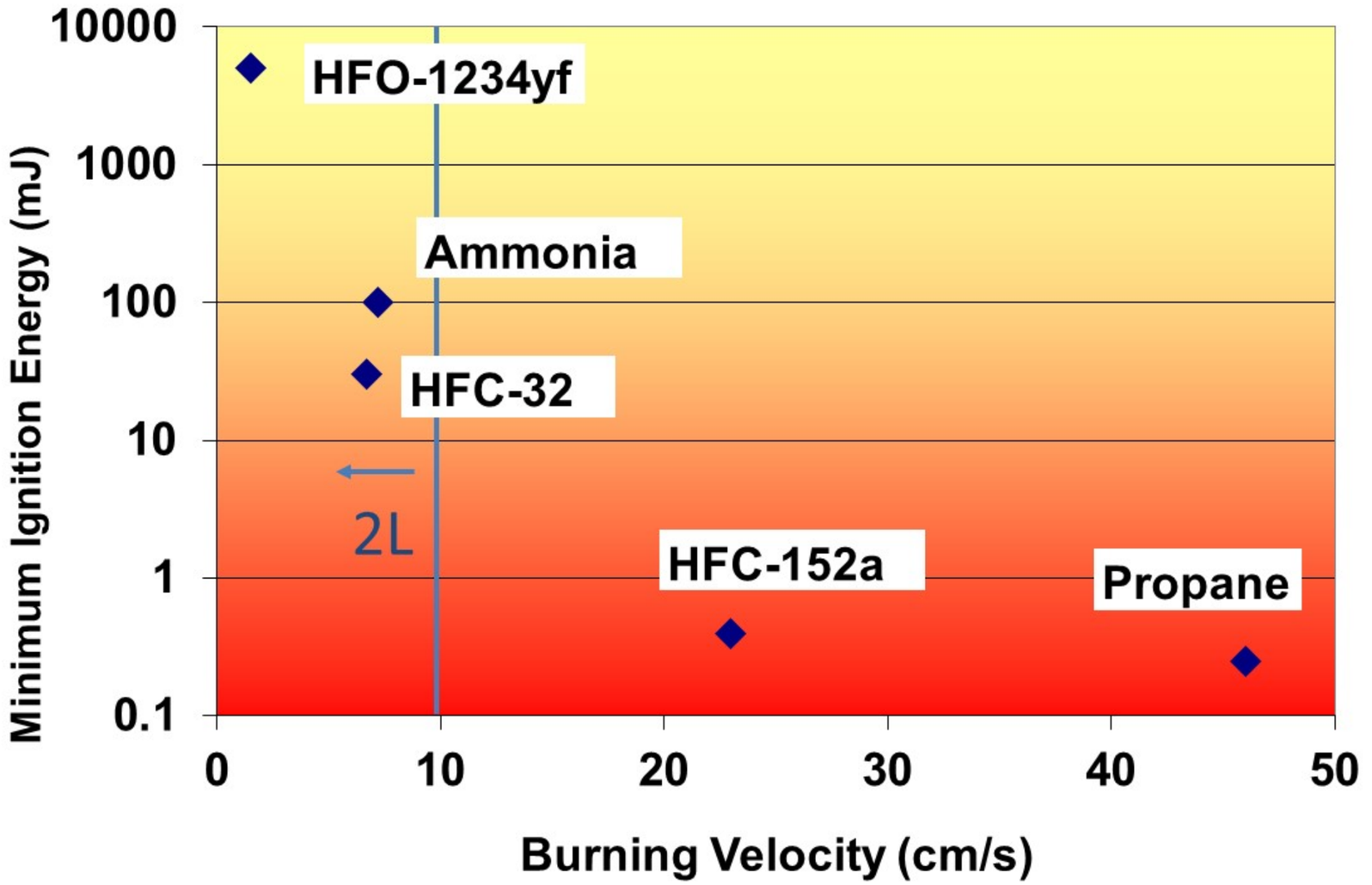
- Same operating conditions as 134a (similar P/T curve)
- Capacity and efficiency similar to HFC-134a





	R-134a	HFO-1234yf
Formula	CH_2FCF_3	$CF_3CF=CH_2$
Molecular Weight	102	114
ODP	0	0
$GWP_{100\ (AR5)}$	1300	<1
T Critical Point	102 ºC	95ºC
Boiling Point	-26ºC	-29ºC

HFO-1234yf – 2L Mildly Flammable



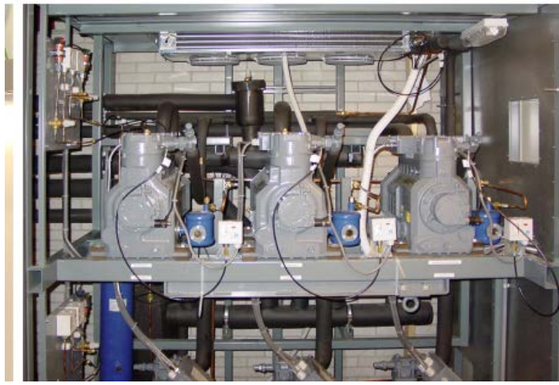
R-1234yf - Difficult to Ignite, Low Burning Velocity

Global Adoption of HFO-1234yf By Automotive Industry

- ✓ **SAE International – HFO-1234yf accepted**
  - **Safe for use; low environmental impact**
- ✓ **HFO-1234yf selected by Auto OEMs globally to meet EU MAC Directive**

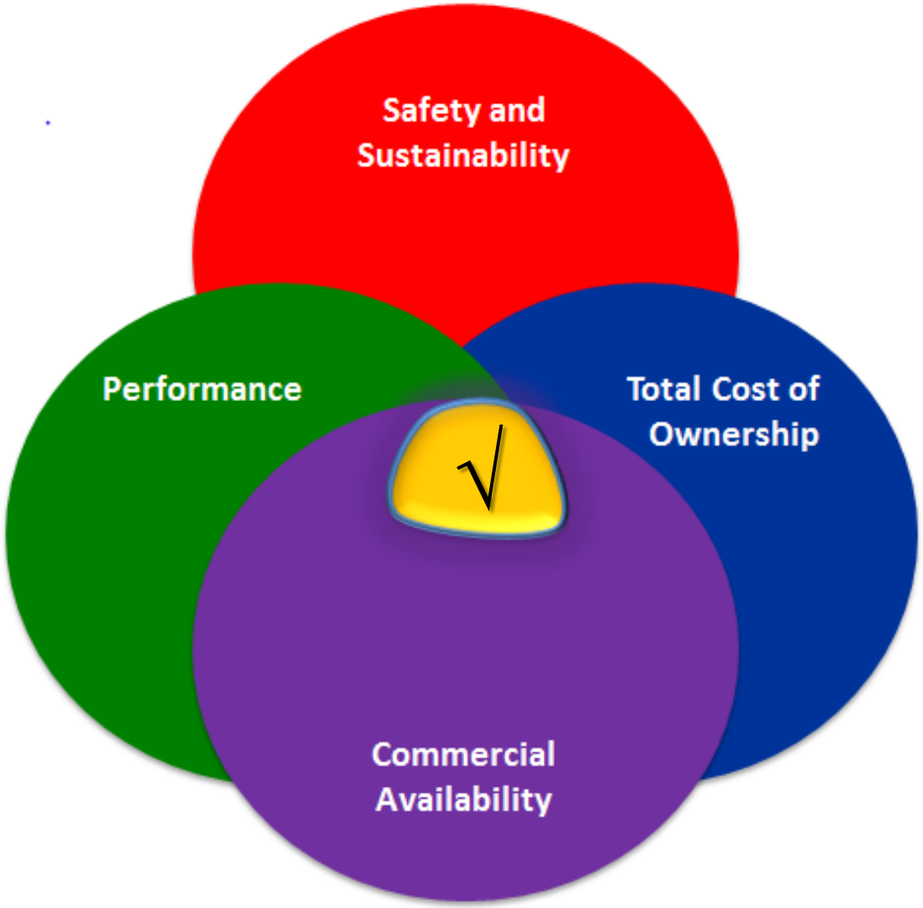
Millions of 1234yf cars on the road, but:

What about Stationary Refrigeration ?



Creating the ~~^Next~~ *New* Generation of Refrigerants

HFOs enable a safe, sustainable, cost-effective future



- Zero ODP
- Low GWP
- No or low flammability

Efficiency + Capacity

Performance

Capital Costs + Operation Costs

Total Cost of Ownership

The HFOs as Building Blocks

HFO- 1234yf
CH2=CF-CF3

HFO- 1234ze
CHF=CH-CF3

HFCO- 1233zd
CF3CH=CH-Cl

HFO- 1336mzz(Z)
CF3CH=CHCF3

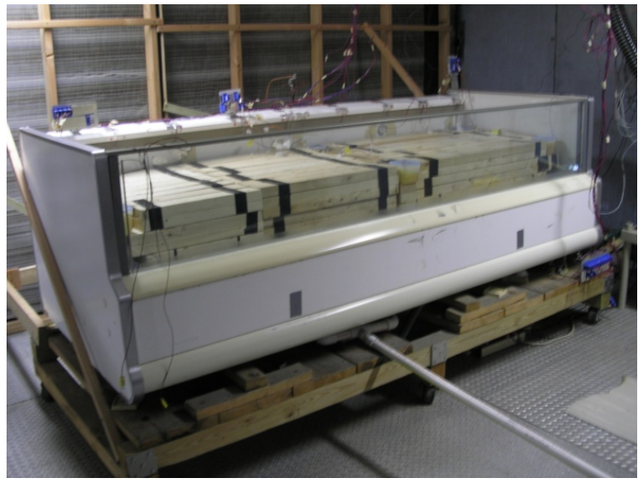
New Low GWP HFO Refrigerant Blends

Replaced	HFO Blend	ASHRAE Class	GWP
R-404A/507	R-449A	A1	1397
	R-454A	A2L	246
R-134a	R-513A	A1	631
	R-1234yf	A2L	4

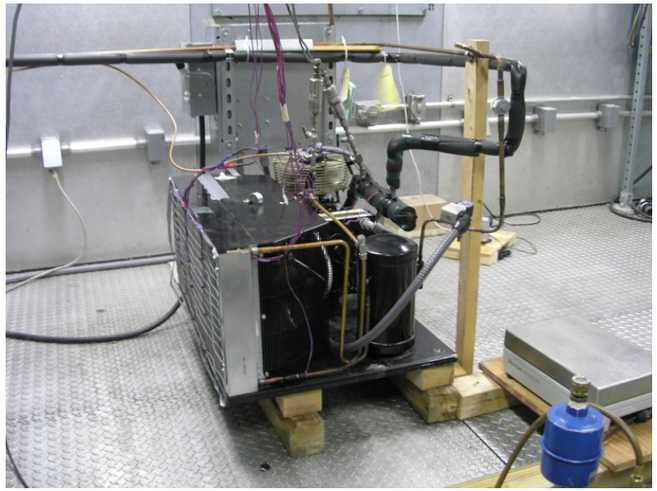
R-449A Compared to R-404A

	R-404A	*R-449A(XP40)*
100 yr GWP	3922	1397
Flammability	None	None
Boiling Point °C (ºF)	-47 (-53)	-46 (-51)
Critical Point °C (ºF)	72 (162)	82 (180)
Vapor Pressure at 25°C in kPa (Psia)	1254 (182)	1274 (185)
Liquid Density at 25°C in kg/m3 (lb/ft^3)	1044 (65.2)	1096 (68.4)
Vapor Density at 25°C in kg/m3 (lb/ft^3)	65.3 (4.08)	49.2 (3.07)

R-449A System Performance
Condensing Unit – Dual LT/MT Case



Open Display Case in Indoor Room



Condensing Unit in Outdoor Room

- 2.5 m (8.0 ft) open food display case designed for R-404A, fully loaded with food simulator
- Reciprocating compressor with POE 32 oil
- Refrigerant charge size ~3.8 kg (8.4 lb), adjusted based on liquid density
- Tested per ASHRAE Standard 72-2005
- Tested at two ambient temps: 28ºC (82ºF) and 35ºC (95ºF) in outdoor room, 24ºC (75ºF) in indoor room
- Only minor TXV adjustment made (1.6 turns closed)
- Tested at low and medium temp conditions

R-449A System Performance
Condensing Unit – Low Temp Results

	Energy Consumed Rel to R404A	Mass Flow Rate, lb/hr	Suct Press , Psia	Disch Press, Psia	Comp Ratio	Avg Food Temp, F	Comp Disch Temp, F
Ambient T = 82 F							
R-404A	100%	32 (71)	112 (16)	1438 (209)	13	-17 (1.4)	78 (172)
XP40 (R-449A)	*97%*	26 (57)	104 (15)	1407 (204)	14	-17 (1.4)	83 (181)
Ambient T = 95 F							
R-404A	100%	33 (73)	127 (18)	1722 (250)	14	-16 (3.2)	87 (189)
XP40 (R-449A)	96%	26 (57)	115 (17)	1685 (244)	15	-15 (5.0)	92 (198)

- *~3% lower energy consumption*
- *Similar pressures and compression ratio*
- *Modest increase in discharge T and slightly lower mass flow rate*

R-449A System Performance
Condensing Unit – Medium Temp Results

	Energy Consumed Rel to R404A	Mass Flow Rate, lb/hr	Suct Press , Psia	Disch Press, Psia	Comp Ratio	Avg Food Temp, F	Comp Disch, F
Ambient T = 28ºC (82ºF)							
R-404A	100%	83	38	224	5.9	36	161
XP40 (R-449A)	*92%*	71	38	217	5.7	36	167
Ambient T = 35ºC (95ºF)							
R-404A	100%	91	36	265	7.4	36	180
XP40 (R-449A)	88%	74	41	260	6.3	37	183

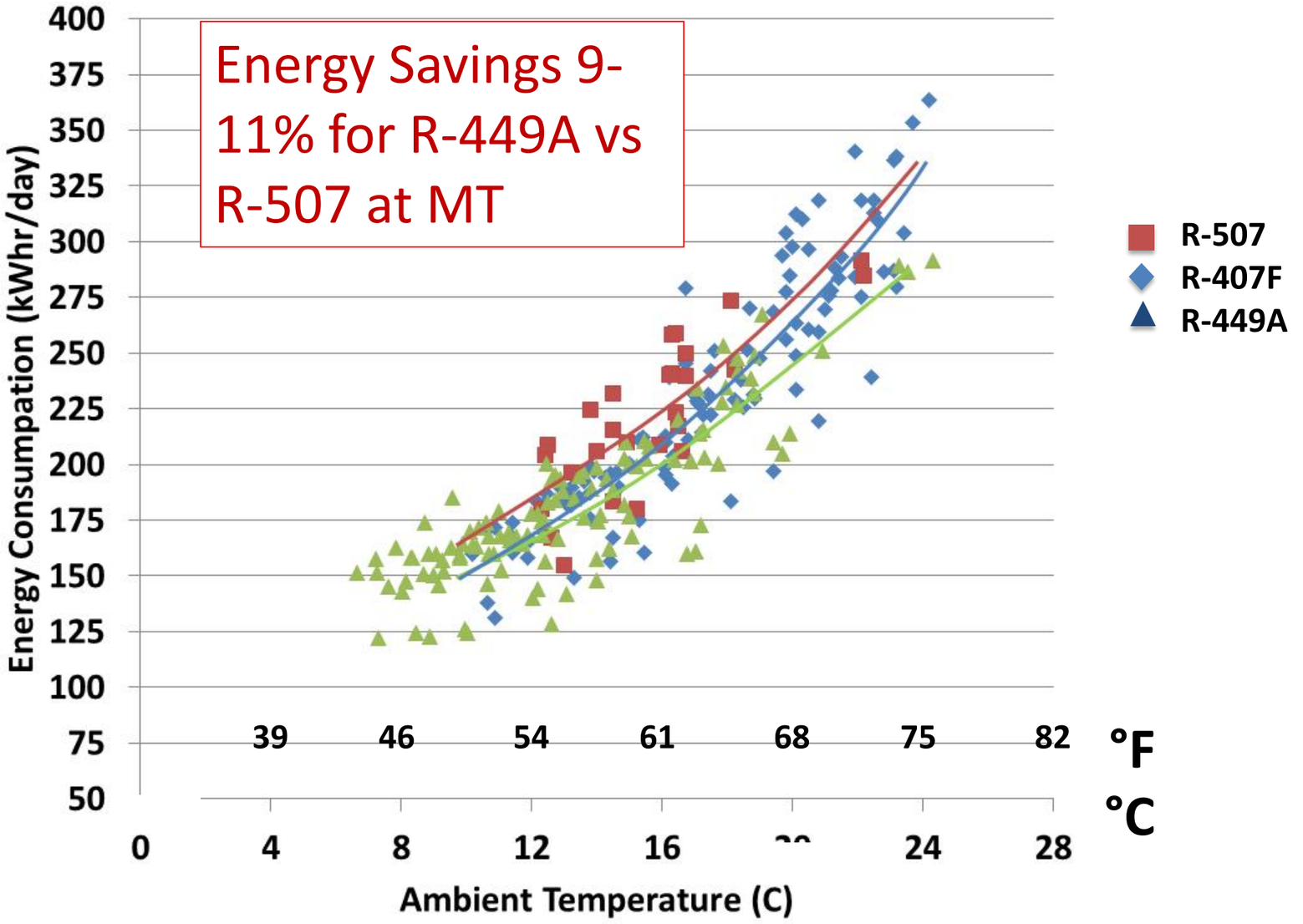
- *8-12 % lower energy consumption*
- *Similar pressures and compression ratio*
- *Less increase in discharge T and slightly lower mass flow rate*

Dutch Retailer Conversion to R-449A

- ❑ System used screw compressors and electronic expansion valves
- ❑ MT/LT racks were converted first to R-407F, then to R-449A
- ❑ Refrigerant was removed and filter drier changed
- ❑ No seals or oil change was required
- ❑ Work took 3-4 hours

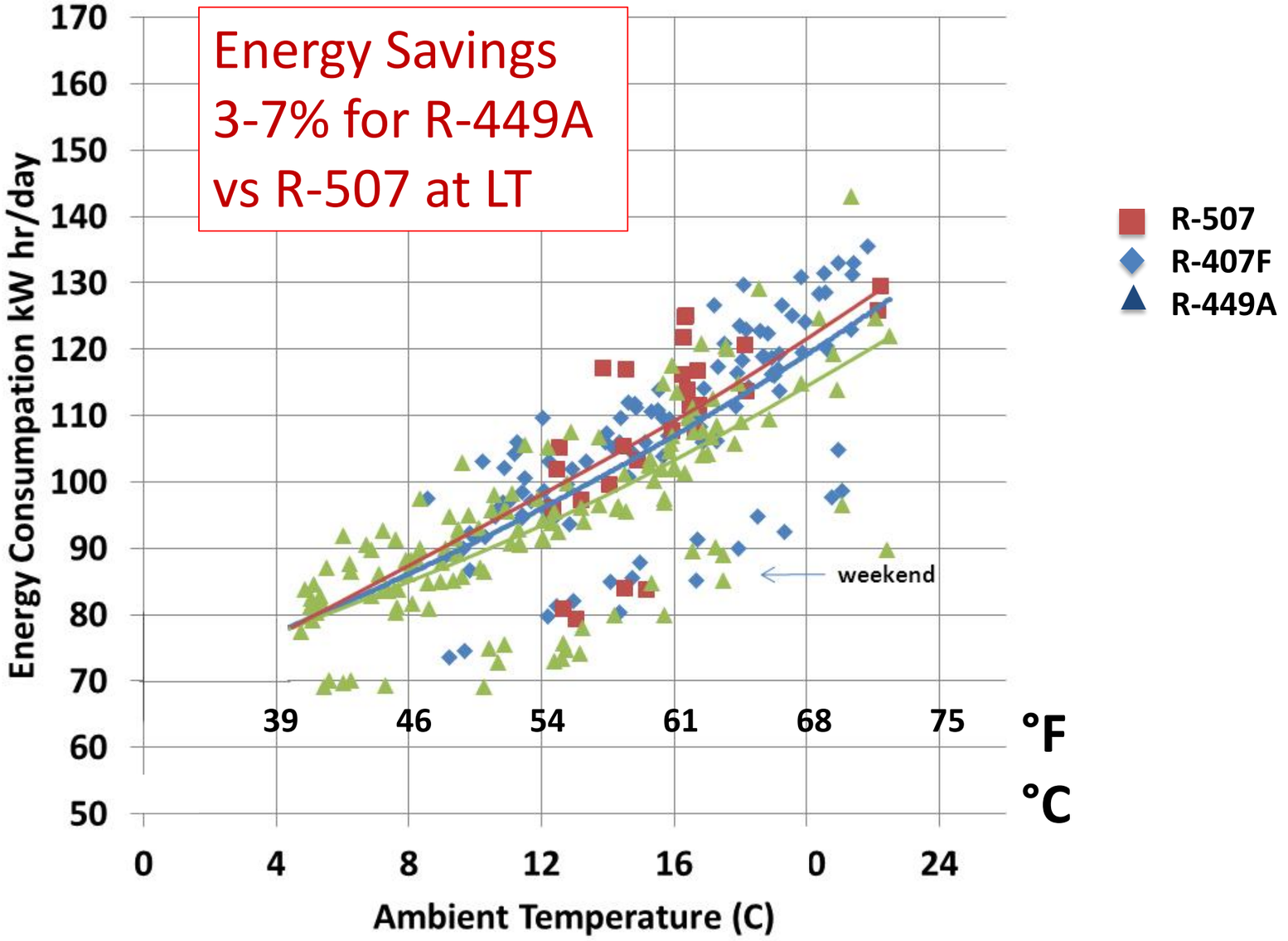
Dutch Retailer Conversion to R-449A

Medium Temp Energy Consumption Vs Ambient Temperature

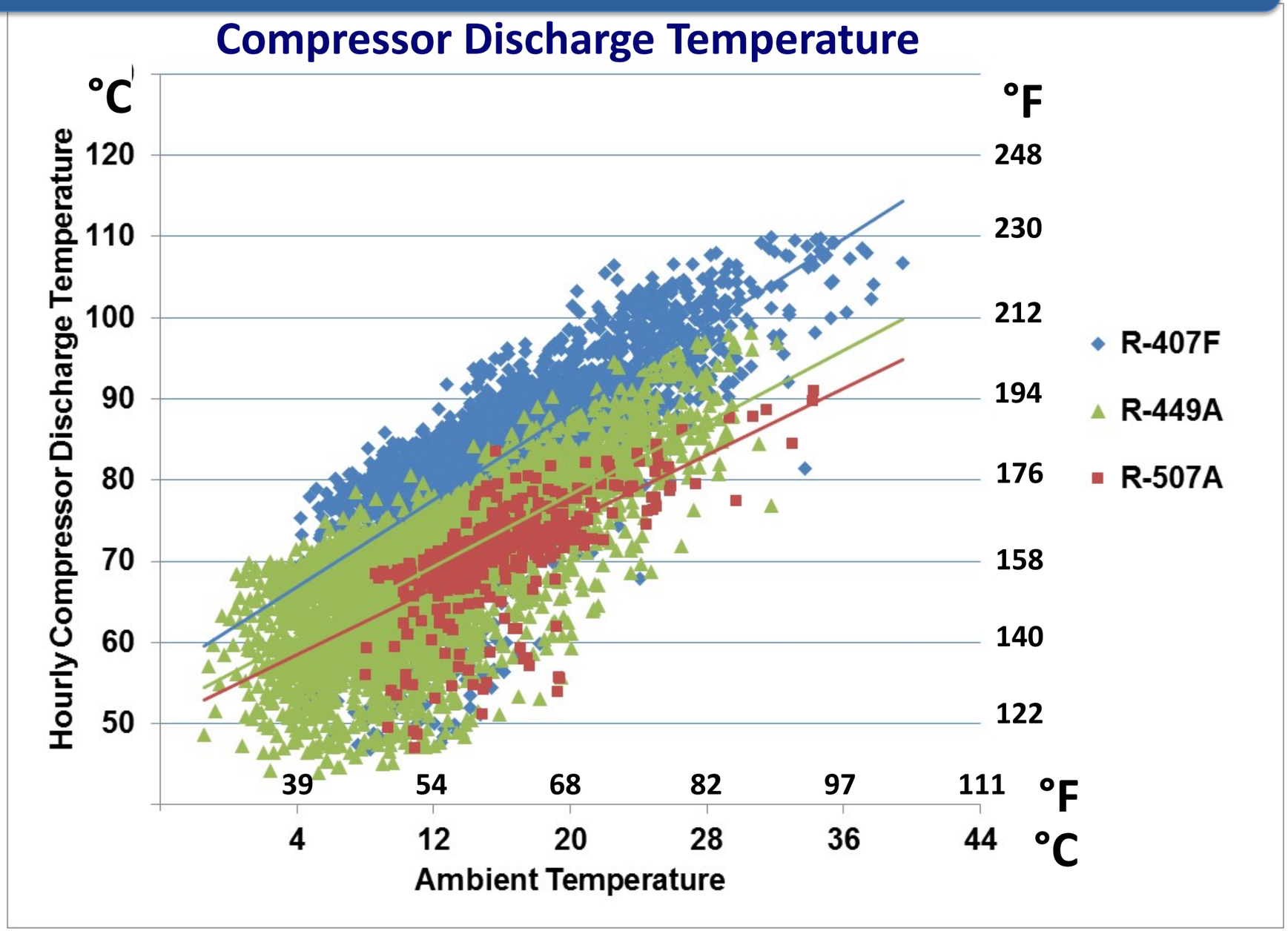


Dutch Retailer Conversion to R-449A

Low Temp Energy Consumption Vs Ambient Temperature



Dutch Retailer Conversion to R-449A

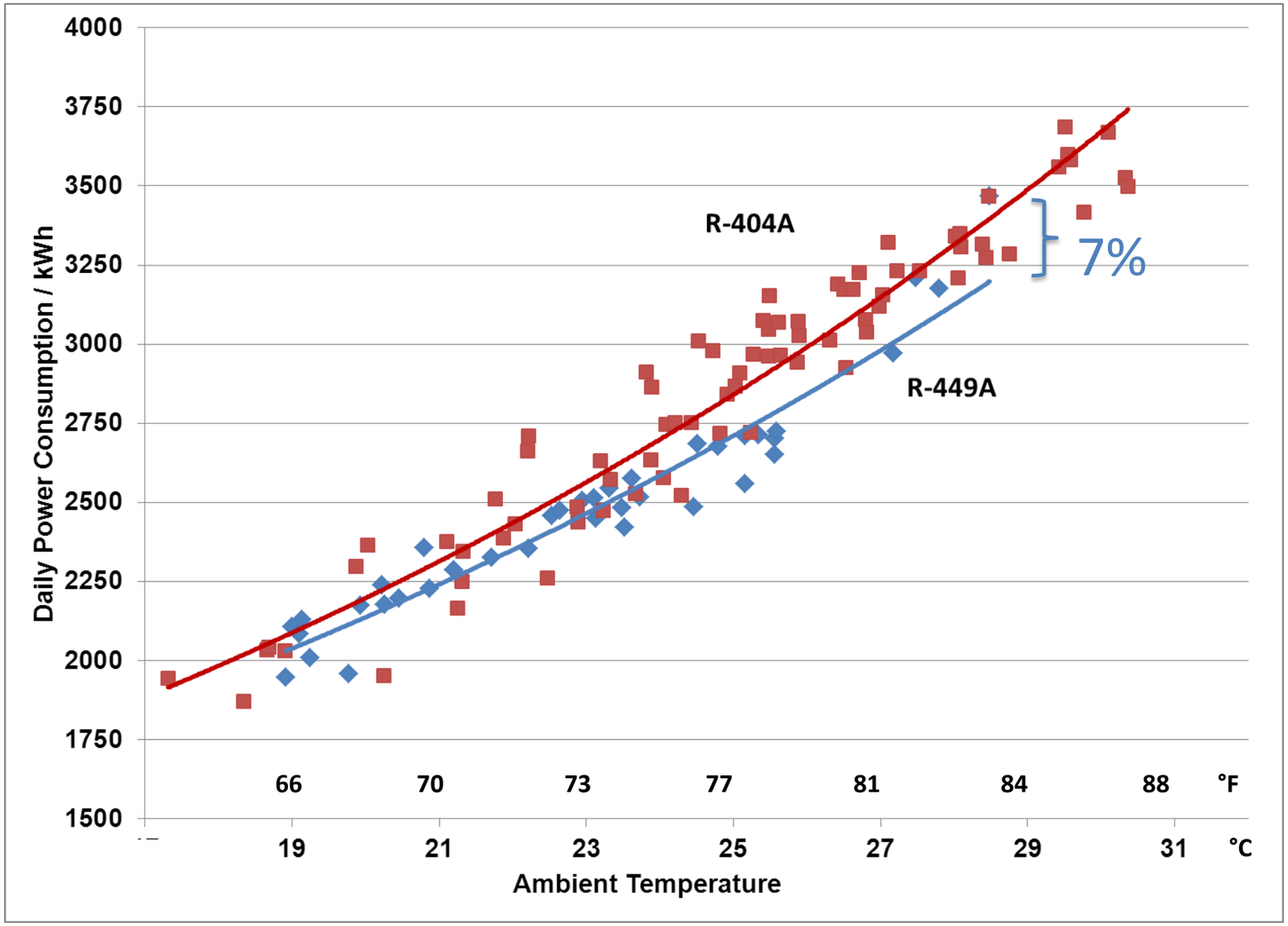


Retrofit of Italian Cascade Supermarket

- R-404A/CO2 hybrid cascade system
- R-404A MT rack with six screw compressors
- System has programmable EEVs
- Covers 73 cabinets and 7 cold store rooms
- Filter drier replaced, EEVs programmed, no other changes

Retrofit of Italian Cascade Supermarket

Energy Consumption



Santa Rosa, California Retailer

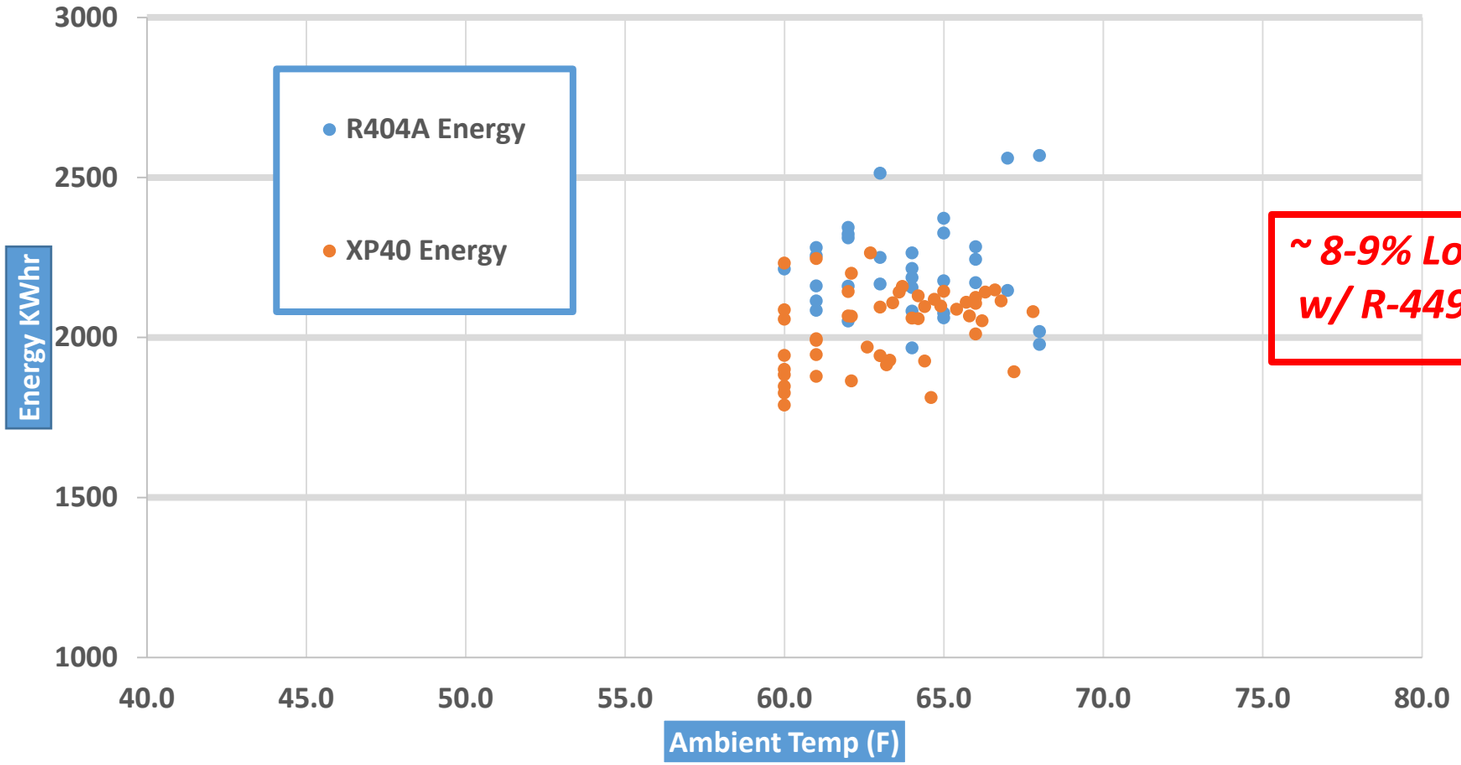
Conversion from 404A to R-449A, Oct-2014

Operational Data – 6 months

Daily Average Value	10/2014	11/2014	4/2015
	R-404A	*R-449A*	*R-449A*
Condensing Pressure, psig	167.3	166.0	167
Discharge Temp, F	140.3	161.8	165.9
Ambient Temp, F	67.4	63.6	62.0
MT Suction P, psig	53.8	49.0	48.8
MT Suction Temp, F	54.0	62.9	66.5
LT Suction P, psig	16.2	12.3	12.3
LT Suction Temp, F	3.9	16.8	17

California Supermarket - Conversion to R-449A

Total Energy Usage for Days @ 60-68F



~ 8-9% Lower Energy Usage w/ R-449A vs R-404A

Retrofit Summary - California Retailer

No changes to equipment, piping, lubricant or seals/gaskets

Adjusted TXVs (turn down) for optimized performance

Meets cooling demand, Stable operation

Energy benefit of 8-9%

HFO Replacement Options for R-134a

	R-134a	R-1234yf	R-513A
Chemical Formula	CF_3CH_2F	$CF_3CF=CH_2$	Azeotrope
100 yr GWP (AR4)	1430	4	631
Toxicity Flammability	A1	A2L	A1
Boiling Point °C	-26	-29	-29
Critical Point °C	101	95	98
Temperature Glide ° C	0	0	0

R-513A

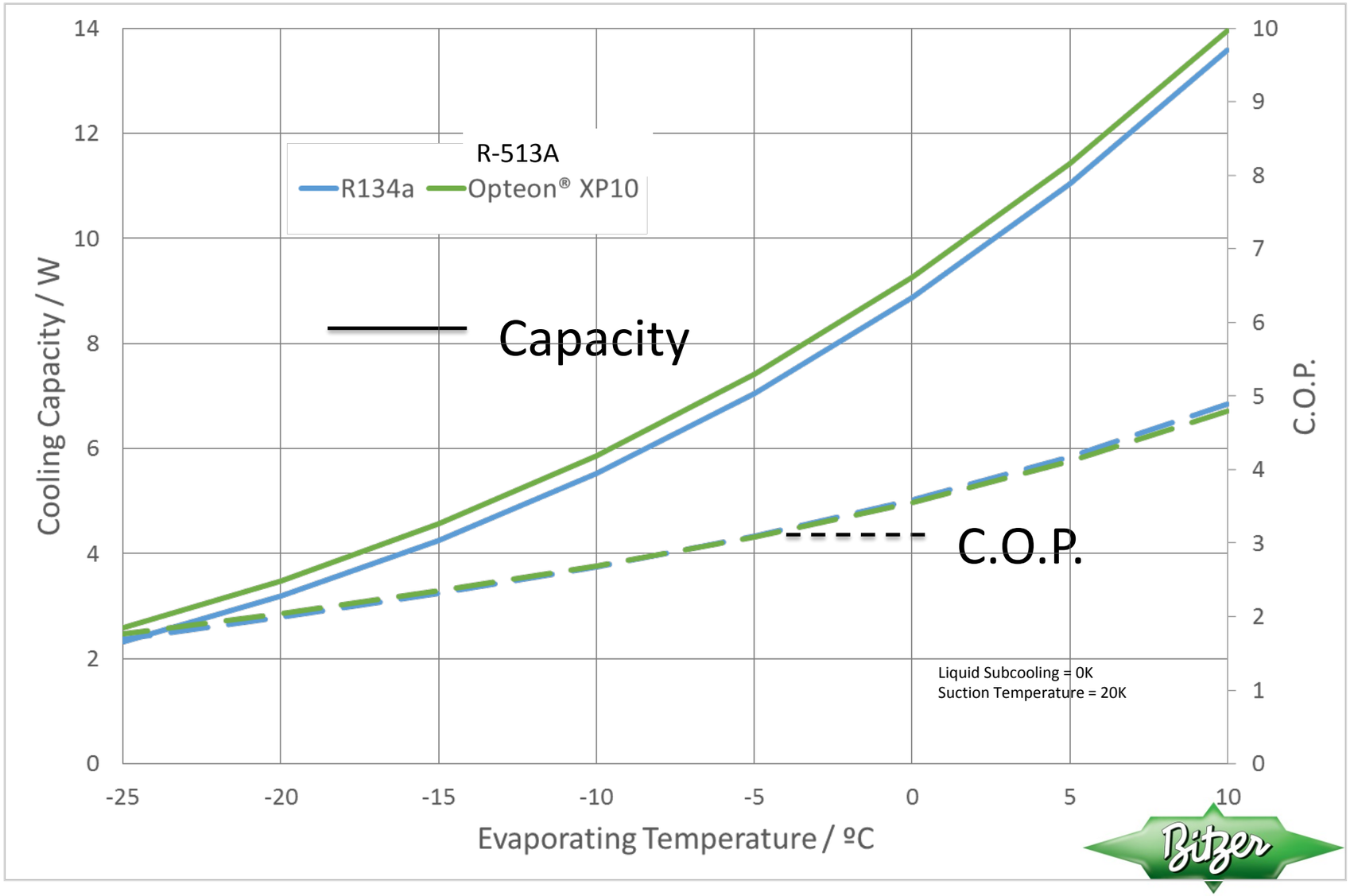
- **HFC/HFO blend:** R1234yf / R134a (56% / 44%)
- **ODP:** Zero Ozone Depletion Potential
- **GWP:** 631
- **ASHRAE safety:** A1 non-flammable
- **Glide:** 0R (Azeotrope)
- **Can be topped off while servicing (do not mix with R-134a)**
- **Compatible with POE lubricants**
- **Major Compressor and OEM approvals**






Compressor Performance Modeling for R-513A

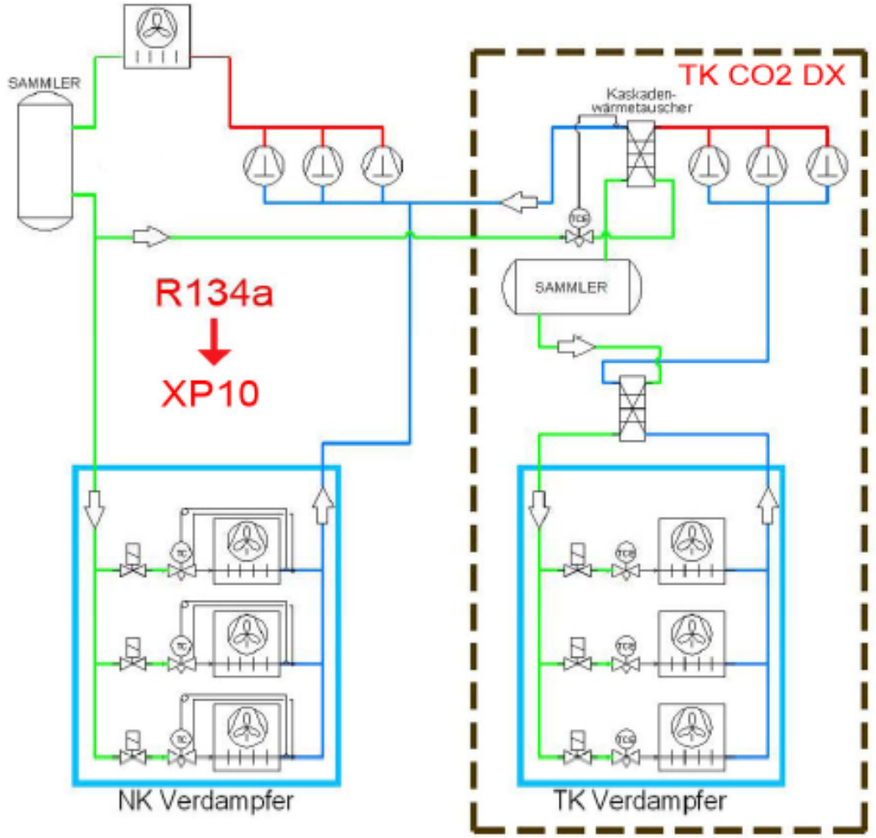
Calculations using Bitzer Software (v.6.4.3 rev1302) in 4FES-3Y Reciprocating compressor, at 40ºC Condensing Temperature



R-513A Evaluation in Supermarket - Hybrid System

- Retrofitted from R-134a MT; CO_2 LT

- Running for three years

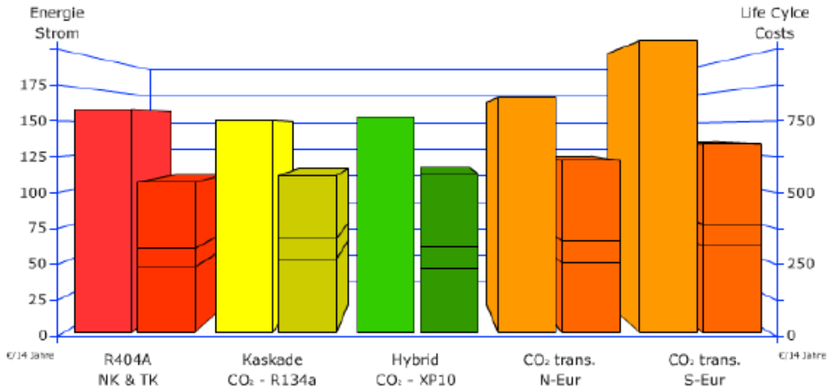


HAUSER

so cool. so beautiful.

Energie – TEWI – LifeCycleCosts

Beispiel Supermarkt: 15lfm Wandkühlregal, 10lfm Kühltheke, 2 NK-Räume / 14lfm TK-Möbel, 1 TK-Raum



The New Generation of HFO Refrigerants

Where Do We Go From Here ?

The New Generation of HFO's Regulatory Approvals

Recent Additions

EPA publishes final rule prohibiting certain high-GWP HFCs as alternatives under SNAP (7/20/15) → R-404A, R-507, and others targeted for delisting

EPA publishes notice expanding list of acceptable climate-friendly alternatives under SNAP (7/16/15) → R-449A, R-513A and others approved

EPA final rule approves climate-friendly refrigerant alternatives under SNAP (4/10/15)

The New Generation of HFO's OEM Approvals/Adoptions

Trane Commercial
@TraneCommercial

#Trane to offer air-cooled chiller using R513A, @DuPontRefrig's low GWP, non-flammable replacement for R134a: bit.ly/1z5u2QY #HVAC

2/26/15, 10:05 AM

R513A an option in new Trane chiller

Posted on Monday, January 26, 2015 · Leave a Comment

SHARE THIS ARTICLE | JOIN OUR NEWSLETTER

USA: Trane is to offer an air-cooled chiller using R513A, DuPont's low GWP, non-flammable replacement for R134a.

The refrigerant, which DuPont markets as Opteon XP10, will be available as an option on Trane's recently launched Sintesis air-cooled chiller. The option will be available in North America and Latin America from June.

The Sintesis is part of Ingersoll Rand's EcoWise portfolio of more sustainable environmental products that Trane announced last year in Europe and includes Trane's Series E CenTraVac running on R1233zd(E) and Thermo King's new truck and trailer refrigeration products using DuPont's Opteon XP44 (R452A).

R513A is a binary mixture of R134a (44%) and R1234yf (56%). It has a GWP of around 630 and carries the ASHRAE safety classification of A1.

The Sintesis air-cooled chiller covers capacities from 300kW to 1500kW. It features a micro-channel condenser coil, flooded evaporator, EC fans and fan diffusers.

Thermo King's new SLXe trailer units with R452A will be available in February, with new factory units and retrofit kits available in the European Union later this year.

Copeland

Refrigerants and lubricants approved for use in Copeland™ compressors

	Refrigerants	Similar to	Application		Lubricant choices			
			Retrofit	New	Preferred	Alternate #1	Alternate #2	Comments
Ozone depleting	CFC R-12		L,M		MIN	AB & MIN		Phased out in 1996
	CFC R-502		L,M		MIN	AB & MIN	POE-32	Phased out in 1996
	HCFC R-22		L,M,H		MIN	AB & MIN	POE-32	No new equipment 2010
Interims	HCFC R-401A	R-12	M,H		AB & MIN	POE-32 & MIN	POE-32	Service only Suva® MP39
	HCFC R-401B	R-12	L,M		AB & MIN	POE-32 & MIN	POE-32	Service only Suva MP66
	HCFC R-402A	R-502	L,M		AB & MIN	POE-32 & MIN	POE-32	Service only Suva HP80
	HCFC R-402B	R-502	L,M		AB & MIN	POE-32 & MIN	POE-32	Service only Suva HP81
	HCFC R-408A	R-502	L,M		AB & MIN	POE-32 & MIN	POE-32	Service only FX10
	HCFC R-409A	R-12	L,M		AB & MIN	POE-32 & MIN	POE-32	Service only FX56
Non-ozone depleting	HFC R-134a	R-12	M,H	M,H	POE-32			
	HFC R-404A	R-502	L,M	L,M	POE-32			Suva HP62, Forane® FX70
	HFC R-507	R-502	L,M	L,M	POE-32			Genetron® AZ50
	HFC R-407A	R-22	L,M	L,M	POE-32			
	HFC R-407C	R-22	L,M,H	L,M,H	POE-32			Suva 9000(X)LEA 56
	HFC R-407F	R-22	L,M	L,M	POE-32			Discus™ and select refrigeration scroll models (ZF/ZB)
	R-448A	R-22	L,M	L,M	POE-32			
	R-449A	R-22	L,M	L,M	POE-32			
	R-450A	R-12	M,H	M,H	POE-32			
	R-513A	R-12	M,H	M,H	POE-32			
	HFC R-410A			Discus = L,M Scroll = M,H	POE-32			ZP & ZB KCP Copeland Scroll™ models and certain Discus models only
	HFC R-422A/D	R-22	L,M		POE-32	MIN	AB	Discus supermarket racks only
	HFC R427A	R-22	L,M		POE-32			Discus supermarket racks only
	HFC R-438A	R-22	L,M		POE-32	MIN	AB	Discus supermarket racks only; ISCEON® MO99
	R-704 helium			Cryogenic	PAG			ZC Copeland Scroll models only
	R-744 CO_2			Sub-critical	POE-68			4MTLS Discus and ZO Copeland Scroll models for CO_2
				Trans-critical	POE-68			4MTLS semi-hermetic compressors for medium temp trans-critical applications
	R-290 propane			L,M	POE-22			For use with specific Copeland compressors designed for R-290, excluding models manufactured in India
					POE-32			For use with specific Copeland compressors manufactured in India for R-290

See legend on reverse ➡

EMERSON Climate Technologies

Thermo King adopts R404A replacement

Posted on Wednesday, September 24, 2014 · Leave a Comment

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BELGIUM: Thermo King has adopted DuPont's new R404A replacement refrigerant R452A as a lower GWP option for its transport refrigeration customers.

The new refrigerant, announced by the *Cooling Post* in July, is a non-flammable blend that closely matches the properties and performance of R404A, including a similarly low compressor discharge temperature. It is considered particularly suitable for transport refrigeration where compressor cooling is difficult to manage under a wide range of ambient conditions. It is also suitable for retrofitting existing R404A systems.

With a GWP of 2140, it might not be considered a low GWP gas but at virtually half the GWP of R404A it could have considerable environmental appeal as a drop-in alternative.

From January, Thermo King will offer the new refrigerant in a new line of trailer and self-powered truck units to customers in Europe, the Middle East, and Africa. At the same time, transport customers wishing to transition their existing units, Thermo King will offer replacement service through its dealer network. In 2016, Thermo King will then offer the same benefits with vehicle powered truck products.

"Our intent is to offer operators a choice of how and when to lower their GHG footprint without compromising the efficiency, reliability and overall product performance they expect from Thermo King," said Ray Pittard, president of Thermo King North America, Europe, Middle East and Africa. "We made a significant investment in research and development, testing and the appropriate ATP approvals in order to bring product and service alternatives to market."

Thermo King selected R452A, also known as Opteon XP44, for this alternative line of transport refrigeration products in anticipation of Europe's revised F-gas regulation.

"Since its inception by Thermo King in 1938, the transport refrigeration industry has been using class A1 refrigerants that are safe, non-flammable and have the lowest toxicity," said Pittard. "R452A when used in our products is the safest, most environmentally responsible, and technically and commercially viable solution for transport refrigeration applications. Plus, it has about half the GWP of refrigerants currently used today."

"The new line of Thermo King products offers the same high level of performance as today's portfolio including the same cooling capacity, pull-down and fuel efficiency," said Dwight Gibson, vice president, Thermo King Europe, Middle East and Africa. "In addition, retrofitting current products with the next generation of refrigerant is a compatible solution which means that operators can increase their return on investment of units they already own with – the least amount of rework, lower fuel consumption and emissions, and retaining the residual value of the equipment."

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Tecumseh backs R452A as R404A alternative

Tecumseh

Carrier TRANSICOLD
United Technologies

Carrier Transicold announces R452A option

FSDF member Carrier Transicold is the latest major transport refrigeration company to offer R452A as an optional alternative to R404A.

At this week's Commercial Vehicle Show in Birmingham, UK, Carrier Transicold said that while it was actively working towards replacing current HFC refrigerants with CO2, it is to offer R452A as a lower GWP option to the existing R404A refrigerant. R452A, it says, has the same cooling capacity, fuel efficiency, reliability and refrigerant charge as R404A, but offers a 45% GWP reduction compared to R404A.

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