Low Global Warming Fluids for Replacement of HFC-245fa and HFC-134a in ORC Applications

Gary Zyhowski* and Andrew Brown†

*Honeywell, 20 Peabody St., Buffalo, NY USA 14210
e-mail: gary.zyhowski@honeywell.com

Agenda

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- Environmental
- Safety
- Properties
- Cycle Comparisons
- Conclusions

Honeywell – A History of Innovation

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Transition Molecules | Montreal Protocol Compliant Molecules | LGWP Molecules

CFCs → **HCFCs** → **HFCs** → **HFOs**

Montreal Protocol
CFCs Phaseout

Montreal Protocol
HCFCs Phaseout

Kyoto Protocol
EU Legislation
F-Gas Regulation

Innovating To Enable Industry Compliance

Environmental / Safety

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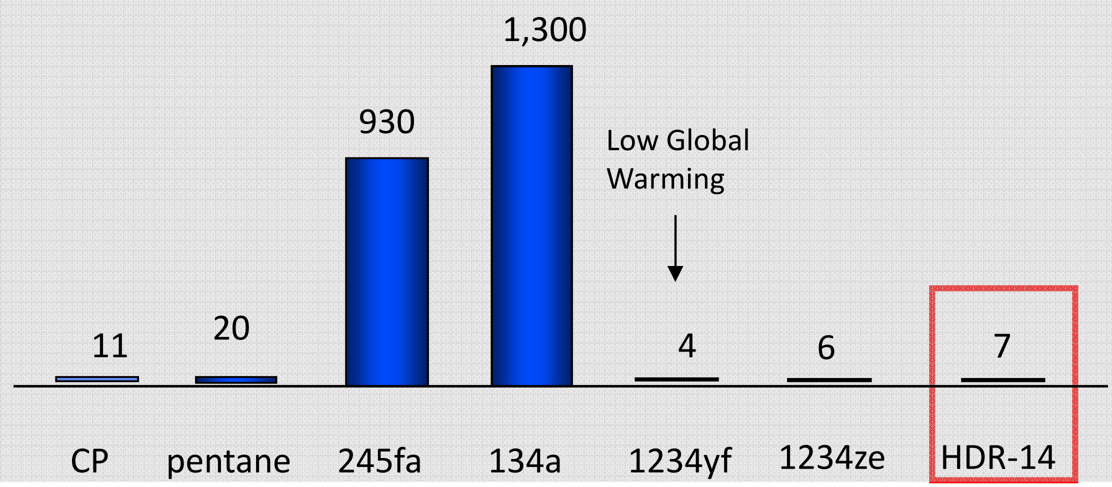
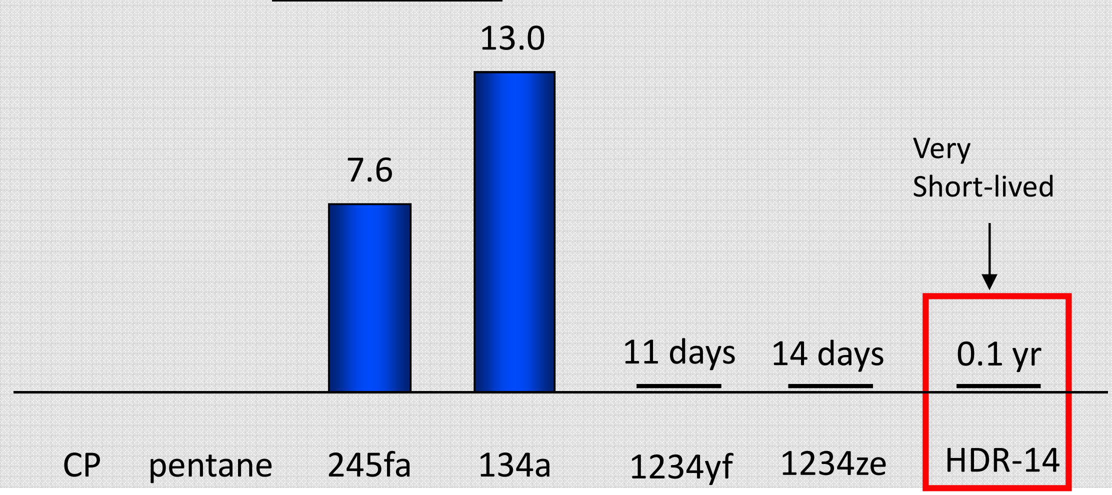
Global Warming Potential (GWP)



Lifetime (yrs)



Next Generation Offers Low GWP

Select Criteria for Replacement Molecules

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- Environmental Properties
  - GWP
  - VOC
- Safety/Health
  - Flammability
  - Toxicity
- Performance
  - Thermodynamic Properties
  - Transport Properties
- Manufacturability
  - Chemistry
  - Cost
  - Raw Materials Cost/Availability
  - Materials Compatibility

Numerous Factors Are Important for Replacement Selection

Environmental / Safety

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Flammability

FLAMMABILITY	NON-FLAMMABLE
• Cyclopentane • Pentane • Isopentane • Butane • Isobutane • 365mfc • HFO-1234yf • HFO-1234ze (>30°C)	• 245fa • 134a • HFO-1234ze (<30°C) • Solkatherm SES36 (365mfc/PFPE) • HDR-14

Higher → Lower

- Risk to operate varies
  - Cost of Insurance
  - Permitting
  - More to the story…

Addition of PFPE to 365mfc lowers cycle efficiency

Volatile Organic Compound (VOC/ POCP)

VOC	NOT VOC
• Cyclopentane • Pentane • Isopentane • Butane • Isobutane	• 245fa • 134a • HFO-1234yf • HFO-1234ze(E) • 365mfc • HDR-14

Possible permitting issue

Next Generation Offers Solid Safety Performance

Environmental / Safety

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FLAMMABLE	Burning Velocity, cm/s	LEL/UEL vol.% in air	Minimum Ignition Energy mJ @ 20C, 1 Atm.
Pentane		1.4/7.6[2]	0.78, 25°C, stoich.[5]
Butane		1.8/8.4[2]	0.26 @ 1atm, ~1.45 stoich.[2]
Isobutane	~31.5[1]	1.8/8.4[2]	
365mfc		3.6/13.3[3]	
HFO-1234yf	1.5	6.2/12.3[4]	5,000 – 10,000[6]
HFO-1234ze	No flame propagation	None at RT 5.7/11.3 (60°C)[4]	No ignition[7] >61,000 <64,000 (54C, 1 Atm.)[7]

Low Rate of Pressure Rise
HFO-1234yf
HFO-1234ze

Difficult to ignite
HFO-1234yf
HFO-1234ze

1 Engineering Journal of the University of Qatar, Vol. 14, 2001, p. 184
2 Us Dept. of the Interior Bureau of Mines Bulletin 680
3 Solvay MSDS
4 Honeywell
5 Combustion, Flames and Explosion of Gases, B. Lewis and Guenther von Elbe, Academic Press Inc., 1987, Orlando, FL 32887
6Measured by DuPont, in-house method
7Measured by Chilworth Technology

HFO-1234yf & HFO-1234ze have lower flammability risk

Environmental / Safety

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	Permissible Exposure Levels
• Pentane	600ppm (8-hr TLV-TWA, ACGIH)[1]
• Isopentane	600ppm (8-hr TLV-TWA, ACGIH)[2]
• Butane	1000ppm (8-hr TLV-TWA, ACGIH)[2]
• Isobutane	1000ppm (8-hr TLV-TWA, ACGIH)[2]
• Solkatherm SES36 (HFC-365mfc/PFPE)	
HFC-365mfc	1000ppm (Solvay limit)[3]
PFPE (1,1,2,3,3-hexafluoro, oxidized, polymerized)	none established for perfluoropolyether[3]
• HFC-245fa	400ppm (TWA, WEEL)[4]
• HFC-134a	1000ppm (TWA, WEEL)[4]
• HFO-1234yf	500ppm (TWA, WEEL)[4]
• HFO-1234ze	800ppm (TWA, WEEL)[4]
• Novec 7000	75ppm[5]
• Novec 649	150ppm[5]

1 ConocoPhillips MSDS
2 Airgas MSDS
3 Solvay Chemicals MSDS
4 Honeywell MSDS
5 3M MSDS

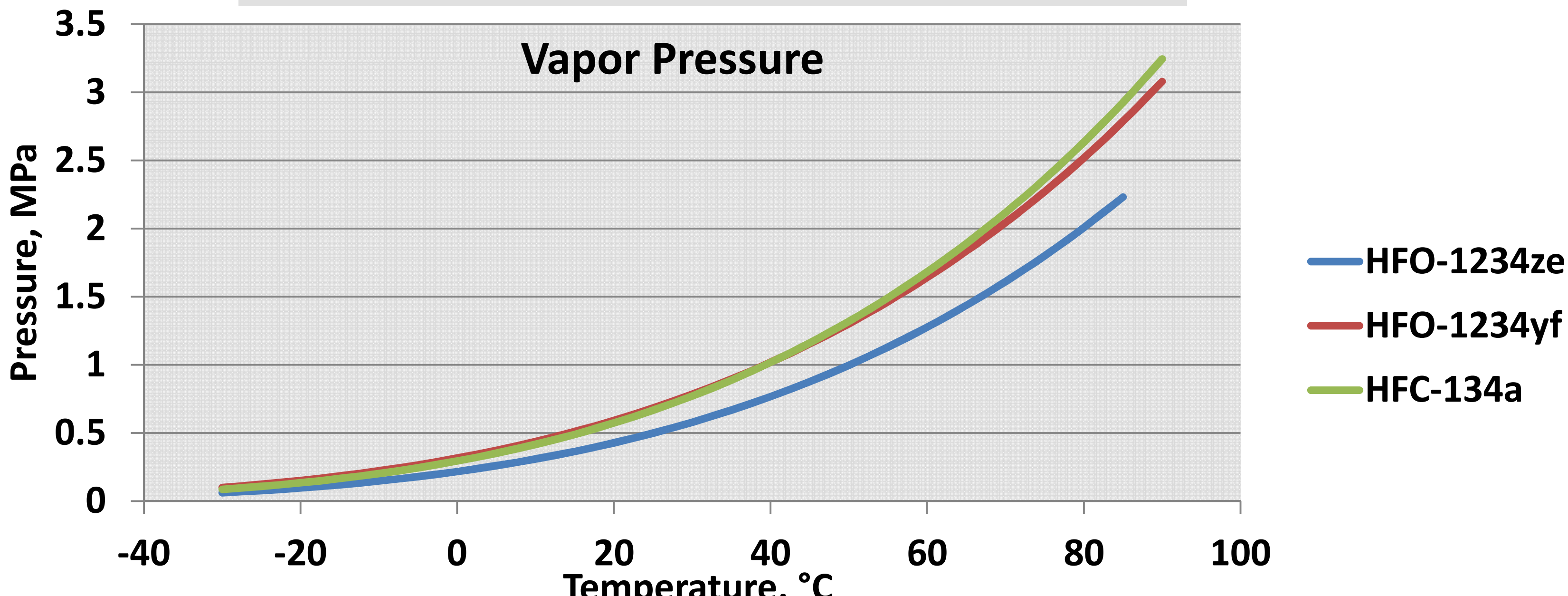
HFC and HFO PELs can be met using typical control measures

HFO-1234yf & HFO-1234ze

Physical Properties

Honeywell

	1234yf*	134a†	1234ze*
Boiling Point, T_b	-29° C	-26° C	-19° C
Critical Point, T_c	95° C	102° C	109° C
Molecular Weight	114.0	102.0	114.0
P_{vap}, MPa (25° C)	0.677	0.665	0.498
P_{vap}, MPa (80° C)	2.44	2.63	2.01
Liquid Density, kg/m^3 (25° C)	1094	1207	1163
Vapor Density, kg/m^3 (25° C)	37.6	32.4	26.4
Latent Heat, kJ/kg (10° C below T_c)	66.6	76.3	73.1



Higher critical temperature for HFO-1234ze

*Honeywell data. † NIST Refprop 8.0.

HFC-134a, HFO-1234yf, HFO-1234ze(E)

ORC Cycle Comparison

Honeywell

Boiler Temp, °C	90.0	Boiler Temp, °C	110.0
Cond Temp, °C	13.0	Cond Temp, °C	13.0
Volume Flow Expander Exit, cm3/s	10.0	Volume Flow Expander Exit, cm3/s	10.0

Fluid	R134a	1234yf	1234ze(E)	R134a	1234yf	1234ze(E)
Thermal Efficiency	0.122	0.117	0.126	0.135	0.128	0.136
Net Work, J/gm	-26.4	-21.5	-26.2	-30.7	-25.5	-30.9
Net Work, J/s	-5.8	-5.4	-4.6	-6.5	-6.0	-5.1
Expander Exit Vapor Density, gm/cm3	0.022	0.025	0.017	0.021	0.024	0.016
Mass Flow, gm/s	0.22	0.25	0.17	0.21	0.24	0.16
Condenser Pressure, psia	66.4	68.8	49.5	66.4	68.8	49.5
Boiler Pressure, psia	430.0	412.7	359.0	565.2	531.1	445.1
Q Boiler, J/gm	216.6	184.0	209.0	227.8	199.2	226.8
Superheat in Boiler, °C	4.4	3.1	0.0	11.0	67.4	9.3

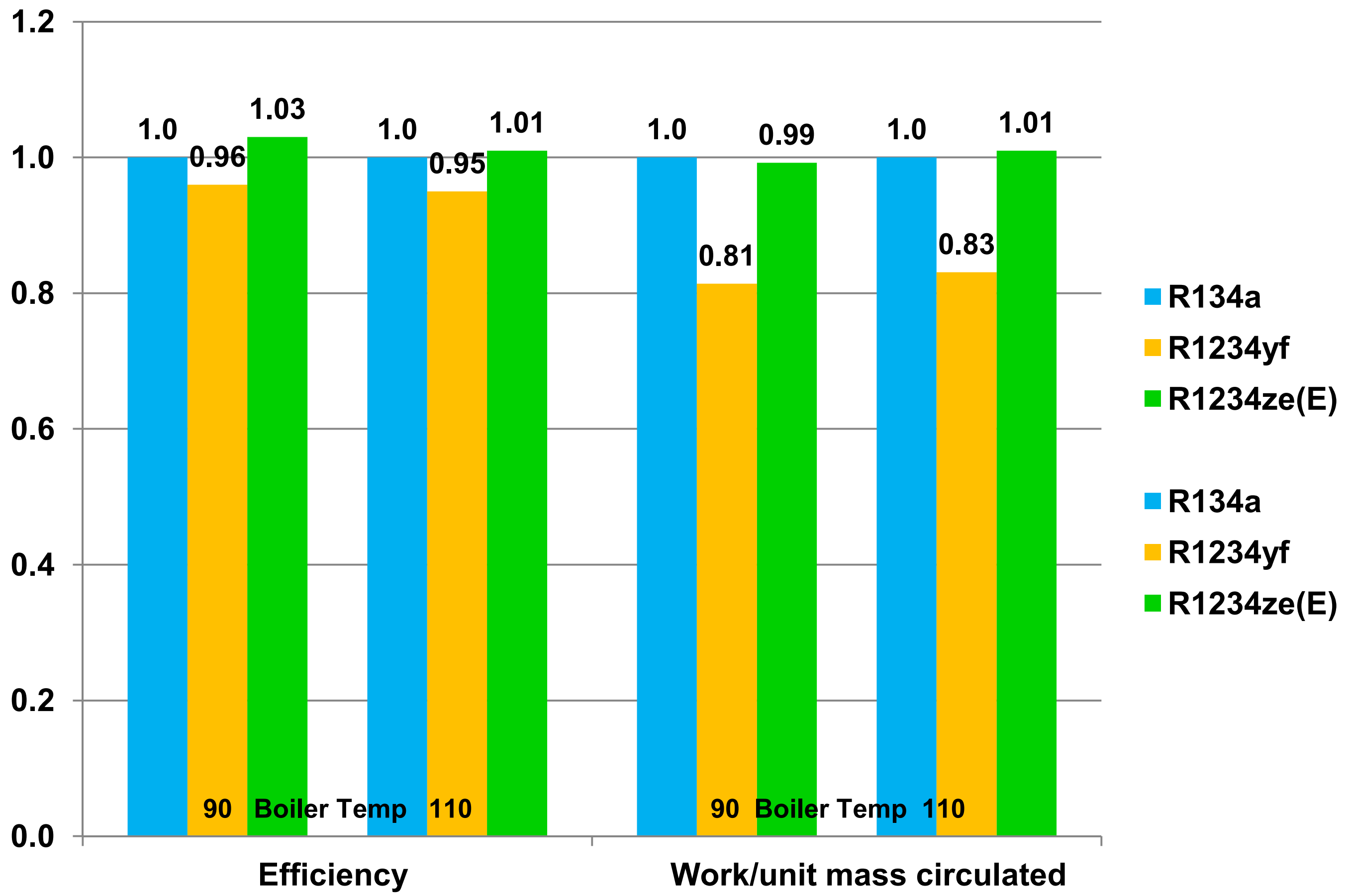
Calculations based on Honeywell data and internal proprietary models

Comparable work and efficiency for HFO-1234ze vs. HFC-134a

HFC-134a, HFO-1234yf, HFO-1234ze(E)

ORC Cycle Comparison (relative to 134a)

Honeywell



Thermodynamic Cycle Comparison - Adjustments to Operating Conditions

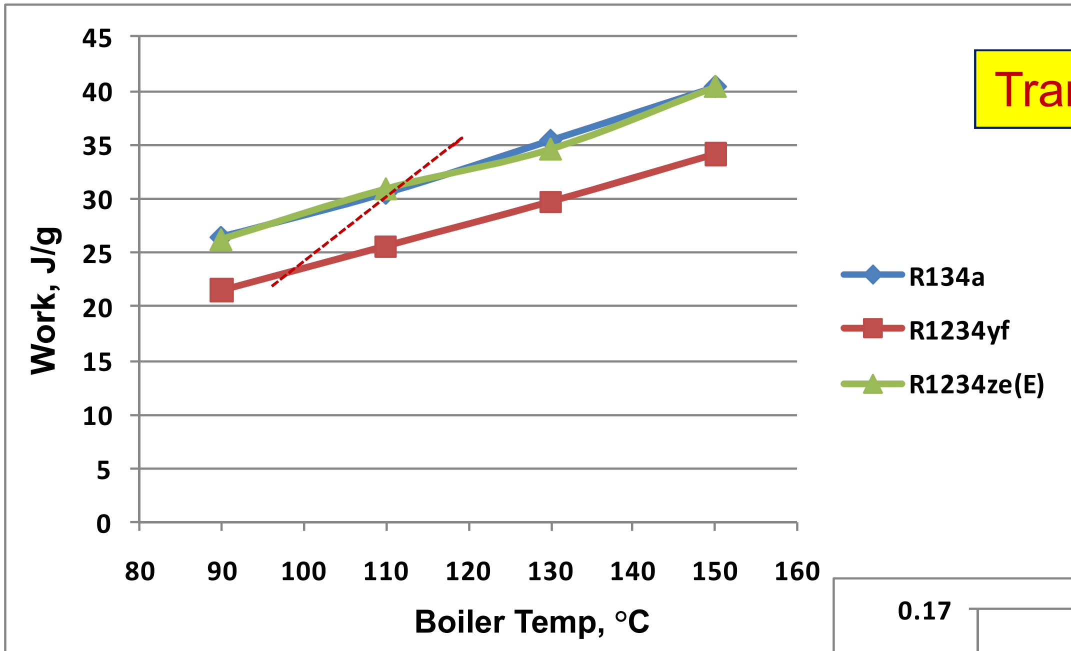
- HFO-1234yf, 110°C boiler temperature : Transcritical cycle optimized for best efficiency
- HFC-134a (90C, 110C boiler) , HFO-1234yf (90C boiler temperature), HFO-1234ze(E) (110C boiler)– boiler pressure lowered from saturation pressure to avoid 2-phase expansion

Comparable work and efficiency for HFO-1234ze vs. HFC-134a

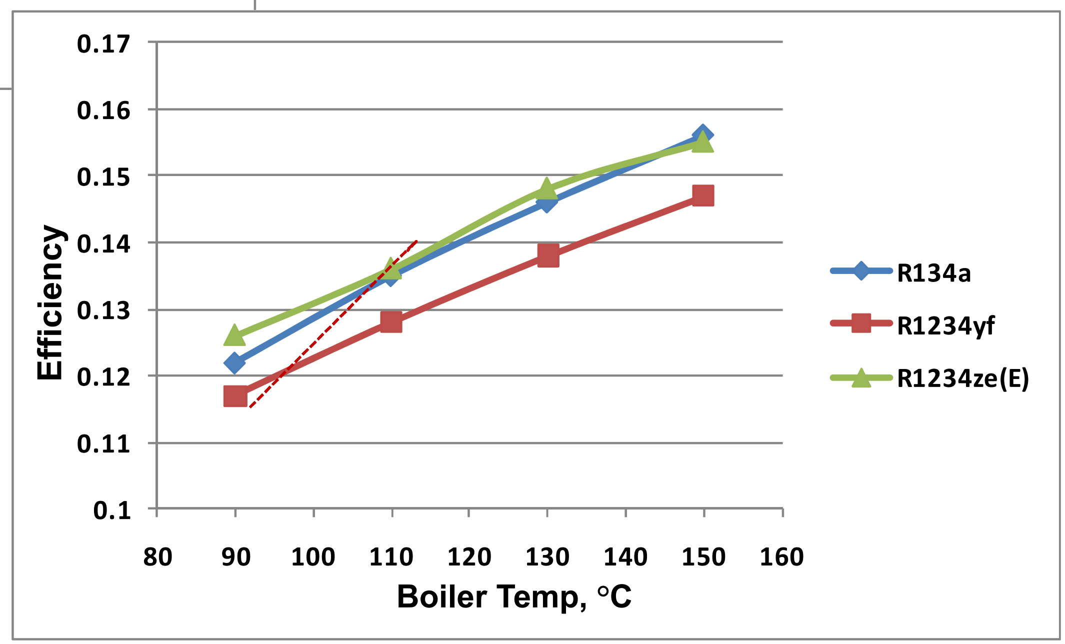
HFC-134a, HFO-1234yf, HFO-1234ze(E)

Work Output and Efficiency vs. Boiler Temperature

Honeywell



Transition from subcritical to trans-critical



HFC-134a, HFO-1234yf, HFO-1234ze(E)

Turbine Impeller Diameter Comparison

Honeywell

	Boiler Temp, °C		90.0	Boiler Temp, °C		110.0
Expander Sizing	R134a	1234yf	1234ze(E)	R134a	1234yf	1234ze(E)
Work Input, kJ/s	5000	5000	5000	5000	5000	5000
Pressure Ratio	6.48	6.00	7.26	8.51	7.72	9.00
Vol Flow, m^3/s	1.05	1.08	1.37	1.03	1.06	1.34
Head, m	4025	3390	4031	4937	4212	4856
Impeller Speed rpm ($n_s = 0.7$)	18296	15803	16021	21451	18815	18598
Mach #	1.89	1.85	1.96	2.05	2.00	2.08
Impeller Diameter m ($d_s = 4$)	0.290	0.309	0.332	0.274	0.289	0.314

Turbine diameter $D = d_s Q^{0.5} / H^{0.25}$ Assume a specific diameter of 4 (Balje Diagram)
Q is the volumetric flow rate (m^3/s)
H is head (m^2/s^2)
d_s is specific diameter (dimensionless)

Head is determined from the equation $PR=[1+(\gamma-1) H/ a^2]^{\gamma/\gamma-1}$

PR is the turbine pressure ratio (dimensionless)
γ is the isentropic exponent (*dimensionless)
*for an ideal gas = heat capacity at constant pressure /heat capacity at constant volume, Cp/Cv
a is the speed of sound in the particular working fluid (m/s)

Speed $N = n_s H^{0.75} Q^{-0.5}$
n_s is specific speed (dimensionless)

Joost Brasz and Patrick Lawless, Design, Analysis and Applications of Centrifugal Compressors, Short Course, Purdue University, July 10-11, 2004.

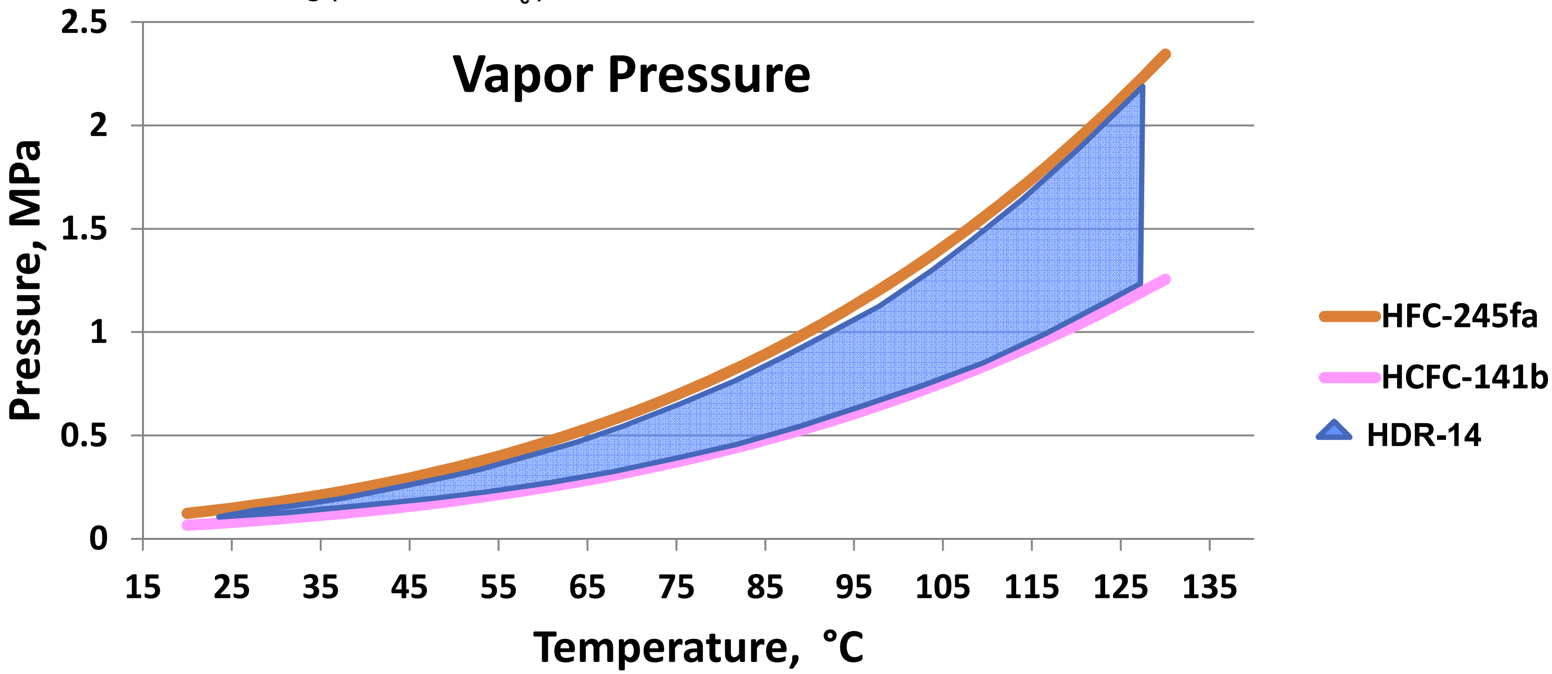
HFO-1234ze bumps up dividing line between low boilers and RT boilers

Comparison of HFC-245fa & Honeywell's Replacement Candidate

Physical Properties

Honeywell

	HFC-245fa*	HDR-14
Boiling Point, T_b	15° C	15° C < >32° C (HCFC-141b)
Critical Point, T_c	154° C	Higher than HFC-245fa
P_{vap}, MPa (25° C)	0.148	Lower than HFC-245fa
P_{vap}, MPa (120° C)	1.93	Lower than HFC-245fa
Liquid Density, kg/m³ (25° C)	1094	Higher than HFC-245fa
Vapor Density, kg/m³ (25° C)	37.6	Lower than HFC-245fa
Latent Heat, kJ/kg (10° C below T_c)	69.3	74.7



Replacement candidate has higher boiling point & T_c

*HFC-245fa properties from NIST Refprop 8.0

HFC-245fa and Honeywell's Replacement Candidate

ORC Cycle Comparison

Honeywell

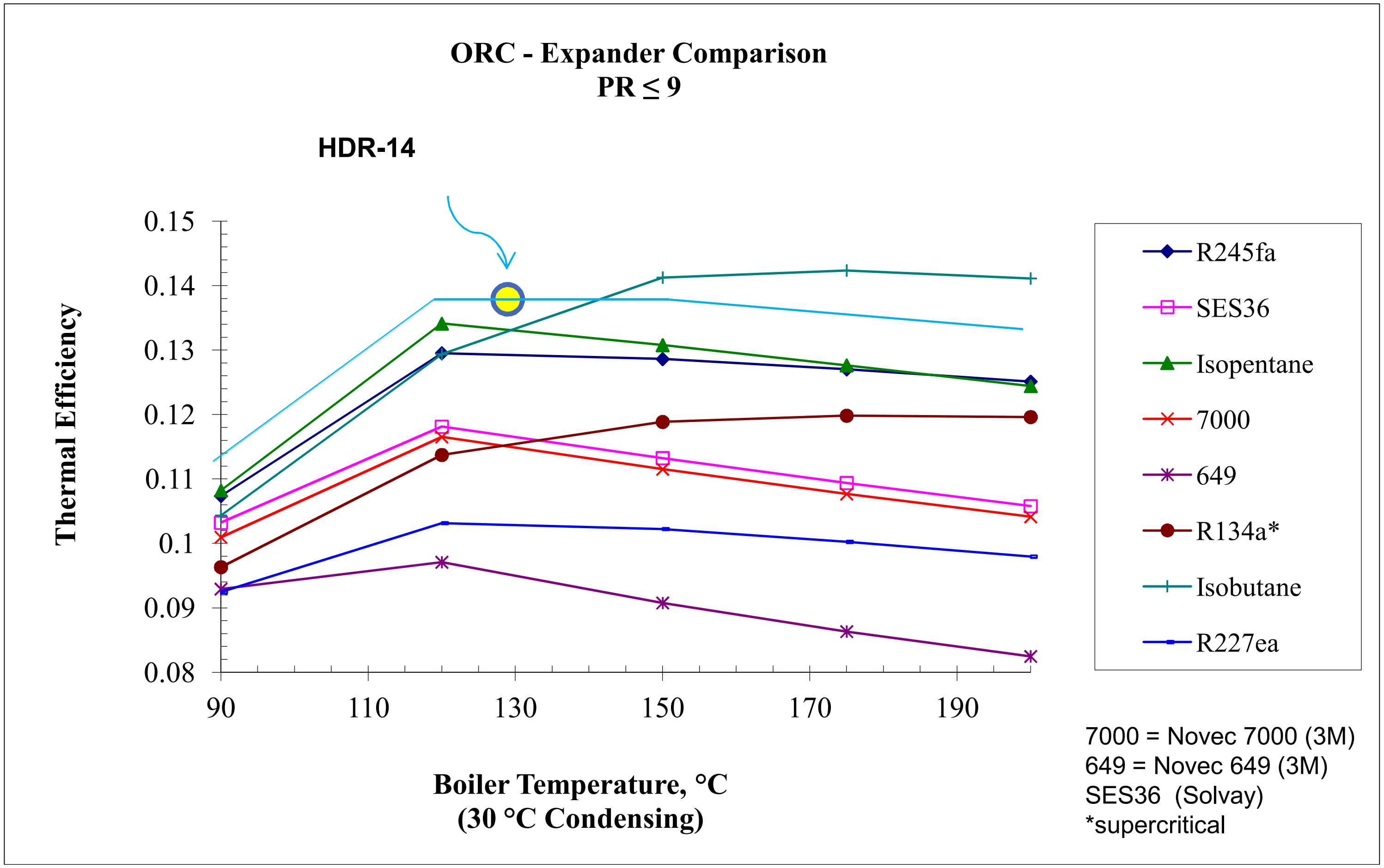
Boiler Temp, °C	130.0
Cond Temp, °C	25.0
Volume Flow Expander Exit, cm3/s	10.0

Fluid	R-245fa	HDR-14
Thermal Efficiency	0.129	0.136
Efficiency, relative to R245fa	1.0	1.05
Net Work, J/gm	-35.8	-36.6
Work relative to R245fa	1.0	1.02
Net Work, J/s	-2.5	-2.2
Work relative to R245fa	1.0	0.88
Expander Exit Vapor Den, gm/cm3	0.007	0.006
Mass Flow, gm/s	0.07	0.06
Mass Flow, relative to R245fa	1.0	0.86
Q Boiler, J/gm	277.4	270.2
Q Boiler, relative to R245fa	1.0	0.97
Superheat in Boiler, °C	27.6	25.8

Replacement candidate efficiency & work output favorable

Thermal Efficiency – A Broader Comparison

Honeywell



HDR-14 Thermodynamic Efficiencies Higher Than A Number of Known Working Fluids

HFC-245fa & Replacement Candidate

ORC Turbine Impeller Diameter Comparison

Honeywell

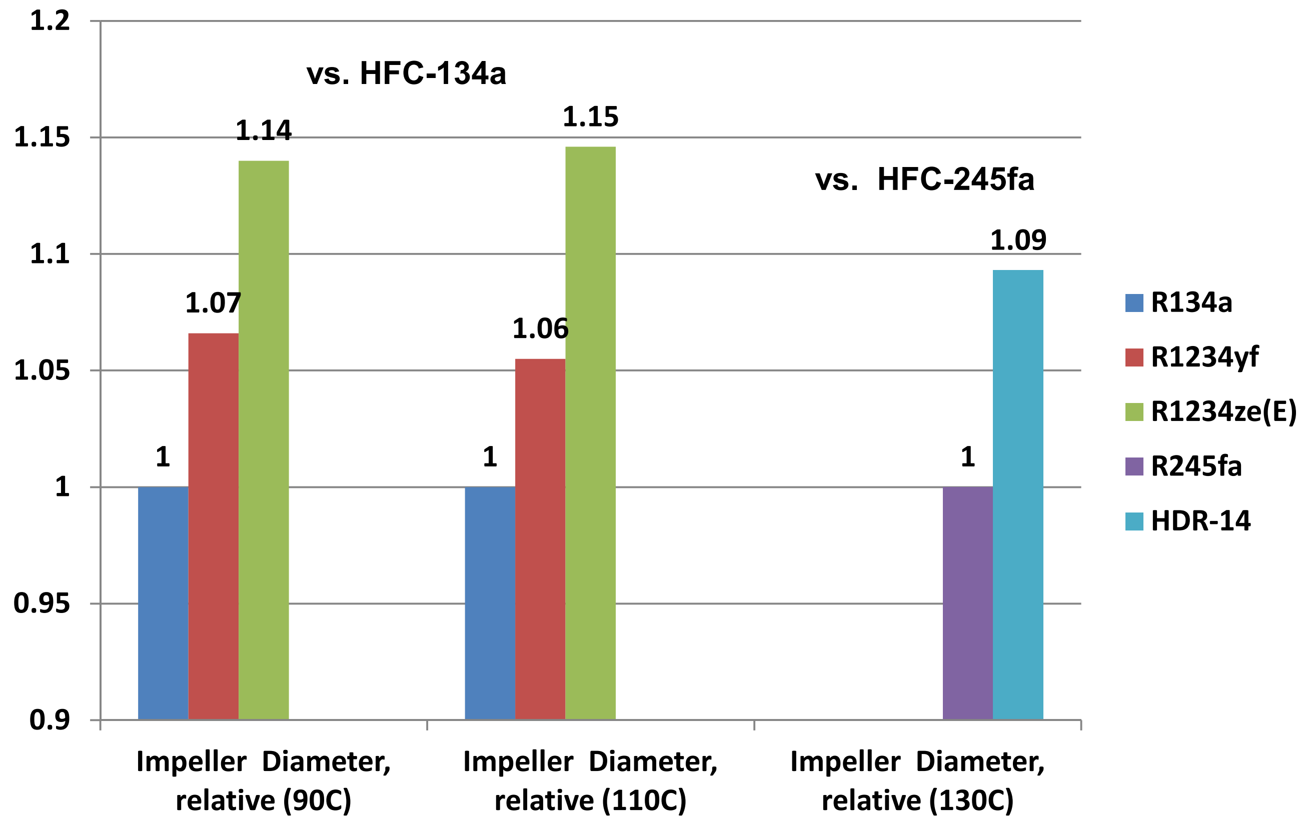
Boiler Temp, °C	130.0
Cond Temp, °C	25.0
Volume Flow Expander Exit, cm3/s	10.0

Expander Sizing	HFC-245fa	HDR-14
Work Input, kJ/s	5000	5000
Pressure Ratio	9.00	9.00
Vol Flow, m3/s	2.57	3.11
Head, m	5000	5108
Impeller Speed rpm (ns = 0.7)	13734	12701
Mach #	2.08	2.08
Impeller Diameter m (ds = 4)	0.431	0.471

HDDR-14 Requires Larger Wheel to Maintain Comparable Volumetric Flow at Expander Exit

ORC Turbine Impeller Sizing Comparison

Honeywell



Conclusions

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- **A low global warming replacement for HFC-245fa in ORC is on the near horizon.**
  - **HDR-14**
    - **Higher thermodynamic efficiency in ORC cycle**
    - **Comparable work output / unit mass circulated**
    - **Non-flammable**

- **Low global warming fluids are available to replace R-134a in ORC**
  - **HFO-1234ze(E)**
    - **Higher boiling point and critical temperature than R-134a**
    - **Comparable thermodynamic efficiency**
    - **Comparable work output / unit mass circulated**

- **Preliminary assessment of Honeywell replacements for 245fa and 134a in ORC is promising; additional testing required to substantiate findings**

- **GWP of HFO-1234yf, HFO-1234ze(E) and HDR-14 are comparable to hydrocarbons**

Keep up to date. Visit www.Honeywell-ORC.com

THANK YOU!

Questions?

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