➢*Increasing Energy prices*
➢*Climate Protection*

Low GWP Working Fluids for Cooling, Heating & Power:

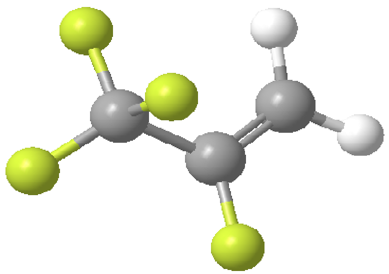
- Com AC
- HTHPs
- ORCs

Weighing the Tradeoffs

ASHRAE -- HELLENIC CHAPTER, Athens, Greece
September 7th, 2011

Kostas Kontomaris, Ph.D.
DuPont Fluorochemicals R&D

HFOs



DuPont Refrigerants
80 Celebrating Years

Low GWP Refrigerants:
An idea whose time has come!

•1824: Joseph Fourier discovered the “Greenhouse Effect”

•1908: Svante Arrhenius calculated that emissions from human industry might someday cause global warming

IPCC
INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE

•2007 Nobel Prize to IPCC

WMO UNEP

•2011: European Union F-Gas Regulation:

GWP<150 for Automobile AC

Growing Pressure on HFCs with High GWPs

Working Fluids Specifications

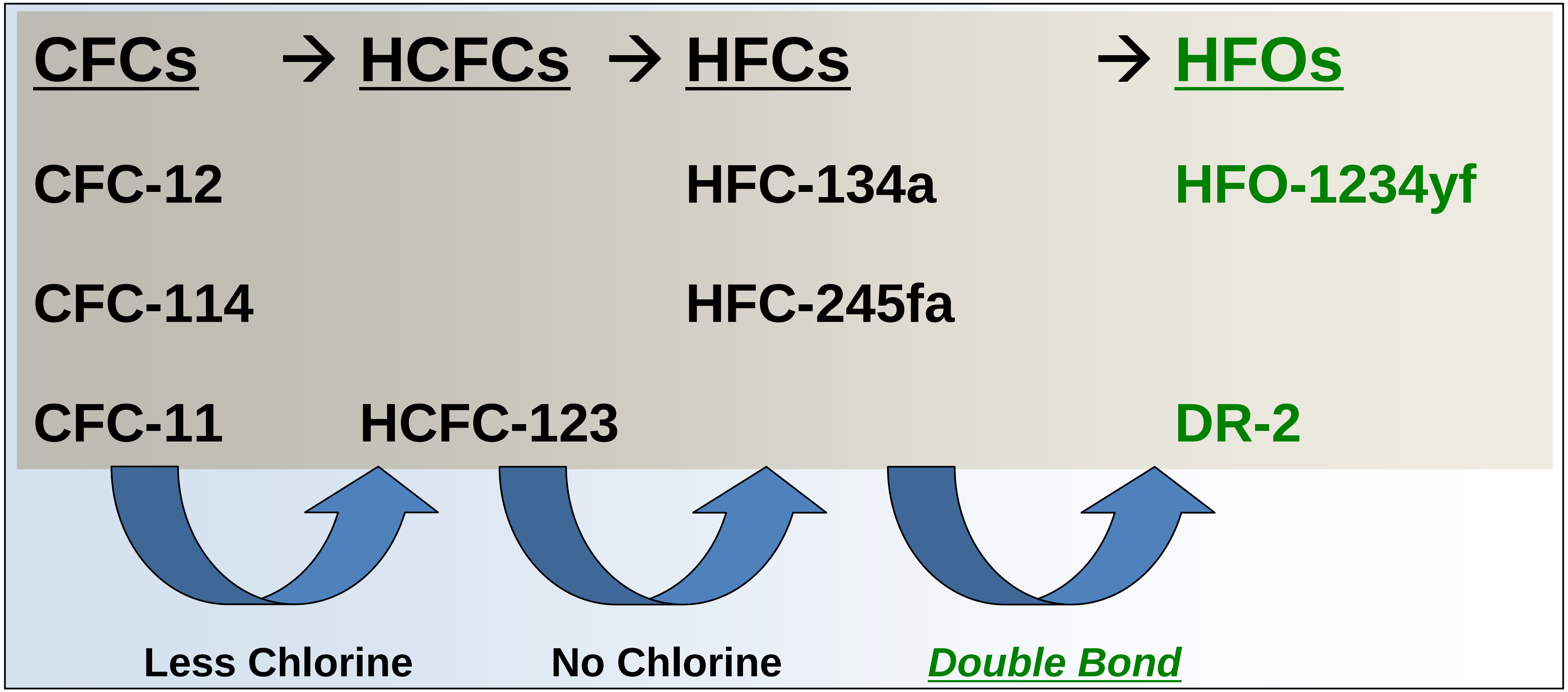
- ✓High energy efficiency
- ✓High volumetric capacity for cooling, heating or power generation
- ✓Low or no temperature glide
- ✓Low toxicity
- ✓Low or no flammability
- ✓High chemical stability
- ✓Compatibility with commercially available lubricants
- ✓Compatibility with common materials of equipment construction
- ✓Short atmospheric life time
- ✓No ozone depletion potential
- ✓Acceptable atmospheric breakdown products
- ✓Acceptable performance in existing equipment with no or little modification
- ✓Low cost AND
- ✓***LOW GLOBAL WARMING IMPACT***

Threading The Needle!

I. HFO-Based Fluids (General Properties)

(II. Applications Later)

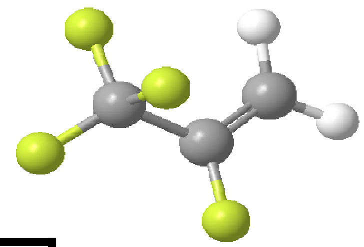
Hydro-Fluoro-Olefins



Conventional Wisdom:
Unsaturated fluorocarbons are not sufficiently stable to be used as refrigerants!

Paradigm Shift:
Unsaturated fluorocarbon refrigerants decompose rapidly in the atmosphere but can remain stable in a system!

Mid-Pressure Fluids: HFO-1234yf



	CFC-12	HFC-134a	HFO-1234yf
Chemical Formula	CCl_2F_2	CH_2FCF_3	$CF_3CF{=}CH_2$
MW	120.9	102	114
Safety Class (ASHRAE Std 34)	A1	A1	A2L
ALT [yrs]	100	14	0.0301 (11 days)
ODP	1.00	None	None
GWP_{100}	10,890	1,430	4
T_{cr} [°C]	112.0	101.1	94.7
P_{cr} [MPa]	4.14	4.06	3.38
T_b [°C]	-29.8	-26.1	-29.5

Marginally Flammable

Very Low GWP

HFO-1234yf Flammability

		Difficulty or Ease to Cause Flame				Consequences	
Refrigerant:	Flamm-ability Class	LFL[a] vol%	UFL[a] vol%	(UFL- LFL) vol%	MIE mJ	HOC kJ/g	BV cm/s
Propane	3	2.2	10.0	7.8	0.25	46.3	46
R152a	2	3.9	16.9	13.0	0.38	16.5	23
R32	2L	14.4	29.3	14.9	30-100[b]	9.4	6.7
Ammonia	2L	15.0	28.0	13.0	100-300[b]	18.6	7.2
HFO-1234yf	2L	6.2	12.3	6.1	5,000-10,000[b]	10.7	1.5[c]

BV<10 cm/s

[a]Flame limits measured at 21 °C, ASTM 681-01

[b]Tests run in 12 liter flask to minimize wall quenching effects

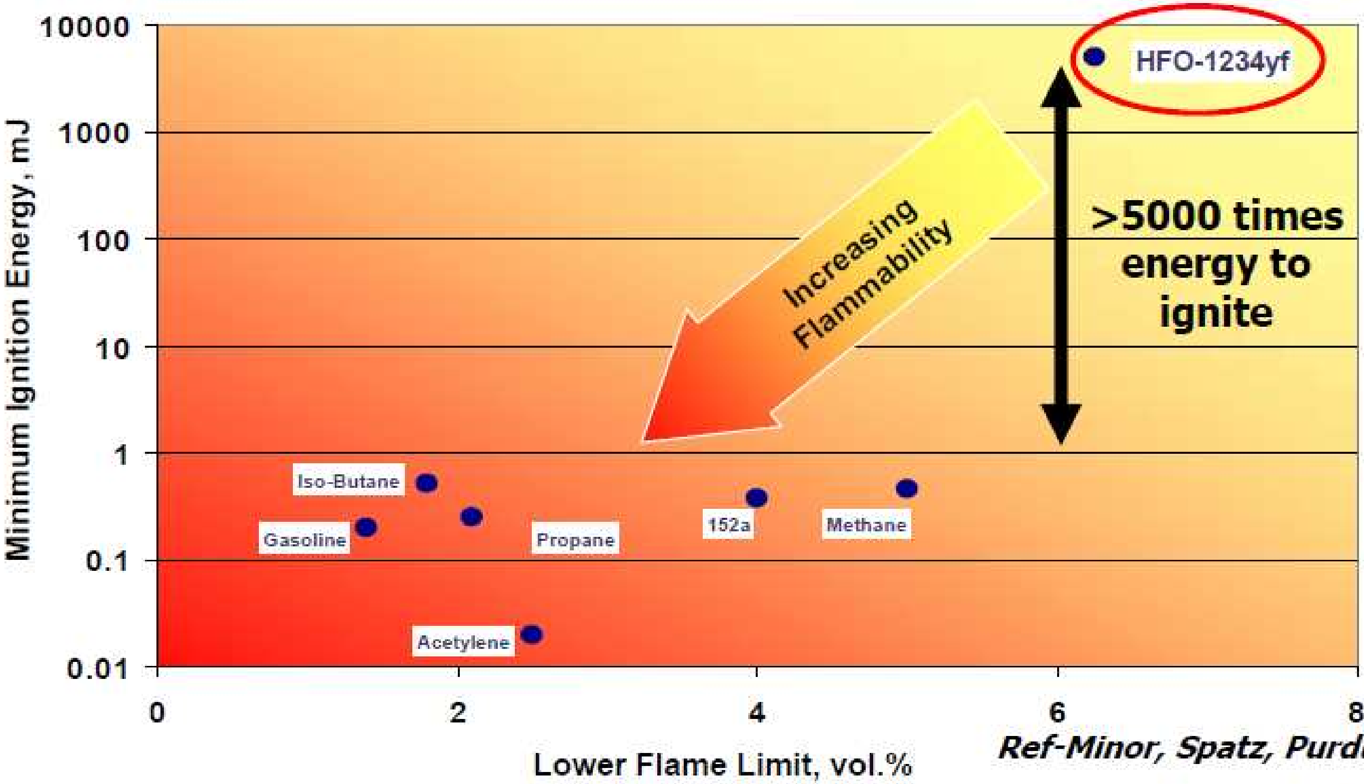
[c]HFO-1234yf BV measured by AIST, Japan

Mildly Flammable – "2L"

HFO-1234yf Flammability Properties- Minimum Ignition Energy

Flammability evaluated by 'Chance of Flame ' and 'Effect of Flame"

- Chance of Flame occurring -> Lower Flame Limit, Minimum Ignition Energy



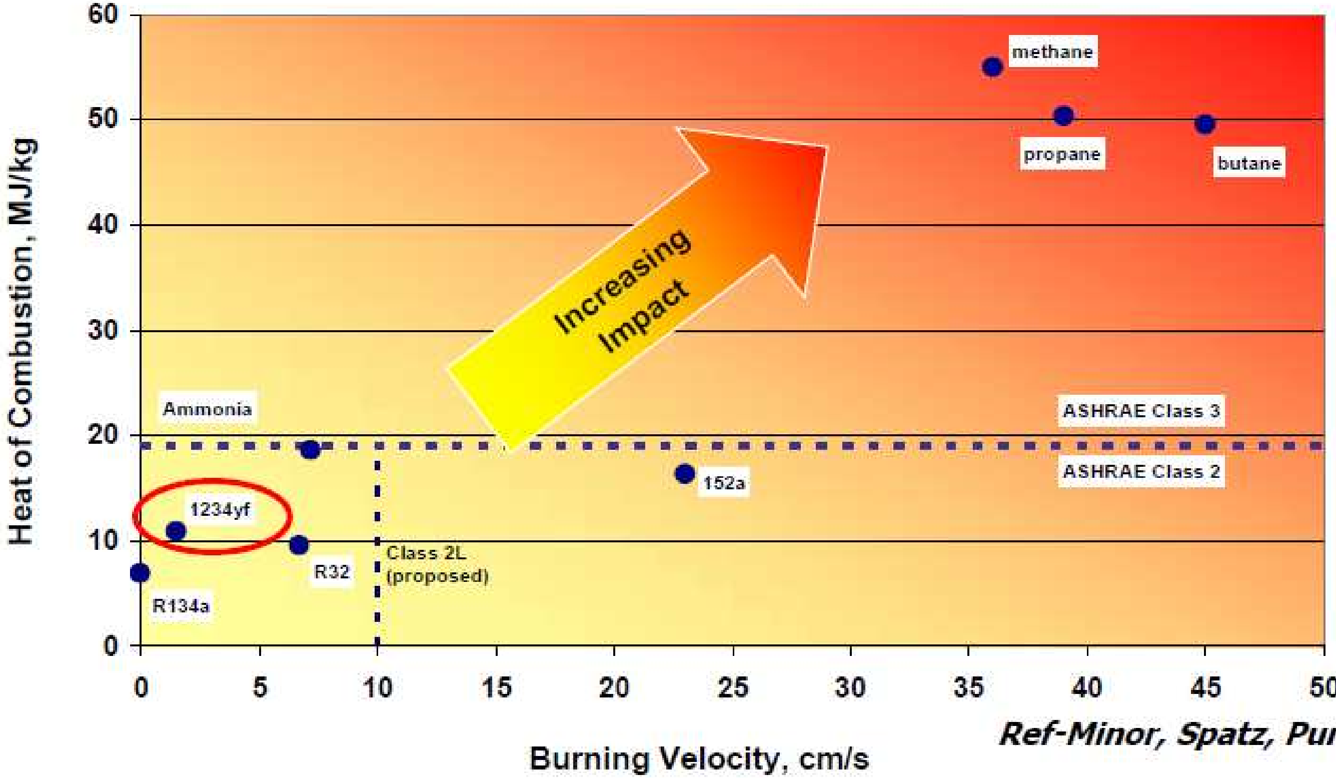
Ref-Minor, Spatz, Purdue 2008

Difficult to ignite HFO-1234yf due to high Minimum Ignition Energy

HFO-1234yf Flammability Properties-Burning Velocity

Flammability is evaluated by 'Chance of Flame' and 'Effect of Flame"

- Effect of Flame occurring -> Heat of Combustion, Buning Velocity



Ref-Minor, Spatz, Purdue 2008

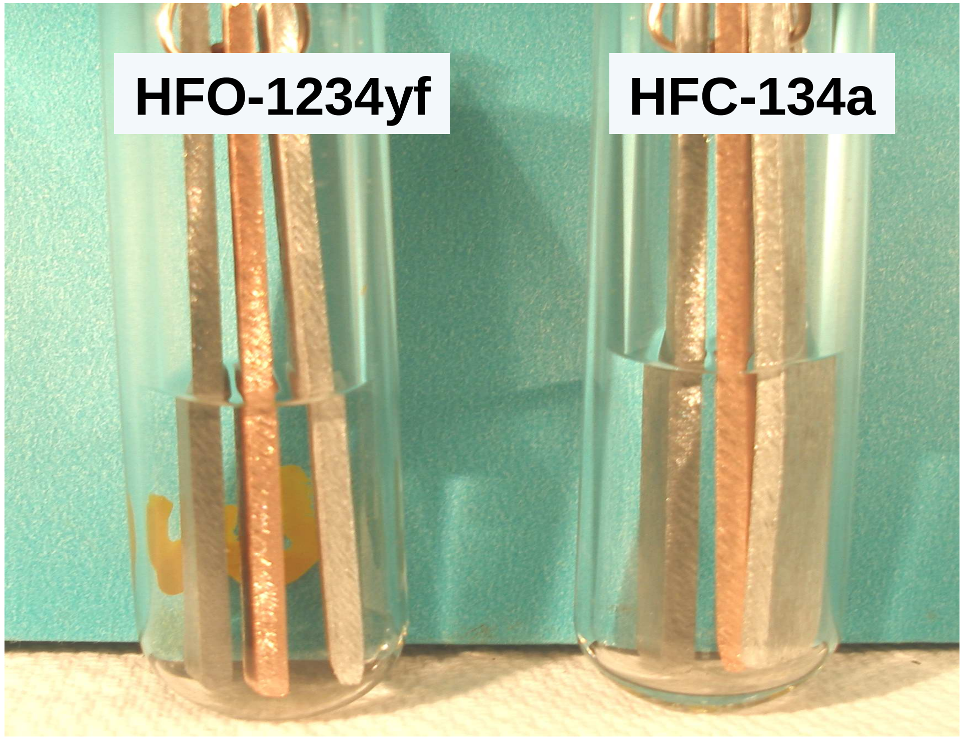
Even if ignited, HFO-1234yf burns weakly, would have limited effect

HFO-1234yf Thermal Stability I

Rapidly decomposing in the atmosphere
But stable under service conditions!

Neat HFO-1234yf vs Neat HFC-134a
After 2 wks @ 200 ºC

Sealed tube testing based on ASHRAE-ANSI STD 97



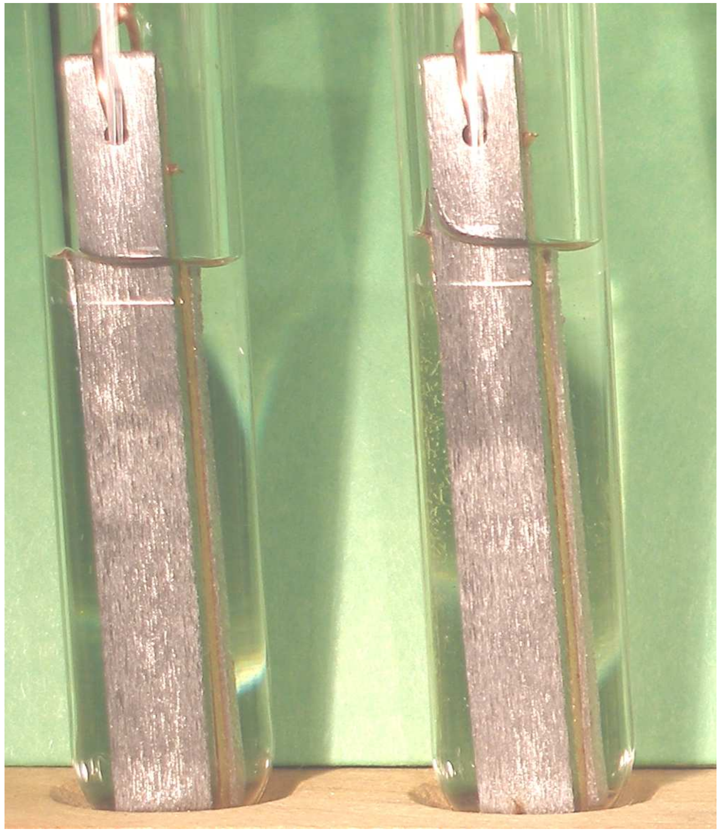
No Detectable Fluoride nor Acid Generation

HFO-1234yf Thermal Stability II

AFTER TWO WEEKS @ 175 °C

HFO-1234yf/POE vs HFC-134a/POE

Front View



HFO-1234yf HFC-134a

Side View

HFO-1234yf HFC-134a

No Detectable Fluoride nor Acid Generation

Compatibility with Plastics

% weight change after 2 wks @ 100ºC in HFO-1234yf vs HFC-134a

Polymer	Immediately after exposure		24 Hrs after exposure	
	HFC-134a	HFO-1234yf	HFC-134a	HFO-1234yf
Polyester Resin	7.6	4.2	2.2	2.3
Nylon Resin	0.3	-0.2	-0.5	-0.4
Epoxy Resin	0.1	-0.1	-0.3	-0.1
Polyester PET	9.3	5.3	5.8	3.8
Polyester PBT	12.5	1.1	12.3	1.1
Polycarbonate	4.2	0.9	3.9	0.8
Polyimide	3.7	3.4	3.2	3.2
Polyethylene	1.3	1.7	1.1	1.3
PTFE	2.7	3.0	2.3	2.4
FEP	3.1	3.8	2.7	3.2
ETFE	6.0	4.9	4.8	4.2
Phenolic Resin	-0.8	-0.8	-1.0	-0.8
Acetal Resin	2.7	0.7	2.1	0.6
PET Film	0.8	-1.0	-1.3	-2.1

Compatibility with Elastomers

% <u>weight change</u> after 2 wks @ 100ºC in HFO-1234yf vs HFC-134a

Elastomer	Immediately after exposure		24 Hrs after exposure	
	HFC-134a	HFO-1234yf	HFC-134a	HFO-1234yf
Neoprene WRT	**2.6**	**2.4**	**1.3**	**1.3**
HNBR	**15.2**	**5.2**	**9.9**	**4.4**
NBR	**14.1**	**5.8**	**8.0**	**4.6**
EPDM (Nordel)	**3.6**	**3.5**	**0.7**	**0.6**
Silicone	**10.6**	**2.0**	**-0.1**	**-0.4**
Butyl Rubber	**4.1**	**5.0**	**3.2**	**4.1**
Terminal seal	**2.2**	**4.8**	**0.8**	**2.0**
Buna S (SBR)	**2.7**	**2.1**	**1.1**	**0.8**
Viton	**47.4**	**20.0**	**8.0**	**8.0**
Hypalon	**3.2**	**2.7**	**2.6**	**2.4**
Neoprene o-ring	**-0.4**	**3.0**	**-0.5**	**2.3**

Overall: Comparable degree of interaction of polymers & elastomers with 1234yf and 134a

Miscibility in ISO 120 POE: HFO-1234yf vs. R-134a

Branched Acid POE Lubricant

Refrigerant: HFO 1234yf							**Temperature**				**(C)**																		
Lubricant: ISO120 Branched Acid POE																													
% POE	**-50**	**-45**	**-40**	**-35**	**-30**	**-25**	**-20**	**-15**	**-10**	**-5**	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**	**85**	**90**
5%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
10%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N
15%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N
20%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N
30%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N
60%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Refrigerant: HFC-134a																													
Lubricant: ISO120 Branched Acid POE							**Temperature**				**(C)**																		
% POE	**-50**	**-45**	**-40**	**-35**	**-30**	**-25**	**-20**	**-15**	**-10**	**-5**	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**	**85**	**90**
5%	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
10%	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
15%	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
20%	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
30%	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
60%	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M

Miscibility in ISO 68 POE: HFO-1234yf vs. R-134a

68 cSt Mixed Acid POE

Refrigerant: HFO 1234yf																													
Lubricant: ISO 68 Mixed Acid POE							Temperature				(C)																		
% POE	-50	-45	-40	-35	-30	-25	-20	-15	-10	-5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90
5%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N
10%	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N	N
15%	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N	N	N
20%	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N	N	N	N
30%	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N	N	N	N	N	N
60%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Refrigerant: HFC-134a																													
Lubricant: ISO 68 Mixed Acid POE							Temperature				(C)																		
% POE	-50	-45	-40	-35	-30	-25	-20	-15	-10	-5	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90
5%	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
10%	N	N	N	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
15%	N	N	N	N	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N
20%	N	N	N	N	N	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N
30%	N	N	N	N	N	N	N	N	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	N
60%	N	N	N	N	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
70%	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M

HFO-1234yf Miscibility in Common Lubricants

Mineral Oil	Non Miscible
Alkyl Benzene	Non Miscible
Polyol Ester	Miscible
PAG	Miscible

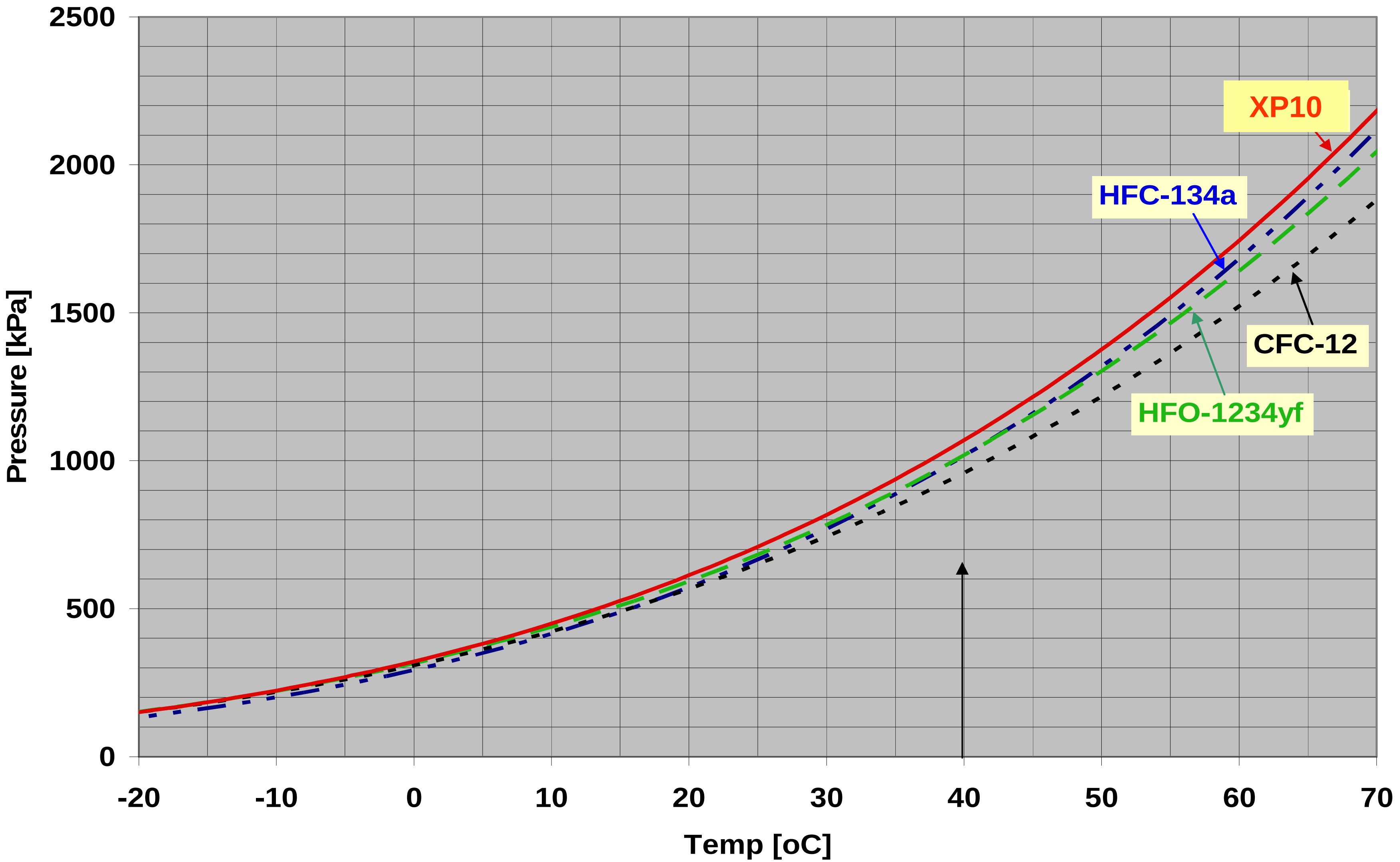
Similar to HFC-134a

Non-Flammable Blend Based on HFO-1234yf: XP10

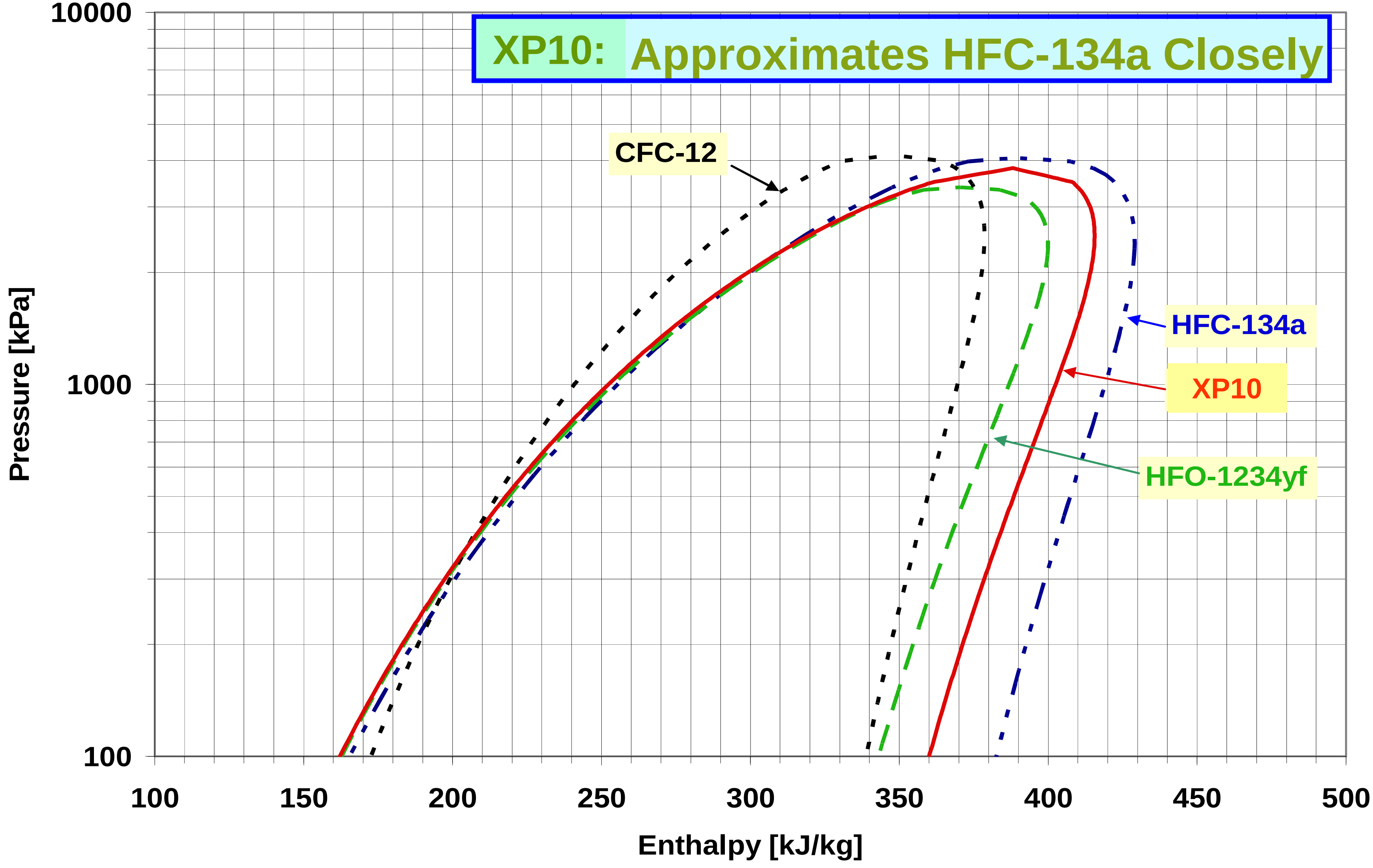
Marginally Flammable → HFO-1234yf   *Non-flammable* → XP10

	CFC-12	HFC-134a	HFO-1234yf	XP10
Chemical Formula	CCl_2F_2	CH_2FCF_3	$CF_3CF=CH_2$	**Azeotrope**
Safety Class (ASHRAE Std 34)	A1	A1	A2L	**A1** (expected)
ODP	1.00	None	None	**None**
GWP_{100}	10,890	1,430	4	**~600**
T_{cr} [^oC]	112.0	101.1	94.7	**97.5**
P_{cr} [MPa]	4.14	4.06	3.38	**3.85**
T_b [^oC]	-29.8	-26.1	-29.5	**-29.2**
Glide [^oC]	N/A	N/A	N/A	**Negligible**

HFO-1234yf and XP10: Vapor Pressure



HFO-1234yf and XP10: P-h Diagram



New Developmental Refrigerant: DR-14

	CFC-12	HFC-134a	HFO-1234yf	XP10	DR-14
Chemical Formula	CCl_2F_2	CH_2FCF_3	$CF_3CF=CH_2$	Azeotrope	**Azeotrope**
Safety Class (ASHRAE Std 34)	A1	A1	A2L	A1 (expected)	**A1 (expected)**
ODP	1.00	None	None	None	**None**
GWP_{100}	10,890	1,430	4	~600	**~380**
T_{cr} [ºC]	112.0	101.1	94.7	97.7	**111.6**
P_{cr} [MPa]	4.14	4.06	3.38	3.85	**3.96**
T_b [ºC]	-29.8	-26.1	-29.5	-29.2	**-20.5**
Glide [ºC]	N/A	N/A	N/A	Negligible	**Negligible**

Apparent Trade-Off: Either Very Low GWP or Non-Flammable

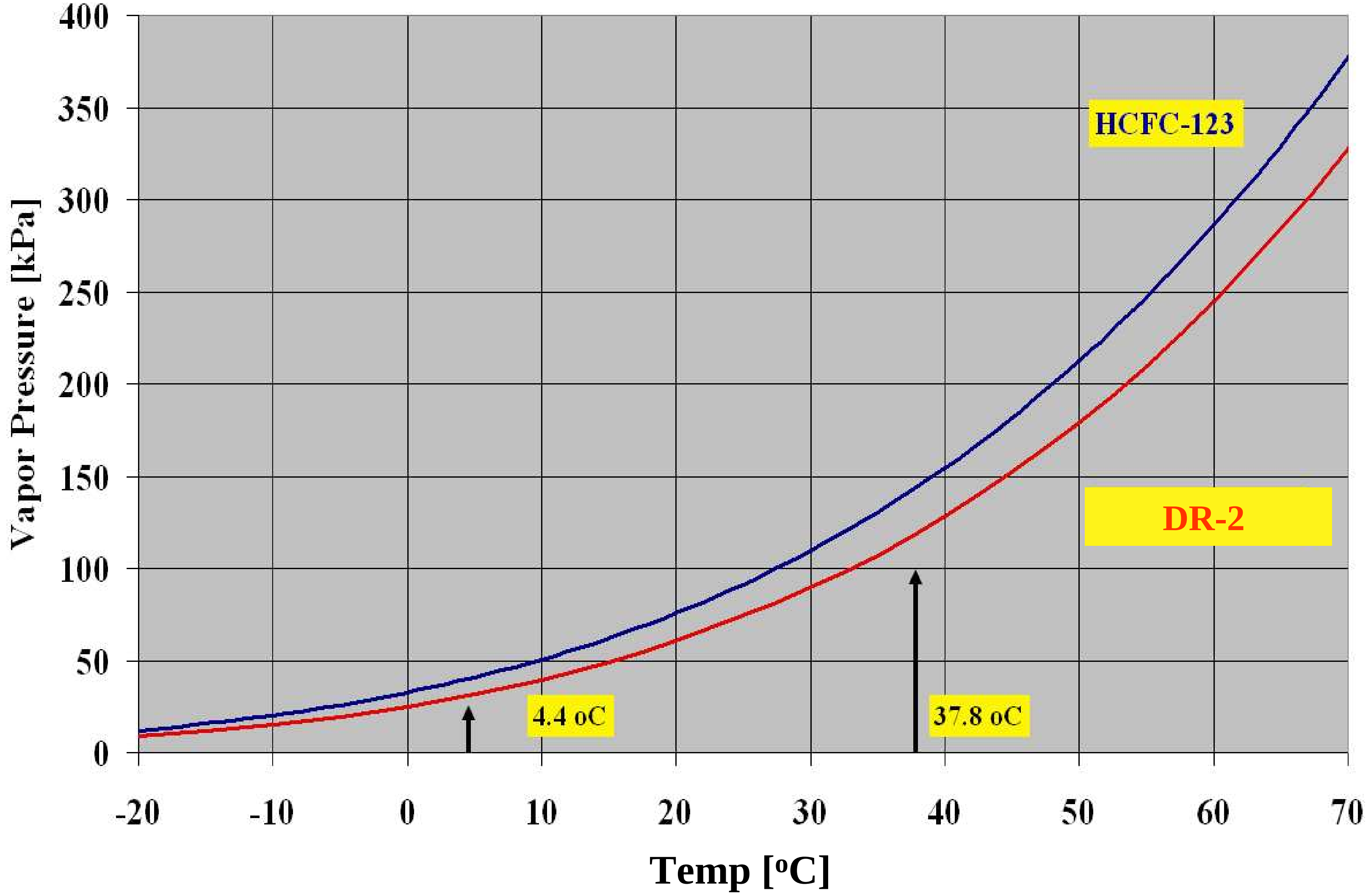
A Low Pressure Candidate: DR-2

HCFC-123 cannot be used in new equipment in EU today and the US in 2020
HCFC-123 production already scheduled for phase-out by 2030

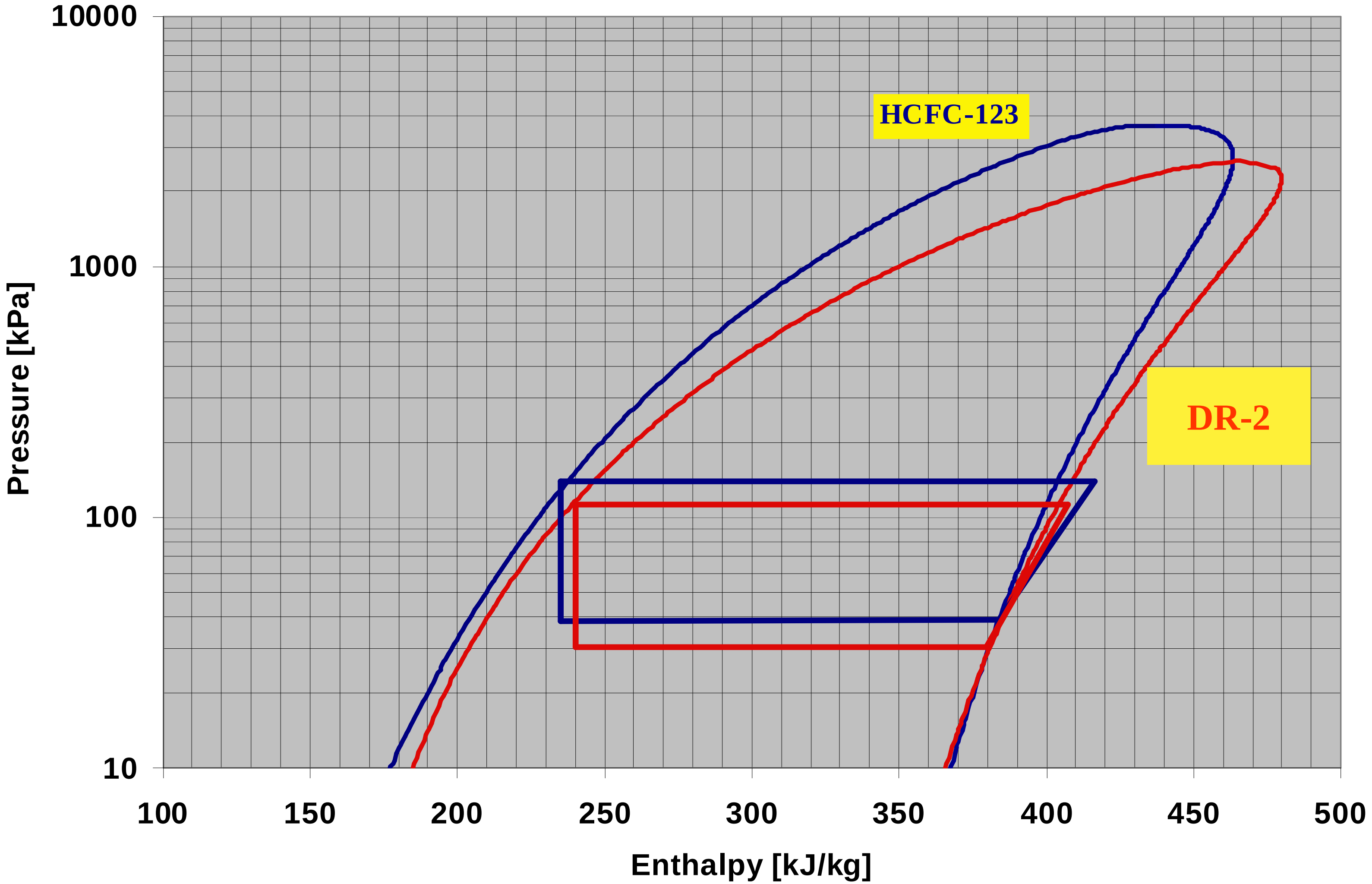
	HCFC-123	DR-2
Safety Class	B1	**A1** (expected)
Atmospheric life time [yrs]	1.3	**0.0658** (24 days)
ODP	0.02	**None**
GWP$_{100\ YR\ ITH}$	77	**<10**
Critical Temperature [ºC]	183.7	**171.3**
Critical Pressure [MPa]	3.7	**2.9**
Normal Boiling Point [ºC]	27.9	**33.4**

Very Low GWP AND Non-Flammable

DR-2 Vapor Pressure vs. HCFC-123



DR-2 P-h Diagram vs. HCFC-123



DR-2: Stable At Least Up to 250 oC

Sealed tube testing based on ASHRAE-ANSI STD 97

Even After 2 Wks @ 250 oC:
Clear Fluid, Clean Coupons
Negligible formation of new compounds

DR-2:
- ***High Thermal Stability***
- ***High Critical Temperature***
- ***Low Vapor Pressure***

→ ***High Temp Apps?***

II. Applications

•Automotive AC: Move away from HFC-134a underway

•Stationary Applications: Longer Term Low GWP Options
  - •Residential & Light Commercial A/C & Heating
  - •Commercial Refrigeration (Bottle Coolers & Supermarket Refrigeration)
  - •Commercial AC (Chillers)

•Low Temperature Heat Utilization
  - •Commercial & Industrial Heating (High Temperature Heat Pumps)
  - •Power from Low Temp Heat (Organic Rankine Cycles)

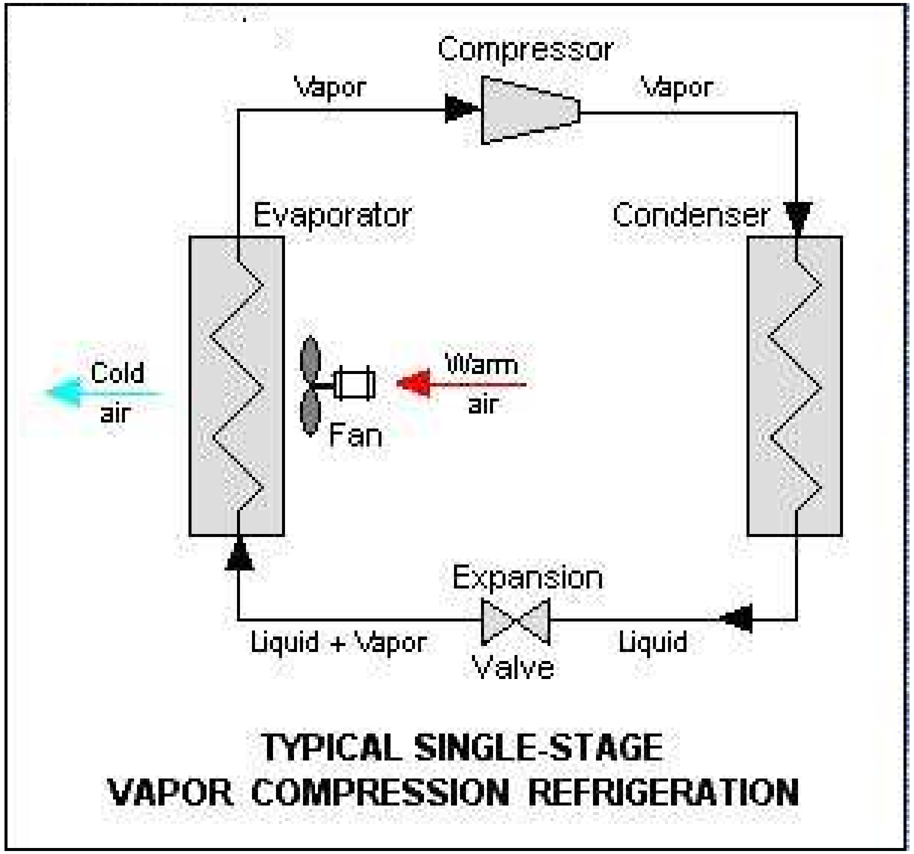
Terminology

Key Performance Parameters:

Volumetric Capacity

(for cooling or heating)

Coefficient of Performance (COP)
(for cooling or heating)



Automotive Air Conditioning

Auto industry is converging to HFO-1234yf

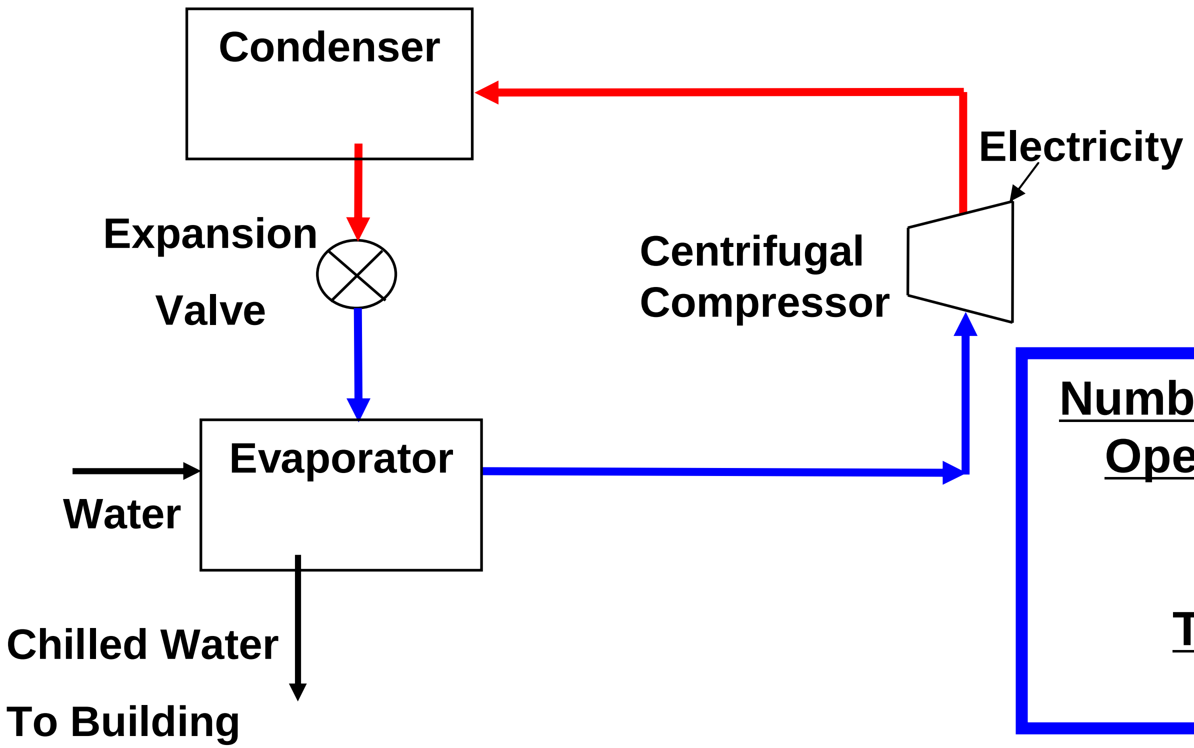
SAE International

HFO1234yf vs R744 Summary

	HFO1234yf	CO_2
Environmental Impact	Lower total greenhouse gas emissions than either 134a or CO_2	10-15% more total global warming emissions than HFO1234yf
Atmospheric Lifetime	11 days	> 100 years
Drop-in Solution?	Near drop-in solution	New system design required
Ability to Cool Auto Interior	Superior performance in all climates	Less effective/efficient in hot climates – where air conditioning is used more
Safety	Safe for use in automotive air conditioning applications with proper mitigation	Safe for use in automotive air conditioning applications with proper mitigation

Chillers

Centrifugal Water Chillers



Number of centrifugal chillers in Operation around the world:
Over 130,000

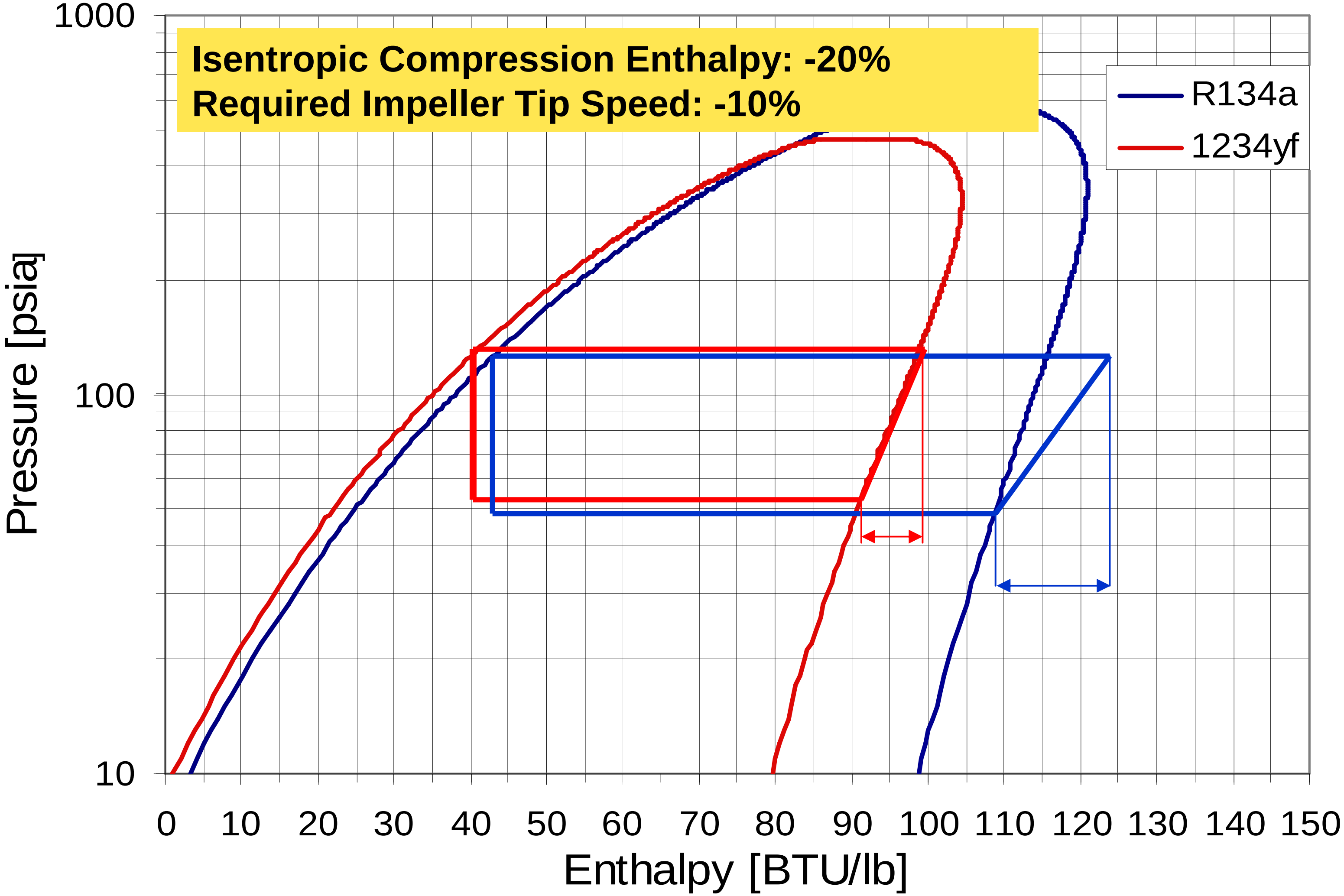
Total refrigerant bank:
ca. 60,000 tonnes

Previous centrifugal chiller refrigerants and transitions

CFC-11→HCFC-123 CFC-12→HFC-134a

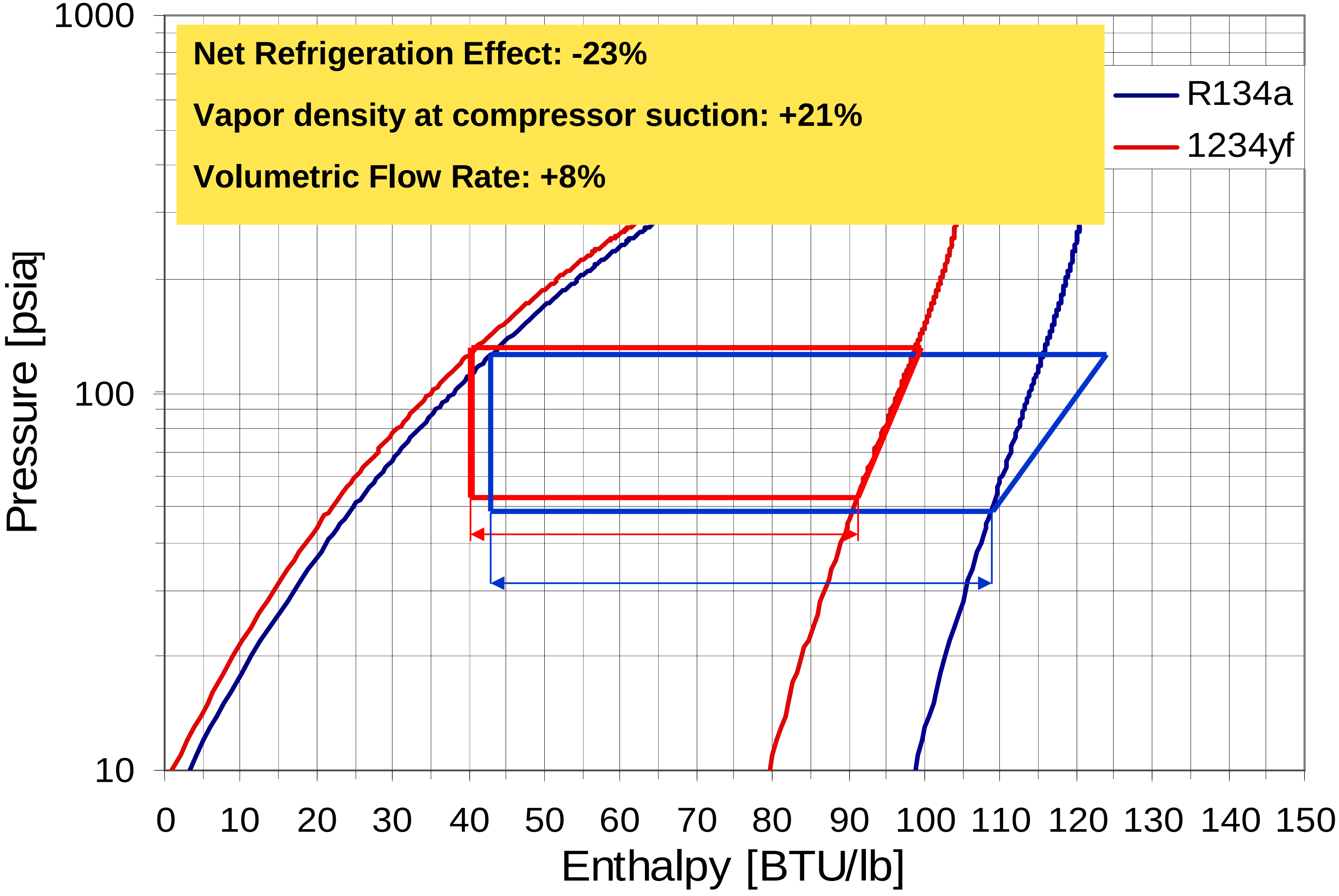
Ozone Depleting ***High GWP***

HFO-1234yf Thermodynamic Performance vs HFC-134a: I



T_{evap}=4.4 ºC; T_{cond}=37.8 ºC; ΔT_{suph}=0 ºC; ΔT_{subc}=0 ºC

HFO-1234yf Thermodynamic Performance vs HFC-134a: II



T_{evap}=4.4 ºC; T_{cond}=37.8 ºC; ΔT_{suph}=0 ºC; ΔT_{subc}=0 ºC

Low GWP Replacements for HFC-134a in Chillers: Summary

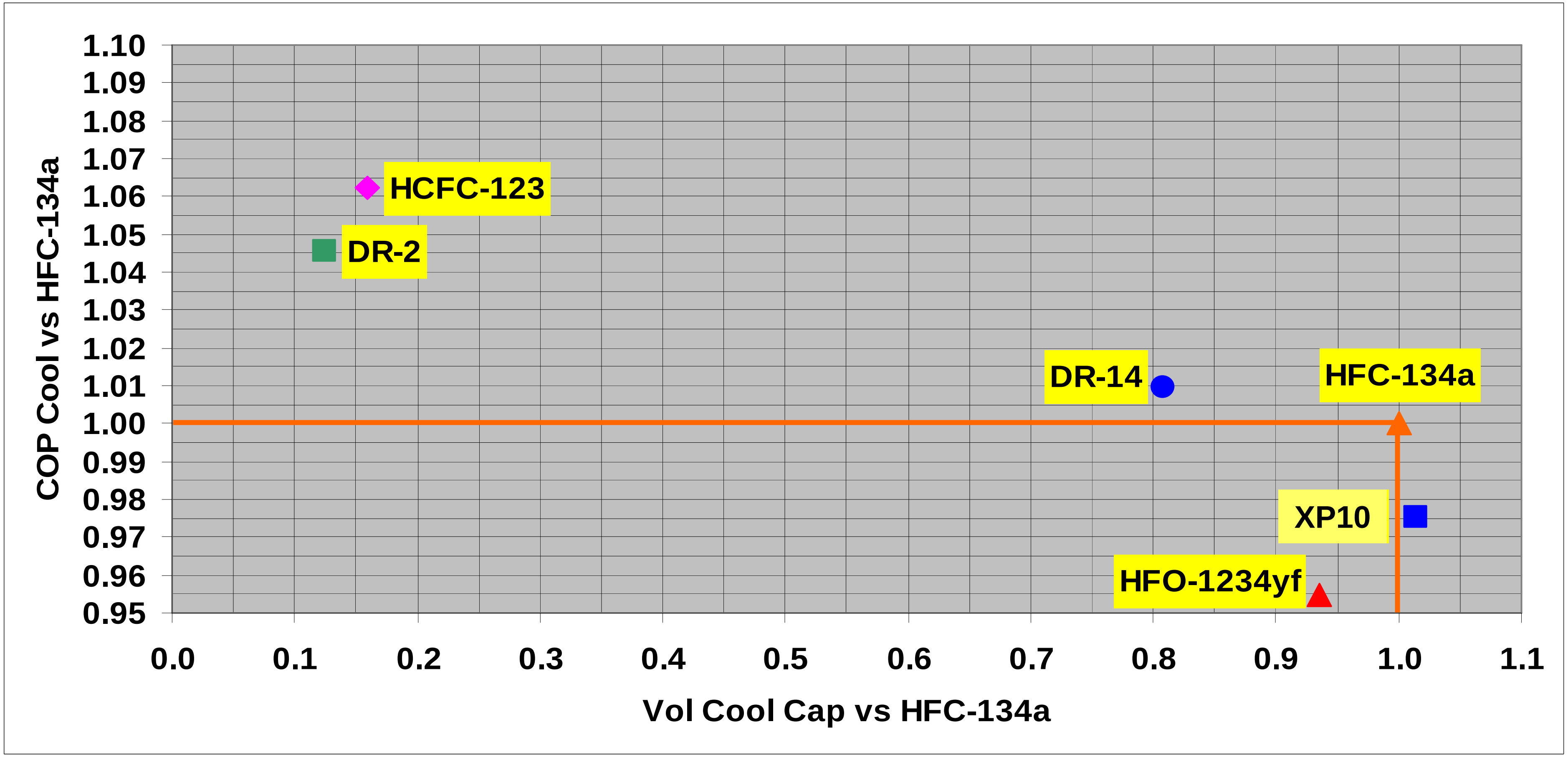
Low Toxicity, Adequate Stability, No ODP

	HFO-1234yf	XP10	DR-14
FLAMMABILITY	Marginal	Nonflammable	Nonflammable
Theoretical Energy Efficiency vs HFC-134a	-4.5%	-2.5 %	+0.7 %
Cooling Capacity vs HFC-134a	-6.5%	+1.5%	-19.3 %
HFC-134a Retrofit	-	Near drop-in	--
GWP_{100}	4	~600	~380

Preferred Refrigerant?

XP10: would require no major equipment and no safety code modifications; it could be adopted earlier and more widely

Low GWP Chiller Refrigerants: Performance



<u>The case for DR-2</u>

DR-2 vs	DR-14	XP10	1234yf
COP	3.6%	7.2 %	9.5%

- ***Higher energy efficiency***
- ***Lower vapor pressure (containment; no pressure rated vessels)***
- ***Favorable safety and environm properties***

Warming Impact of Low GWP Chiller Refrigerants

$$TEWI = EM_{NRG} + EM_{RFG} + EM_{EOLrf}$$

EM_{NRG} [kgCO_2-eq] = CI x E

E [kwh] = P(COP) x HRS x N

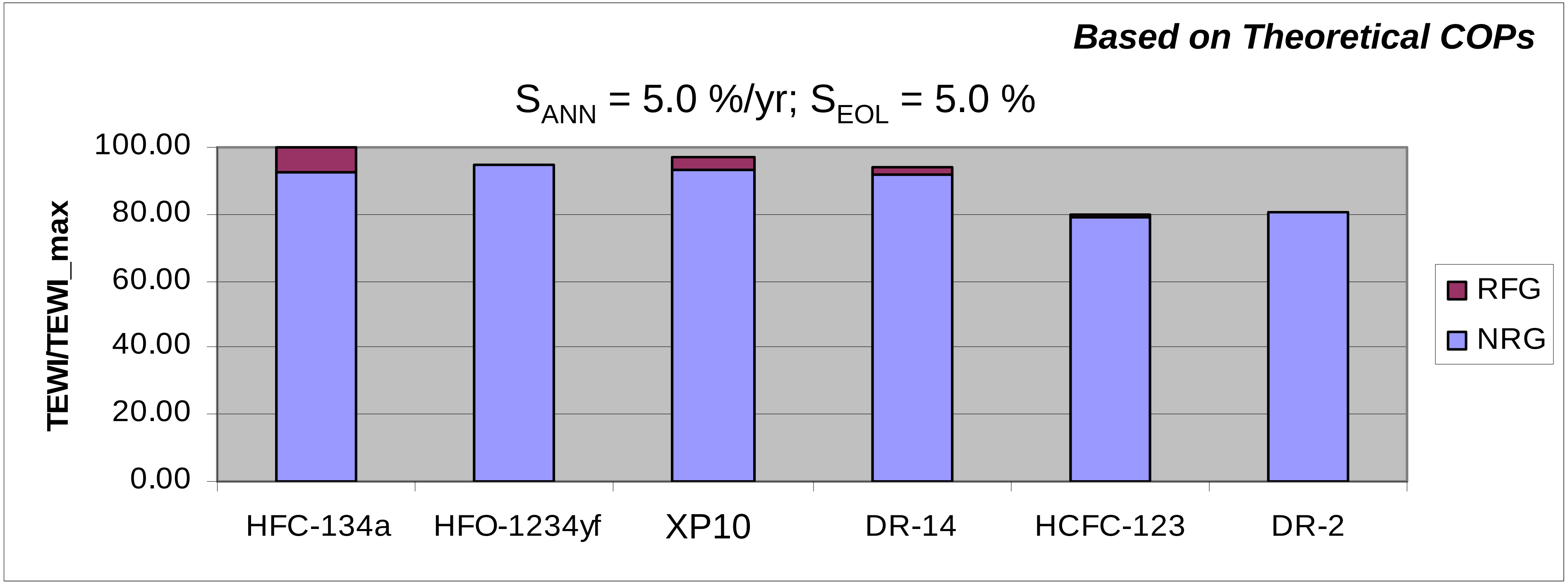
$EM_{RFG} = M_r \times S_{ANN} \times N \times GWP$

S_{ANN} = annual % charge loss

$EM_{EOLrf} = M_r \times S_{EOL} \times GWP$

S_{EOL} = End-Of-Life % charge loss

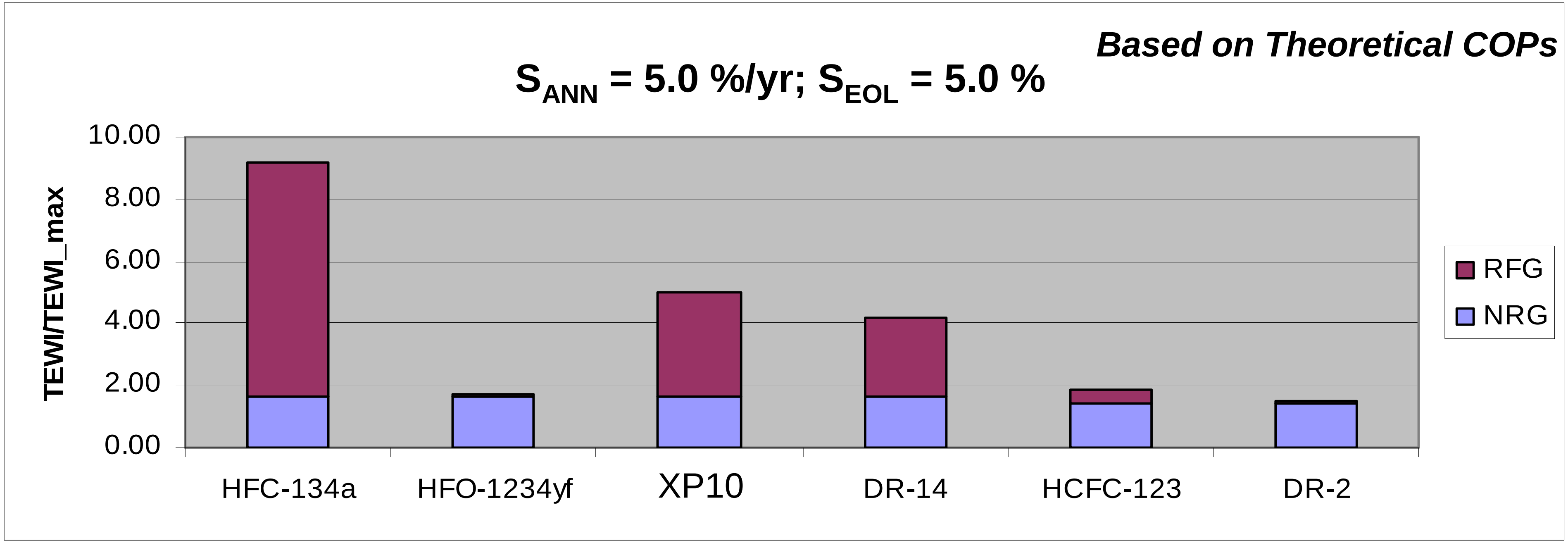
TEWI: High Carbon Intensity Scenario
(0.8445 kgCO_2-eq/kwh--China)



GWP=1,430 4 ~600 ~380 77 ~10

Minimization of GWP does not necessarily lead to maximum Warming Impact reduction

TEWI: Low Carbon Intensity Scenario
(0.0150 kgCO_2-eq/kwh--Switzerland)

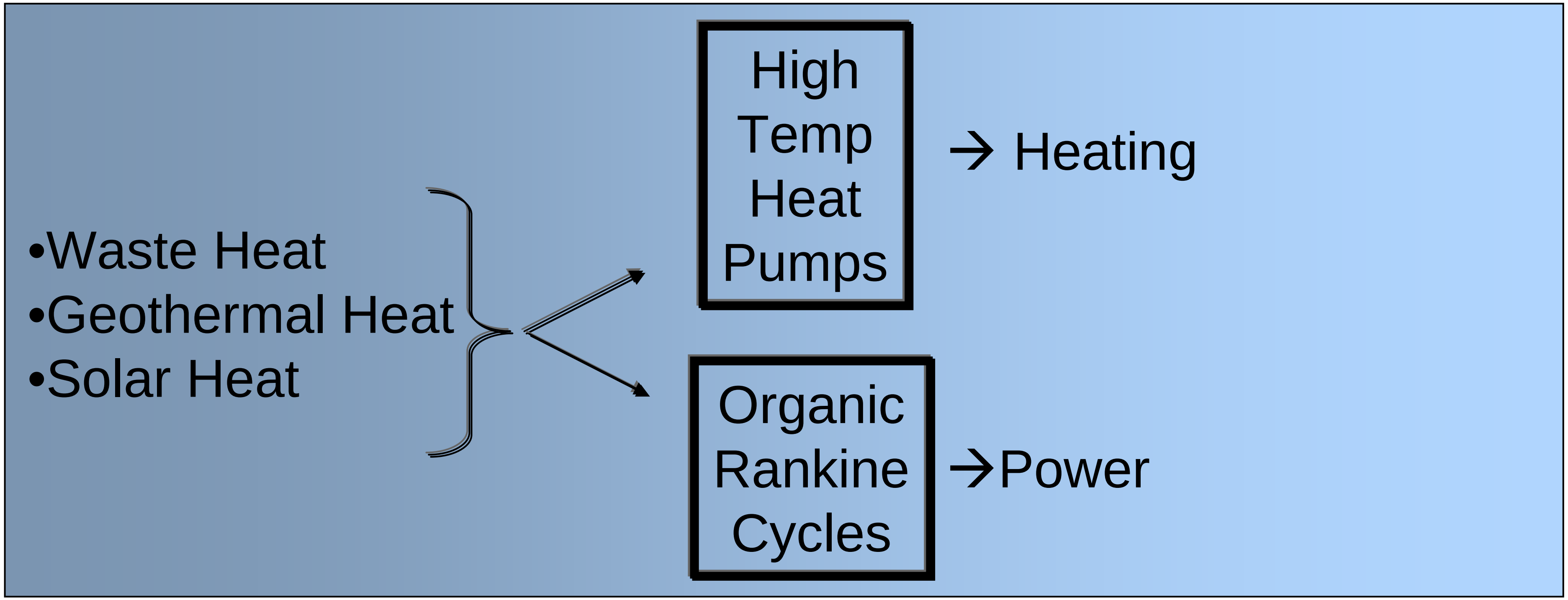


GWP=1,430 | 4 | ~600 | ~380 | 77 | ~10

DR-2 for Low Temp Heat Utilization

➢Reduce energy costs

➢Reduce environmental impact from energy use



DR-2: Stable at high temperatures; High critical temperature; Low vapor pressure

High Temperature Heat Pumps: DR-2

Heating Duty: T_{cond} = 155 ^{o}C

P_{cond} = 2.18 MPa

ΔT_{suph}= 15 ^{o}C; ΔT_{subc}= 10 ^{o}C; η_{compr}=0.80

T_{evap}	^{o}C	80	100	120
P_{evap}	MPa	0.43	0.70	1.10
PR		5.08	3.09	1.98
COP_h		**2.975**	**4.568**	**8.034**
CAP_h	kJ/m^3	2,331.42	4,121.62	7,003.43

Potential Applications?

Power from Heat through ORCs: DR-2 vs HFC-245fa

		HFC-245fa	DR-2
Chemical Formula		$CHF_2CH_2CF_3$	Proprietary
T_b	ºC	15.1	33.4
T_{cr}	ºC	154	171.3
P_{cr}	MPa	3.65	2.90
Safety Class		B1	A1 (expected)
ALT	yrs	7.6	0.0658 (24 days)
GWP_{100}		1030	9.4

Power from Heat through ORCs: DR-2 vs HFC-245fa

P_{evap}=2.18 MPa

T_{cond}=40 ºC; ΔT_{suph}= 0 ºC; ΔT_{subc}= 0 ºC; η_{exp}=0.85; η_{pump}=0.85

		HFC-245fa	DR-2	DR-2 vs HFC-245fa %
T_{evap}	oC	126.2	155	
P_{cond}	MPa	0.25	0.13	
Efficiency		0.1348	0.1551	+15.06
CAP_e	kJ/m3	409.85	272.20	-33.59

Summary-Conclusions

HFOs: a rich class of low GWP compounds each with each own idiosyncrasies; pipeline of candidates tailor-made for various applications emerging

XP10: a sensible nearer-term replacement for HFC-134a in emissive chiller applications

DR-2: promising longer-term, low-pressure fluid for commercial air conditioning and low temperature heat utilization

Refrigerant selection should consider application impact, not just refrigerant attributes: e.g. refrigerant with lowest GWP may not lead to maximum warming impact reduction

Flexible climate protection regulations to allow acceptance of optimum refrigerants/trade-offs

Thank you!

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