

**Zero-ODP, Lower GWP,
Non-Flammable Refrigerants for
Marine Applications:
R-452A, R-449A, R-513A, R-1336mzz(Z)
for improved sustainability and energy savings**

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DuPont Fluorochemicals

Athens, Greece

May 23rd, 2015



The miracles of science™



Cooling, Heating & Power Generation: On-Board & On-Shore Applications

- Refrigeration
- Air Conditioning
- Water Heating/Steam Generation
- Mechanical or Electrical Power Generation

Cooling, Heating & Power Generation: On-Board & On-Shore Applications

- Refrigeration
- Air Conditioning
- **Water Heating/Steam Generation**
- **Power Generation**

From Low Temperature Waste Heat?

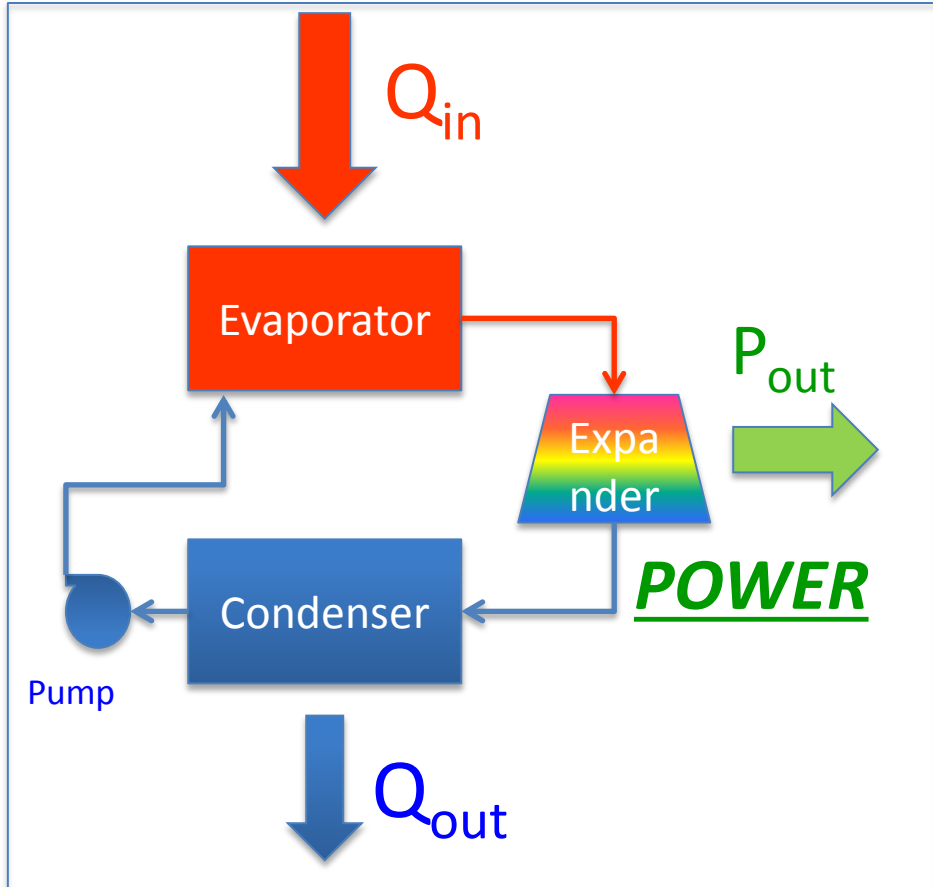


Cooling, Heating & Power Generation: On-Board & On-Shore Applications

- Refrigeration
- Air Conditioning
- Water Heating/Steam Generation
- Power Generation

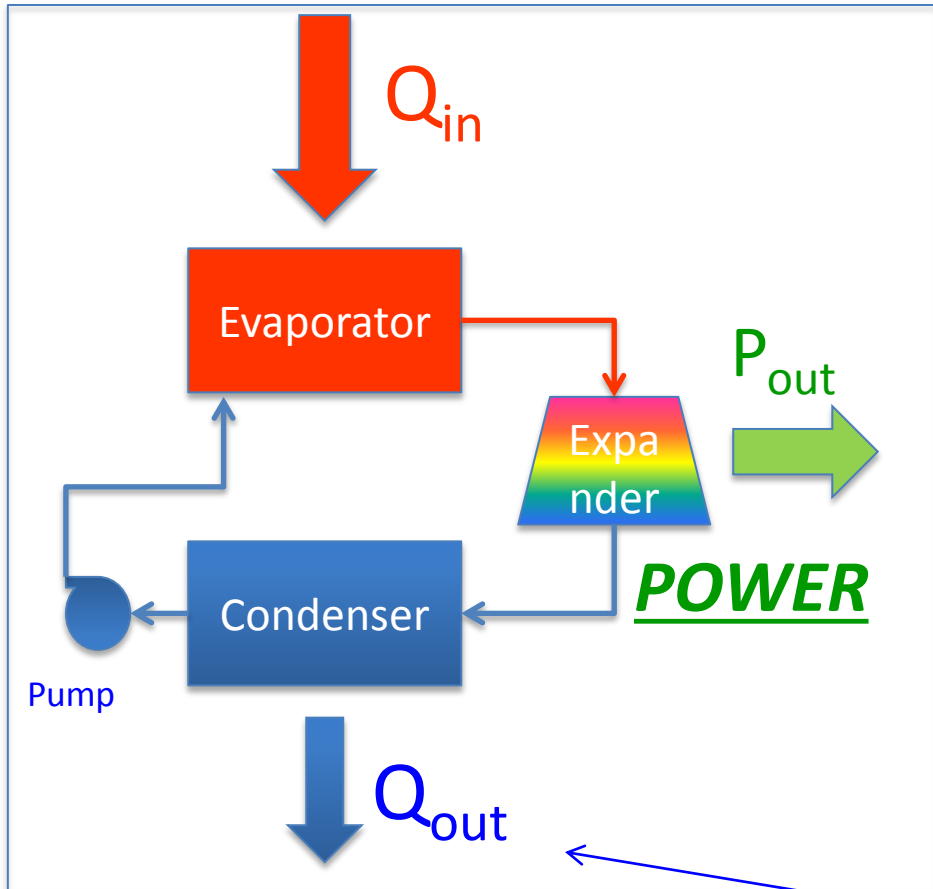
HIGH ENERGY USE
HIGH ENVIRONMENTAL IMPACT
(including CO₂ & Refrigerant Emissions)

The Rankine Cycle



Organic Rankine Cycle (ORC)

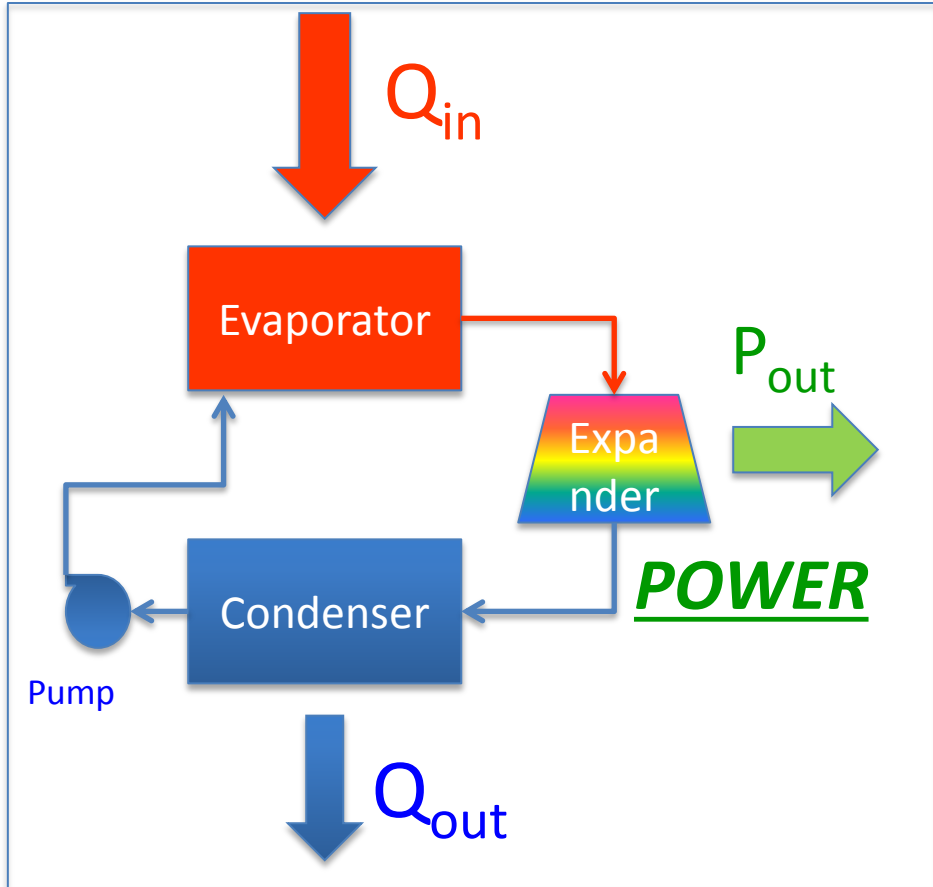
The Rankine Cycle



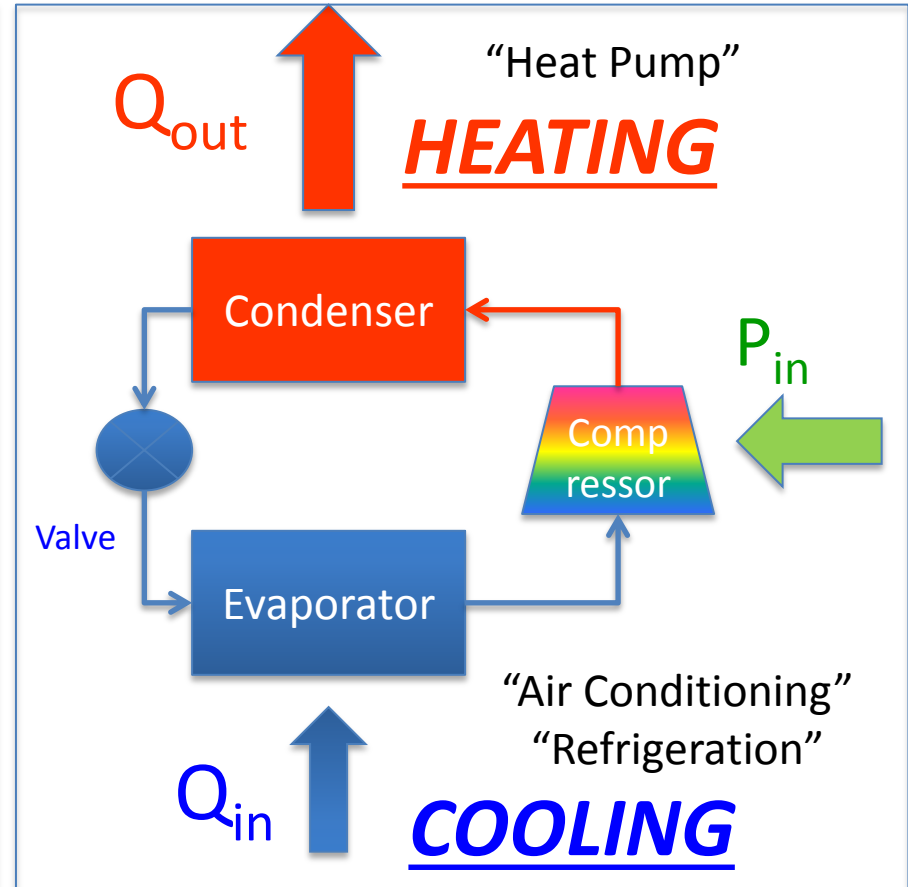
Organic Rankine Cycle (ORC)

Reject Heat to Sea Water

The Rankine Cycle

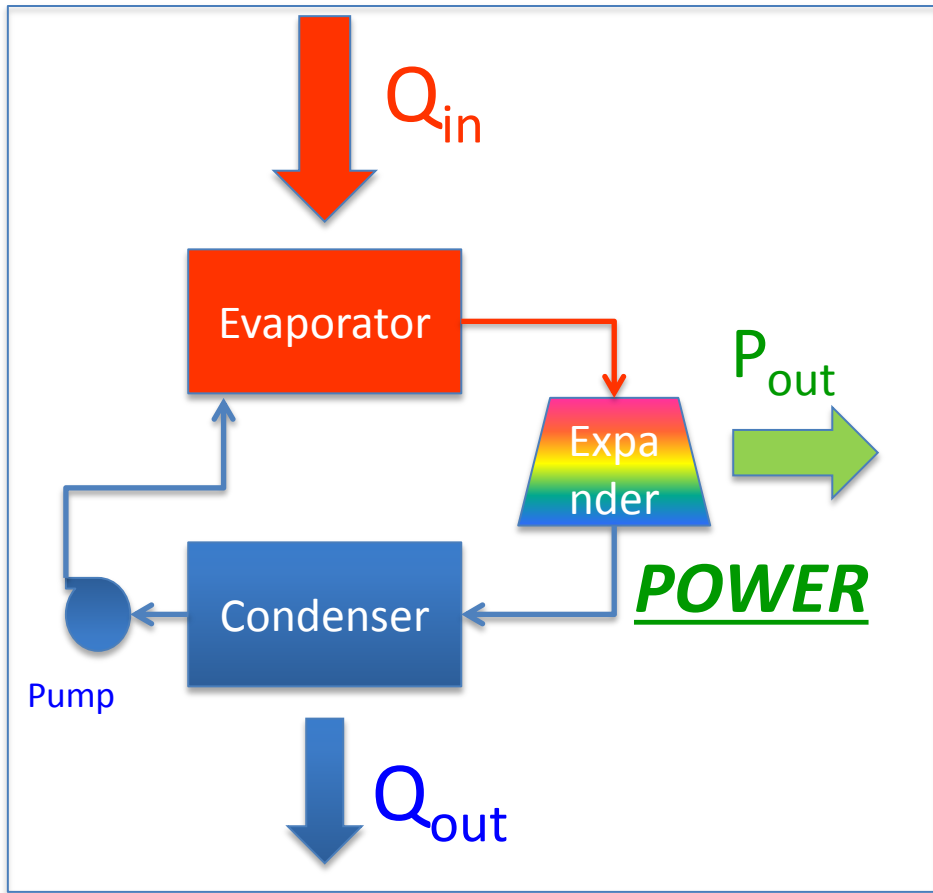


Organic Rankine Cycle (ORC)

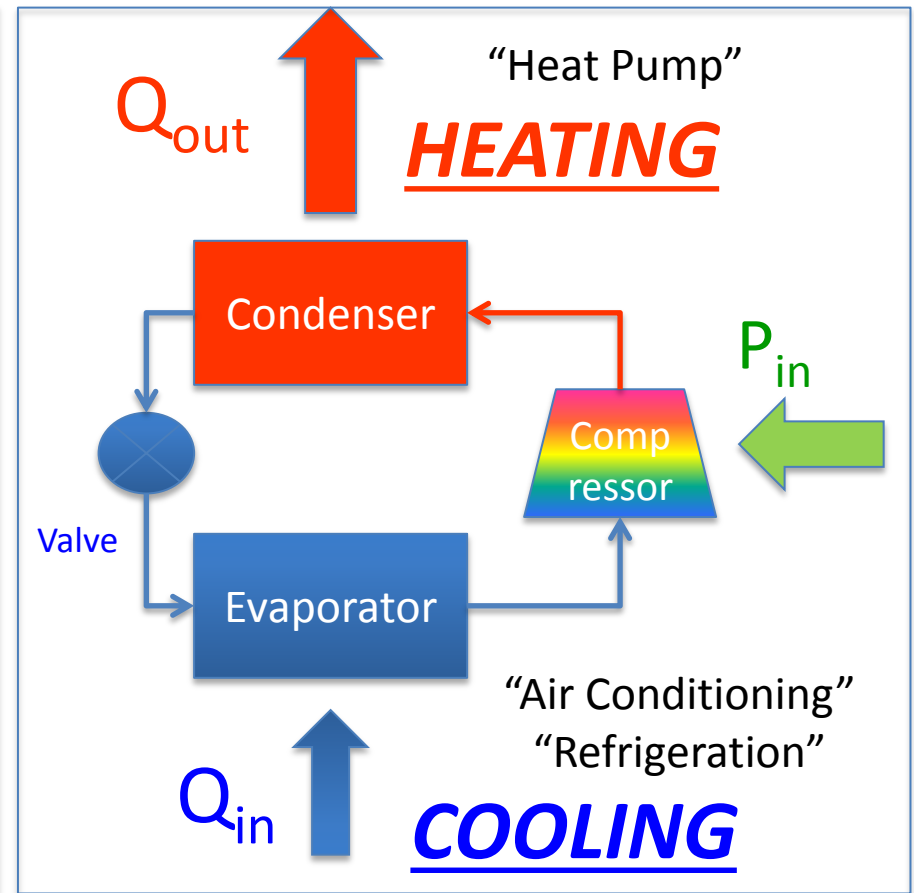


Reverse Rankine Cycle

The Rankine Cycle



Organic Rankine Cycle (ORC)



Reverse Rankine Cycle

Working Fluid?

Working Fluids Requirements

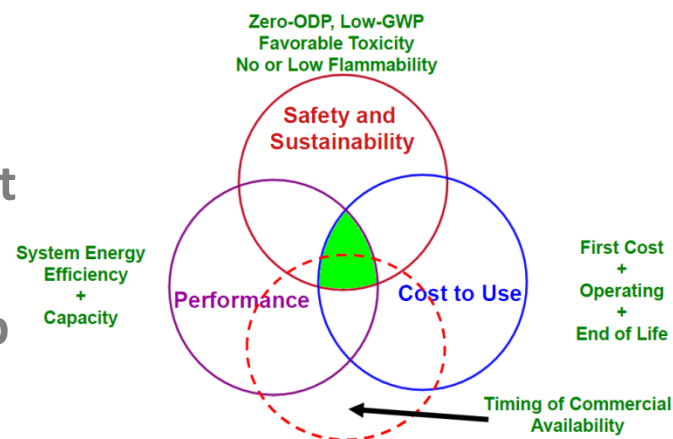
- ✓ High energy efficiency
- ✓ High volumetric capacity for cooling, heating or power generation
- ✓ Low or no temperature glide
- ✓ Low toxicity
- ✓ Low or no flammability
- ✓ High chemical and thermal stability
- ✓ Compatibility with commercially available lubricants
- ✓ Compatibility with common materials 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 fluid cost and low total cost of ownership
- ✓ **AND LOW GLOBAL WARMING IMPACT**

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- ✓ **AND LOW GLOBAL WARMING IMPACT**

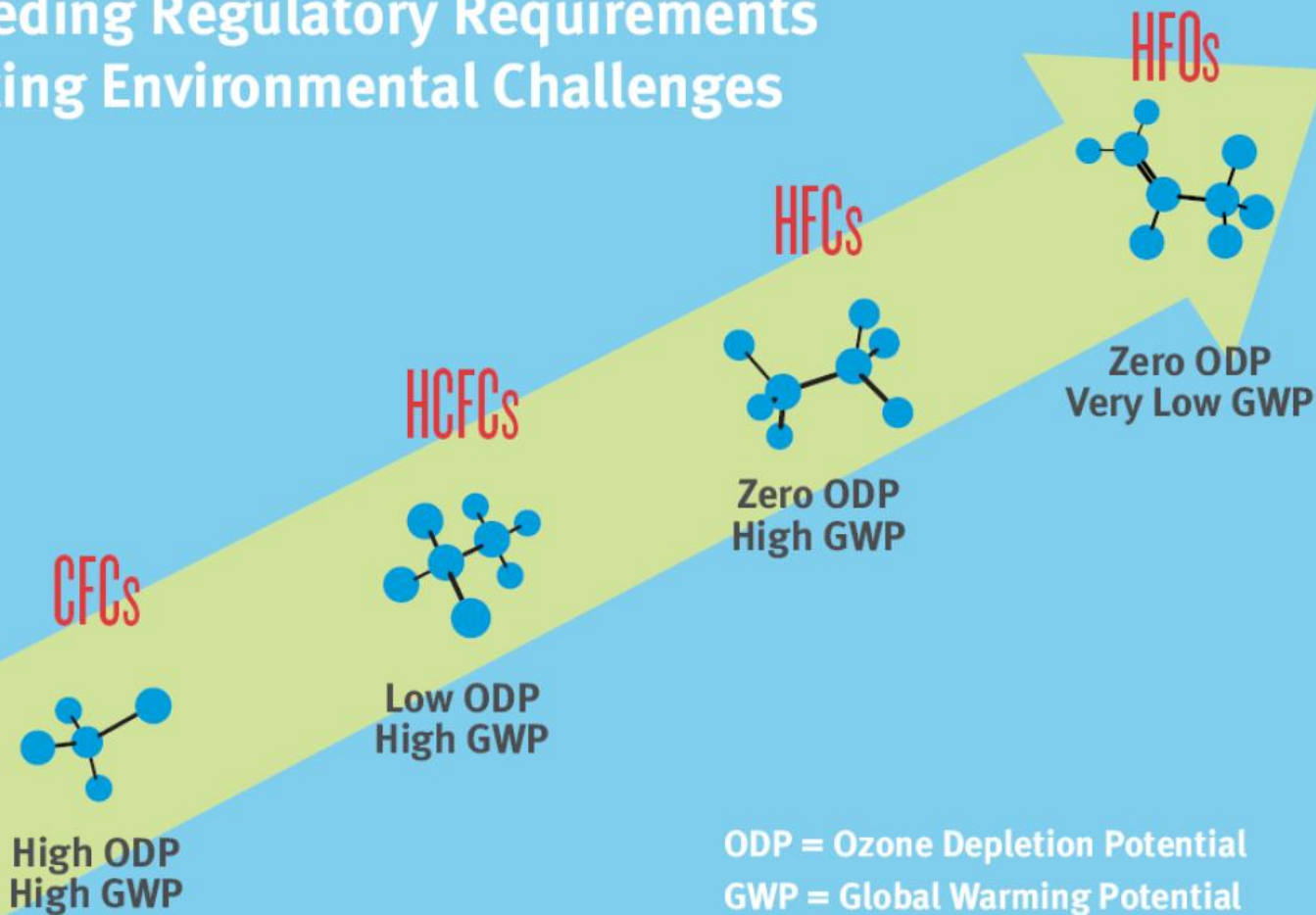
**Threading
The
Needle!**

Optimal Balance of Properties for Each App

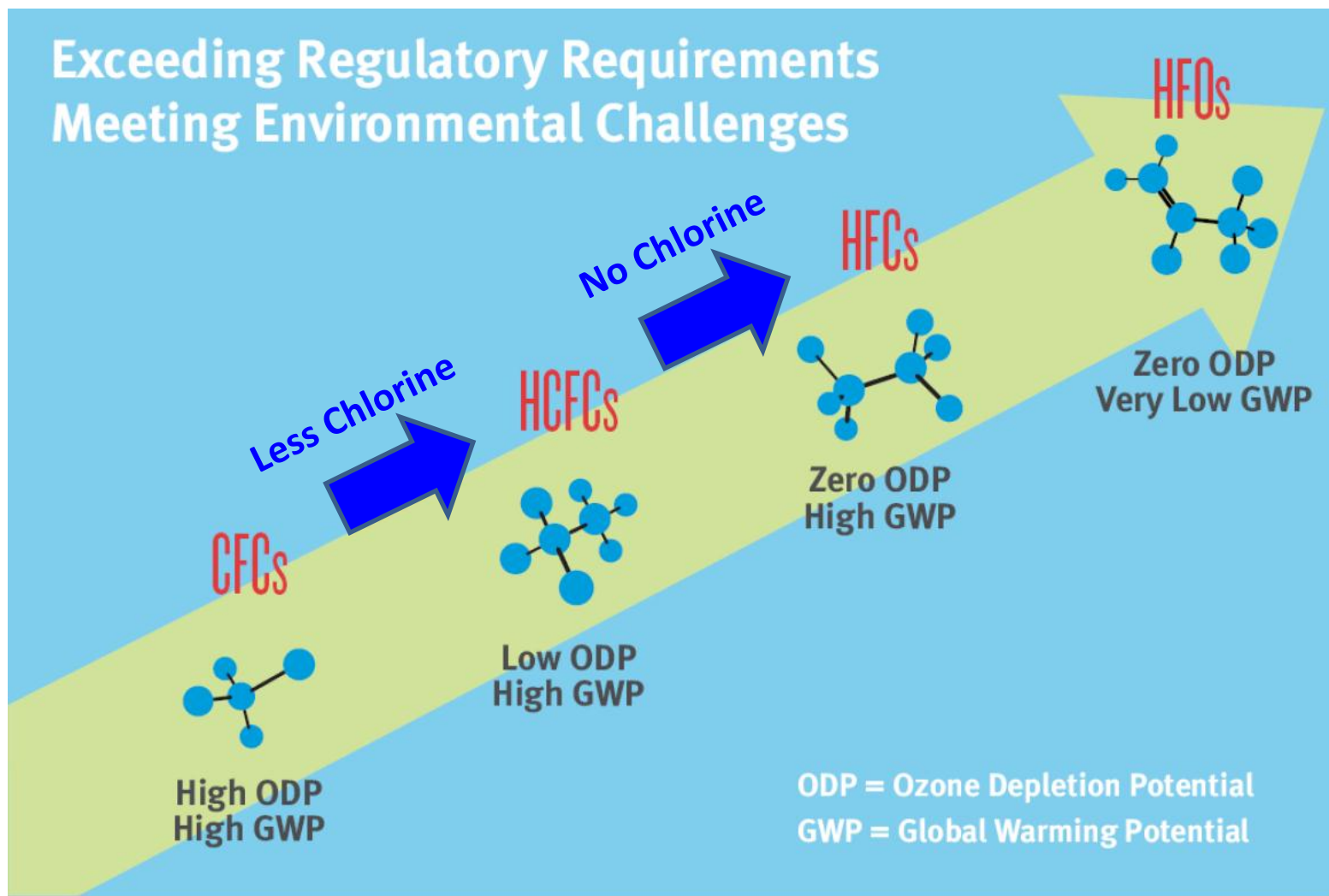


Working Fluids Transitions

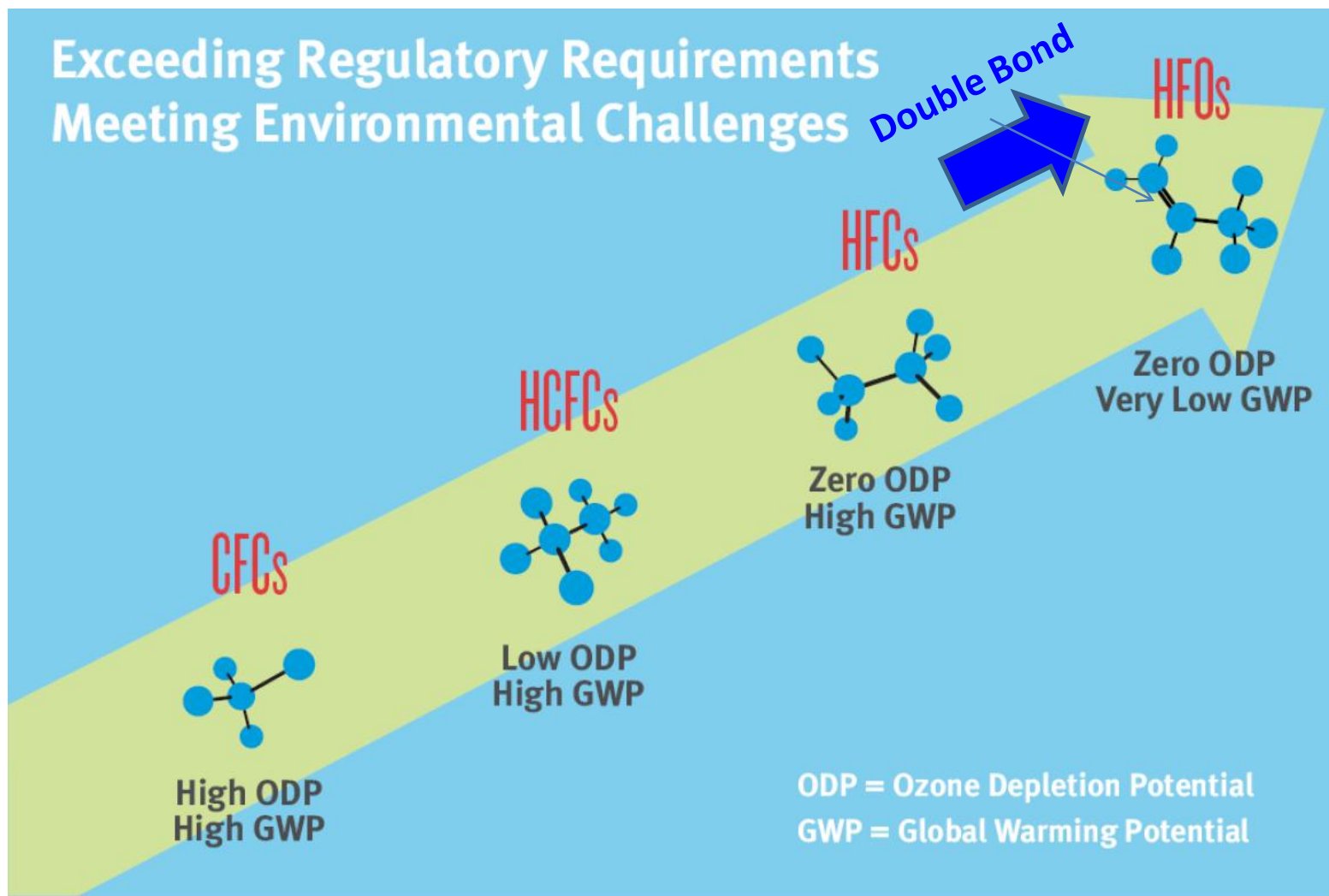
Exceeding Regulatory Requirements
Meeting Environmental Challenges



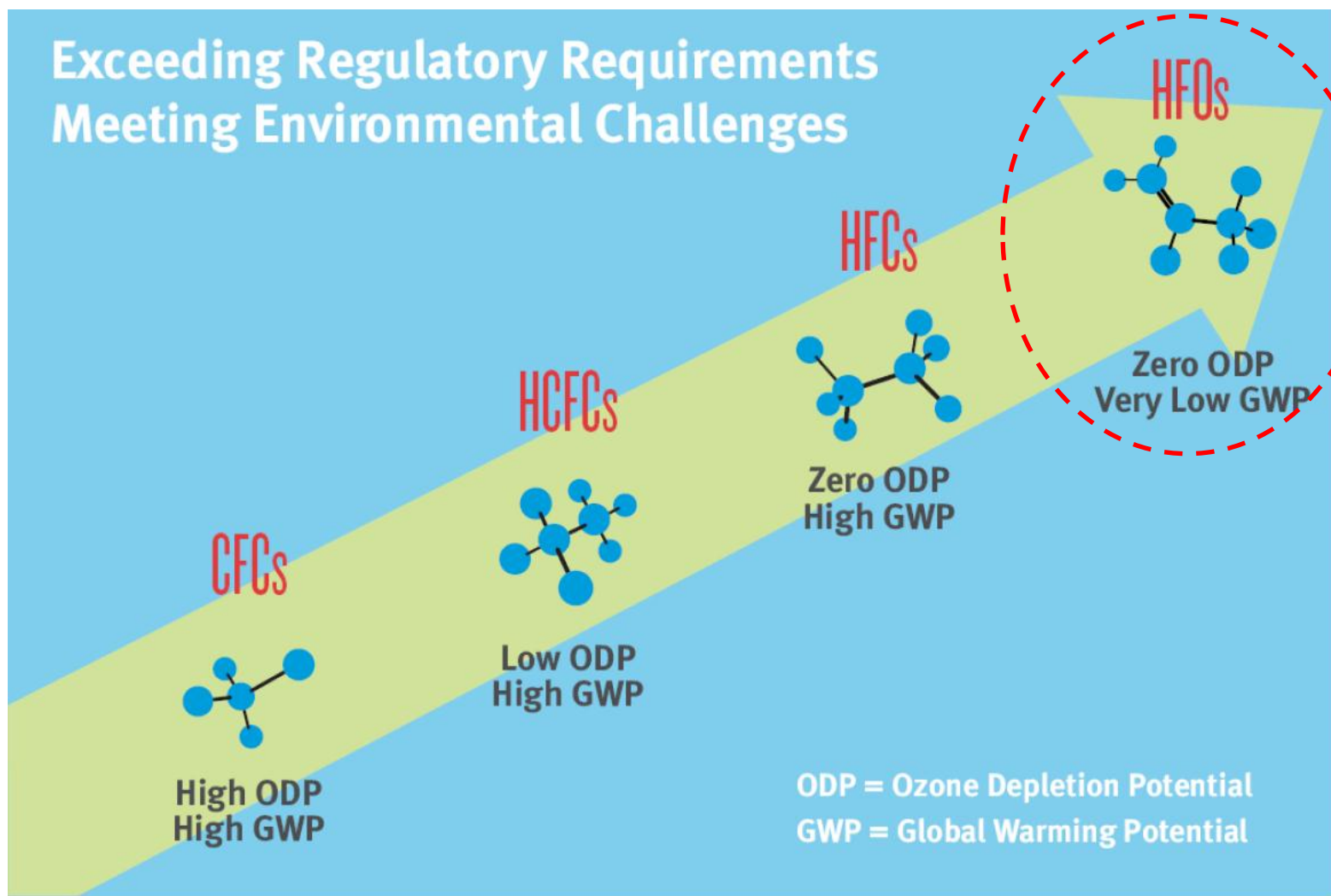
Working Fluids Transitions



Working Fluids Transitions



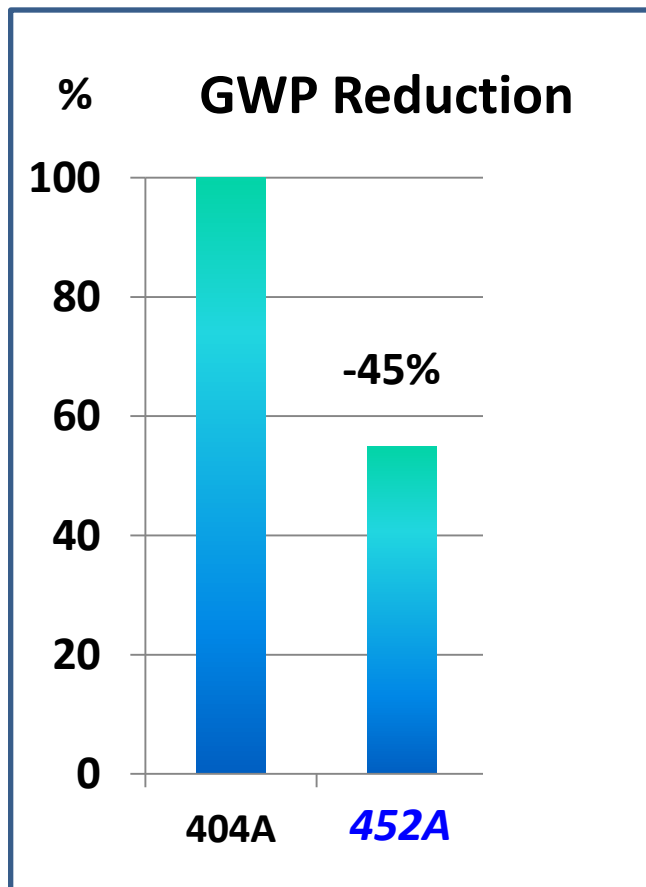
Hydro-Fluoro-Olefins (HFOs)



Next: HFO-Based Fluids for Current and Emerging Applications

Transport Refrigeration: Lower GWP Replacements for R-404A

R-404A GWP=3922



R-452A (GWP=2140)

(HFO-1234yf/HFC-32/HFC-125)

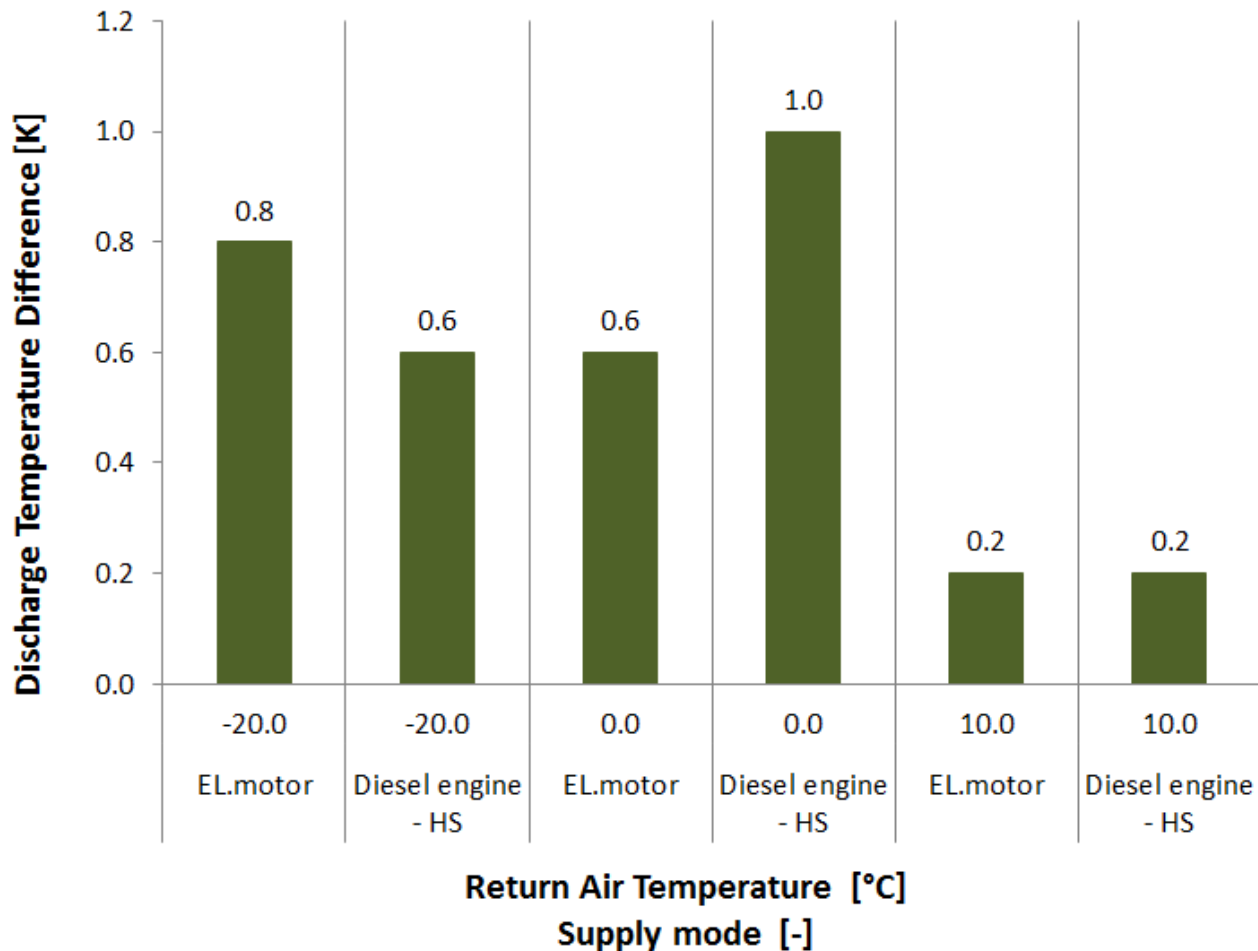
- Close performance with 45% lower GWP than R-404A
- Nonflammable**; ideal for marine transport refrigeration
- New and retrofit with no equipment or oil change
- Energy Efficiency is comparable to R-404A

Compliance With F-Gas Regulation

R-452A for Truck & Trailer Refrigeration: Test Results

Minor & Gerstel - Chillventa, 2014

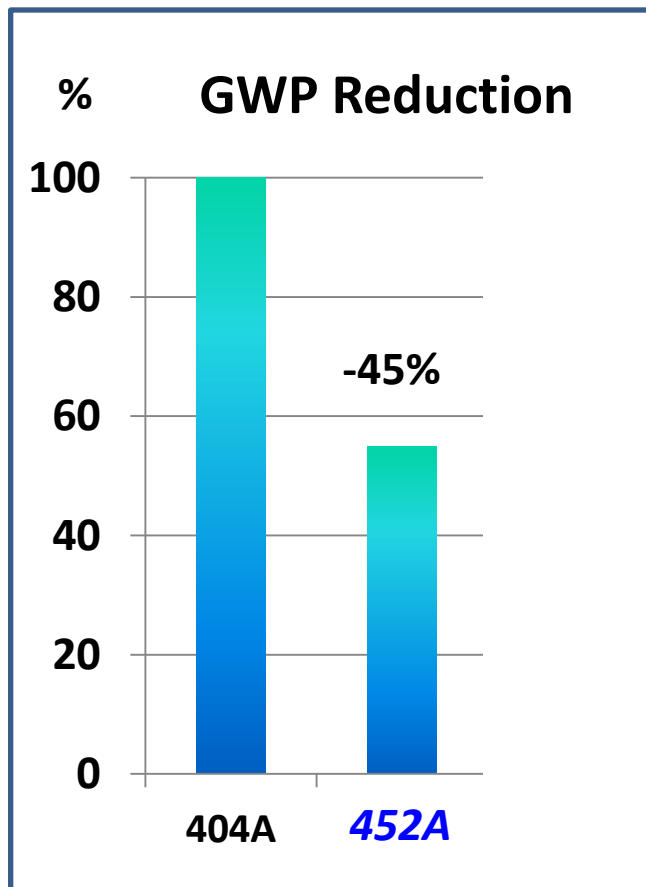
Compressor discharge temperature at ambient temperature 30 °C
(ATP conditions)



Compressor Discharge Temperature with R-452A within 1K vs. R-404A

Transport Refrigeration: Lower GWP Replacements for R-404A

R-404A GWP=3922



Compliance With F-Gas Regulation

R-452A (GWP=2140)

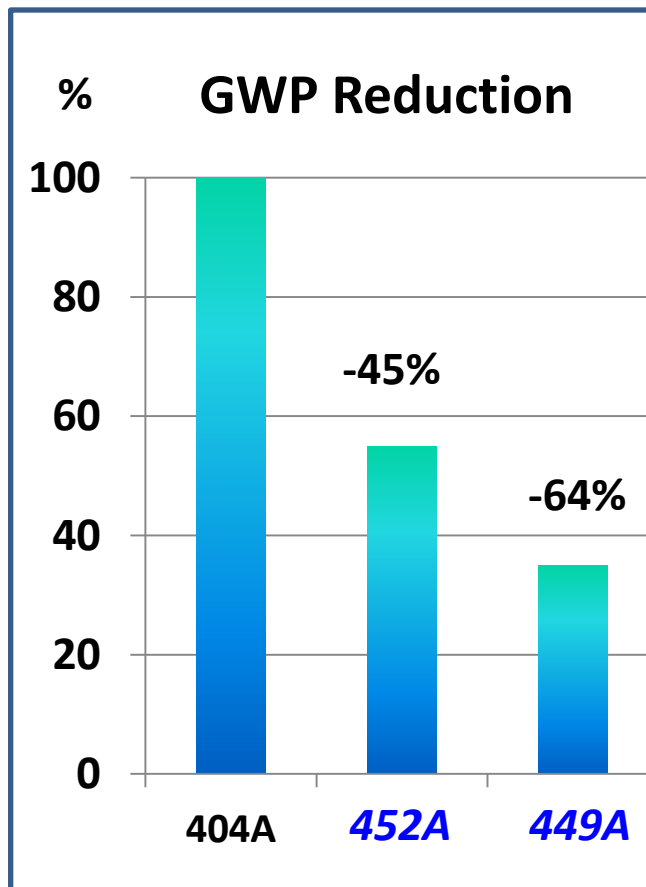
(HFO-1234yf/HFC-32/HFC-125)

- Close performance with 45% lower GWP than R-404A
- Nonflammable; ideal for transport refrigeration
- New and retrofit with no equipment or oil change
- Energy Efficiency is comparable to R-404A
- For use where lowest discharge temperature required

Refrigeration:

Lower GWP Replacements for R-404A

R-404A GWP=3922



R-449A (GWP=1397)

(HFO-1234yf/HFC-32/HFC-125/HFC-134a)

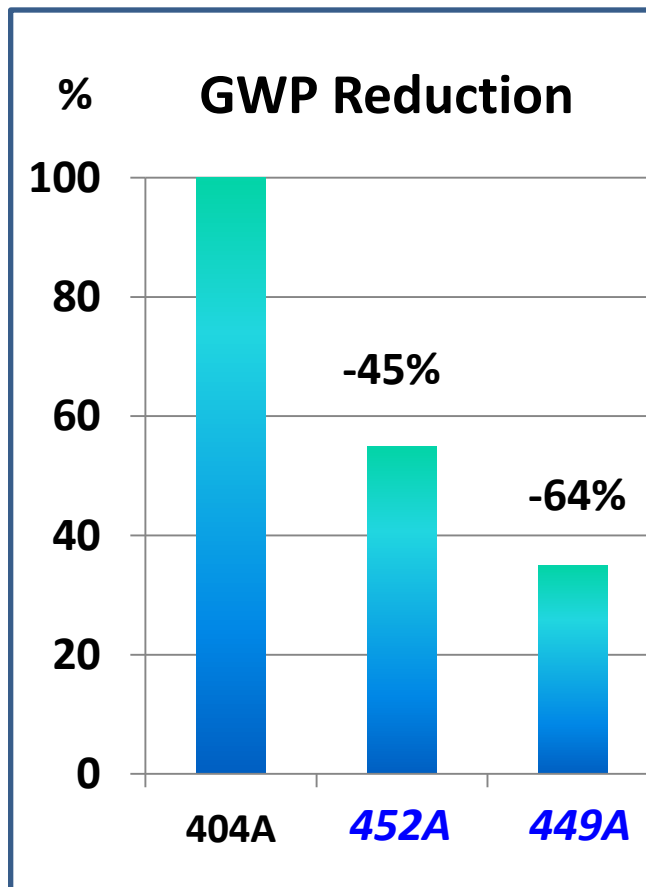
- Close performance with **64% lower GWP** than R-404A
- Nonflammable**; ideal for on-board applications
- New and retrofit with **no equipment or oil change**

Compliance With F-Gas Regulation

Refrigeration:

Lower GWP Replacements for R-404A

R-404A GWP=3922



R-449A (GWP=1397)

(HFO-1234yf/HFC-32/HFC-125/HFC-134a)

- Close performance with 64% lower GWP than R-404A
- Nonflammable; ideal for on-board applications
- New and retrofit with no equipment or oil change
- Potential energy efficiency benefit based on system tests: **8-12% MT** and **~3% LT**

Compliance With F-Gas Regulation

Chillers:

Lower GWP Replacement for HFC-134a

	R-134a	R-513A
Chemical Formula	CF ₃ CH ₂ F	HFC-134a/HFO-1234yf (44/56 wt%)
GWP (100 yr) AR4 (AR5)	1430 (1300)	631 (573)
Boiling Point °C	-26.1	-29.2
Critical Point °C	101	97
Temp Glide (K)	0	0 (Azeotrope)
Tox/Flamm	A1	A1

R-513A: Near Drop-In Replacement for HFC-134a in Chillers

Kontomaris et. al, HVAC & R Research, Vol. 19, Issue 7, 857-864, 2013

R-513A:

Lower GWP Replacement for HFC-134a

	R-134a	R-513A
Chemical Formula	CF ₃ CH ₂ F	HFC-134a/HFO-1234yf (44/56 wt%)
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Boiling Point °C	-26.1	-29.2
Critical Point °C	101	97
Temp Glide (K)	0	0 (Azeotrope)
Tox/Flamm	A1	A1

Also for Refrigeration!

Improve Fuel Efficiency to Reduce:

➤ **Fuel Costs**

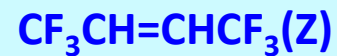
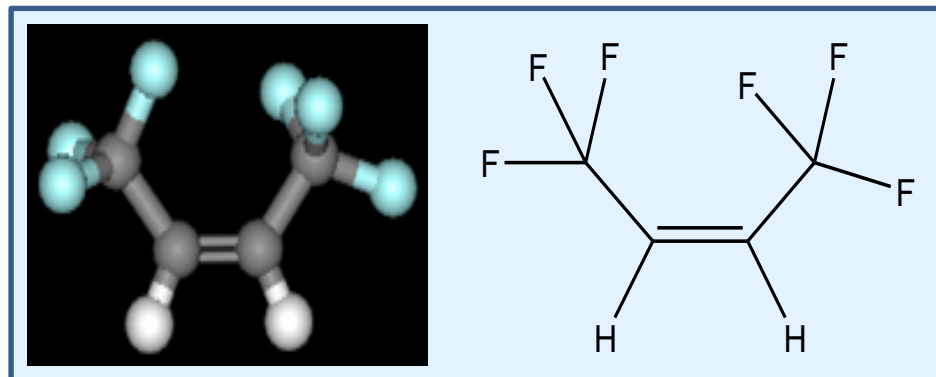
➤ **Environmental Impact**

**Power from Engine Waste Heat:
R-1336mzz(Z)**

Novel Working Fluid: HFO-1336mzz(Z)

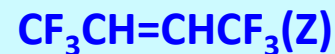
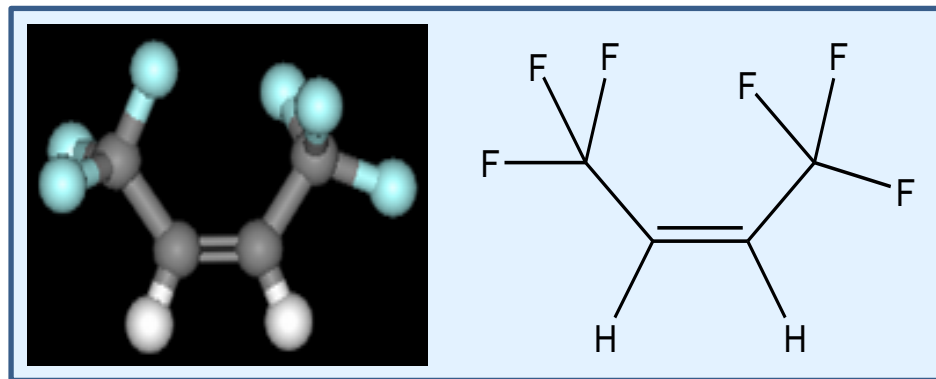
Chemical Formula

**HFO-
1336mzz(Z)**



Novel Working Fluid: HFO-1336mzz(Z)

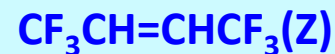
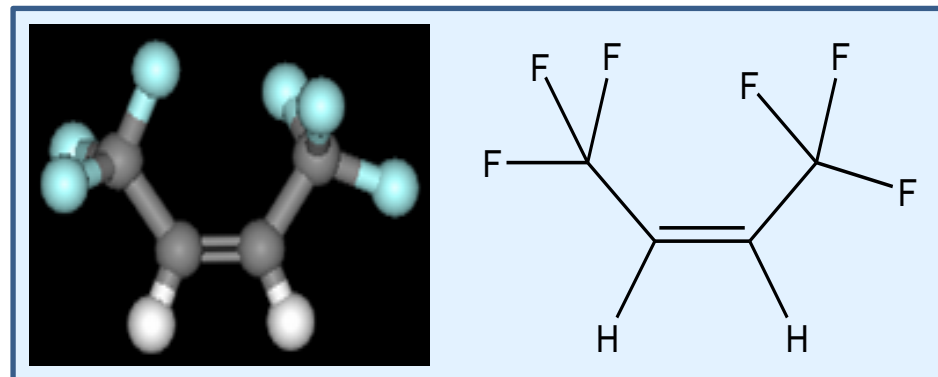
Chemical Formula	HFO-1336mzz(Z)
OEL [ppm]	500
Flammability	Non-Flam
ODP	None
GWP ₁₀₀	2
T _{cr} [°C]	171.3
P _{cr} [MPa]	2.90
T _b [°C]	33.4



R-1336mzz(Z) recommended for a safety classification of A1 (low toxicity, no flammability) with an OEL of 500 ppm by ASHRAE Standing Standard Project Committee 34, pending public review

Novel Working Fluid: HFO-1336mzz(Z)

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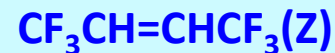
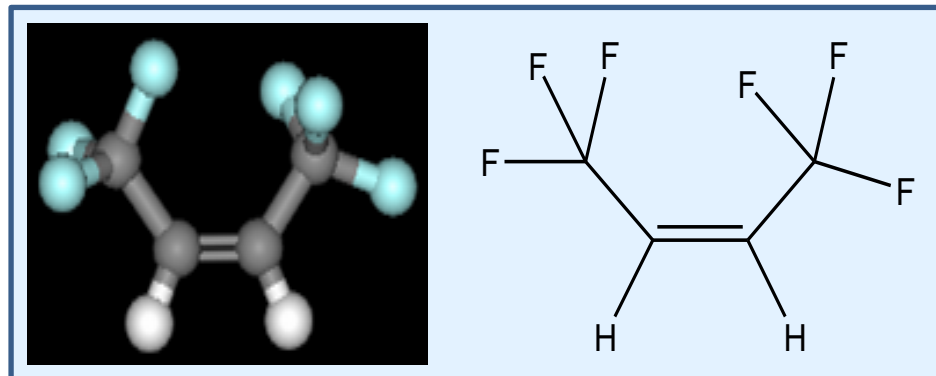


**Very Low GWP
And
Non-Flammable**

Novel Working Fluid: HFO-1336mzz(Z)

Chemical Formula

**HFO-
1336mzz(Z)**



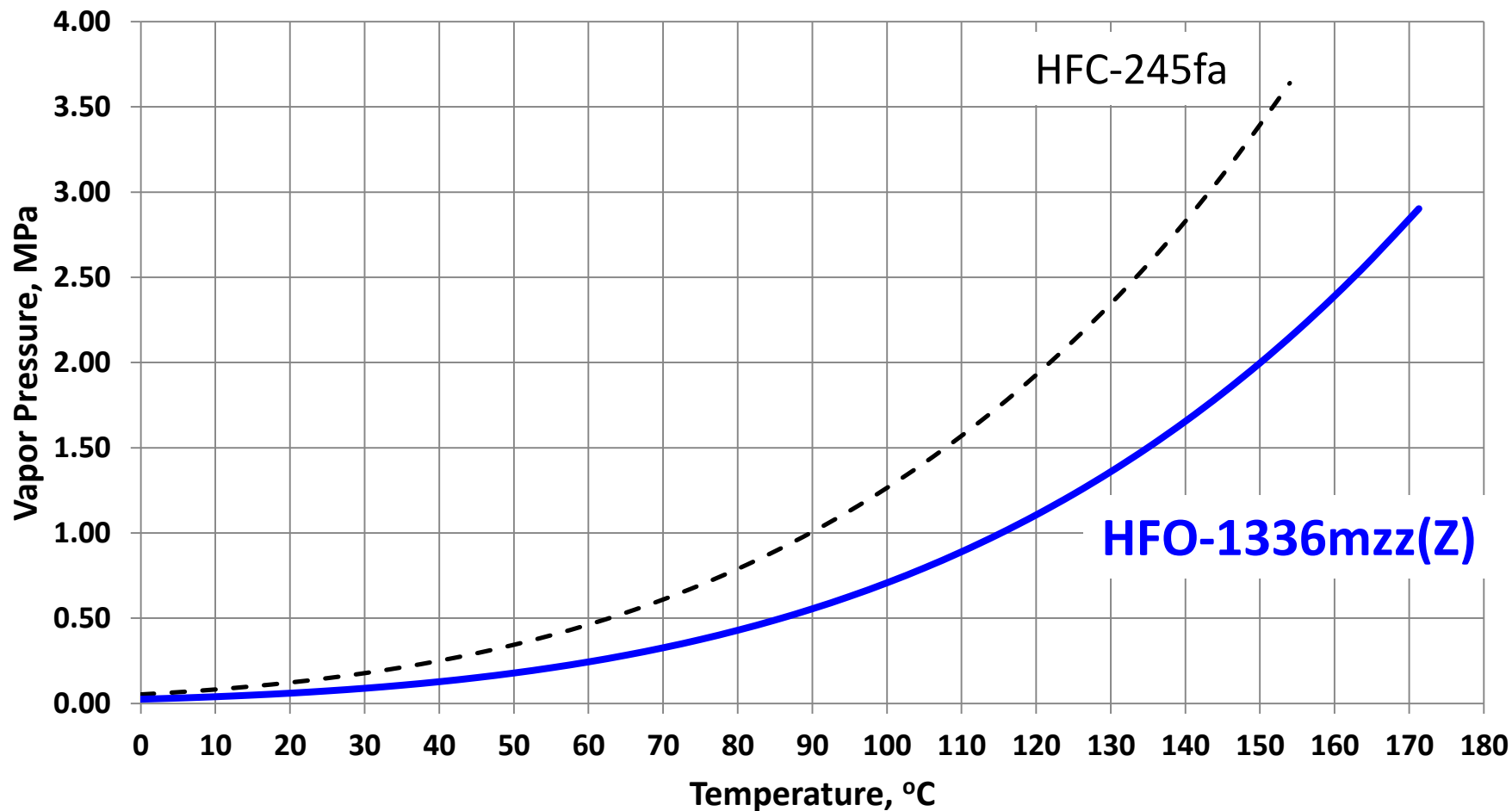
No Chlorine:
**Dramatically Increased Chemical Stability to
Various Transformation Mechanisms at High Temps¹**

¹Kontomaris, K.: 15th Inter. Refrig. & Air Cond. Conf. at Purdue, West Lafayette, IN, USA, July 14-17, 2014.

Reference Fluid: HFC-245fa

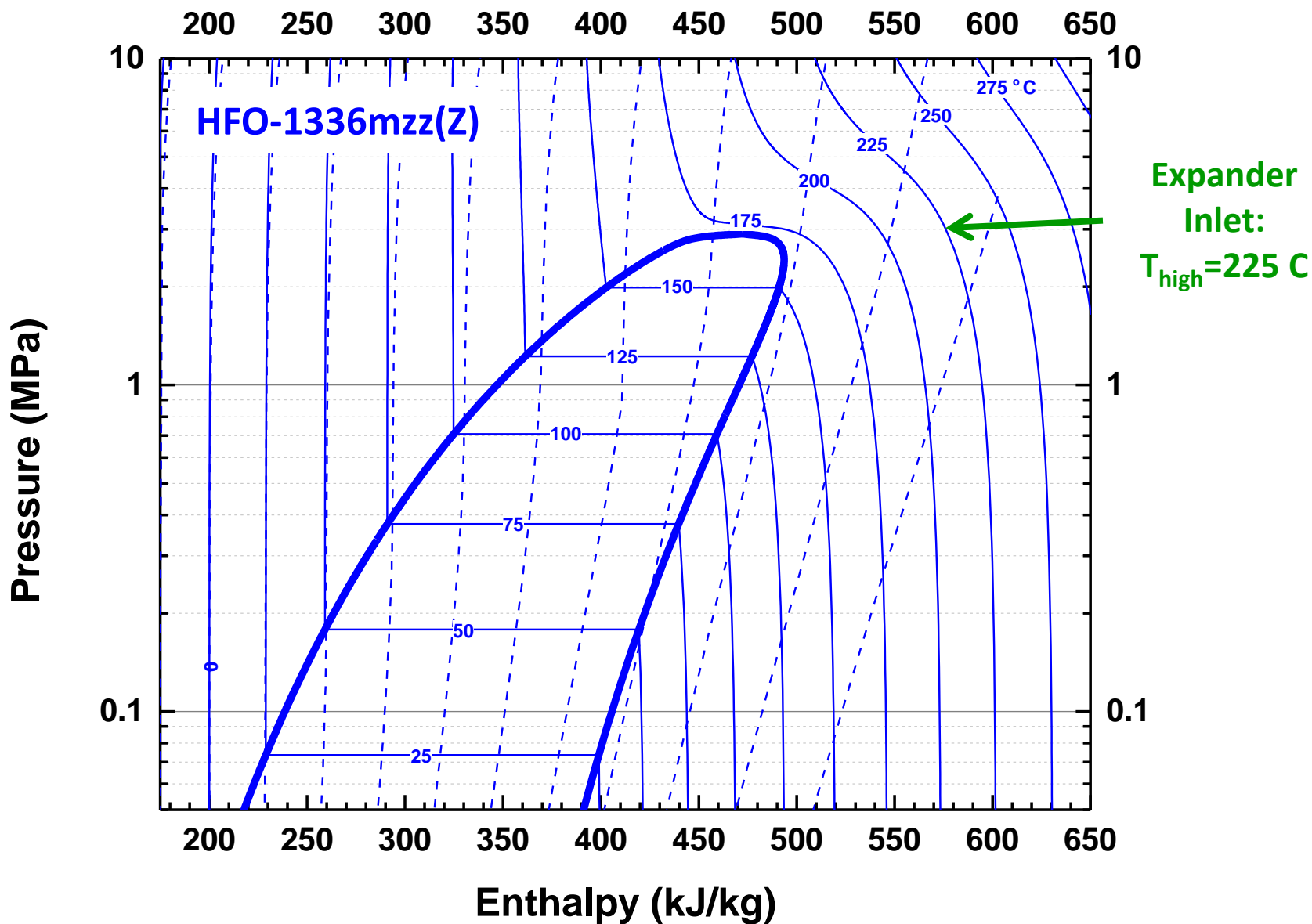
	HFC-245fa	HFO-1336mzz(Z)
Chemical Formula	$\text{CF}_3\text{CH}_2\text{CHF}_2$	$\text{cis-CF}_3\text{CH=CHCF}_3$
OEL/AEL [ppm]	300	500
Flammability	Non-Flam	Non-Flam
ASHRAE Std 34 Safety Class	B1	A1
ODP	None	None
GWP_{100}	858	2
ALT [yrs]	7.7	0.060274 (22 days)
T_{cr} [°C]	154	171.3
P_{cr} [MPa]	3.65	2.90
T_{b} [°C]	15.1	33.4
T_{freez} [°C]	-107	-90.5

HFO-1336mzz(Z): Vapor Pressure

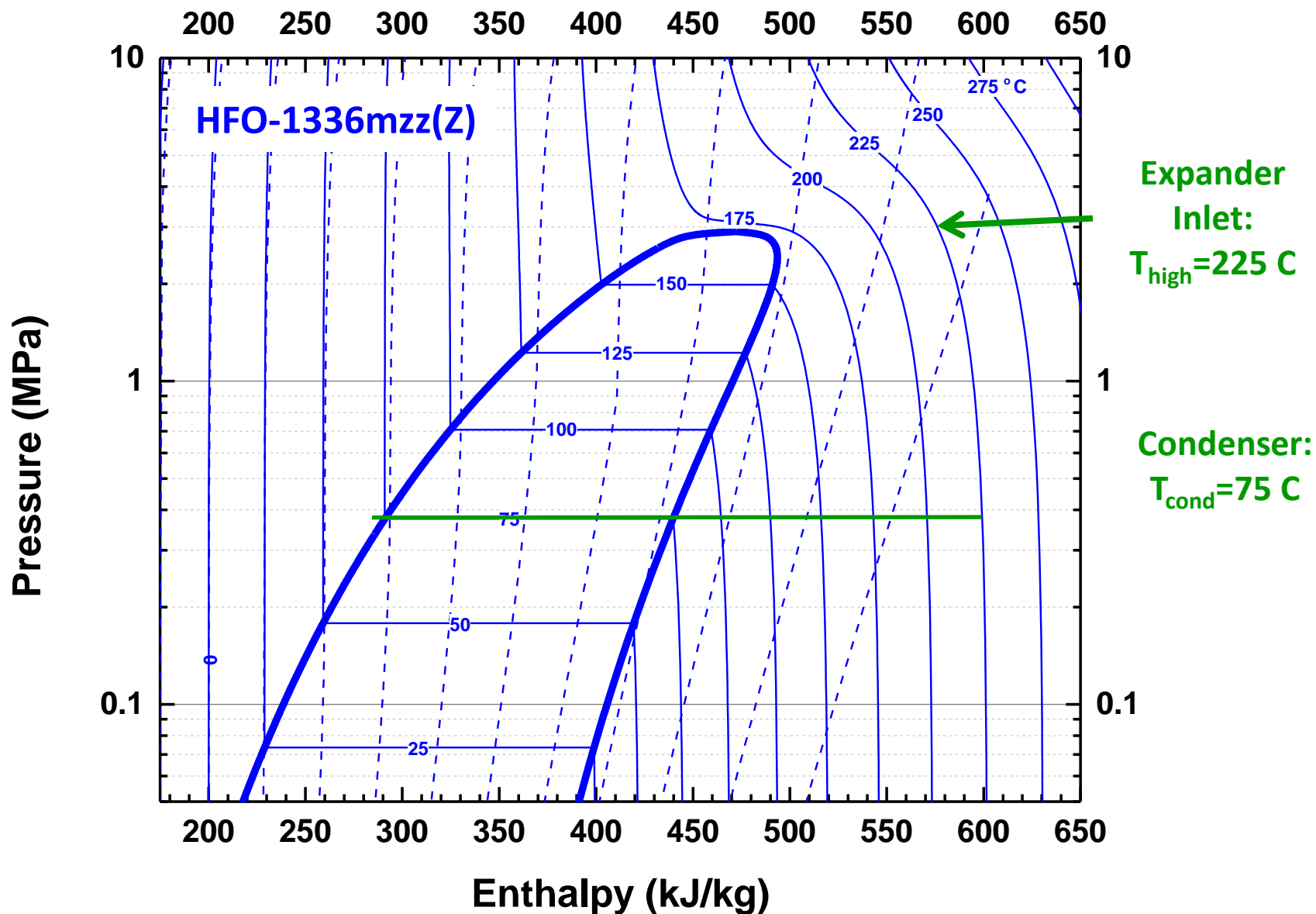


	HFC-245fa	HFO-1336mzz(Z)
T_{cr} [°C]	154.0	171.3

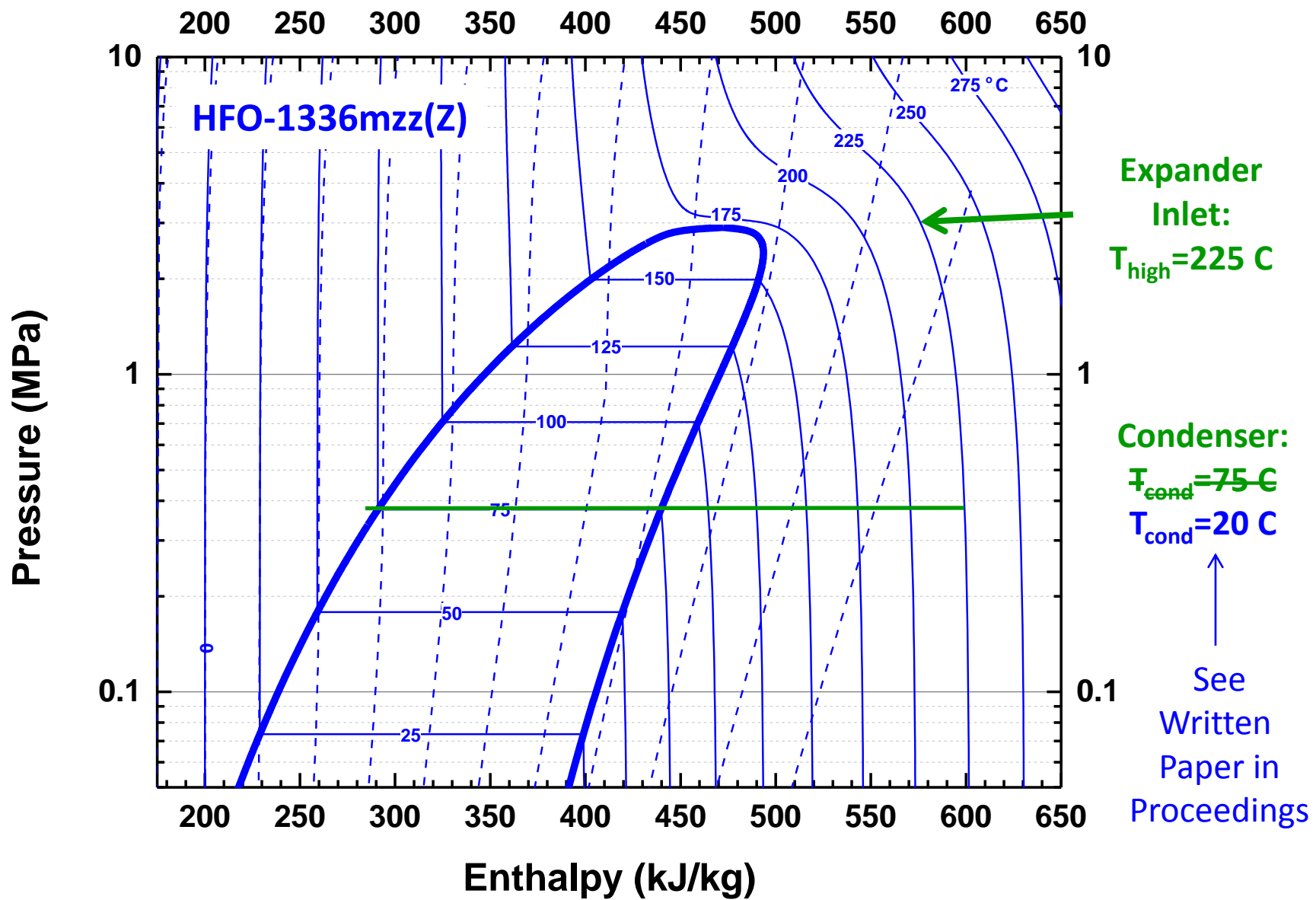
Heat Source Temp > T_{cr}



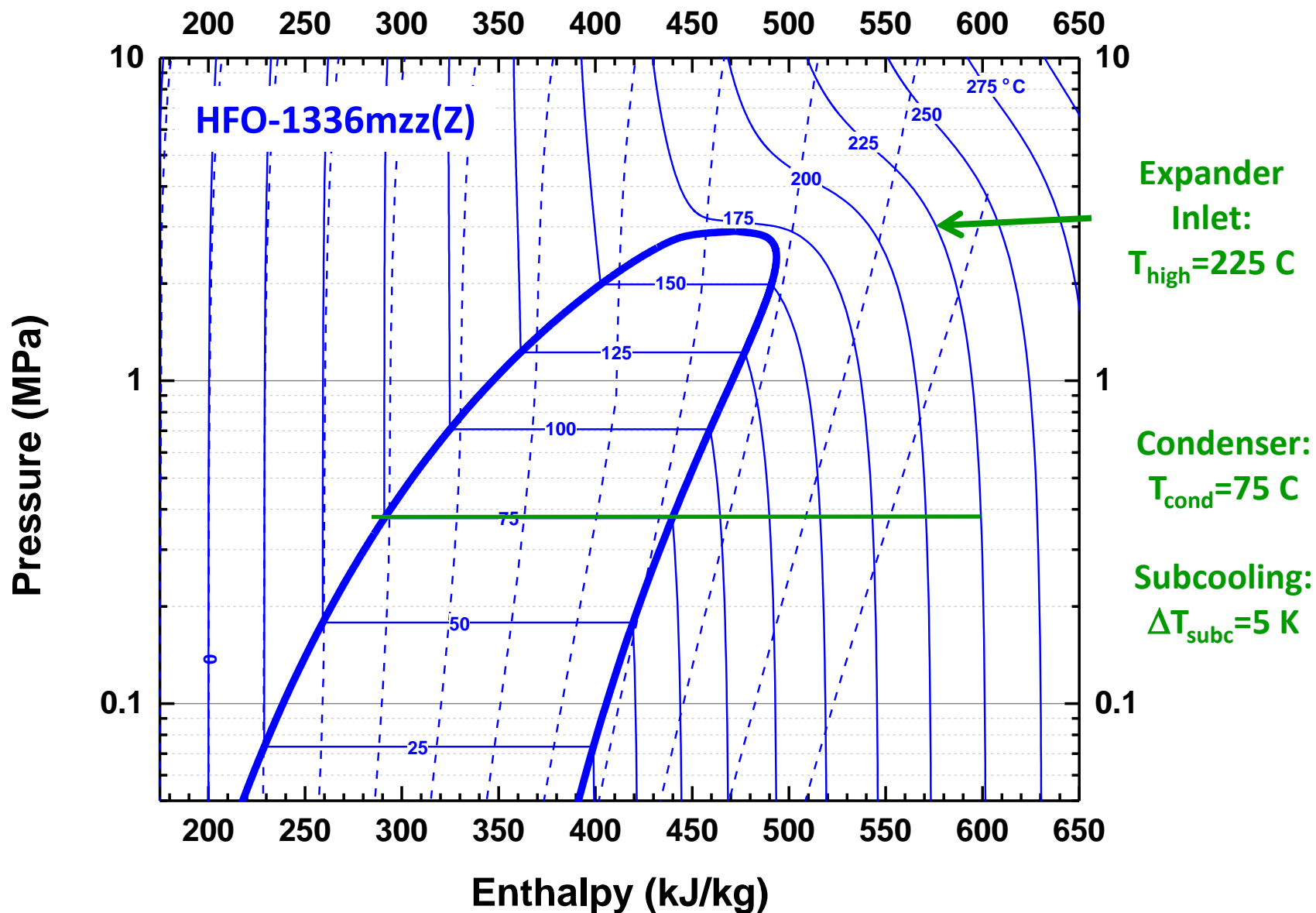
Representative Cycle Conditions



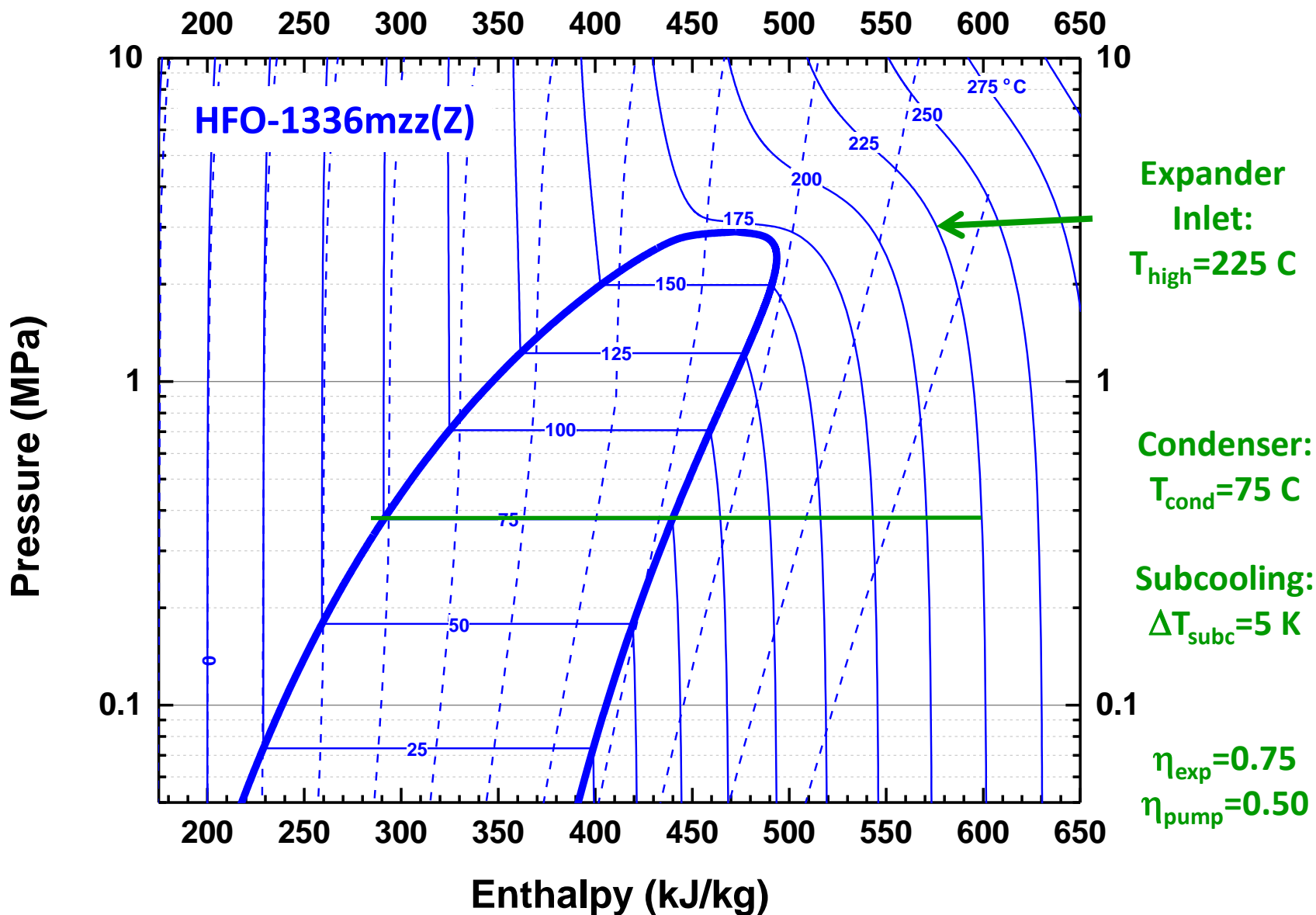
Representative Cycle Conditions



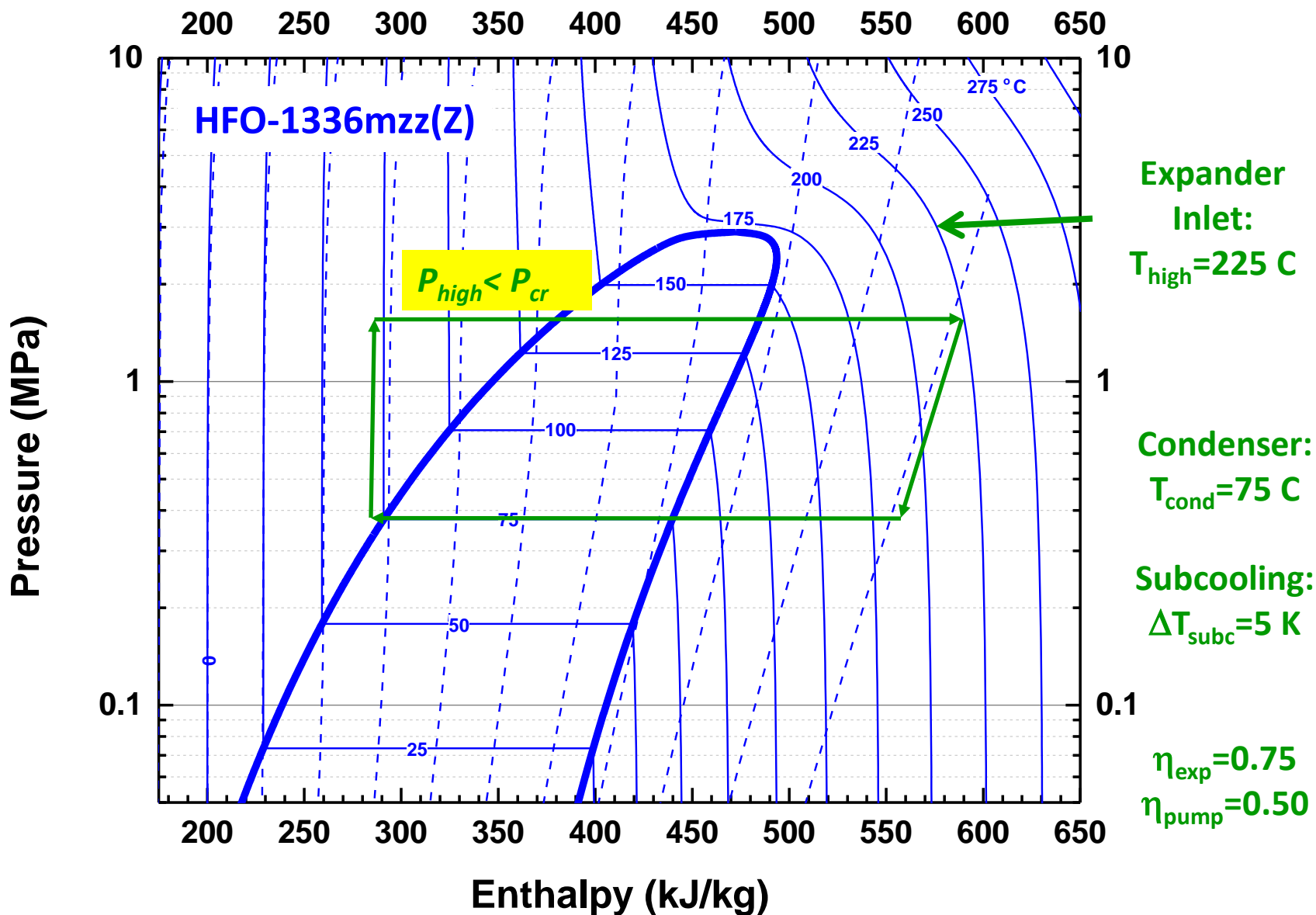
Representative Cycle Conditions



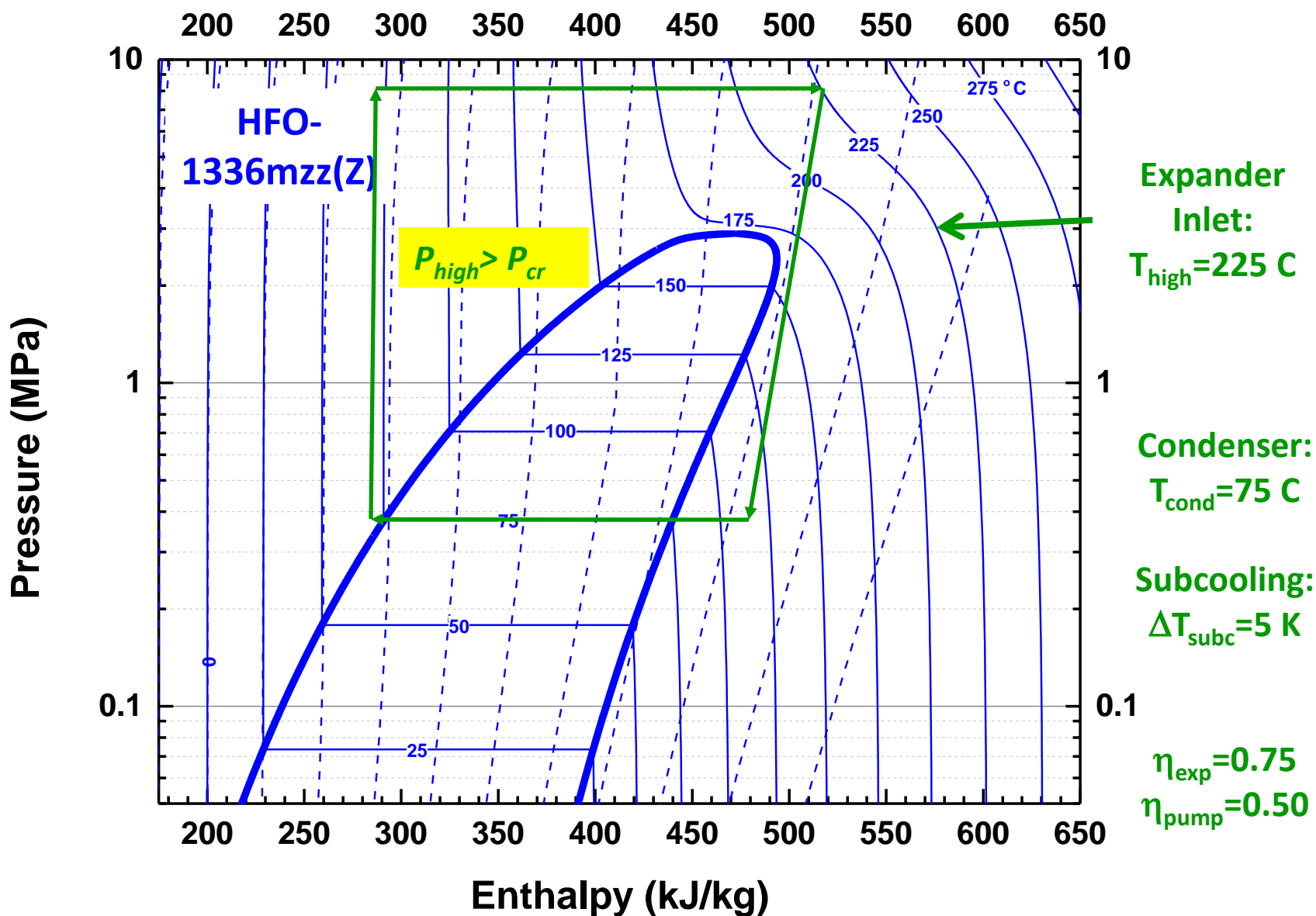
Representative Cycle Conditions



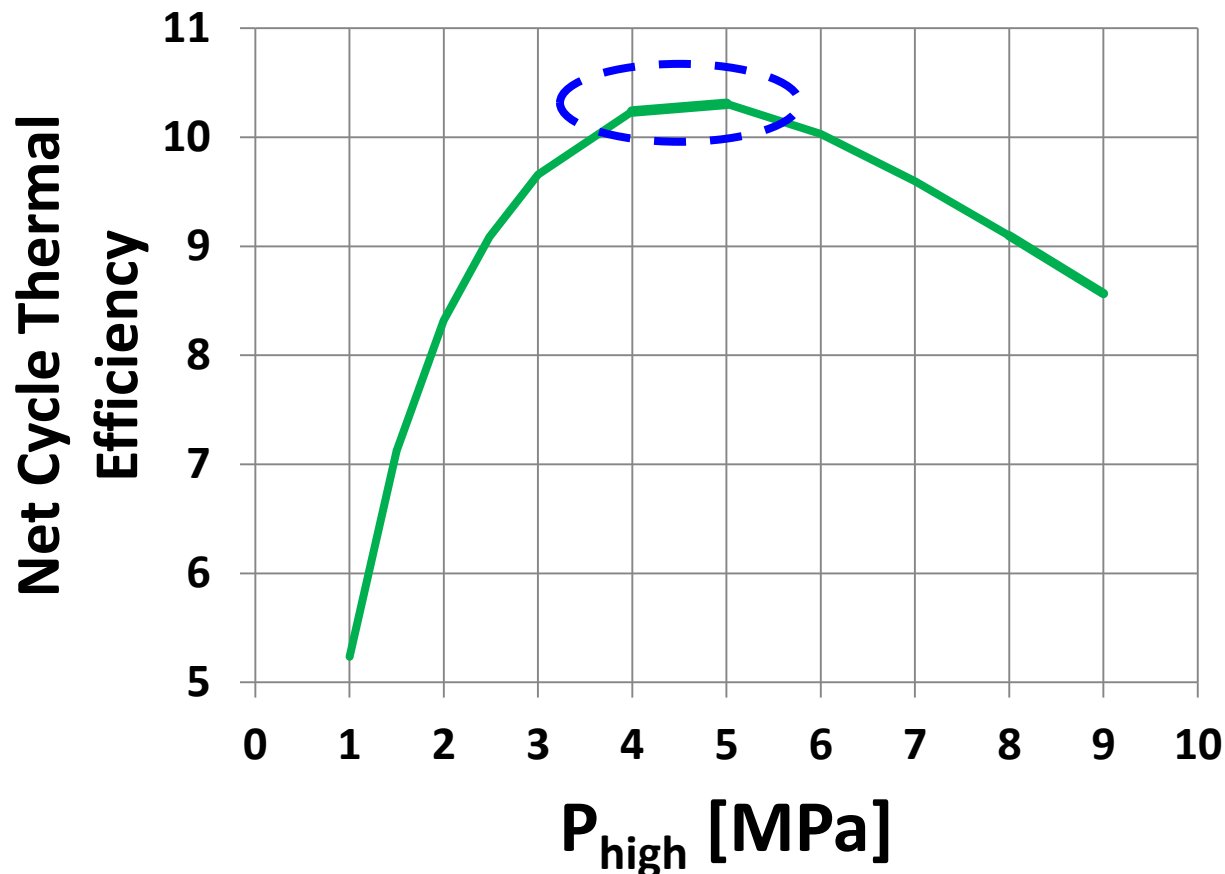
Optimization of High-Side Pressure



High-Side Pressure: Upper Limit

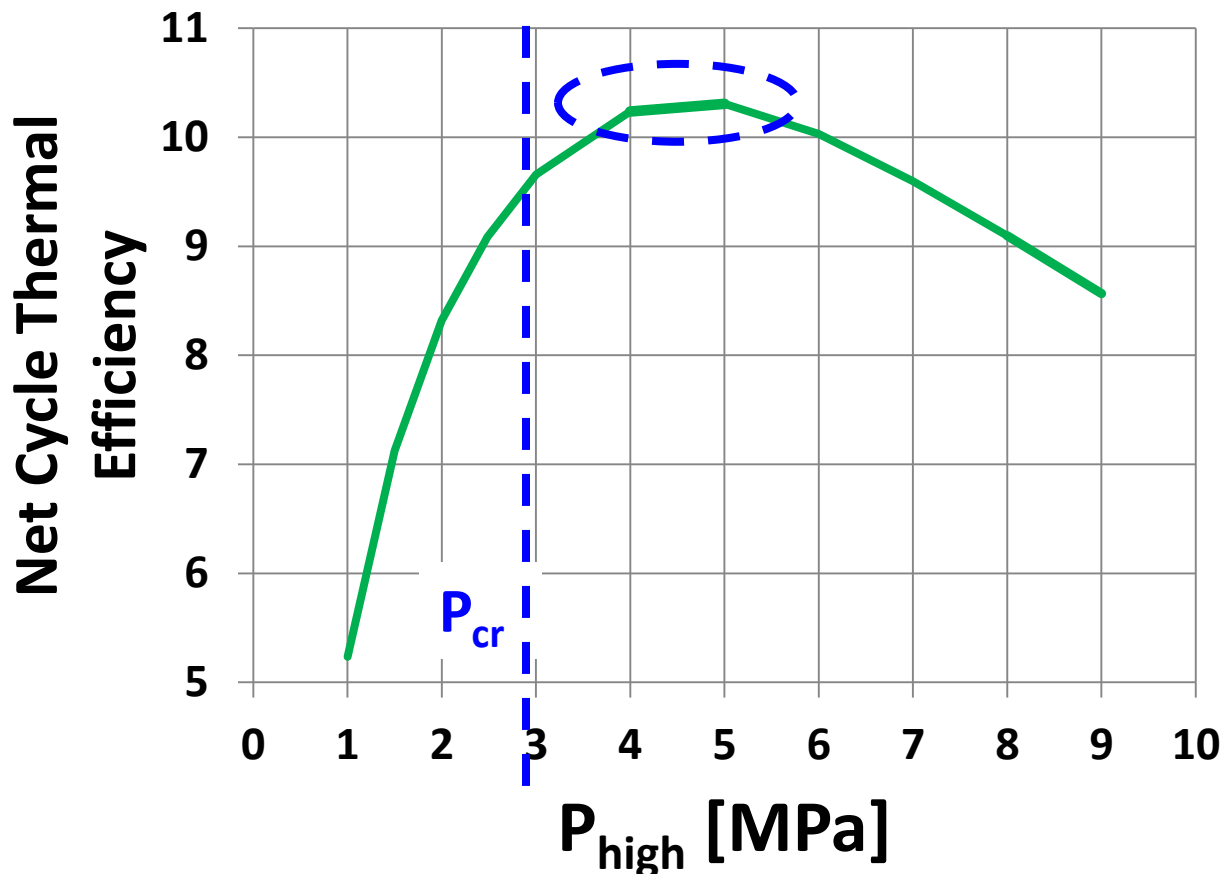


HFO-1336mzz(Z): Maximization of Thermal Efficiency



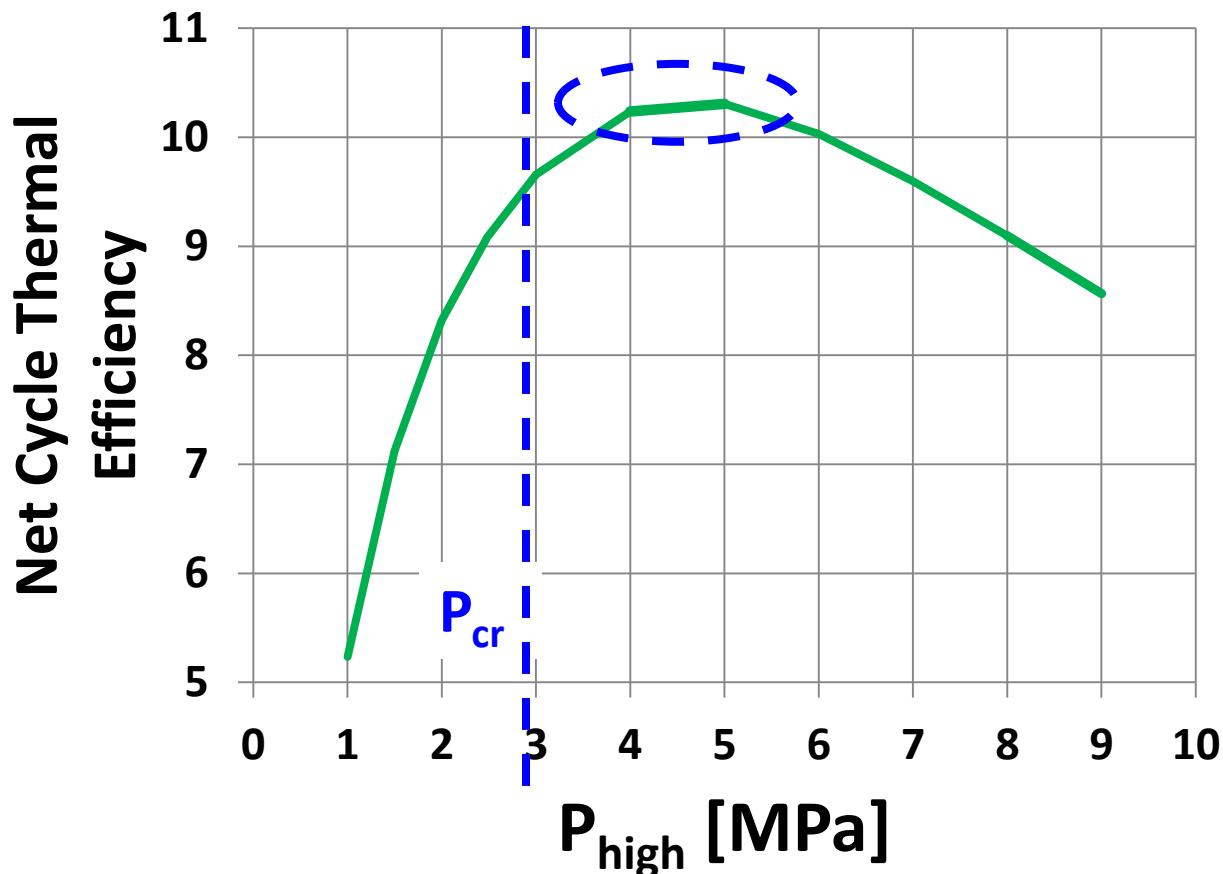
Net Cycle Efficiency Exhibits Maximum

HFO-1336mzz(Z): Maximization of Thermal Efficiency



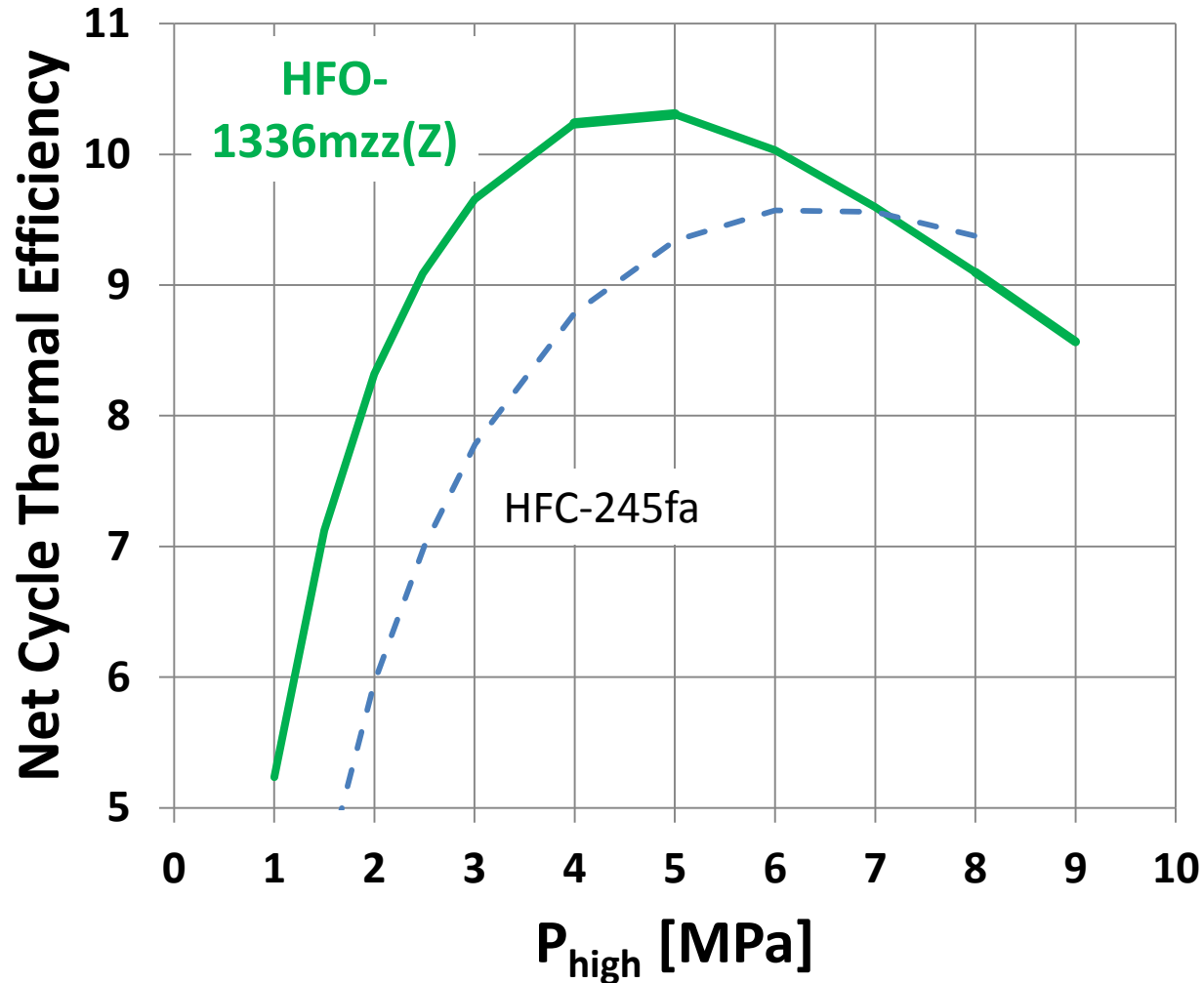
**Maximum Efficiency at $P_{high} > P_{cr}$
10-15% Higher Than Subcritical Cycle Efficiency**

HFO-1336mzz(Z): Maximization of Thermal Efficiency



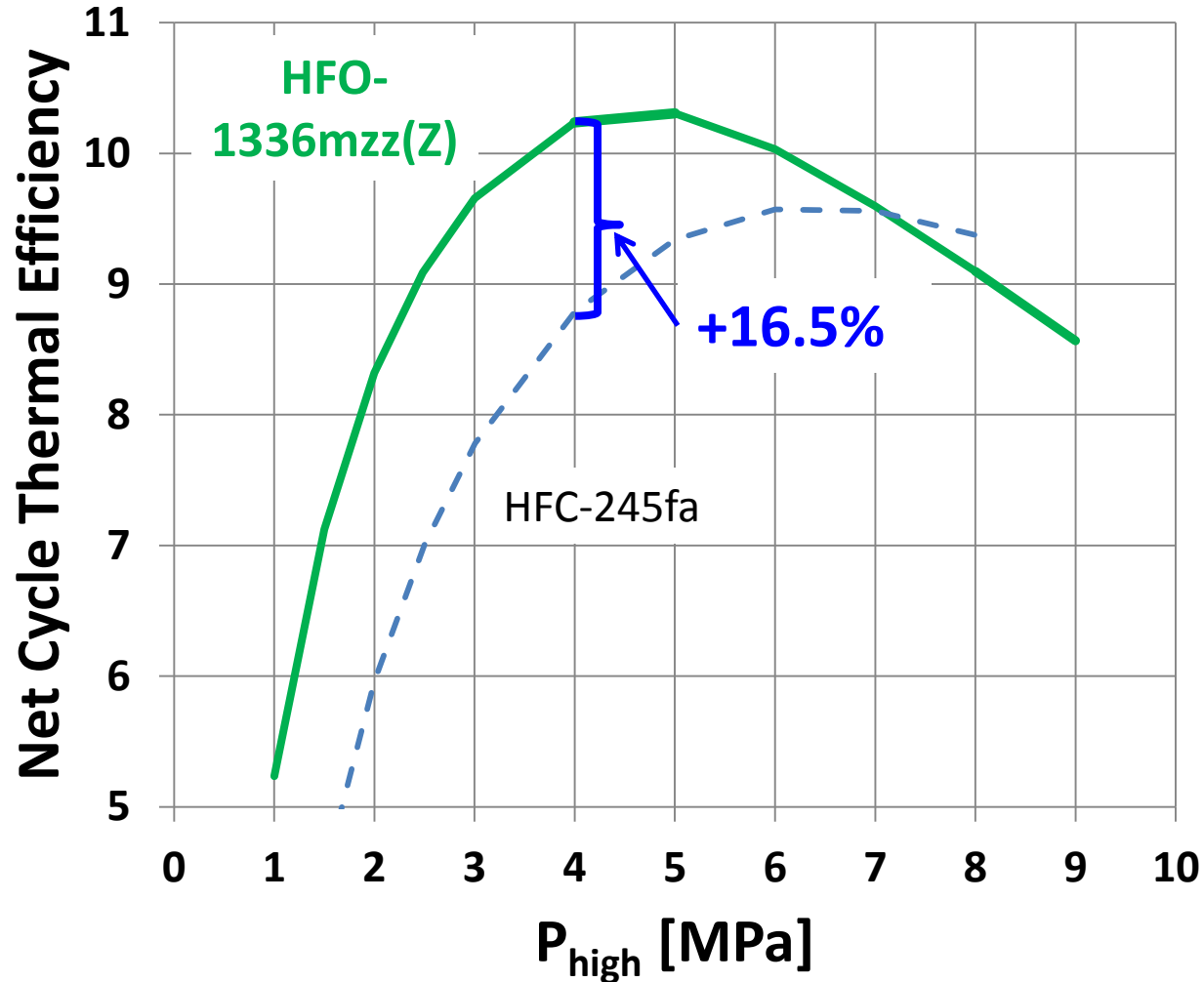
P_{high} [MPa]	4
PR	10.7

HFO-1336mzz(Z) vs. HFC-245fa: Cycle Efficiency



Basic ORC (No Recuperator)		
T_{high}	C	225
T_{cond}	C	75
ΔT_{subc}	K	5
η_{exp}		0.75
η_{pump}		0.50

HFO-1336mzz(Z) vs. HFC-245fa: Cycle Efficiency



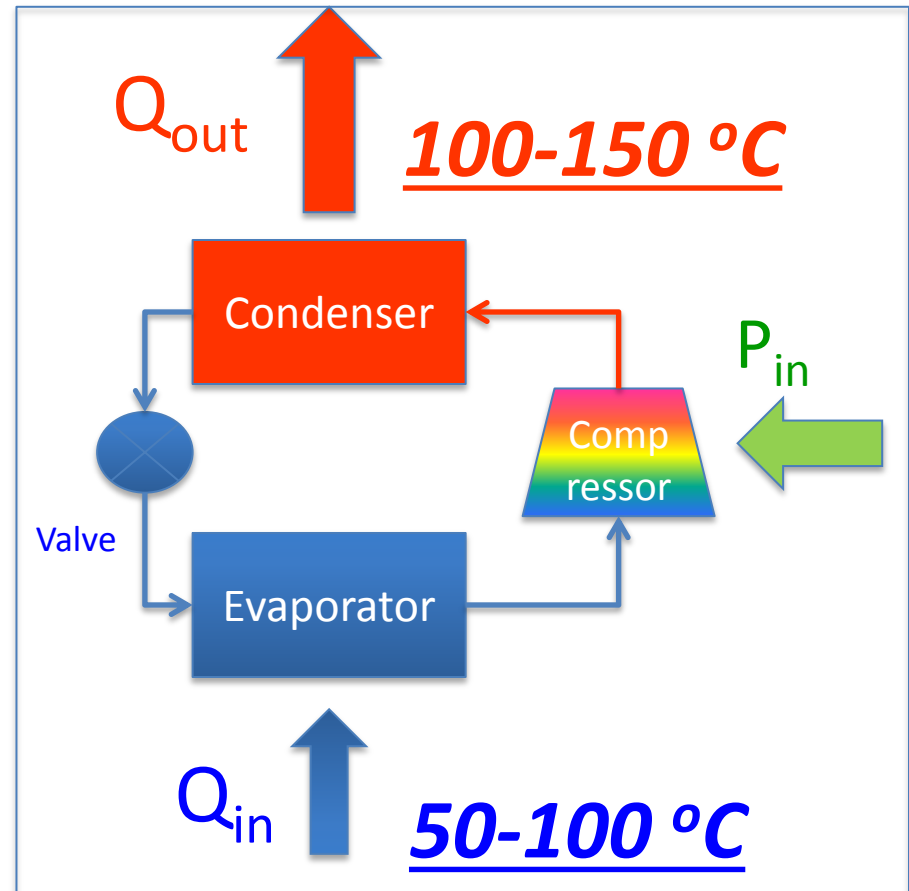
Basic ORC (No Recuperator)		
T_{high}	C	225
T_{cond}	C	75
ΔT_{subc}	K	5
η_{exp}		0.75
η_{pump}		0.50

HFO-1336mzz(Z): 99.8% Lower GWP and 16.5% Higher Efficiency!

HFO-1336mzz(Z)

Heat Pump Steam Generator

*Use heat
from
engine jacket
cooling water
to
generate
steam?*



Reverse Rankine Cycle

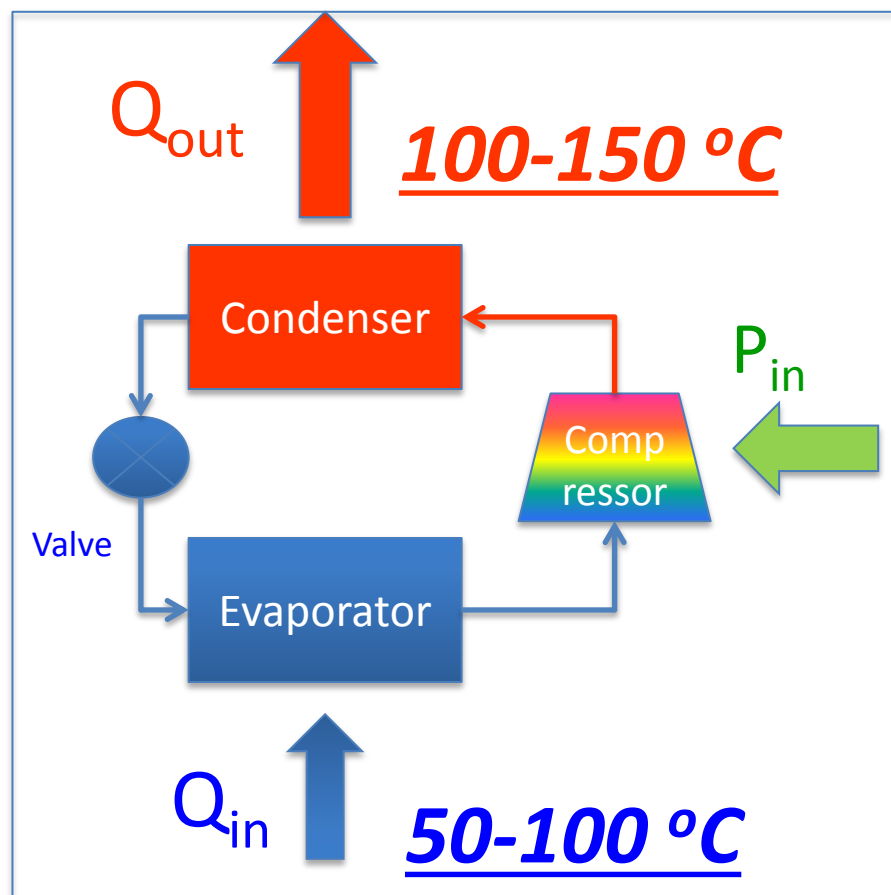
HFO-1336mzz(Z)

Heat Pump Steam Generator

Energy Efficiency Metric:

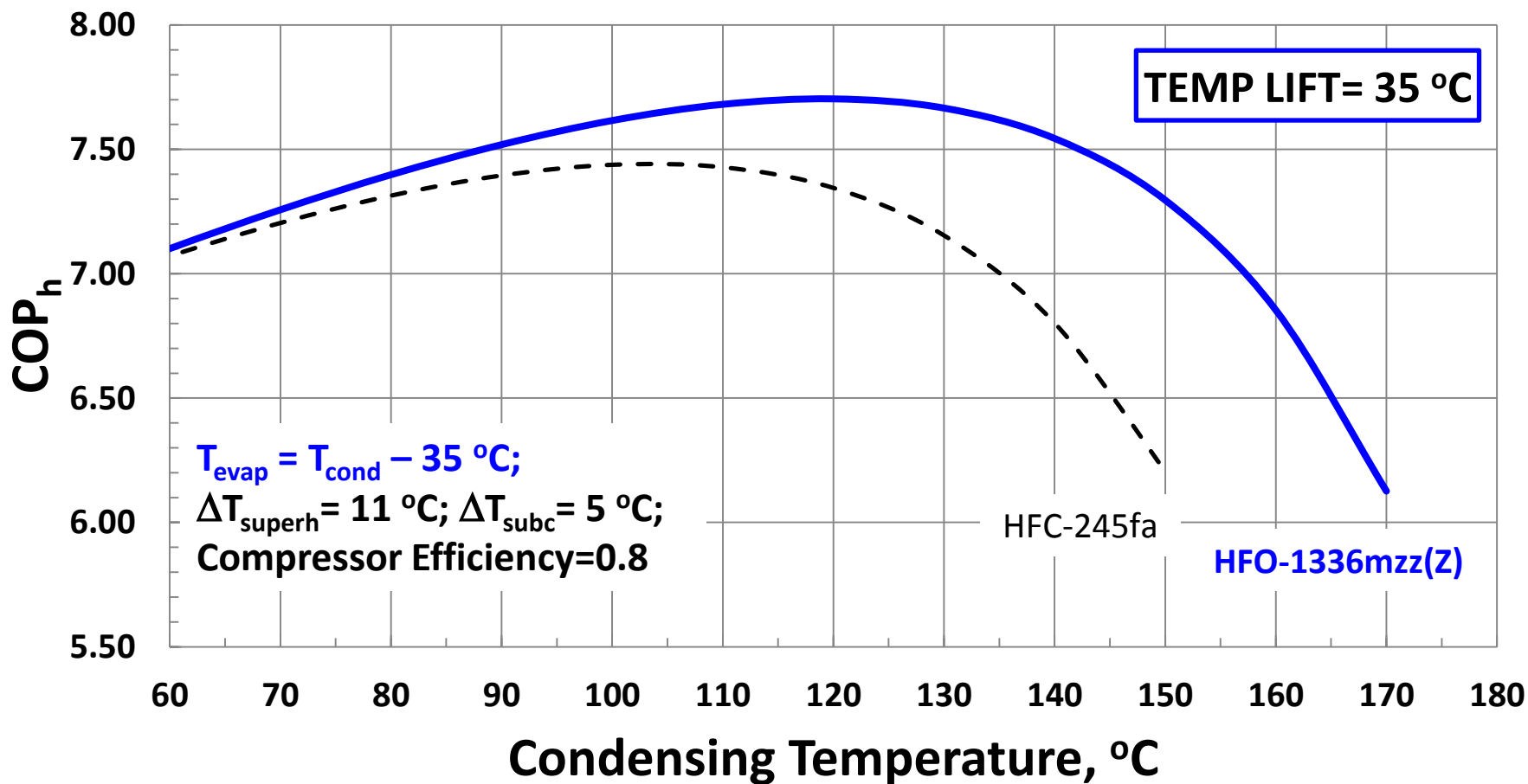
$$\text{COP}_h = Q_{\text{out}} / P_{\text{in}}$$

“Coefficient of
Performance for
Heating”



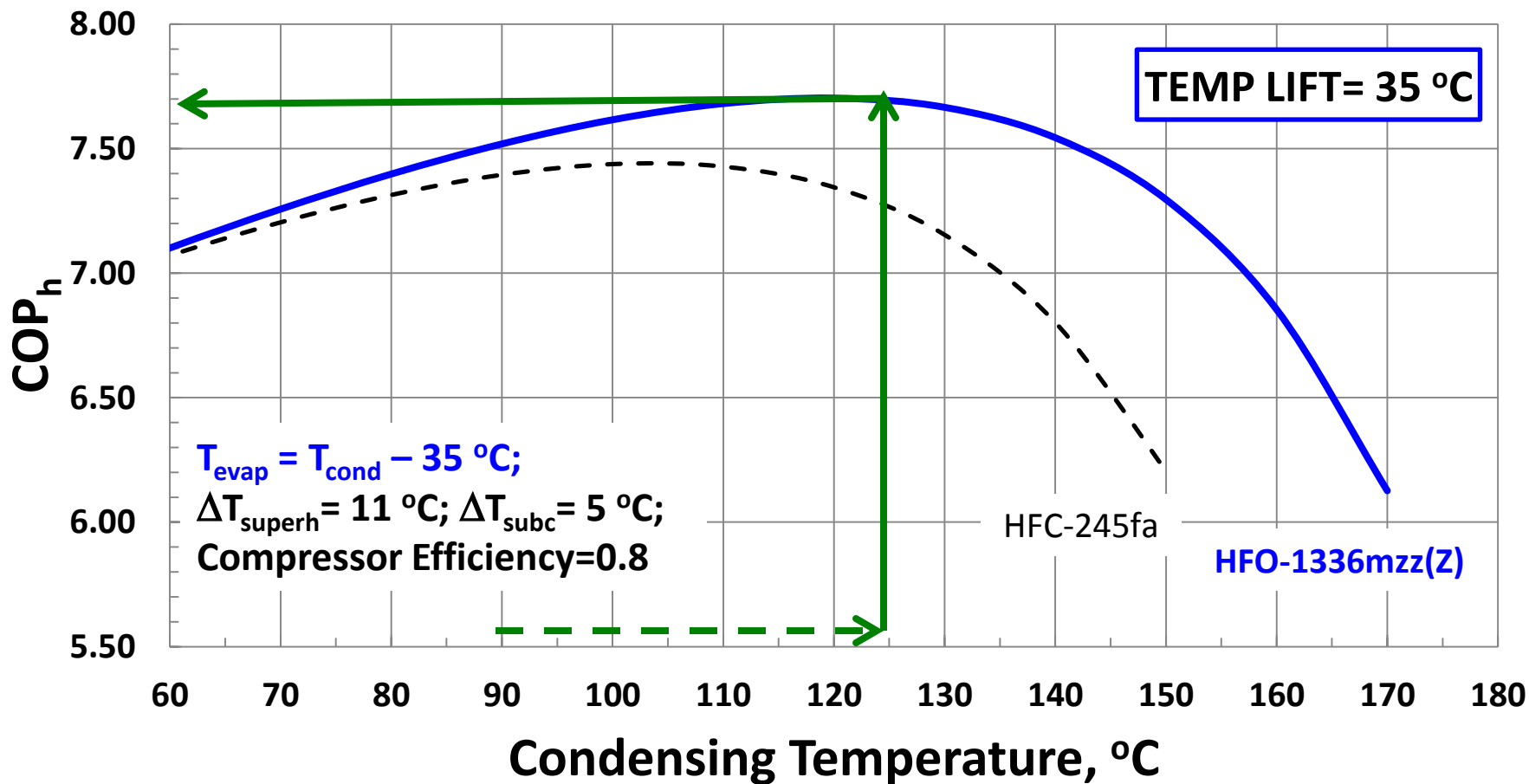
Reverse Rankine Cycle

HFO-1336mzz(Z) High Temp Heat Pump: Predicted Simple Cycle Performance



ATTRACTIVE COP_h

HFO-1336mzz(Z) High Temp Heat Pump: Predicted Simple Cycle Performance



Summary

Newly Registered **Non-Flammable, Lower GWP** ASHRAE Refrigerants:

R-452A:

R-404A replacement with lower compressor discharge temperature

R-449A:

R-404A replacement with lower GWP and energy consumption

R-513A:

Near drop-in replacement for HFC-134a

R-1336mzz(Z):

**Unique combination of properties for
power and heating from low temp waste heat
for increased fuel efficiency and reduced environmental impacts**

Zero-ODP, Lower GWP, Non-Flammable Refrigerants and Working Fluids for Cooling, Heating and Power Generation

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