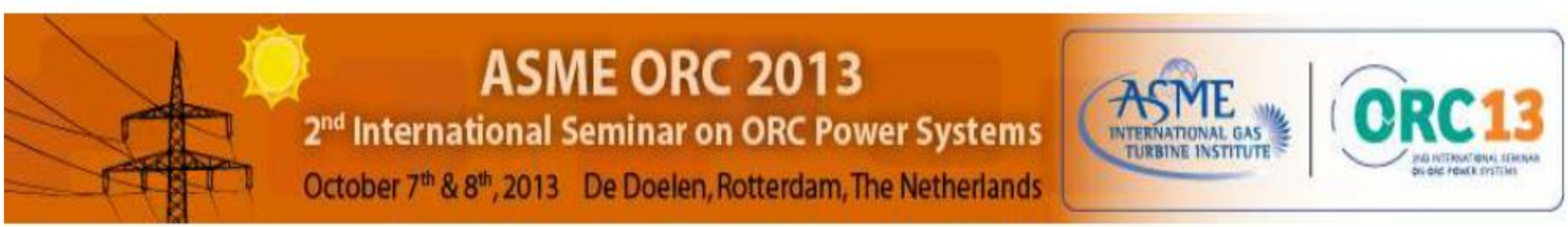
Ban-Ki Moon:
"The heat is on!"
Stockholm, Sep. 27, 2013

Low GWP Working Fluid for Organic Rankine Cycles: DR-2

Chemical Stability at High Temperatures

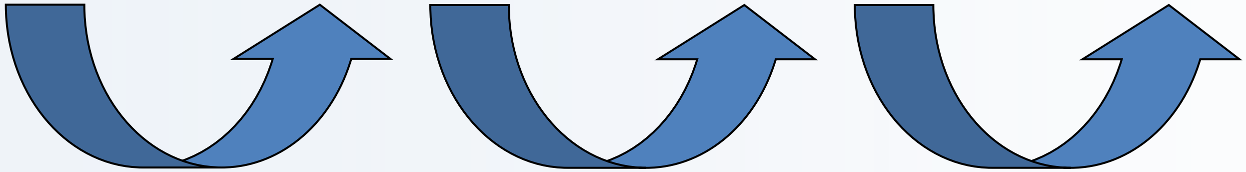


Kostas Kontomaris, Barbara Minor, Bianca Hydutsky
DuPont Fluorochemicals

October 8th, 2013

Hydro-Fluoro-Olefins

CFCs →	HCFCs →	HFCs →	HFOs
CFC-12		HFC-134a	HFO-1234yf, XP10, DR-14
CFC-114		HFC-245fa	DR-12, DR-40
CFC-11	HCFC-123		DR-2



Less Chlorine **No Chlorine** ***Double Bond***

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!

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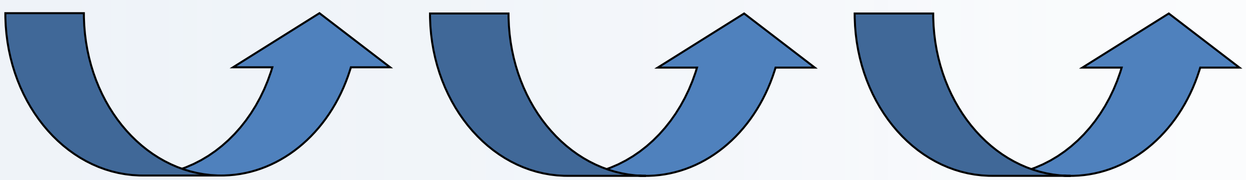

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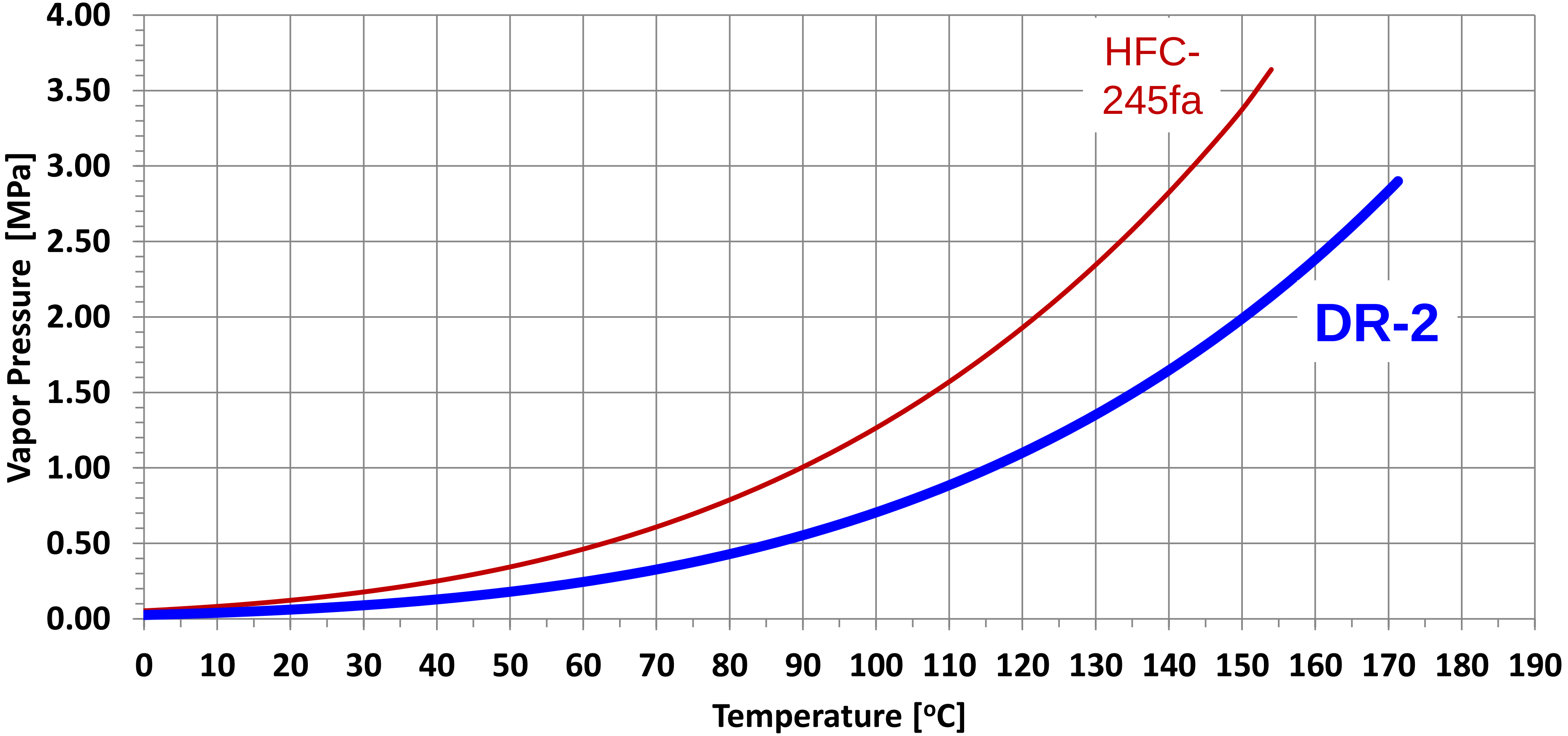
Developmental Refrigerant: DR-2

	HFC-245fa	DR-2
Chemical Formula	$CF_3CH_2CHF_2$	
ASHRAE Std 34 Safety Class	B1	A1 (expected)
ALT [yrs]	7.6	0.0658 (24 days)
ODP	None	None
GWP_{100}	1,030	9
T_b [°C]	15.1	33.4
T_{cr} [°C]	154	171.3
P_{cr} [MPa]	3.65	2.9

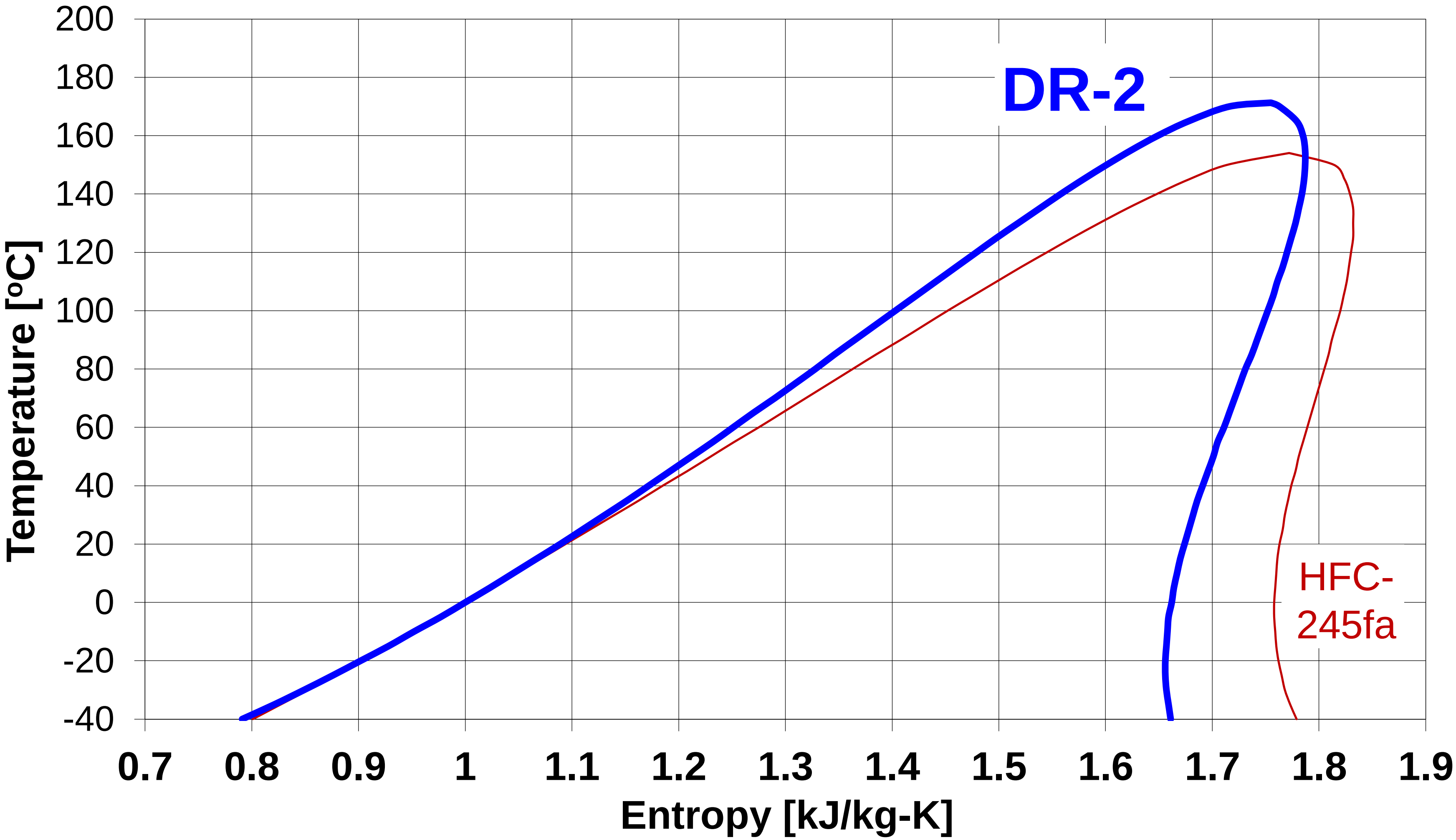
Very Low GWP AND Non-Flammable

Vapor Pressure

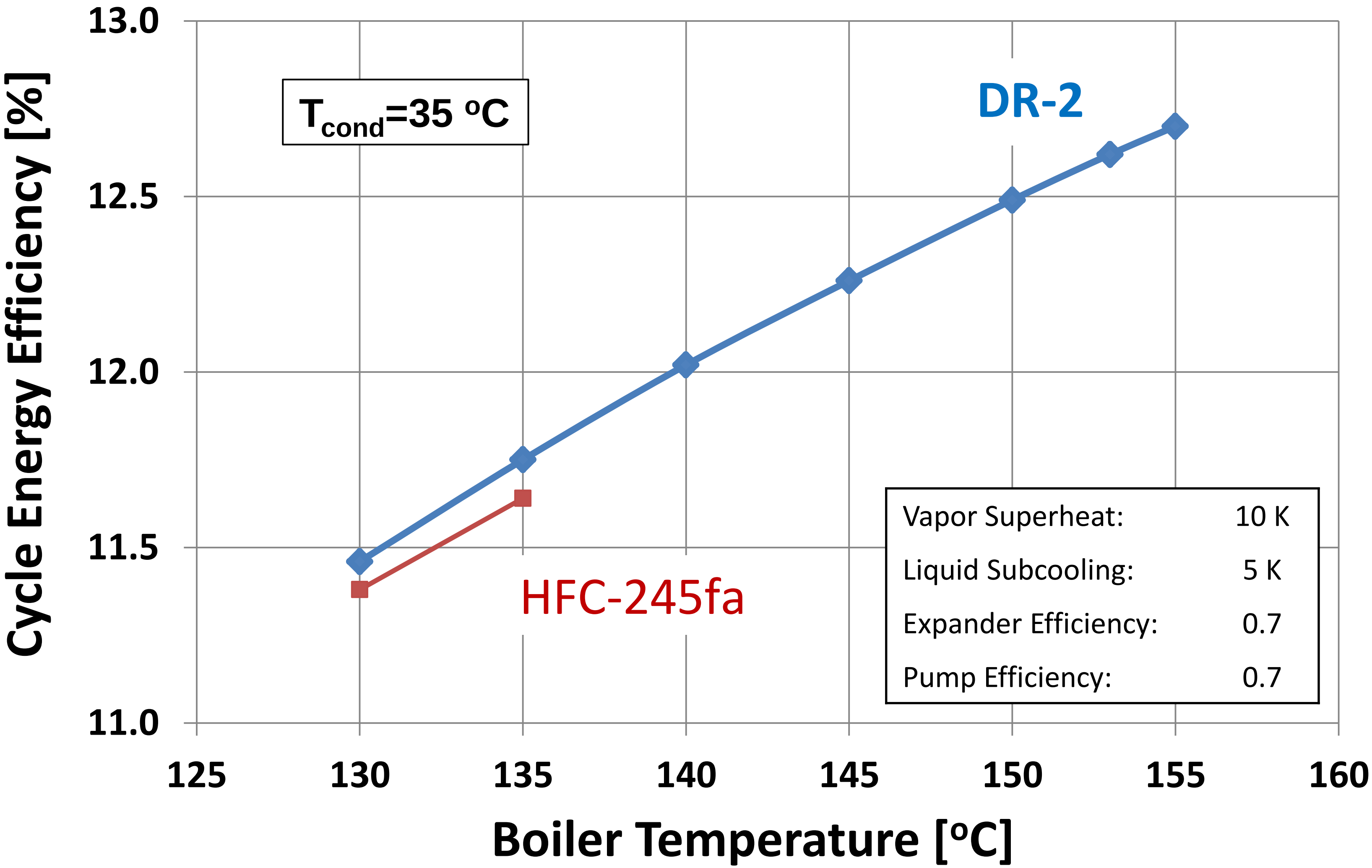


	HFC-245fa	DR-2
T_{cr}, °C	154.0	171.3

DR-2 Temp-Entropy Diagram vs HFC-245fa



ORC Energy Efficiency



Thermal Stability Testing

ASHRAE Standard 97 Sealed Glass Tube Method

1. **Copper, steel and aluminum coupon bundles are placed in glass tubes.**

2. **Working fluid and optionally lubricant, air and/or moisture are loaded into tubes**

3. **Tubes are sealed and aged at a selected temperature for selected times.**

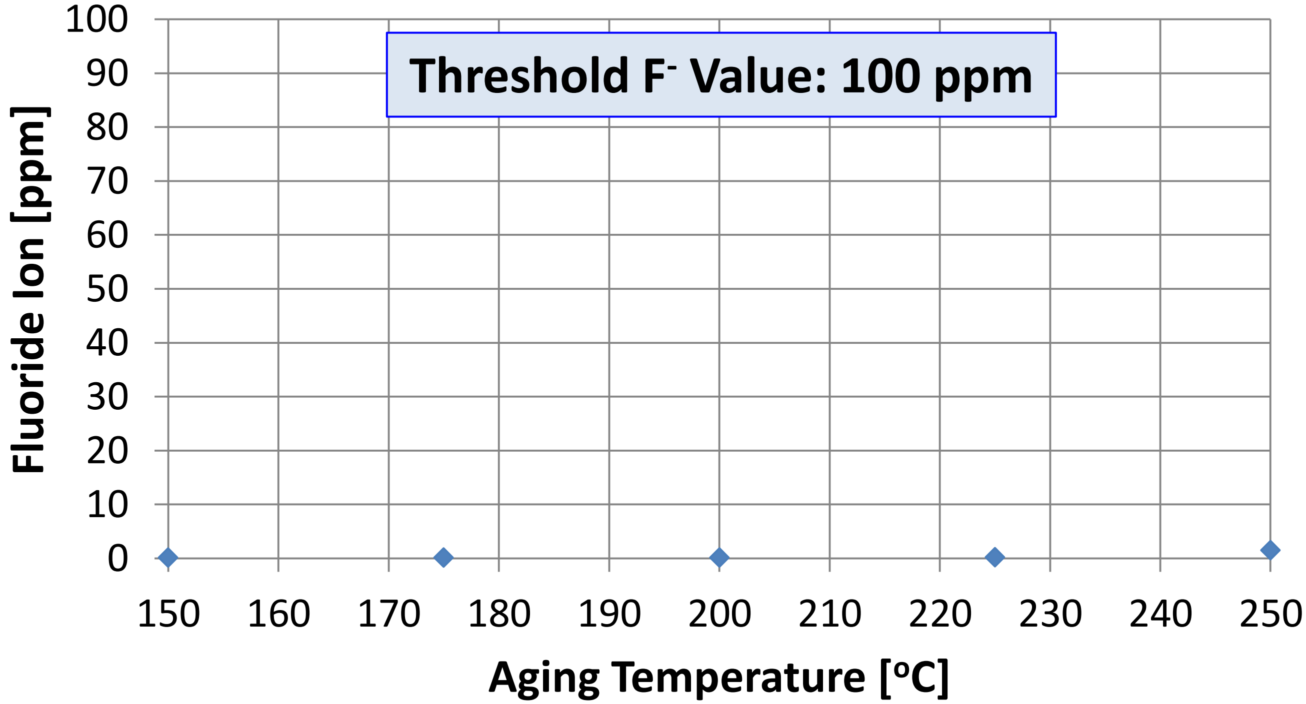
4. **Post-aging, liquid is analyzed for:**
   -Fluoride and Chloride concentration
   -Total Acid Number (TAN) when lubricant is present

Thermal Stability of DR-2: In the Presence of Metals

Aging for 14 Days at Increasing Temperatures

After 14 days @ 250 °C: Clear Fluid, Clean Coupons

Aging Temp [°C]	F^- [ppm]
150	<0.15
175	<0.15
200	0.18
225	0.23
250	1.50



Thermal Stability of DR-2:
In the Presence of Metals

Aging for 14 Days at Increasing Temperatures

Aging Temp [^oC]	Newly Formed Compounds [ppm] by GCMS
150	0.5
175	4.0
200	25.0
225	77.1
250	425.5

After 14 days @ 250 ^oC:

Negligible Formation of Decomposition Products

Reference Fluids

Working Fluid Family	Name	Formula
Hydro-**F**luoro-**O**lefin	DR-2	
Hydro-**C**hloro-**F**luoro-**C**arbon	123	$CHCl_2CF_3$
Hydro-**F**luoro-**C**arbon	245fa	$CF_3CH_2CHF_2$
Hydro-**F**luoro-**E**ther	HFE-449sl	$C_4F_9OCH_3$
Hydro-**C**hloro-**F**luoro-Olefin	1233zd-E	$CF_3CH{=}CHCl$

Thermal Stability in the Presence of Metals: DR-2 vs Reference Fluids

After 1 day @ 250 °C

Fluid	Visual Observations
HFO DR-2	clear liquid; clean coupons
HCFC-123	slight yellow tint
HFC-245fa	clear liquid; clean coupons
HFE-449sl	Cu migration to steel
HCFO-1233zd-E	slight dulling of Cu; darkening of steel

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Thermal Stability in the Presence of Metals: DR-2 vs Reference Fluids

After 7 days @ 250 ^{o}C

Fluid	Visual Observations
HFO DR-2	clear liquid; clean coupons
HCFC-123	dark brown liquid, brown on glass, brown on coupons
HFC-245fa	clear liquid; clean coupons
HFE-449sl	dulling of Cu; darkening of the steel
HCFO-1233zd-E	steel discoloured, dark residue

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Thermal Stability in the Presence of Metals: DR-2 vs Reference Fluids

AGING @ 250 ^{o}C

Fluoride Ion Concentration [ppm]

AGING [DAYS]	HFO DR-2	HCFC -123	HFC-245fa	HFE-449sl	HCFO-1233zd-E
1	<3	328	<3	330	14
7	8	2,460	8	159	118

Chloride Ion Concentration [ppm]

AGING [DAYS]	HCFC-123	HCFO-1233zd-E
1	496	219
7	63	530

Threshold Cl^-, F^- Value: 100 ppm

Thermal Stability in the Presence of Metals: DR-2 vs Reference Fluids

AGING @ 250 ^{o}C

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7	63	530

Threshold Cl^-, F^- Value: 100 ppm

DR-2 Thermal Stability: In the Presence of Metals, Air and Moisture

AGING @ 250 ºC

Air: 7.6 mmHg; Moisture: 200 ppm

Metal Coupons:
No Significant Change in Appearance

Fluoride Ion Concentration [ppm]

AGING [DAYS]	HFO DR-2	HFC-245fa
1	6	4
7	11	20

Threshold F^- Value: 100 ppm

Stability of POE Lubricants: CPI/Lubrizol POE

At 250 ^oC With Metal Coupons; No Refrigerant Added

Dried and De-aerated

AGING [DAYS]	Acidity, TAN [mg KOH/g]
1	0.2
7	1.3

7.6 [mm Hg] of Air and 200 [ppm] of Moisture

AGING [DAYS]	Acidity, TAN [mg KOH/g]
1	0.6
7	1.6

Threshold TAN Value: 3

Thermal Stability of DR-2/POE Blends: At 250 ºC In the Presence of Metals

CPI/Lubrizol POE Lubricant

Dried and De-aerated

Acidity, TAN [mg KOH/g]

AGING [DAYS]	HFO DR-2/POE (50/50 vol%)	HFC-245fa/POE (50/50 vol%)
1	1.4	?
7	1.5	1.5

Threshold TAN Value: 3

Thermal Stability of DR-2/POE Blends:

At 250 ºC In the Presence of Metals, Air and Moisture

CPI/Lubrizol POE Lubricant

7.6 [mm Hg] of Air and 200 [ppm] of Moisture

Acidity, TAN [mg KOH/g]

AGING [DAYS]	HFO DR-2/POE (50/50 vol%)	HFC-245fa/POE (50/50 vol%)
1	1.6	1.3
7	2.3	2.2

Threshold TAN Value: 3

In Summary

- DR-2, remarkably, exhibits comparable thermal stability to HFC-245fa at the severe conditions tested (up to 250ºC) despite its unsaturated chemical nature!!

- DR-2 and HFC-245fa demonstrate the highest thermal stability among the fluids tested (HCFC-123, HCFO-1233zd-E and HFE-449sl).

- However, DR-2 provides the highest thermal stability with the lowest GWP (99 % reduction vs. HFC-245fa).

DR-2:

Attractive Safety, Health and Environmental Properties

Favorable Thermodynamics

High Thermal Stability

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Thank you!

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