A NON-FLAMMABLE, ZERO-ODP, LOW GWP WORKING FLUID FOR HIGH TEMPERATURE HEAT PUMPS: DR-148

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Abstract: This paper introduces a new developmental refrigerant, DR-148, as a potential working fluid for high temperature heat pumps. DR-148 is a non-flammable, hydrofluoro-olefin-based fluid with an ozone depletion potential of zero and a global warming potential of 148. The components of DR-148 remained chemically stable in the presence of metals up to the maximum temperature tested of 250 ^{o}C. DR-148 thermodynamic performance under cycle conditions representative of potential high temperature heat pump applications was evaluated through computational modeling. DR-148 has a relatively high critical temperature, generates relatively low vapor pressures and enables high cycle energy efficiencies. It could enable more environmentally sustainable heat pump platforms for the utilization of abundantly available low temperature heat to meet heating duties at higher temperatures and with higher energy efficiencies than incumbent working fluids.

Key Words: heat recovery, low global warming potential (GWP), Hydro-Fluoro-Olefin (HFO), refrigerants, energy efficiency

1 INTRODUCTION

Current trends shaping the global energy landscape suggest an expanding utilization of low temperature heat (i.e. heat at temperatures lower than about 100 ^{o}C) in the near future. Motivation for low temperature heat utilization is provided by increasing energy prices and a growing awareness of the environmental impacts, in general, and the threat to the earth's climate, in particular, from the use of fossil fuels and associated greenhouse gas emissions.

Low temperature heat may be recovered from various commercial or industrial operations, can be extracted from geothermal or hydrothermal reservoirs or can be generated through solar collectors. Elevation of the temperature of available heat through high temperature mechanical compression heat pumps (HTHPs) to meet heating requirements is one promising approach to using low temperature heat. (Use of low temperature heat for cooling, heating or power generation through absorption cycles is beyond the scope of this paper.) A proliferation of technologies is emerging that could expand the easily accessible low temperature heat resource (e.g. local, stand-alone, remote, supplemental or backup distributed power generation and cogeneration of heat and power for commercial, industrial and military end use from a variety of primary energy sources including biomass, municipal and other waste, natural gas and bio-gas, bio-diesel, and solar or geothermal heat).

Heat pumps operating according to a reverse Rankine cycle require the use of working fluids (also referred to as "refrigerants"). Working fluids currently in common use for HTHPs either are controlled as ozone depleting substances under the Montreal Protocol (e.g. CFC-114) or are coming under increasing scrutiny because of their high global warming potentials (GWPs) (e.g. HFC-245fa). Clearly, there is an increasing need for more environmentally sustainable working fluids for HTHPs, especially given that environmental sustainability is a primary motivation for low temperature heat utilization.

A new generation of refrigerants with low GWPs, known as Hydro-Fluoro-Olefins (HFOs), may enable the design and operation of energy efficient HTHPs with reduced environmental impact. Three new low GWP developmental refrigerants based on HFOs, DR-14, DR-12 and DR-2 (HFO-1336mzz-Z; $CF_3CH=CHCF_3$), have been recently introduced as working fluids for HTHPs in a series of papers by Kontomaris (2011a, 2011b, 2012a, 2012b, 2012c, 2013a, 2013b). They have increasing critical temperatures (DR-14: 111.6 ^oC; DR-12: 137.7 ^oC; DR-2: 171.3 ^oC) and atmospheric boiling temperatures (DR-14: -20.5 ^oC; DR-12: 7.5 ^oC; DR-2: 33.4 ^oC).

This paper introduces a novel, near-azeotropic, fluid blend, DR-148, based on HFO technology, as a working fluid for HTHPs. DR-148 has a critical temperature, 167.4 ^oC, and atmospheric boiling temperature (average of atmospheric bubble and dew temperatures), 26.33 ^oC, intermediate to those of DR-2 and DR-12. DR-148 could be proven advantageous for utilizing heat at temperatures approaching its critical temperature. The main objective of this paper was to evaluate the potential of DR-148 as a working fluid for HTHPs.

Table 1 summarizes key thermodynamic, safety, health and environmental characteristics of DR-148. It compares DR-148 to two alternative low GWP fluid candidates, DR-2 and DR-12, and to three familiar reference fluids (HCFC-123, CFC-114 and HFC-245fa). CFC-114 and HFC-245fa have been widely used for HTHPs. HCFC-123 has not been widely used at condensing temperatures higher than about 100 ^oC, despite its attractive thermodynamic properties, apparently because of its limited thermal stability.

2 METHODS

The thermo-physical properties of DR-148 were estimated using group contribution methods and equations of state from measurements of the liquid density and vapor pressure of the blend and its constituent components over a wide temperature range. The thermodynamic performance of DR-148 in illustrative idealized cycles representative of potential applications was computed and compared to the performance of HFC-245fa. Quantifying the effect of DR-148 transport properties on system performance, although clearly of practical significance, was beyond the scope of this paper. The thermal stability of the DR-148 components in the presence of aluminum, steel and copper was assessed according to the familiar sealed glass tube methodology of ASHRAE-ANSI Standard 97.

3 RESULTS

3.1 Thermodynamic Properties

Figure 1 compares the average vapor pressure of DR-148 (quantified as the average of the DR-148 dew and bubble pressures at a given temperature) to the vapor pressures of HFC-245fa and DR-2. DR-148 generates vapor pressures intermediate to those of HFC-245fa and DR-2. As a result of its lower vapor pressure, use of DR-148 could allow higher condensing temperatures for HTHPs than HFC-245fa without exceeding the maximum design working pressure of commonly available low cost equipment. For example, the maximum permissible working pressure for some commonly available heat pumps may be limited to values below 2.5 MPa. DR-148 and HFC-245fa would allow condensing temperatures of up to about 150 ^oC and 133 ^oC, respectively, without exceeding a vapor pressure of 2.5 MPa. Furthermore, the higher critical temperature of DR-148 (T_{cr}=167.4 ^oC) would also be advantageous for use in HTHPs because it would allow heat release under conventional subcritical operation (i.e. through condensation) at higher temperatures than HFC-245fa (T_{cr}=154 ^oC). The higher vapor pressure of DR-148 relative to DR-2 would result in higher volumetric heating capacity in applications in which the range of operating condensing temperatures and pressures would allow the use of either DR-148 or DR-2.

Table 1: Key properties of DR-148 compared to incumbent and alternative low GWP working fluids; fluids listed in increasing order of atmospheric boiling temperature.

		CFC-114(1)	DR-12	HFC-245fa(1)	DR-148	HCFC-123(1)	DR-2
Chemical Identity		$CClF_2CClF_2$	Proprietary	$CHF_2CH_2CF_3$	Proprietary	$CHCl_2CF_3$	HFO-1336mzz-Z; $CF_3CH=CHCF_3$
Atmosph. Bubble Temp	°C	N/A	N/A	N/A	**25.81**	N/A	N/A
Atmosph. Dew Temp	°C	N/A	N/A	N/A	**26.85**	N/A	N/A
Temp Glide at Atmosph. Pressure	K	N/A	N/A	N/A	**1.04**	N/A	N/A
Average Atmosph. Boiling Temp	°C	3.6	7.5	15.1	**26.33**	27.8	33.4
Critical Temp	°C	145.7	137.7	154	**167.4**	183.7	171.3
Critical Pressure	MPa	3.26	3.15	3.65	**3.41**	3.66	2.90
OEL	ppmv	1,000	TBD(2)	300	**TBD(2)**	50	500(3)
LFL	vol%	None	None(4)	None	**None(4)**	None	None(4)
Tox Class(5)		A	TBD(2)	B	**TBD(2)**	B	A(6)
Flam Class(5)		1	1(6)	1	**1(6)**	1	1(6)
Ozone Depletion Potential		1.000	0(7)	0	**0(7)**	0.020	0(7)
Atmosph Life Time	yrs	300	0.243836(8)	7.6	**N/A**	1.3	0.06027(8)
GWP_{100}(9)		10,040	32(8)	1,030	**148**	77	8.9(8)

(1) From Calm and Hourahan (2007); (2) To Be Determined; (3) DuPont Allowable Exposure Limit (AEL); (4) According to ASTM E681-2001; (5) According to ASHRAE Standard 34; (6) Not established yet, but meets criteria of ASHRAE Standard 34; (7) No halogen atoms in DR-148, DR-12 or DR-2 other than fluorine; (8) National Oceanic and Atmospheric Admin., 2010; (9) One hundred years Integrated Time Horizon

Figures 2 and 3 compare the pressure-enthalpy and temperature-entropy diagrams of DR-148 to those of DR-2 and HFC-245fa. The DR-148 heat of vaporization is larger than that of DR-2. Similarly to HFC-245fa and DR-2, DR-148 would require some superheat at the inlet of the compressor under some HTHP cycle conditions to ensure dry compression. The significance of the apparent differences in the pressure-enthalpy and temperature-entropy diagrams depicted in Figures 2 and 3 is best illustrated through the cycle performance comparisons in the following section.

3.2 Thermodynamic Cycle Performance

Tables 2-6 compare the thermodynamic performance of DR-148 in representative high temperature heat pump cycles to HFC-245fa and DR-2. The condensing temperatures, T_{cond}, in Tables 2-6 were selected in the range from 100 ^{o}C to 160 ^{o}C. Two values for the temperature lift, ΔT_{Lift}, were specified at each selected condensing temperature: 35 ^{o}C and 70 ^{o}C. The evaporating temperature, T_{evap}, is then specified as: $T_{evap}= T_{cond} - \Delta T_{Lift}$. The superheat of the vapor entering the compressor, ΔT_{superh}, the subcooling of the liquid before the expansion valve, ΔT_{subc}, and the compressor efficiency were kept at constant values for all cycle calculations in Tables 2-6: ΔT_{superh}= 20 K; ΔT_{subc}= 10 K; Compressor Efficiency=0.7. The primary purpose of the results summarized in Tables 2-6 was to illustrate the thermodynamic properties of DR-148. No attempt was made to optimize the superheat or subcooling values or address other system design issues.

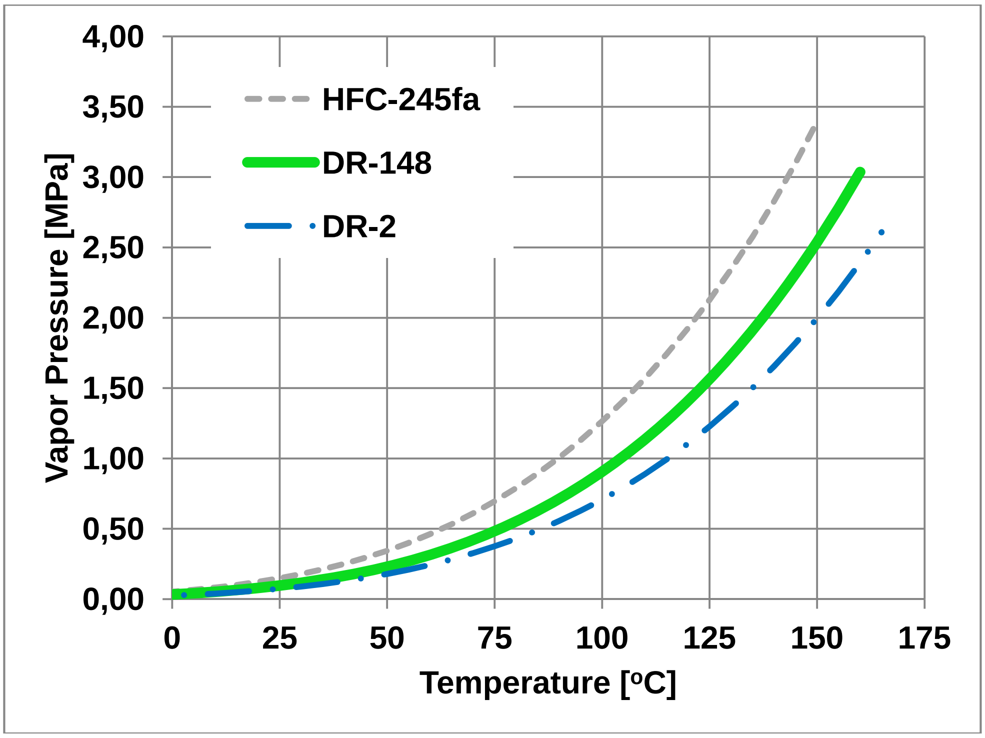

Figure 1: DR-148 average vapor pressure (average of bubble and dew pressures at a given temperature) compared to the vapor pressures of HFC-245fa and DR-2.

Heating at temperatures in the range of 85-100 ^{o}C is often needed for various commercial or industrial applications (e.g. district heating, hydronic space heating, water or other solvent heating for equipment or parts cleaning or disinfection, boiler water preheating, drying or other process heating). Table 2 compares the thermodynamic performance of DR-148 to HFC-245fa and DR-2 for a hypothetical heat pump application meeting a heating duty requiring a condensing temperature of 100 ^{o}C. The heat pump uses available heat (e.g. condenser or process water heat, solar or low grade geothermal heat) supplied to the evaporator operating at 30 ^{o}C or 65 ^{o}C. DR-148 could enable such an application with attractive coefficients of performance for heating, COP_h, in the range of approximately 3.3-7.3. The COP_h, with DR-148 would be 1.9-2.5% higher than with HFC-245fa. The volumetric heating capacity, CAP_h, with DR-148 would be about 27-30% lower than HFC-245fa, as expected given the lower vapor pressure of DR-148.

Table 3 exemplifies the use of a HTHP to meet a heating duty requiring a condensing temperature of 115 ^{o}C (e.g. lumber drying or solvent evaporation). Available heat supplied to the evaporator allows evaporating temperatures of either 45 ^{o}C or 80 ^{o}C. The resulting COP_h values with DR-148 of 3.3-7.4 suggest that heat pump heating for the range of conditions in Table 3 could be quite attractive relative to heating with fossil fuel heaters. The energy efficiency/volumetric heating capacity trade-off expected among fluids of different vapor pressures is observed in Table 3: DR-148 has a 2.8-3.4% higher COP_h and a 25-27% lower CAP_h relative to HFC-245fa. The condensing pressures and compressor discharge temperatures over the range of conditions in Table 3 remain manageable with largely existing compressor technology.

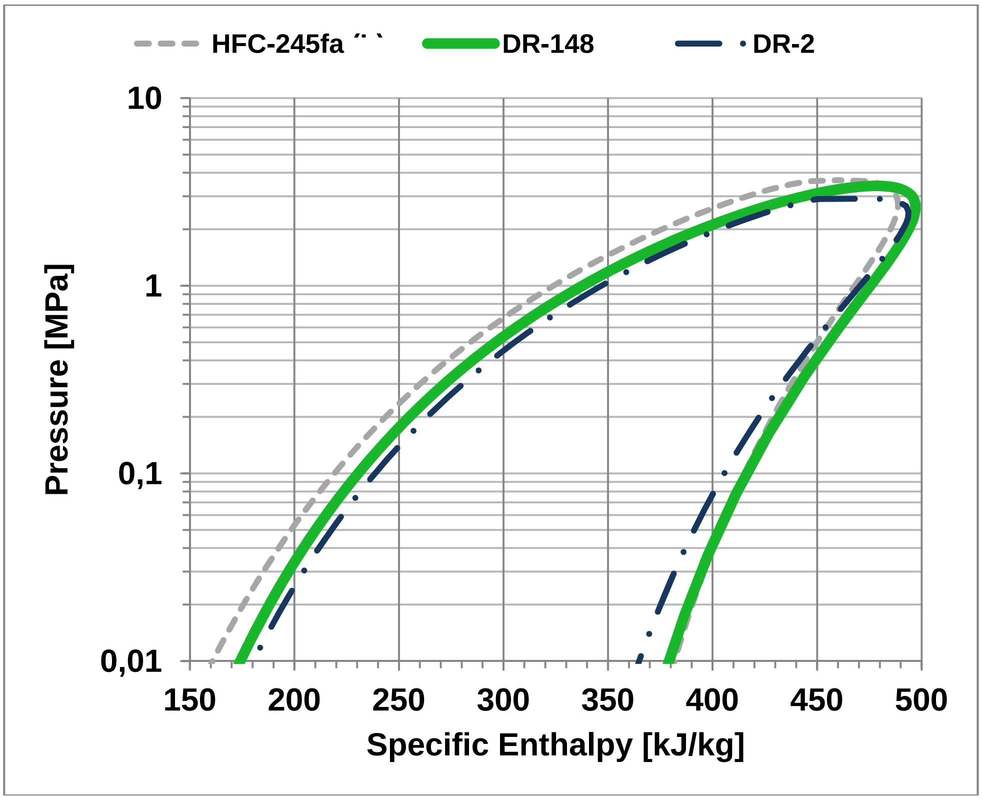

Figure 2: DR-148 pressure-enthalpy diagram compared to HFC-245fa and DR-2.

Table 4 exemplifies the use of a HTHP to meet a heating duty requiring a condensing temperature of 130 ^oC (e.g. low temperature steam generation). Available heat supplied to the evaporator allows evaporating temperatures of either 60 ^oC or 95 ^oC. The resulting COP_h values with DR-148 of 3.3-7.4 suggest that heat pump heating for the range of conditions in Table 4 could be quite attractive relative to heating with fossil fuel heaters. The energy efficiency/volumetric heating capacity trade-off expected among fluids of different vapor pressures is observed in Table 4: DR-148 has a 4.4-5.0% higher COP_h and a 23-25% lower CAP_h relative to HFC-245fa. The compressor discharge temperatures over the range of conditions in Table 4 would pose a challenge to commonly available compressor technology. The condensing pressure with HFC-245fa exceeds the maximum design working pressure for commonly available centrifugal compressors.

Table 5 exemplifies the use of a HTHP to meet a heating duty requiring a condensing temperature of 145 ^oC (e.g. process heating). Available heat supplied to the evaporator allows evaporating temperatures of either 75 ^oC or 110 ^oC. The resulting COP_h values with DR-148 of 3.2-7.3 suggest that heat pump heating for the range of conditions in Table 5 could be attractive relative to heating with fossil fuel heaters. The energy efficiency/volumetric heating capacity trade-off expected among fluids of different vapor pressures is observed in Table 5: DR-148 has a 7.3-7.8% higher COP_h and an about 21% lower CAP_h relative to HFC-245fa. The performance of DR-148 relative to HFC-245fa improves at higher operating temperatures. The condensing pressure with DR-148 remains within the limits of existing compressor technology. However, the compressor discharge temperatures in Table 5 would pose a substantial challenge to commonly available compressor technology.

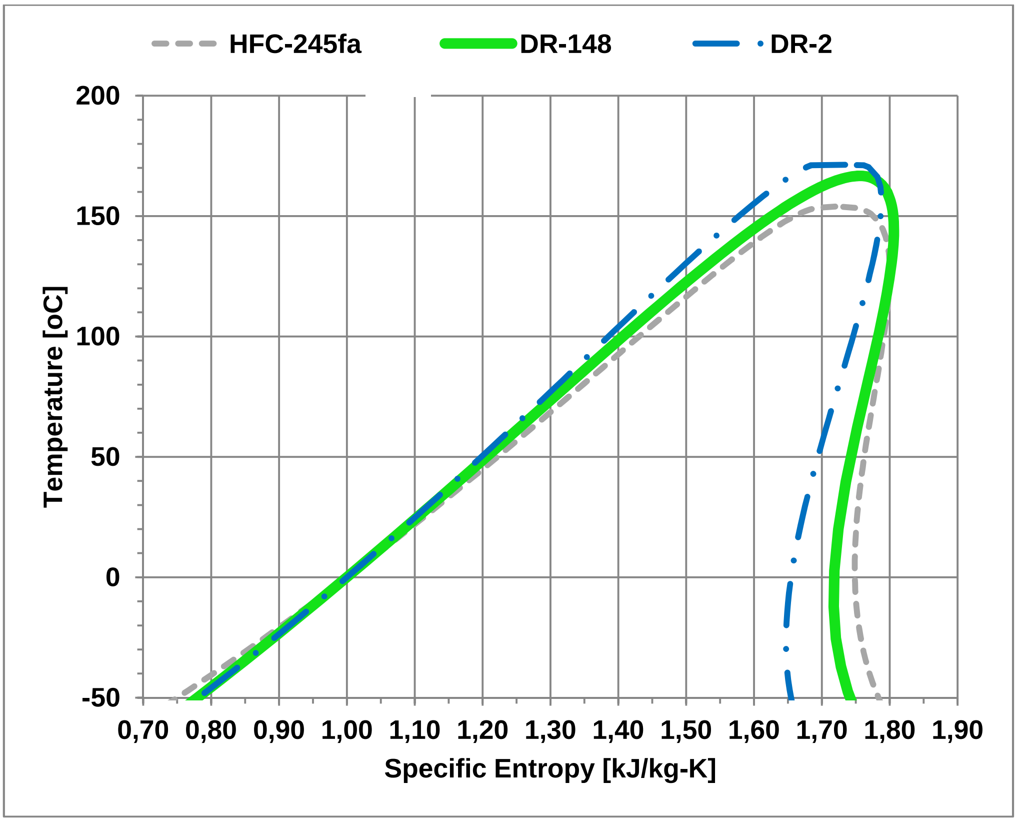

Figure 3: DR-148 temperature-entropy diagram compared to HFC-245fa and DR-2.

Table 6 assesses the possibility of using a heat pump operating with DR-148 to deliver a condensing temperature of 160 ^{o}C to meet some industrial process heating duty (e.g. high temperature steam generation). Attractive COP_h and CAP_h values are enabled when input heat allows evaporating temperatures higher than 90 ^{o}C. The DR-148 condensing pressure at 160 ^{o}C remains manageable. However, equipment modifications would likely be required to mitigate the effects of the high compressor discharge temperatures (e.g. liquid or vapor injection). HFC-245fa could not be used for this application with conventional subcritical heat release through condensation because the required condensing temperature exceeds the critical temperature of HFC-245fa.

3.3 DR-148 Chemical Stability and Lubricant Compatibility

The thermal stability of the DR-148 components was assessed separately according to the sealed glass tube methodology of ASHRAE-ANSI Standard 97. Tubes each containing a carbon steel, a copper and an aluminum coupon (with the copper coupon placed between the other two coupons) immersed in a selected DR-148 fluid component were prepared. The tubes were aged in a heated oven at 250 ^{o}C for two weeks. Visual inspection of the tubes after thermal aging indicated clear liquids with no discoloration, residues or other visible deterioration of the refrigerant. Moreover, there was no change in the appearance of the metal coupons indicating corrosion, insoluble residues or other degradation. Chemical analyses of the refrigerant liquids after aging indicated a negligible degree of degradation.

DR-148, based on its chemcial composition, would be expected to be compatible and miscible with polyol ester (POE) type lubricants. It would also be expected to be compatible with common plastic and elastomeric materials of equipment construction. However, compatibility with either lubricants or polymers at the high operating temperatures of the intented applications remains to be verified.

Table 2: Predicted thermodynamic performance of HTHP cycles: T_{cond} = 100 °C; ΔT_{superh}= 20 °C; ΔT_{subc}= 10 °C; Compressor Efficiency=0.7

T_{evap} =	°C	30			65		
Lift=	°C	70			35		
		HFC-245fa	DR-148	DR-2	HFC-245fa	DR-148	DR-2
P_{cond}	MPa	1.26	0.90	0.70	1.26	0.90	0.70
P_{evap}	MPa	0.18	0.12	0.09	0.53	0.36	0.28
PR		7.1	7.8	7.9	2.4	2.5	2.5
T_{compr_disch}	°C	116.4	116.2	109.0	116.7	116.7	113.1
$Glide_{condenser}$	K	N/A	1.31	N/A	N/A	1.31	N/A
$Glide_{evaporator}$	K	N/A	0.64	N/A	N/A	1.02	N/A
COP_h		3.221	3.301	3.264	7.137	7.275	7.308
COP_h vs HFC-245fa	%		+2.5	+1.3		+1.9	+2.4
CAP_h	kJ/m³	1,604	1,129	866	4,606	3,369	2,657
CAP_h vs HFC-245fa	%		-29.6	-46.0		-26.8	-42.3

Table 3: Predicted thermodynamic performance of HTHP cycles: T_{cond} = 115 °C; ΔT_{superh}= 20 °C; ΔT_{subc}= 10 °C; Compressor Efficiency=0.7

T_{evap} =	°C	45			80		
Lift=	°C	70			35		
		HFC-245fa	DR-148	DR-2	HFC-245fa	DR-148	DR-2
P_{cond}	MPa	1.74	1.25	0.99	1.74	1.25	0.99
P_{evap}	MPa	0.29	0.19	0.15	0.79	0.55	0.43
PR		5.93	6.41	6.50	2.21	2.28	2.31
T_{compr_disch}	°C	129.1	128.4	121.7	131.4	131.0	127.6
$Glide_{condenser}$	K	N/A	1.24	N/A	N/A	1.24	N/A
$Glide_{evaporator}$	K	N/A	0.64	N/A	N/A	1.03	N/A
COP_h		3.204	3.314	3.287	7.199	7.403	7.457
COP_h vs. HFC-245fa	%		+3.4	+2.6		+2.8	+3.6
CAP_h	kJ/m³	2,332	1,694	1,313	6,218	4,660	3,713
CAP_h vs. HFC-245fa	%		-27.4	-43.7		-25.0	-40.3

4 SUMMARY-DISCUSSION

DR-148 is a relatively low pressure, non-flammable, HFO-based developmental refrigerant with attractive environmental characteristics (zero ODP and GWP lower than 150). DR-148 offers both a low GWP and non-flammability, thus breaking an early stereotype about fluids based on HFOs. Moreover, it is based on components that offer both low GWP values and high chemical stability at least up to 250 °C (the highest temperature tested to date). DR-148 provides a combination of thermodynamic and chemical stability properties that could enable HTHPs delivering condensing temperatures in the range of about 85 °C to 150 °C with high energy efficiencies provided that suitable heat sources are available at temperatures that limit the required temperature lifts to about 75 °C. For higher required temperature lifts, cascade heat pumps with DR-148 in the upper stage could prove attractive. The vapor pressure of DR-148 remains moderate even at temperatures exceeding 150 °C. However, the high compressor discharge temperatures for condensing temperatures exceeding 130 °C could pose challenges in compressor heat management, selection of lubricants and selection of plastic and elastomeric materials of equipment construction.

Table 4: Predicted thermodynamic performance of HTHP cycles: T_{cond} = 130 °C; ΔT_{superh}= 20 °C; ΔT_{subc}= 10 °C; Compressor Efficiency=0.7

T_{evap} =	°C	60			95		
Lift=	°C	70			35		
		HFC-245fa	DR-148	DR-2	HFC-245fa	DR-148	DR-2
P_{cond}	MPa	2.34	1.70	1.35	2.34	1.70	1.35
P_{evap}	MPa	0.46	0.31	0.24	1.13	0.79	0.63
PR		5.08	5.44	5.53	2.08	2.14	2.16
T_{compr_disch}	°C	143.4	141.8	135.8	146.8	145.8	142.7
$Glide_{condenser}$	K	N/A	1.11	N/A	N/A	1.11	N/A
$Glide_{evaporator}$	K	N/A	0.63	N/A	N/A	0.99	N/A
COP_h		3.125	3.282	3.271	7.126	7.440	7.526
COP_h vs HFC-245fa	%		+5.0	+4.7		+4.4	+5.6
CAP_h	kJ/m³	3,170	2,384	1,869	7,999	6,165	4,976
CAP_h vs HFC-245fa	%		-24.8	-41.0		-22.9	-37.8

Table 5: Predicted thermodynamic performance of HTHP cycles: T_{cond} = 145 °C; ΔT_{superh}= 20 °C; ΔT_{subc}= 10 °C; Compressor Efficiency=0.7

T_{evap} =	°C	75			110		
Lift=	°C	70			35		
		HFC-245fa	DR-148	DR-2	HFC-245fa	DR-148	DR-2
P_{cond}	MPa	3.09	2.25	1.81	3.09	2.25	1.81
P_{evap}	MPa	0.69	0.48	0.37	1.57	1.12	0.89
PR		4.45	4.74	4.83	1.97	2.02	2.05
T_{compr_disch}	°C	159.2	156.7	151.4	162.7	161.2	158.5
$Glide_{condenser}$	K	N/A	0.89	N/A	N/A	0.89	N/A
$Glide_{evaporator}$	K	N/A	0.57	N/A	N/A	0.89	N/A
COP_h		2.951	3.181	3.193	6.831	7.330	7.466
COP_h vs HFC-245fa	%		+7.8	+8.2		+7.3	+9.3
CAP_h	kJ/m³	4,015	3,150	2,505	9,741	7,785	6,389
CAP_h vs HFC-245fa	%		-21.5	-37.6		-20.1	-34.4

A HTHP could, in principle, be operated to simultaneously provide heating (e.g. hot water for hydronic heating) and cooling (e.g. chilled water for air conditioning). Such a mode of operation would impose a high required temperature lift and, therefore, it would require a large amount of compression work to lift a unit of mass of the working fluid from the thermodynamic state of the evaporator to that of the condenser. The resulting COP for cooling and COP for heating would, generally, be lower than the values expected from machines specifically operated to provide solely either cooling or heating. However, the combined COP for both cooling and heating could still be attractive. For example, a heat pump with DR-148 operated at an evaporator temperature of 5 °C and a condenser temperature of 85 °C (with 20 K of vapor superheat at the evaporator exit, 10 K of liquid sub-cooling at the condenser exit, and a compressor efficiency of 0.70) would achieve an ideal cycle COP for cooling of 1.793 and a COP for heating of 2.793, for a total COP for both cooling and heating of 4.586.

Table 6: Predicted thermodynamic performance of HTHP cycles: T_{cond} = 160 °C; ΔT_{superh}= 20 °C; ΔT_{subc}= 10 °C; Compressor Efficiency=0.7

T_{evap} =	°C	90			125		
Lift=	°C	70			35		
		HFC-245fa	DR-148	DR-2	HFC-245fa	DR-148	DR-2
P_{cond}	MPa	N/A	2.9	2.4	N/A	2.9	2.4
P_{evap}	MPa	N/A	0.7	0.6	N/A	1.5	1.2
PR		N/A	4.2	4.3	N/A	1.9	2.0
T_{compr_disch}	°C	N/A	172.7	168.3	N/A	177.1	174.9
$Glide_{condenser}$	K	N/A	0.53	N/A	N/A	0.53	N/A
$Glide_{evaporator}$	K	N/A	0.46	N/A	N/A	0.73	N/A
COP_h		N/A	2.975	3.021	N/A	6.977	7.189
CAP_h	kJ/m^3	N/A	3,877	3,142	N/A	9,298	7,805

High temperature heat pumps, including heat pumps for heating at temperatures higher than 100 °C, have been attracting a rapidly growing interest in Europe and other parts of the world in recent years. High temperature heating with DR-148 heat pumps could contribute to reducing energy use, in general, and non-renewable primary energy, in particular, environmental impacts associated with energy use, including greenhouse gas emissions, and heating costs relative to fossil fuel heating.

NOMENCLATURE

CAP_h: Volumetric heating capacity; the amount of heat delivered at the condenser (including the compressed vapor superheat and liquid sub-cooling) per unit volume of the working fluid entering the compressor
COP_h: Coefficient of Performance for Heating; ratio of the heat delivered at the condenser (including the compressed vapor superheat and the liquid sub-cooling) and the work of compression
GWP: Global Warming Potential (one hundred year integrated time horizon)
HFO: Hydro-Fluoro-Olefin
HTHP: High Temperature Heat Pump (mechanical compression)
LFL: Lower Flammability Limit
OEL: Occupational Exposure Limit
P_{cond}: Condenser pressure
P_{cr}: Critical pressure
P_{evap}: Evaporator pressure
PR: Pressure Ratio (condenser pressure over evaporator pressure)
T_b: Boiling point at 1 atm
T_{compr_disch}: Compressor discharge temperature
T_{cond}: Condenser temperature
T_{cr}: Critical temperature
T_{evap}: Evaporator temperature
ΔT_{subc}: Liquid sub-cooling at the condenser exit
ΔT_{superh}: Vapor superheat at the evaporator exit

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