Seminar 35 - Advances in
Low Global Warming Potential
Refrigerants

Zero-ODP, Low-GWP, Nonflammable Working Fluids for High Temperature Heat Pumps

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2014 ASHRAE Annual Conference, Seattle, Washington
July 1st, 2014

Reduce:

- ***Primary Energy Use***
- ***Environmental Impact***

LEARNING OBJECTIVES:

- Explain recent development activities related to low GWP refrigerants including air conditioning alternatives to R-410A and R-22 and refrigeration alternatives, including recent drivers in Europe requiring the development of these refrigerants.
- **Describe new low GWP fluids under development for high temperature heat pump applications which have excellent thermal stability and cooling/heating performance at high temperatures.**
- Share refrigerant/lubricant property data and trends including miscibility, solubility and viscosity date for low GWP refrigerants with lubricants
- Describe results for thermodynamic cycle modeling and system performance testing of several low GWP refrigerants in various applications.

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PROSPECTIVE APPLICATIONS

CAP_h [kw] / T_{cond} [^oC]	1-10	10-100	100-1,000	1,000-10,000
150-175		Steam Generation	Steam Generation	
125-150		Evaporation Distillation	Evaporation Distillation	
100-125		Liquid Heating Drying	Liquid Heating Drying	District Heating
75-100	DHW-JPN	Liquid Heating Drying	Liquid Heating Drying	District Heating
50-75	DHW-xJPN Clothes Drying	Liquid Heating Drying	Liquid Heating Drying	

PROSPECTIVE APPLICATIONS

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100-125		Liquid Heating Drying	Liquid Heating Drying	District Heating
75-100	DHW-JPN	Liquid Heating Drying	Liquid Heating Drying	District Heating
50-75	DHW-xJPN Clothes Drying	Liquid Heating Drying	Liquid Heating Drying	

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Large Untapped Potential for Industrial/Process Heating

PROSPECTIVE APPLICATIONS

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Replacement of Fossil Fuel Steam Boilers By Heat Pumps

PROSPECTIVE APPLICATIONS

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Diverse Markets:

Segments, Temp and Capacity Ranges,
Equipment Technologies, Fluid Specifications

Comprehensive Fluid Portfolio Needed

HFO-Based Developmental Fluids

In order of increasing T_{cr} (& NBP)

	DR-14A
Chemical Formula	Azeotropic Blend
GWP_{100}	~415
T_{cr} [°C]	110.7
P_{cr} [MPa]	3.96
T_b [°C]	-20.5
Temp Glide [K] (@ P=1 atm)	0.04

HFO-Based Developmental Fluids

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T_{cr} [ºC]	110.7
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Temp Glide [K] (@ P=1 atm)	0.04

Negligible Temperature Glide
Suitable for Large Heat Pumps (and Chillers) with Flooded Heat Exchangers

HFO-Based Developmental Fluids

	DR-14A	DR-12
Chemical Formula	Azeotropic Blend	Confidential
GWP_{100}	~415	32
T_{cr} [ºC]	110.7	137.7
P_{cr} [MPa]	3.96	3.15
T_b [ºC]	-20.5	7.5
Temp Glide [K] (@ P=1 atm)	0.04	N/A

HFO-Based Developmental Fluids

DR-12: Very Low GWP and Non-Flammable

	DR-14A	DR-12
Chemical Formula	Azeotropic Blend	Confidential
GWP_{100}	~415	32
T_{cr} [°C]	110.7	137.7
P_{cr} [MPa]	3.96	3.15
T_b [°C]	-20.5	7.5
Temp Glide [K] (@ P=1 atm)	0.04	N/A

HFO-Based Developmental Fluids

	DR-14A	DR-12	DR-40A
Chemical Formula	Azeotropic Blend	Confidential	Near-Azeo Blend
GWP_{100}	~415	32	<170
T_{cr} [ºC]	110.7	137.7	166.5
P_{cr} [MPa]	3.96	3.15	3.50
T_b [ºC]	-20.5	7.5	25.5
Temp Glide [K] (@ P=1 atm)	0.04	N/A	0.86

HFO-Based Developmental Fluids

	DR-14A	DR-12	DR-40A	DR-2
Chemical Formula	Azeotropic Blend	Confidential	Near-Azeo Blend	
GWP_{100}	~415	32	<170	2
T_{cr} [ºC]	110.7	137.7	166.5	171.3
P_{cr} [MPa]	3.96	3.15	3.50	2.90
T_b [ºC]	-20.5	7.5	25.5	33.4
Temp Glide [K] (@ P=1 atm)	0.04	N/A	0.86	N/A

HFO-Based Developmental Fluids

	DR-14A	DR-12	DR-40A	DR-2
Chemical Formula	Azeotropic Blend	Confidential	Near-Azeo Blend	HFO-1336mzz(Z)
GWP_{100}	~415	32	<170	2
T_{cr} [ºC]	110.7	137.7	166.5	171.3
P_{cr} [MPa]	3.96	3.15	3.50	2.90
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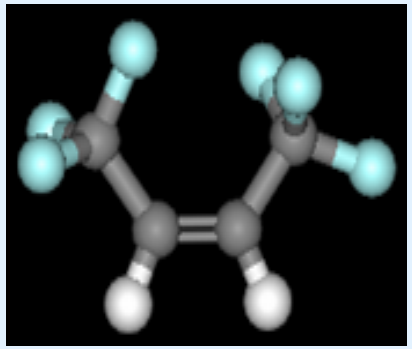

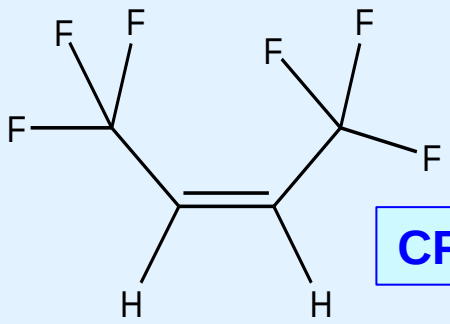

$CF_3CH=CHCF_3(Z)$

HFO-Based Developmental Fluids

DR-2: Very Low GWP and Non-Flammable

	DR-14A	DR-12	DR-40A	DR-2
Chemical Formula	Azeotropic Blend	Confidential	Near-Azeo Blend	HFO-1336mzz(Z)
GWP_{100}	~415	32	<170	2
T_{cr} [ºC]	110.7	137.7	166.5	171.3
P_{cr} [MPa]	3.96	3.15	3.50	2.90
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Temp Glide [K] (@ P=1 atm)	0.04	N/A	0.86	N/A

No Chlorine(*):

-Zero ODP

-Dramatically Increased Chemical Stability at High Temps

(*) or other halogen atoms other than fluorine

DR-2: Unique Combination of Attributes

- **Very Low GWP**
- **No Flammability**

DR-2: Unique Combination of Attributes

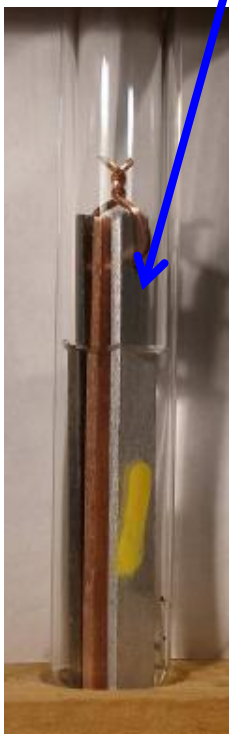
- Very Low GWP
- No Flammability
- **Surprisingly High Chemical Stability at High Temperatures (to Polymerization, Decomposition/De-hydrofluorination, Oxidation and Hydrolysis)**

DR-2: High Chemical Stability

AGING @ 250 °C

w/ Metals; Air: 7.6 mmHg; Moisture: 200 ppm

Sealed tube testing based on ASHRAE-ANSI STD 97



Fluoride Ion Concentration After Aging [ppm]		
AGING [DAYS]	HFO DR-2	HFC-245fa
1	6	4
7	11	20

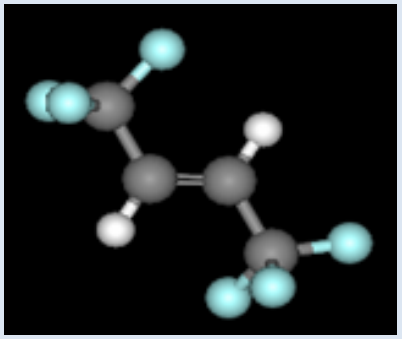
DR-2 as Stable as a Saturated HFC Widely Used in High Temp Apps

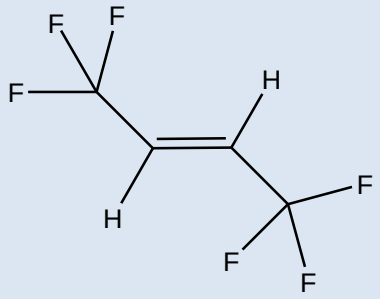
DR-2: Stereo-Isomerization Stability

Aging in the Presence of Metals for 14 Days

Aging Temp [°C]	HFO-1336mzz-E [ppm]
Un-aged Stock	Not Present
150	24
175	39
200	117
225	343
250	3,023

HFO-1336mzz(E)





DR-2 Stable to Stereo-Isomerization Despite Thermodynamic Driving Force!

DR-2: Unique Combination of Attributes

- Very Low GWP
- No Flammability
- Surprisingly High Chemical Stability at High Temps
- **Compatible with Many Plastics and Elastomers**

DR-2 Compatibility with Plastics & Elastomers: (I)

Weight changes of polymeric specimens after exposure to HFO-1336mzz-Z/POE Lubricant blends for 14 days at 100 °C

Material	Immediately after Exposure %	Twenty Four Hours after Exposure %
Neoprene	-0.55	-0.98
EPDM	2.39	0.84
Polyester Resin	10.04	4.94
Nylon Resin	-0.74	-0.79
Epoxy	0.66	0.56
Polyester PET	3.73	3.54
Polyester PBT	1.15	1.13
Polycarbonate	0.74	0.75
Polyimide	0.79	0.79
Teflon PTFE	3.05	2.72
Teflon FEP	3.29	3.09
Tefzel ETFE	6.25	5.61
Phenolic	-0.18	-0.31
PVC	0.68	0.70
PEEK	-0.06	0.01

Mild Interactions between HFO-1336mzz-Z and Many Plastics and Elastomers

DR-2 Compatibility with Plastics & Elastomers: (II)

Hardness changes of polymeric specimens after exposure to HFO-1336mzz-Z/POE Lubricant blends for 14 days at 100 °C

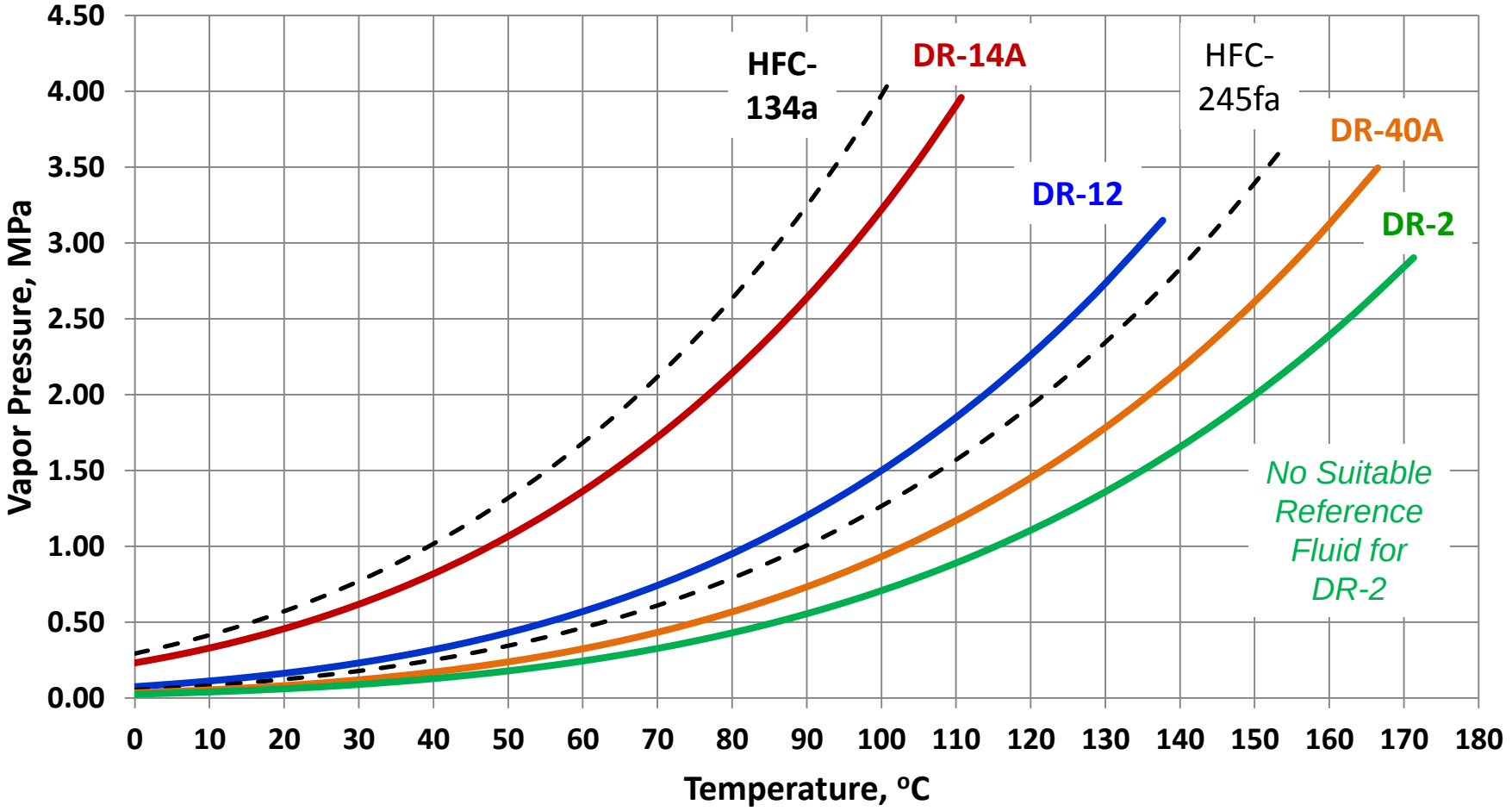
Material	Immediately after Exposure %	Twenty Four Hours after Exposure %
Neoprene	7.10	2.58
EPDM	2.56	0.64
Polyester Resin	-1.01	-0.51
Nylon Resin	-1.00	-2.00
Epoxy	-1.01	-3.54
Polyester PET	0.00	0.00
Polyester PBT	-1.00	-1.00
Polycarbonate	-1.00	0.00
Polyimide	0.00	0.00
Teflon PTFE	-0.50	0.00
Teflon FEP	0.00	-0.51
Tefzel ETFE	0.00	0.00
Phenolic	0.00	0.00
PVC	0.00	0.00
PEEK	0.00	0.00

Mild Interactions between HFO-1336mzz-Z and Many Plastics and Elastomers

DR-2: Unique Combination of Attributes

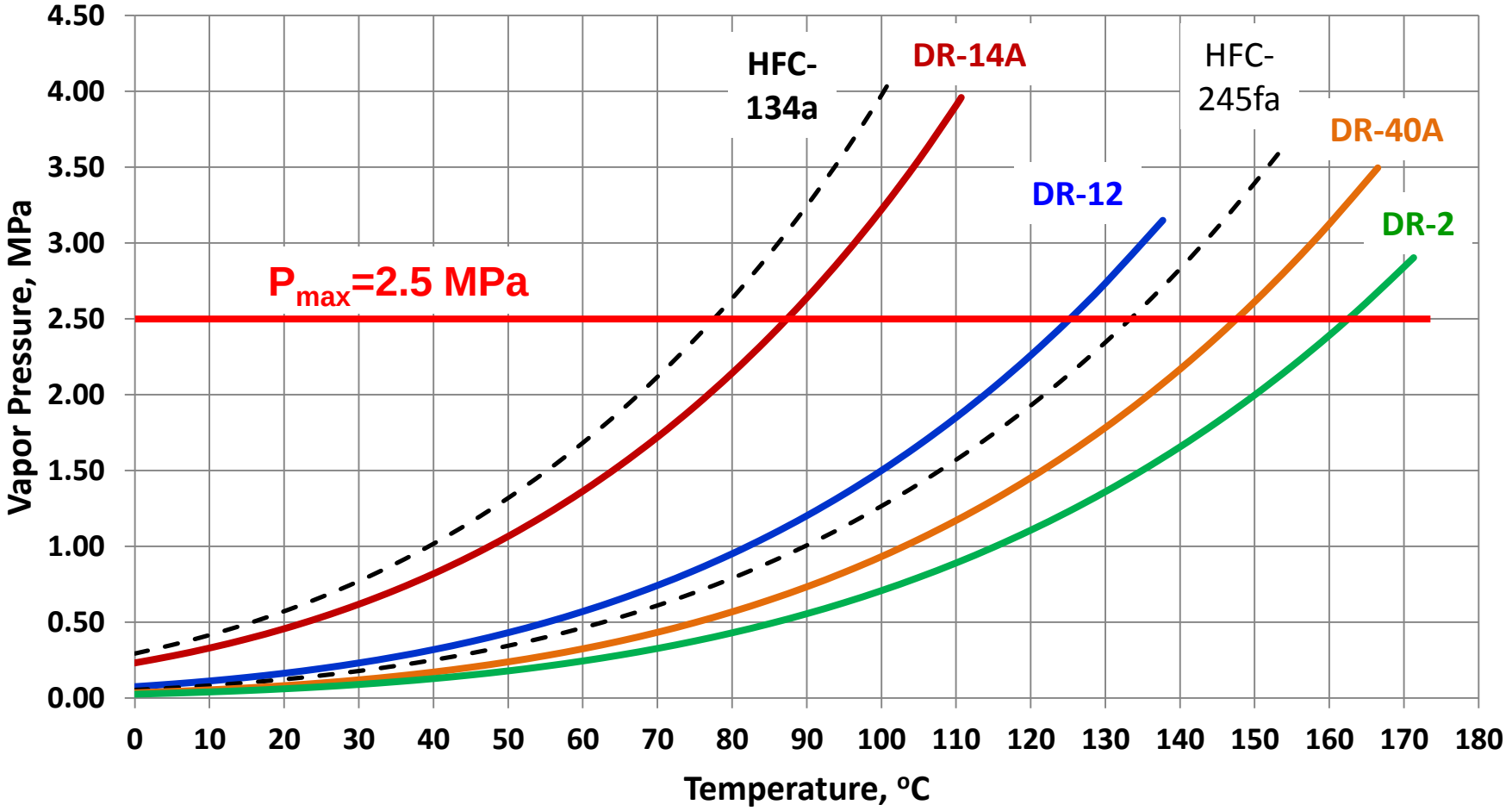
- Very Low GWP
- No Flammability
- Surprisingly High Chemical Stability at High Temps
- Compatibility with Many Common Plastics and Elastomers
- **Attractive Thermodynamic Properties for High Temperature Applications**
  - **High Critical Temperature**
  - **Low, Easy to Confine Vapor Pressure**
  - **High Cycle Efficiency**

Vapor Pressure



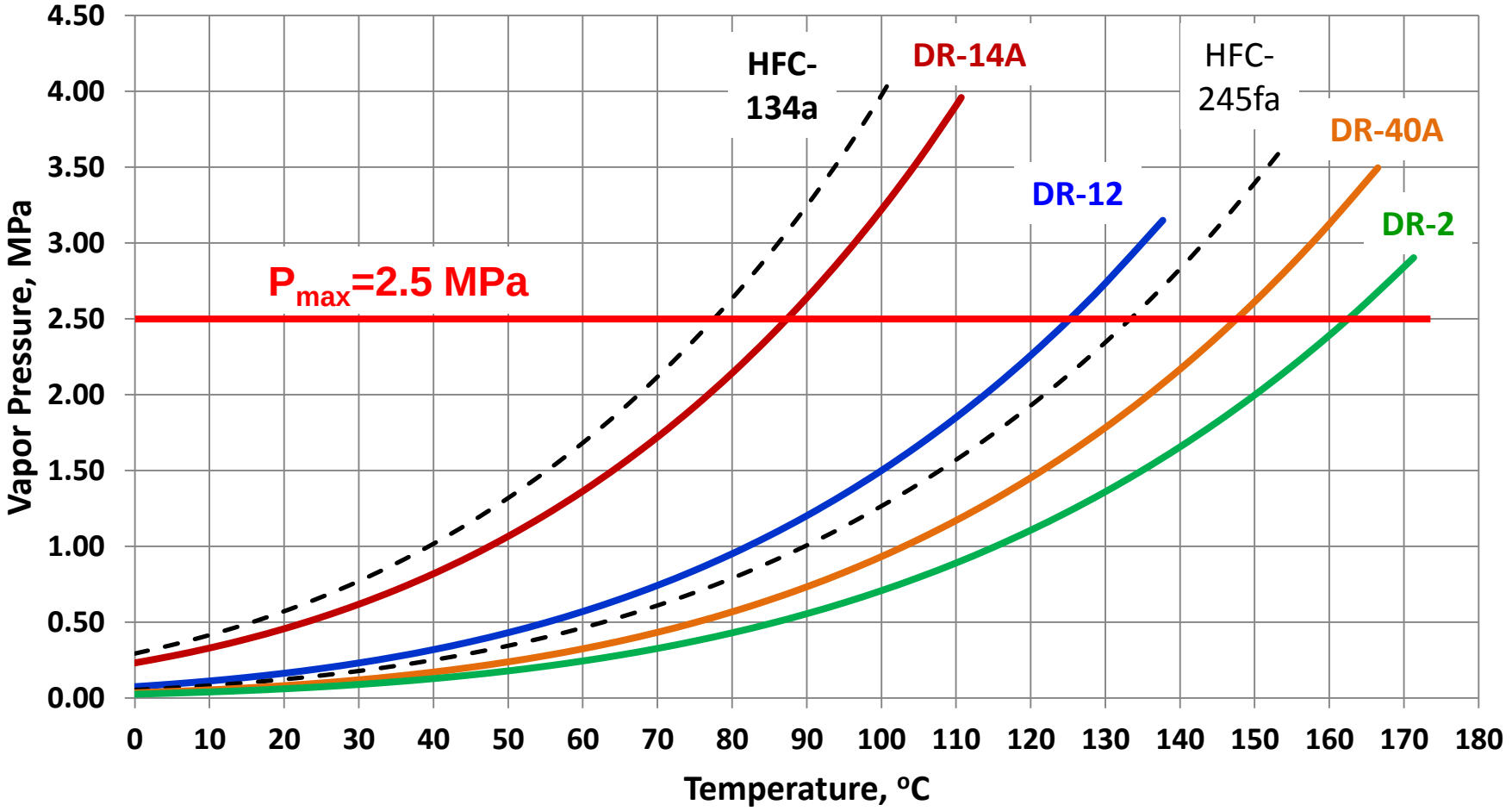
	HFC-134a	DR-14A	DR-12	HFC-245fa	DR-40A	DR-2
T_{cr}, °C	101.1	110.7	137.7	154.0	166.5	171.3

Vapor Pressure



	HFC-134a	DR-14A	DR-12	HFC-245fa	DR-40A	DR-2
$T_{2.5MPa}$, °C	77.5	87.8	125.3	133.4	149.2	162.8

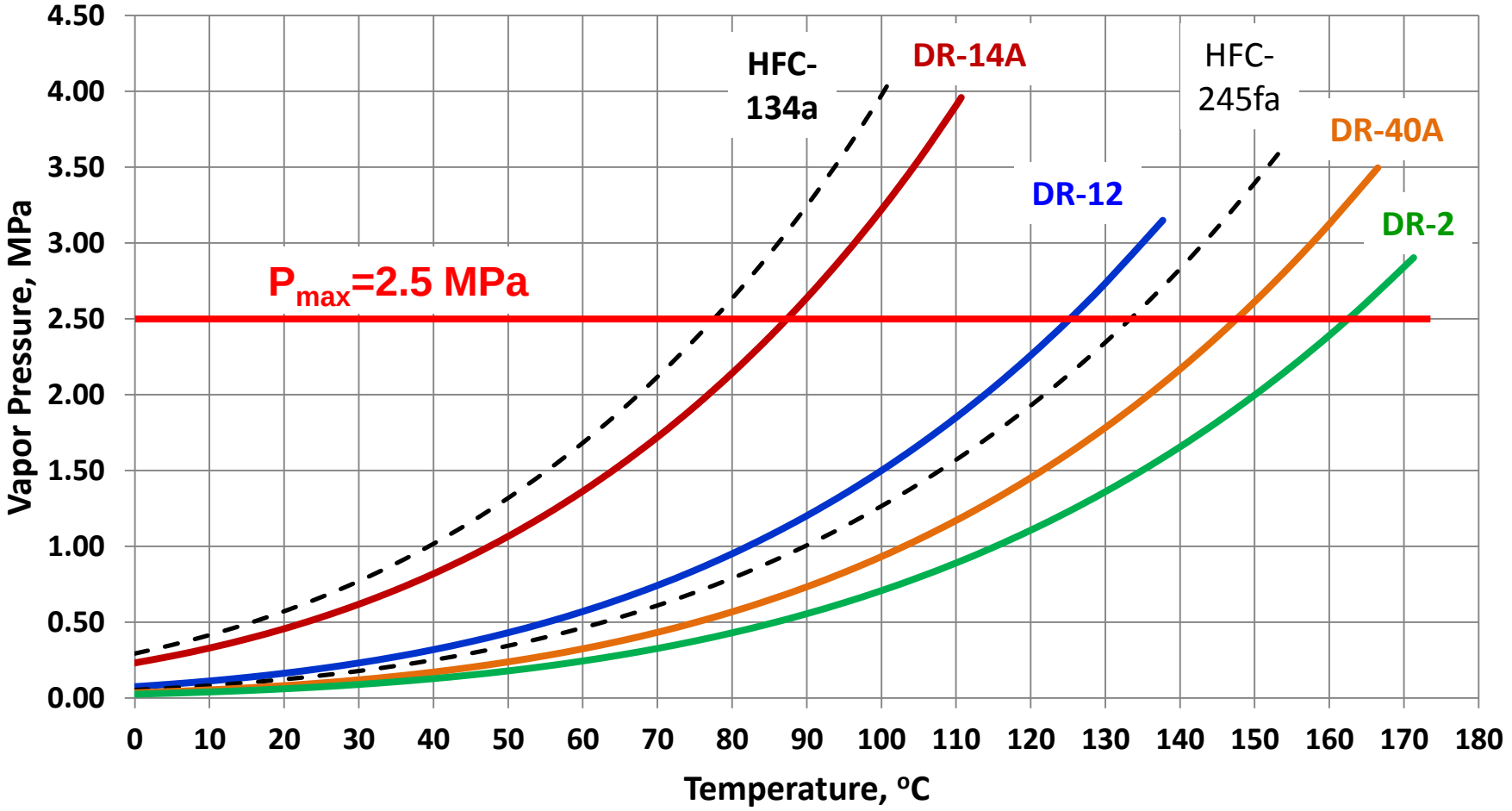
Vapor Pressure



	HFC-134a	DR-14A	DR-12	HFC-245fa	DR-40A	DR-2
$T_{2.5MPa}$, °C	77.5	87.8	125.3	133.4	149.2	162.8

+10.3 °C

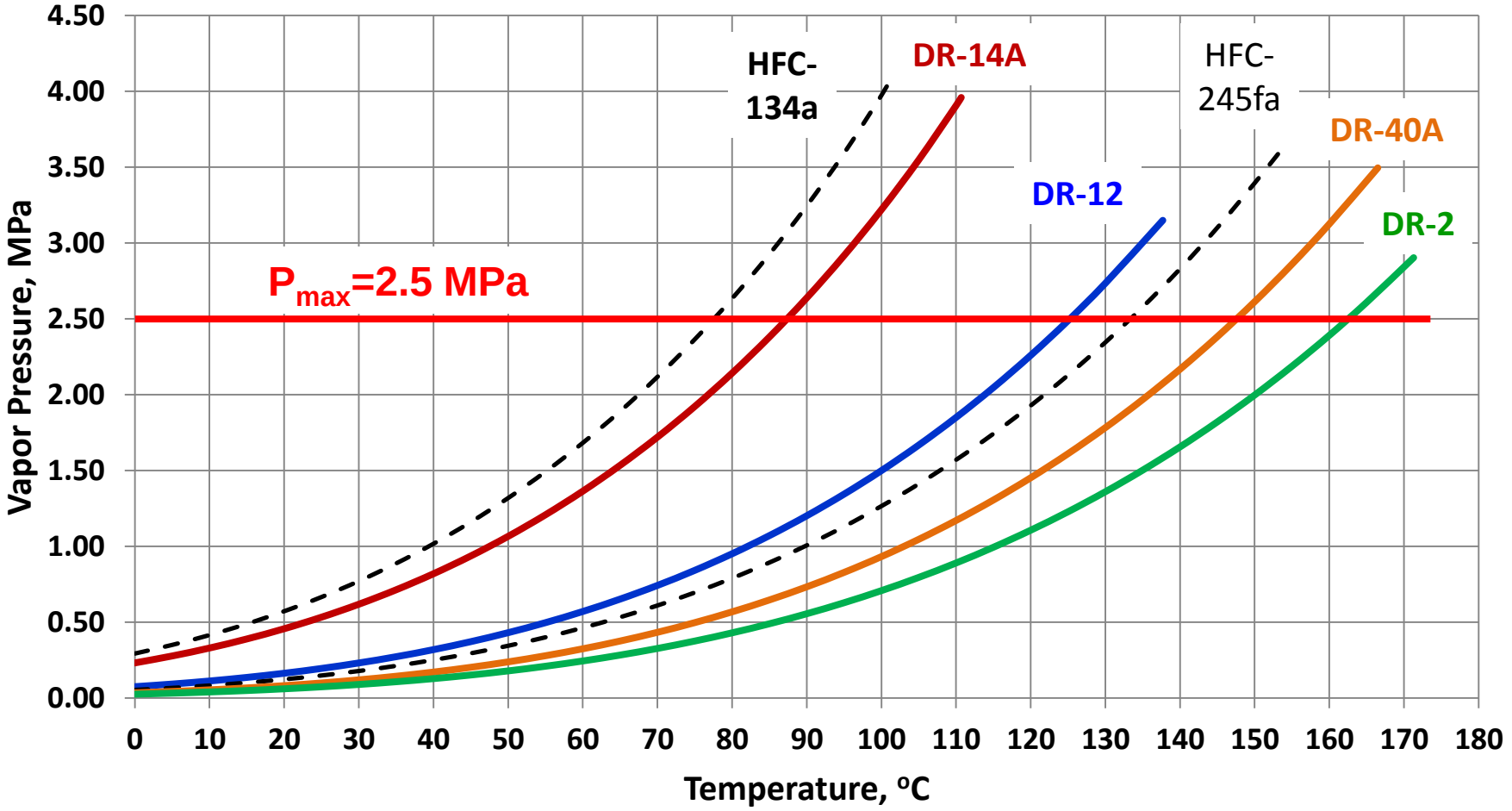
Vapor Pressure



	HFC-134a	DR-14A	DR-12	HFC-245fa	DR-40A	DR-2
$T_{2.5MPa}$, °C	77.5	87.8	125.3	133.4	149.2	162.8

+15.8 °C

Vapor Pressure

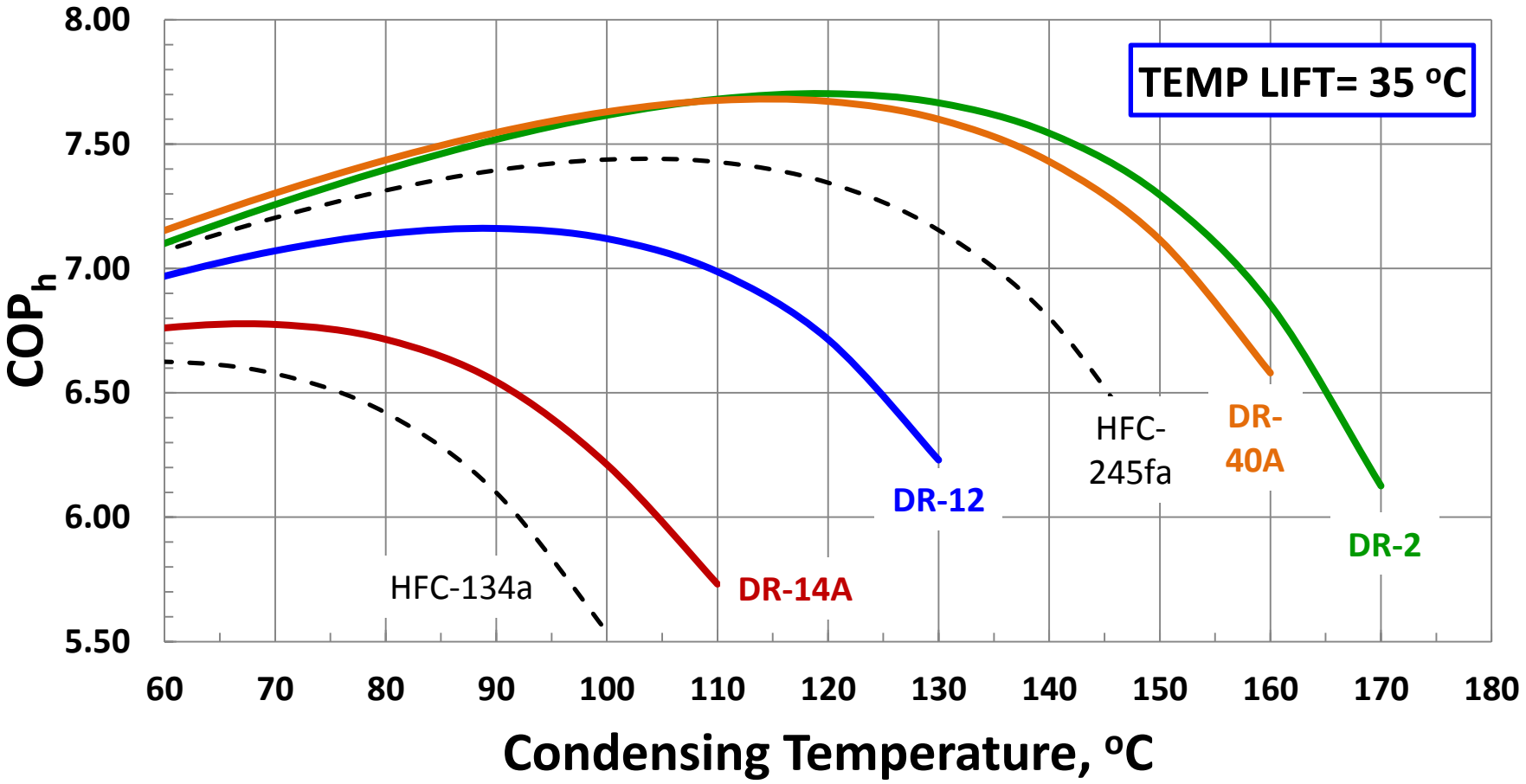


	HFC-134a	DR-14A	DR-12	HFC-245fa	DR-40A	DR-2
$T_{2.5MPa}$, °C	77.5	87.8	125.3	133.4	~~149.2~~	162.8

+29.4 °C

Predicted Simple Cycle Performance

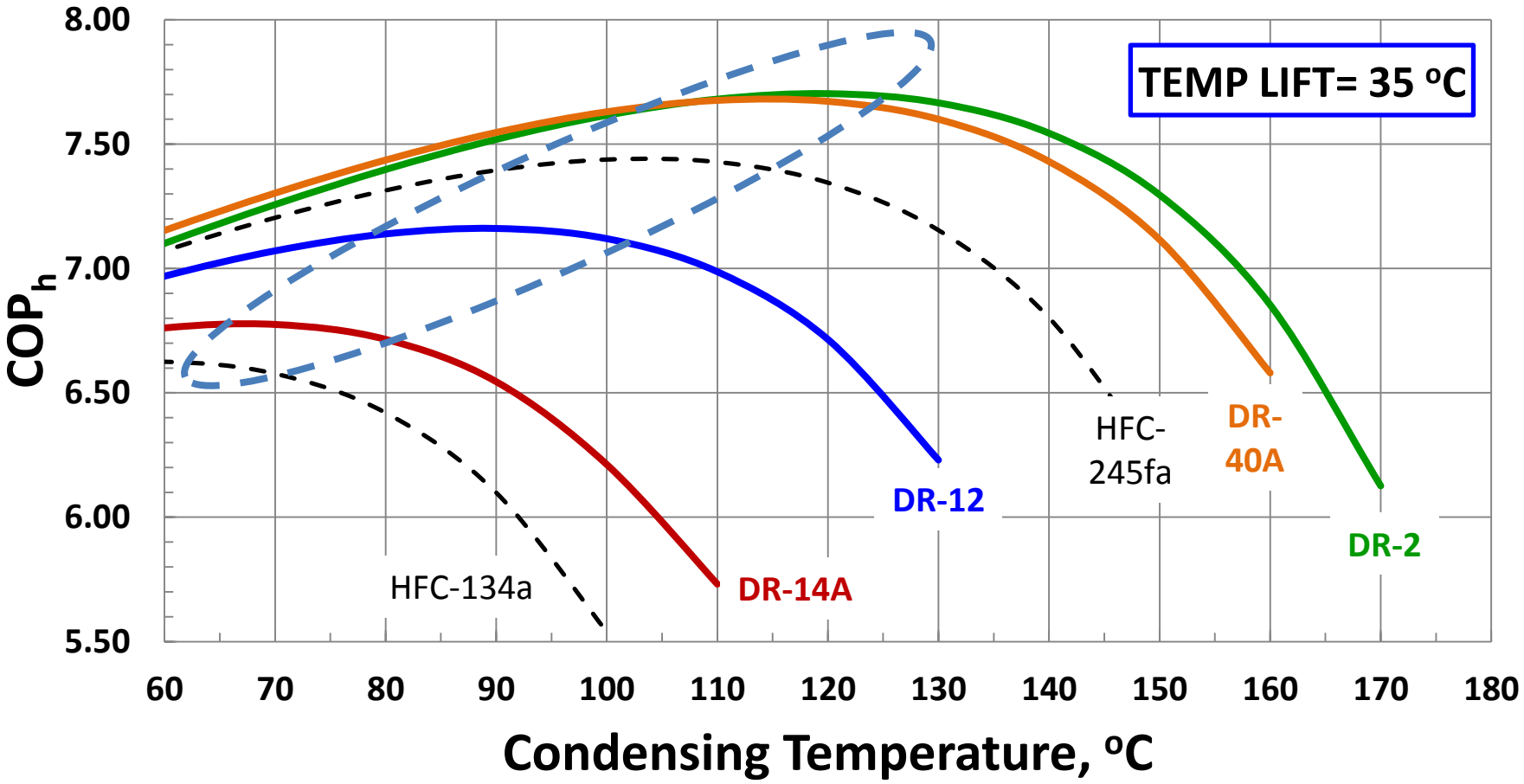
ΔT_{superh}= 11 °C; ΔT_{subc}= 5 °C; Compressor Efficiency=0.8



$$T_{evap} = T_{cond} - 35\ ^{o}C$$

Predicted Simple Cycle Performance

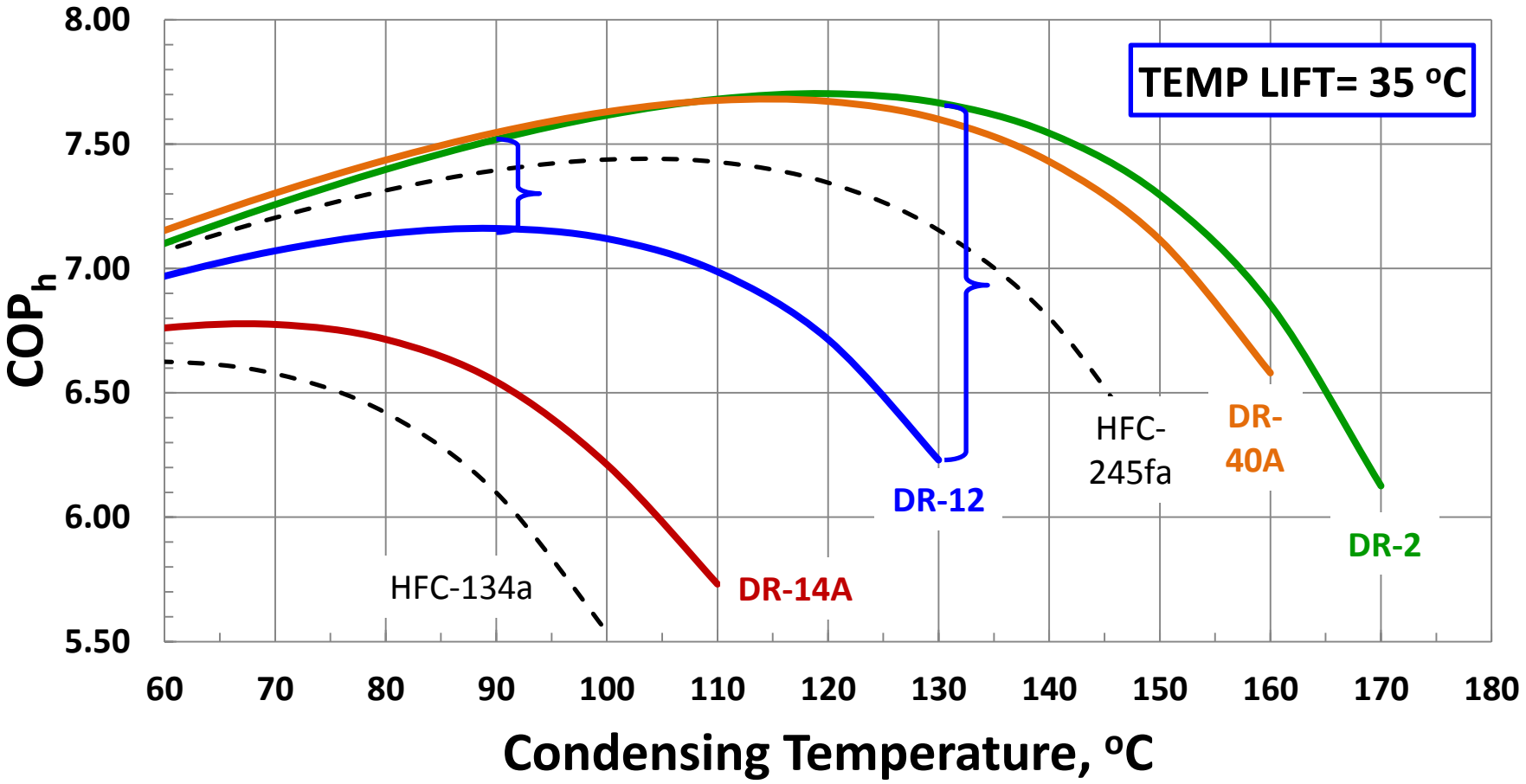
ΔT_{superh}= 11 °C; ΔT_{subc}= 5 °C; Compressor Efficiency=0.8



COP$_h$ DECREASES CLOSE TO T_{cr}

Predicted Simple Cycle Performance

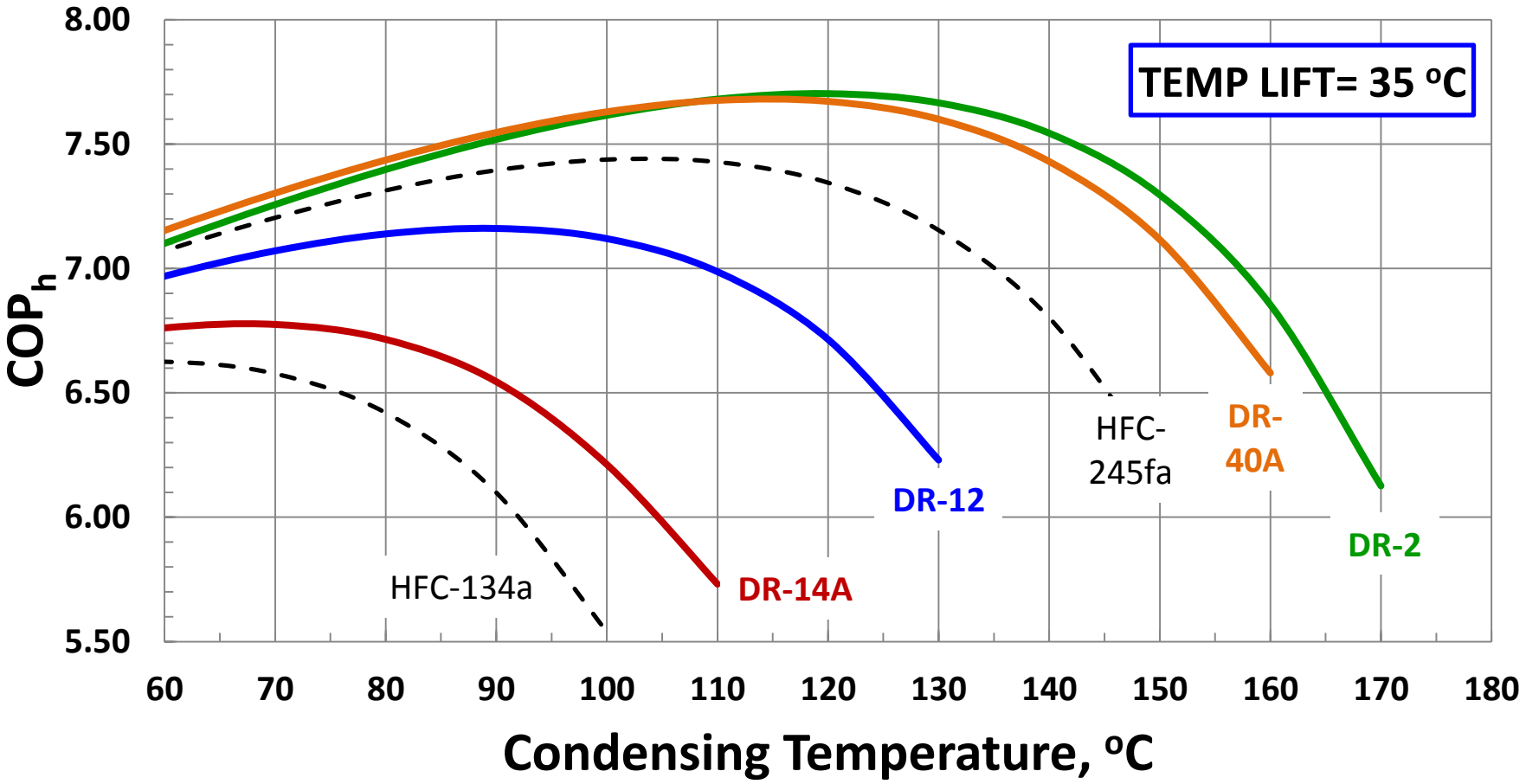
ΔT_{superh}= 11 °C; ΔT_{subc}= 5 °C; Compressor Efficiency=0.8



COP_h DIFFERENCES AMONG FLUIDS MAGNIFIED AT HIGHER TEMPS

Predicted Simple Cycle Performance

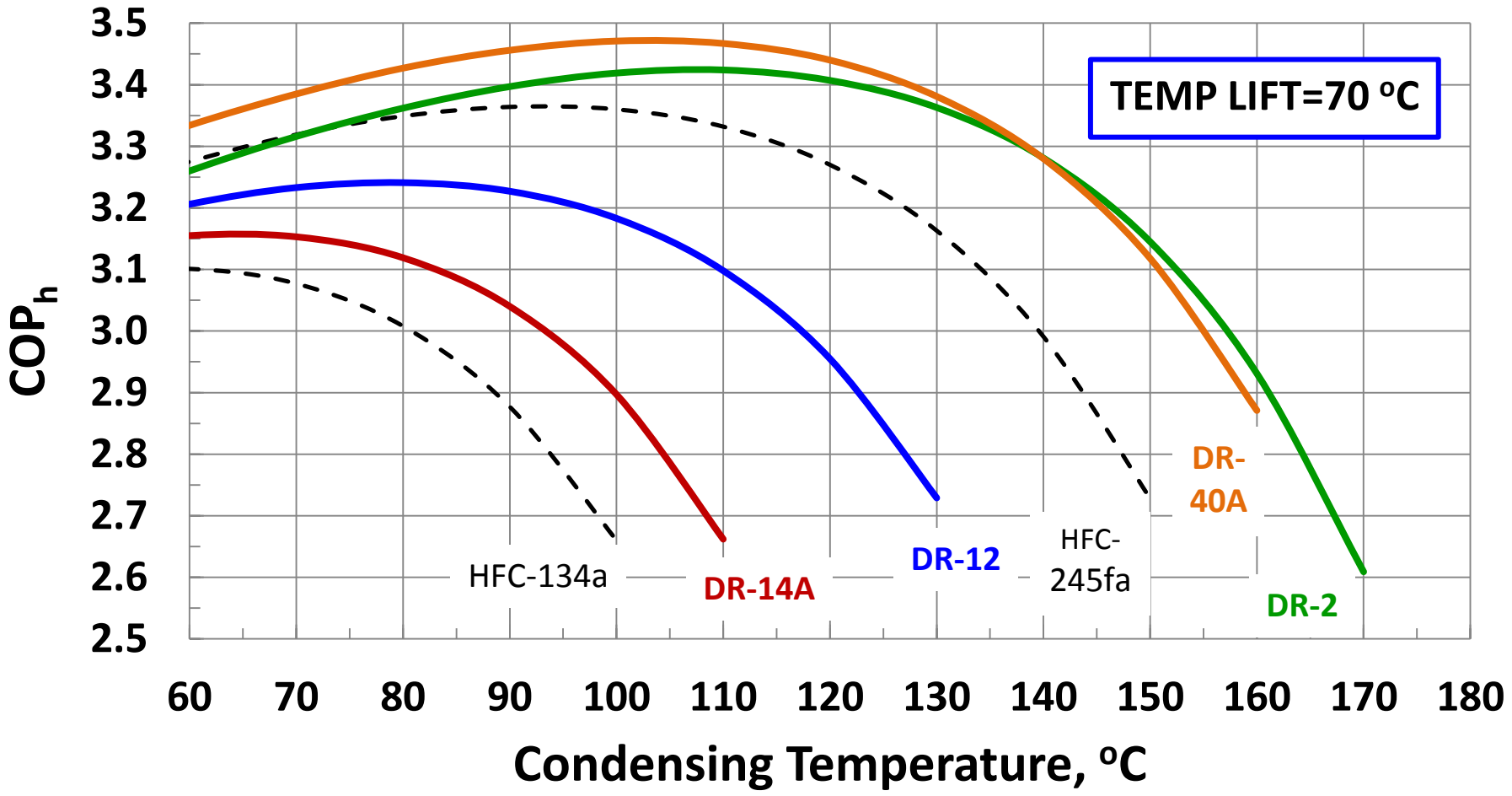
ΔT_{superh}= 11 °C; ΔT_{subc}= 5 °C; Compressor Efficiency=0.8



ATTRACTIVE COP$_h$ UNDER ALL FEASIBLE CONDITIONS

Predicted Performance: COP_h at High Temp Lift

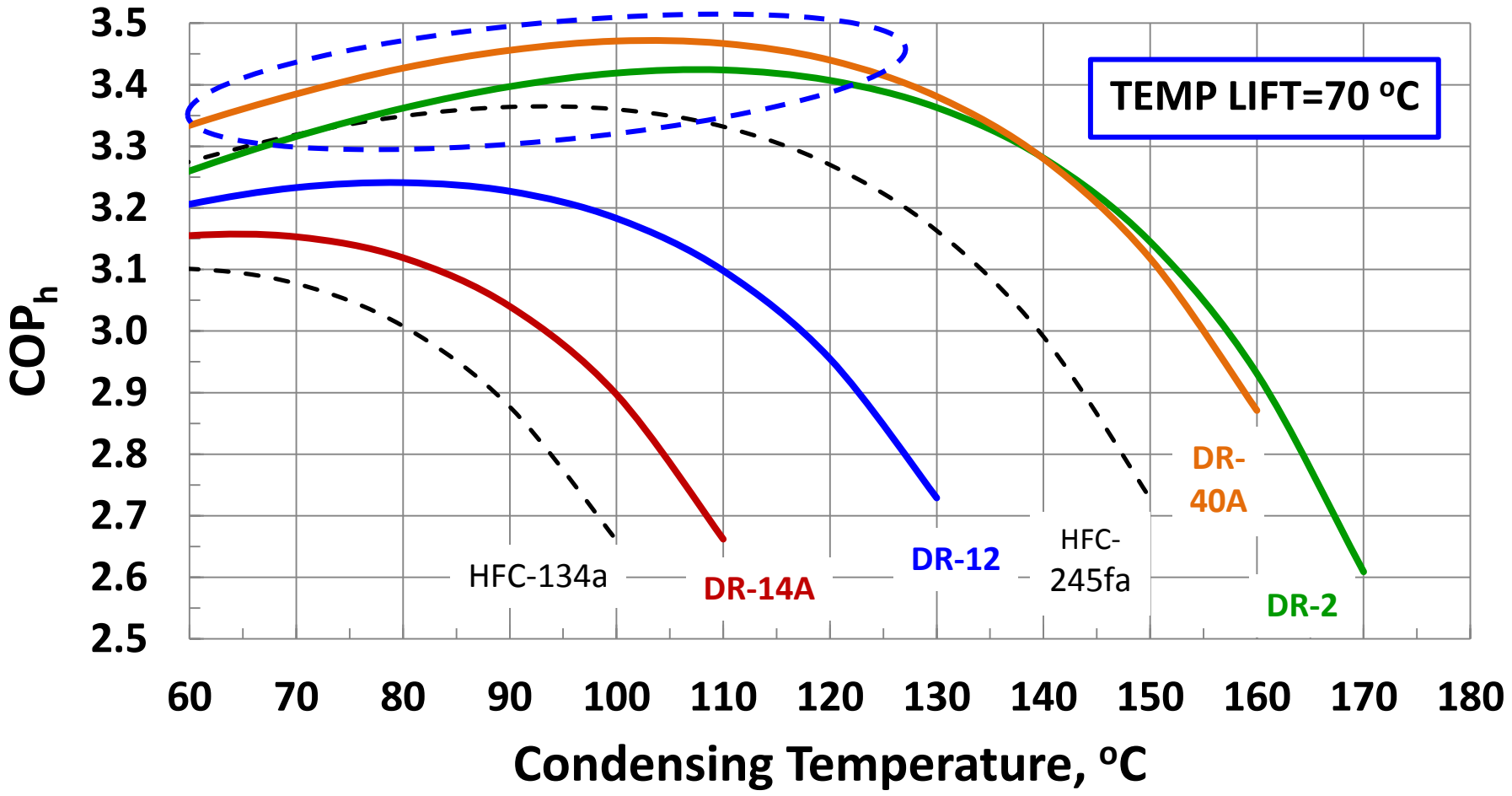
ΔT_{superh}= 20 °C; ΔT_{subc}= 5 °C; Compressor Efficiency=0.8



COP_h LOWER AT HIGHER LIFT BUT STILL ATTRACTIVE UNDER BROAD CONDITIONS

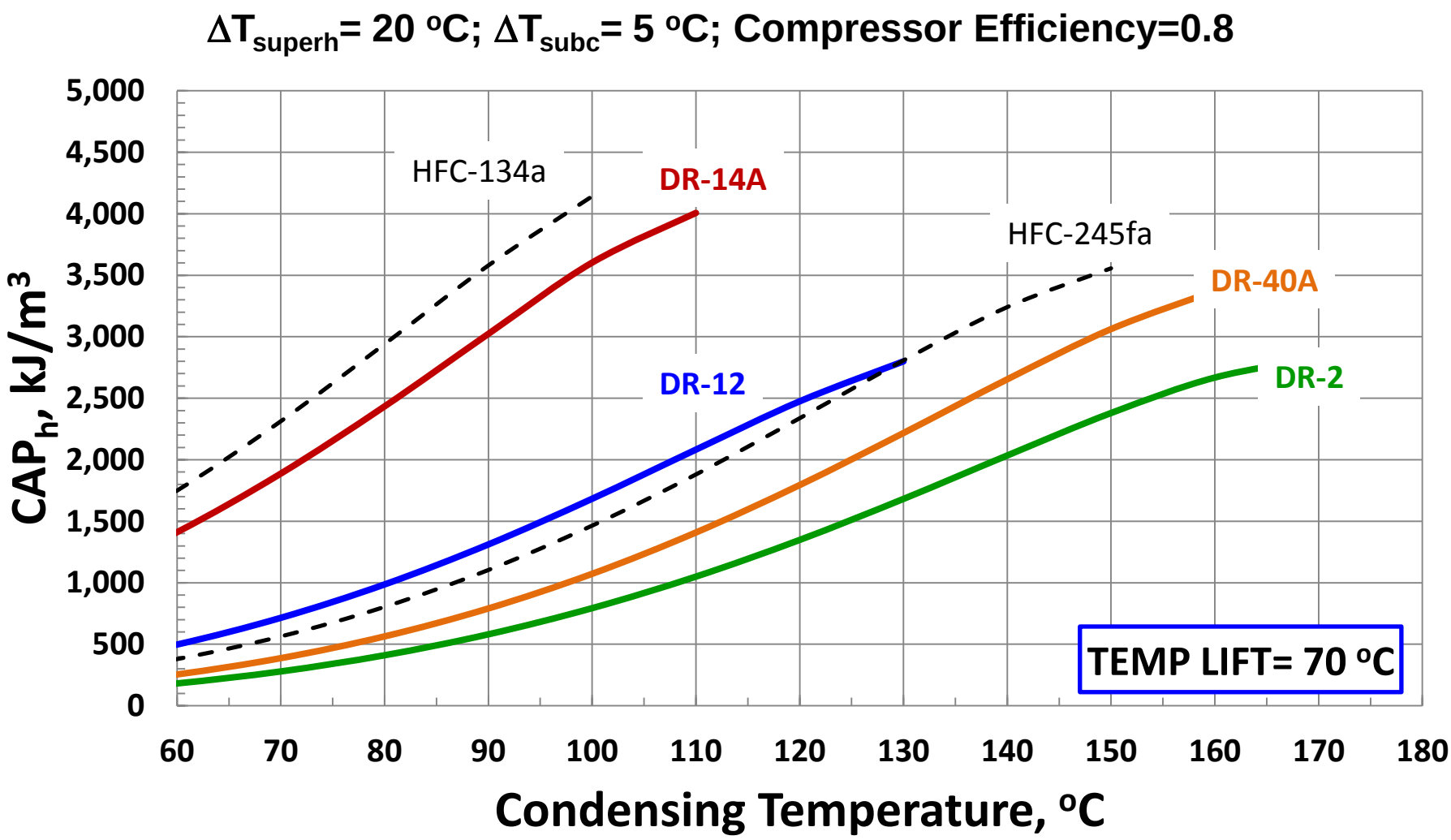
Predicted Performance: COP_h at High Temp Lift

ΔT_{superh}= 20 °C; ΔT_{subc}= 5 °C; Compressor Efficiency=0.8



DR-40A: HIGHEST COP_h FOR T_{cond}< ~140 °C

Predicted Performance: CAP_h at High Temp Lift



In Inverse Order to COP_h
Practical Under Broad Conditions Even at the Higher Lift

Summary

Efforts to increase energy efficiency and reduce environmental impacts from the use of fossil fuels could encourage wider adoption of heat pumps for heating including at higher temperatures than it has been common in the past

Non-flammable, HFO-based, developmental fluids DR-14A, DR-12, DR-40A and DR-2 could enable heat pumps delivering condensing temperatures up to 160 ºC with attractive energy efficiencies

Questions?
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Thank you!