Screening of Future-Proof Working Fluids for Industrial High-Temperature Heat Pumps up to 250°C

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CONTENT

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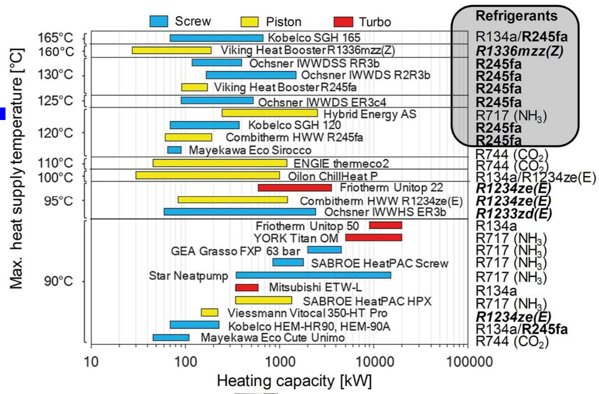
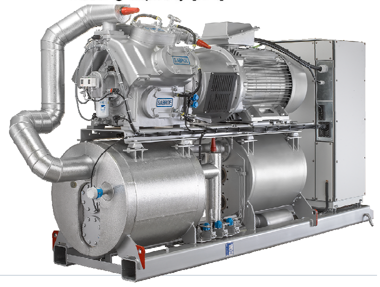
Introduction

- The EU has decided to reduce the CO_2 emissions by 55% by 2030
- IEA has estimated that if we are to achieve the goals given in the Paris agreement we have to install 500 MW heat pump capacity every month until 2050
- The decarbonisation includes reducing burning fossil fuels for heating where electrically driven heat pumps can be used e.g. space heating in our buildings, production processes up to 250°C or higher
- Within the EU alone we have an estimated population of boilers around 5 million units
- Fuels to be cut back include oil, coal, gas, bio-fuels, and wood-chips
- Fuels like hydrogen and ammonia will be the fuel of the future





Literature studied

Refrigerants	R600	R600a	R601	R601a	R290	R1270	R134a	R22	R717	R718	R1234ze (E)	R1234ze (Z)	R1233zd (E)	R1336mzz(Z)	R1224yd(Z)	R744
GWP	0.09	0.09	0.39	0.39	0.18	0.05	1'292	1'700	0	0.2	>1	>1	1	2	>1	1
ODP	0	0	0	0	0	0	0	0.05	0	0	0	0	0.00034	0	0.00012	0
References	Literature data studied															
Palm (2007)		X			X	X	X	X	X							
Bamigbetan et al. (2017a)	X	X	X	X					X	X	X	X	X			
Bamigbetan et al. (2017b)	X	X	X	X	X				X	X						X
Zühlsdorf et al. (2018)	X								X		X					
Wolf et al. (2012)	X								X							X
Bamigbetan et al. (2017c)	X								X							
Papapetrou et al. (2018)																
Mateu-Royo et al. (2019)	X		X						X		X	X	X	X	X	
Arpagaus et al. (2018, 2019)	X	X	X						X	X	X	X	X	X	X	X

Refrigerant overview

Type	Refrigerant	Description	Chemical formula	T_c [°C]	P_c [bar]	ODP [-]	GWP [-]	Safety Class	NBP [°C]	M [g/mol]	Relative price [-]
CFC	**R113**	1,1,2-trichloro-1,2,2-trifloroethane	CCl_2FCClF_2	214.0	33.9	0.85	5’820	A1	47.6	187.4	Prohibited by Montreal Protocol
	R114	1,2-trichloro-1,1,2,2-tetrafluoroethane	$CClF_2CClF_2$	145.7	32.6	0.58	8’590	A1	3.8	170.9	
HCFC	**R123**	2,2-dichloro-1,1,1-trifluoroethane	$C_2HCl_2F_3$	183.7	36.6	0.03	79	B1	27.8	152.9	
	R21	Dichlorofluoromethane	$CHCl_2F$	178.5	51.7	0.04	148	B1	8.9	102.9	
	R142b	1,1-dichloro-1-fluoroethane	CH_3CCl_2F	137.1	40.6	0.065	782	A2	-10	100.5	
	R124	1-chloro-1,2,2,2-tetrafluoroethane	C_2HClF_4	126.7	37.2	0.03	527	A1	-12	136.5	
HFC	**R365mfc**	1,1,1,3,3-pentafluorobutane	$CF_3CH_2CF_2CH_3$	186.9	32.7	0	804	A2	40.2	148.1	8.9
	SES36	R365mfc/perfluoro-ether	R365mfc/PFPE (65/35)	177.6	28.5	0	3’126	A2	35.6	184.5	10.5
	R245ca	1,1,2,2,3-pentafluoropropane	$CHF_2CF_2CH_2F$	174.4	39.3	0	718	n.a.	25.1	134	n.a.
	R245fa	1,1,2,2,3-pentafluoropropane	$CHF_2CH_2CF_3$	154	36.5	0	858	B1	14.9	134	6.6
	R236fa	1,1,1,3,3,3-hexfluoropropane	$CF_3CH_2CF_3$	124.9	32	0	8’060	A1	-1.4	152	10.2
	R152a	1,1-difluorethane	CH_3CHF_2	113.3	45.2	0	138	A2	-24	66.1	n.a.
	R227ea	1,1,1,2,3,3,3-heptafluoropropane	CF_3CHFCF_3	101.8	29.3	0	3’350	A1	-15.6	170	6.9
	R134a	1,1,1,2-tetrafluoroethane	CH_2FCF_3	101.1	40.6	0	1’300	A1	-26.1	102	1.2
	R410A	R32/R125 (50/50% mixture)	CH_2F_2/CHF_2CF_3	72.8	49	0	2’088	A1	-51.5	72.6	2.9
HFO	**R1336mzz(Z)**	1,1,1,4,4,4-hexafluoro-2-butene	$CF_3CH{=}CHCF_3$(Z)	171.3	29	0	2	A1	33.4	164.1	n.a.
	R1234ze(Z)	cis-1,3,3,3-tetrafluoro-1-propene	$CF_3CH{=}CHF$(Z)	150.1	35.3	0	< 1	A2L	9.8	114	n.a.
	R1336mzz(E)	trans-1,1,1,4,4,4-hexafluoro-2-butene	$CF_3CH{=}CHCF_3$(E)	137.7	31.5	0	18	A1	7.5	164.1	n.a.
	R1234ze(E)	trans-1,3,3,3-tetrafluoro-1-propene	$CF_3CH{=}CHF$(E)	109.4	36.4	0	< 1	A2L	-19	114	5.6
	R1234yf	2,3,3,3-tetrafluoro-1-propene	$CF_3CF{=}CH_2$	94.7	33.8	0	< 1	A2L	-29.5	114	13.8
HCFO	**R1233zd(E)**	1-chloro-3,3,3-trifluoro-propene	$CF_3CH{=}CHCl$(E)	166.5	36.2	0.00034	1	A1	18	130.5	6.3
	R1224yd(Z)	1-chloro-2,3,3,3-tetrafluoro-propene	$CF_3CF{=}CHCl$(Z)	155.5	33.3	0.00012	< 1	A1	14	148.5	n.a.
HC	**R601**	Pentane	$CH_3CH_2CH_2CH_2CH_3$	196.6	33.7	0	0.39	A3	36.1	72.2	4.9
	R601a	Iso-pentane	$(CH_3)_2CHCH_2CH_3$	187.2	33.8	0	0.39	A3	27.8	72.15	n.a.
	R600	Butane	$CH_3CH_2CH_2CH_3$	152	38	0	0.09	A3	-0.5	58.1	1.8
	R600a	Isobutane	$CH(CH_3)_2CH_3$	134.7	36.3	0	0.09	A3	-11.8	58.1	1
	R290	Propane	$CH_3CH_2CH_3$	96.7	42.5	0	0.18	A3	-42.1	44.1	1.1
	R1270	Propene	$CH_3CH{=}CH_2$	91.1	45.6	0	0.05	A3	-47.6	42.1	1
	R602	Hexane	$CH_3(CH_2)_4CH_3$	234.7	30.4	0	3	A3	68.7	86.18	n.a.
	n.a.	Benzene	C6H6	288.9	43.1	0	n.a.	B3	80.1	78.11	n.a.
	R603	Heptane	$CH_3(CH_2)_5CH_3$ (C_7H_{16})	267.1	27.4	0	3	A3	98.4	100.2	n.a.
CF6	**Novec 649**	Dodecafluoro-2-methyl-3-pentanone	$CF_3CF_2C(O)CF(CF_3)_2$	168.7	18.8	0	< 1	n.a.	49	316	6.8
Ether	**E170**	Dimethyl ether	CH_3OCH_3	127.2	53.4	0	1	A3	-24.8	46.1	39
Natural	**R718**	Water	H_2O	373.9	220.6	0	0	A1	100	18	5.6
	R717	Ammonia	NH_3	132.3	113.3	0	0	B2L	-33.3	17	27

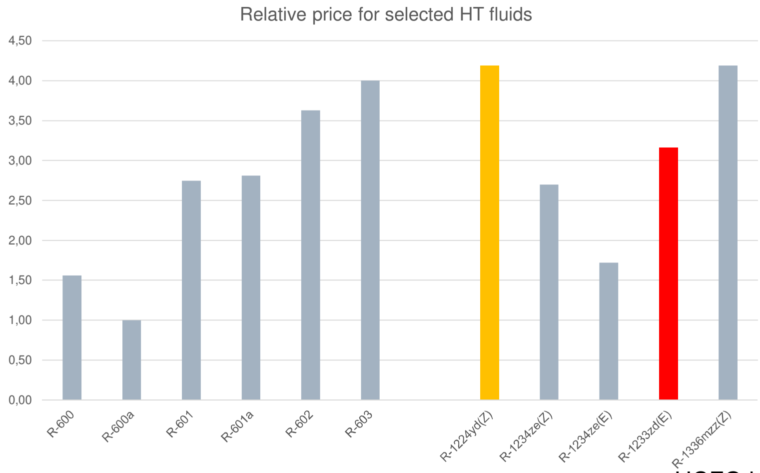
Deutsche Kälte- und Klimatagung

Literature mentions many refrigerant options

	Safety class	Normal boiling point (°C)	Critical temperature (°C)	Critical pressure (bar)	ODP	GWP
R1123	2L	-59,15	58.58	45.46	0	3
R1130(E)	B2	47.7	234.1			1,13
R1132a	A2	-83	30.1		0	4.4
R1132(E)	N/A		76.95	67.7		1.9
R1224yd(Z)	A1	14.5	155.5	33.37	0,00012	
R1225ye(E)	2L	-15	113.65	34.01	0	2.9
R1225ye(Z)	2L	-20	106.15	33.35	0	2.9
R1225zc	2L	-21.8	103.45	33.12	0	4.3
R1233zd(E)	A1	18.1	166.5	35.7	0,0034	1.0
R1233xf	A1	-1.67				
R1234yf	A2L	-29.5	94.7	33.8	0	4.0
R1234ze(E)	A2L	-19.0	109.4	36.3	0	6.0
R1234ze(Z)	A2L	9.7	150.1	35.3	0	1.4
R1234ye(E)	2L	-22	106.75	35.34	0	2.3
R1243zf	2L	-25.4	103.8	35.2	0	1.2
R1336mzz(Z)	A1	33.4	171.4	29.0	0	2.0
R1336mzz(E)	A1	7.4	137.7		0	16.0
R13I1	A1	-21.9	123.3		0,008	0.4

Deutsche Kälte- und Klimatagung DKV

Price levels of working fluids relative to R-600a (based on current budget prices)



HCFO is regarded as an ODS in some regulations
HCFO-1224yd is not globally available

TEWI calculations

- TEWI calculations will give different results from country to country because the CO_2 emissions per kWh electricity is different
- Also the climates are different from region to region
- It is not a static value
- Some values are difficult to get
- A more complete calculation has been proposed but that does not move the individual values much

Beregning af TEWI - for konstante driftsforhold

Fælles

Genindvinding	10	%
CO2-emission - elproduktion	0,15	kg CO2/kWh
Genvindings/genbrugsfaktor	0,10	-

System 1			System 2		
Kølemiddel	R717		Kølemiddel	R1234ze	
Fyldning	50	kg	Fyldning	166	kg
Lækrate	10	%/år	Lækrate	10	%/år
Anlægslevetid	10	år	Anlægslevetid	10	år
Effektoptag	39	kW	Effektoptag	51	kW
Årlig driftstid	7.200	timer/år	Årlig driftstid	7.200	timer/år
GWP_100 år	0	kg CO2	GWP_100 år	6	kg CO2
Årlig driftstid	82	% af året	Årlig driftstid	82	% af året
Lækage	5	kg/år	Lækage	17	kg/år
Energiforbrug	280.800	kWh/år	Energiforbrug	367.200	kWh/år

TEWI 1			TEWI 2		
Lækage-andel	0	kg CO2	Lækage-andel	996	kg CO2
Genindvindings-andel	0	kg CO2	Genindvindings-andel	896	kg CO2
Energiforbrugs-andel	421.200	kg CO2	Energiforbrugs-andel	550.800	kg CO2
Samlet TEWI	**421.200**	**kg CO2**	**Samlet TEWI**	**552.692**	**kg CO2**
Referencen	100	%	I forhold til referencen	131	%

Refrigerant quality

- AHRI standard 700 is a good reference for refrigerant quality
- NH_3 and CO_2 are available in different qualities
- CO_2 is more difficult to clean up than NH_3 when it comes to non-condensables
- Water is easy to handle in CO_2 if the concentration is not too high
- NH_3 quality 3.8 and CO_2 quality 3 as a minimum
- Some gases can be difficult to get in some markets

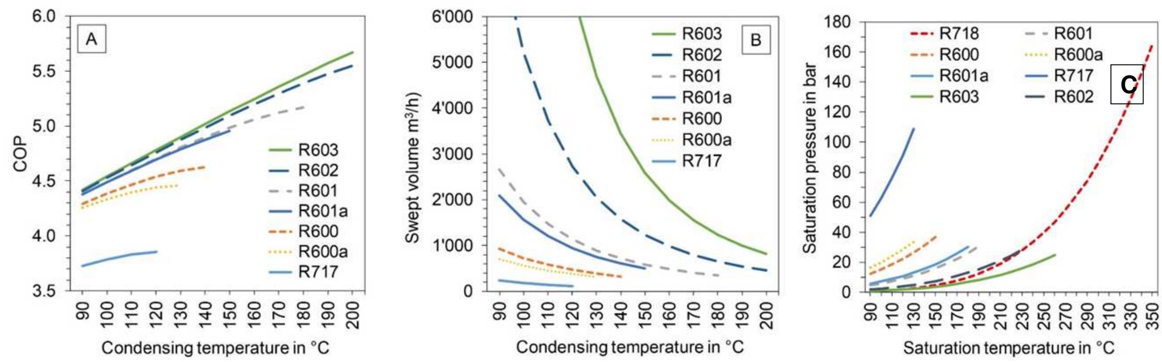
Quality requirements for ammonia as refrigerant		
Refrigerant	Subject	Max. contamination in new refrigerant
Ammonia (R717)	Purity	Min. 99.98%
	Water	<200 ppm
	Oil	<5 ppm
	Non-	

Table 1C Carbon Dioxide Refrigerant Characteristics and Allowable Levels of Contaminants

	Reporting Units	R-744
CHARACTERISTICS:		
Sublimation Point[1]	°C at 101 kPa	-78.4
Sublimation Point Range[1]	K	± 0.3
VAPOR PHASE[2]:		
Air and other non-condensables, Maximum	% by Volume at 10°C below the critical temperature and measure non-condensable directly	1.5
LIQUID PHASE[3]:		
Water, Maximum	ppm by weight	10
Hoigh Boiling Residue, Maximum	% by weight	0.0005
Particulates/Solids	Pass or Fail	Visually Clean
Minimum Purity	% by weight	99.9

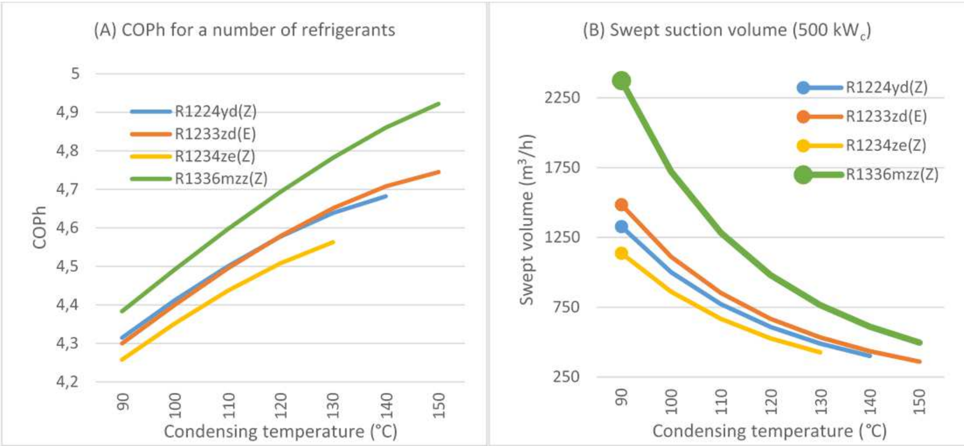
Notes:
1. Sublimation Point, sublimation point range, although not required, are provided for informational purposes. Refrigerant data compiled from Refprop 9.1.
2. Sample taken from vapor phase.
3. Sample vaporized from liquid phase.

The first considerations – What is important?

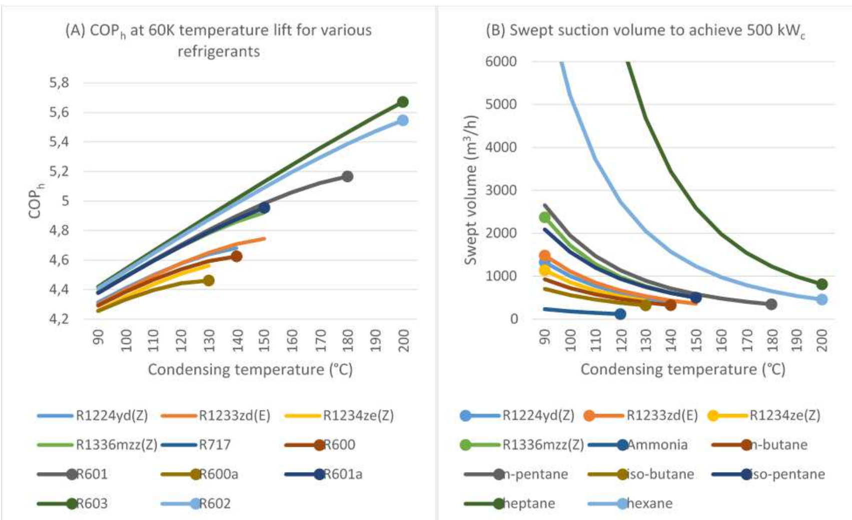


Assumptions:
500 kW cooling capacity
Temperature lift 60K
Superheat 20K and subcooling 20K

Selected new refrigerants



All in one – most fluids up to 150°C

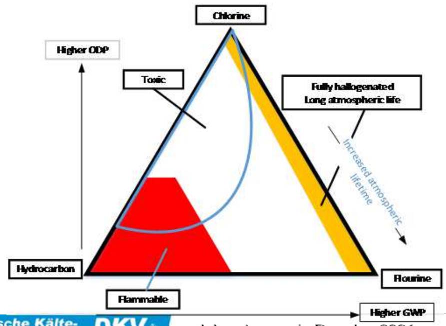


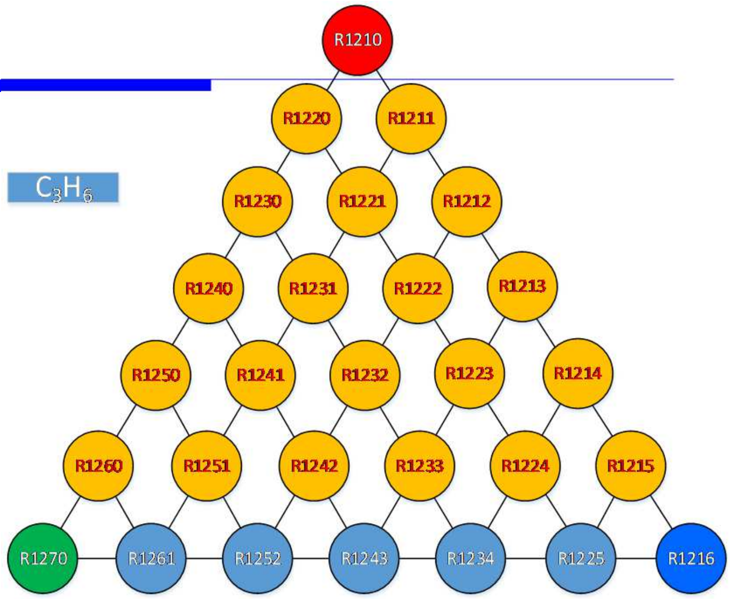
About refrigerants

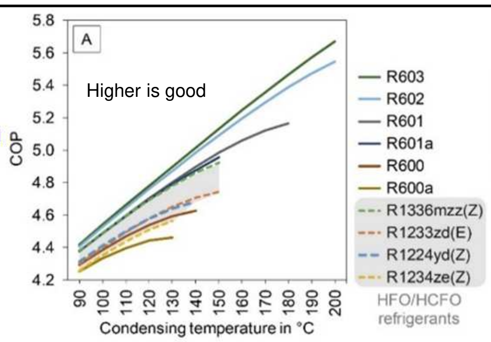
Not all fluids an Ozone Depleting Potential

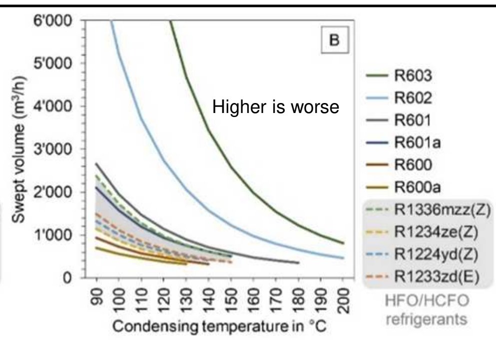
In some cases sunlight can break the refrigerant molecule in to R-23

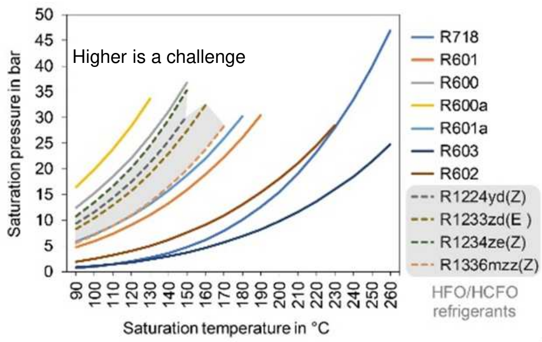
Some members can be toxic





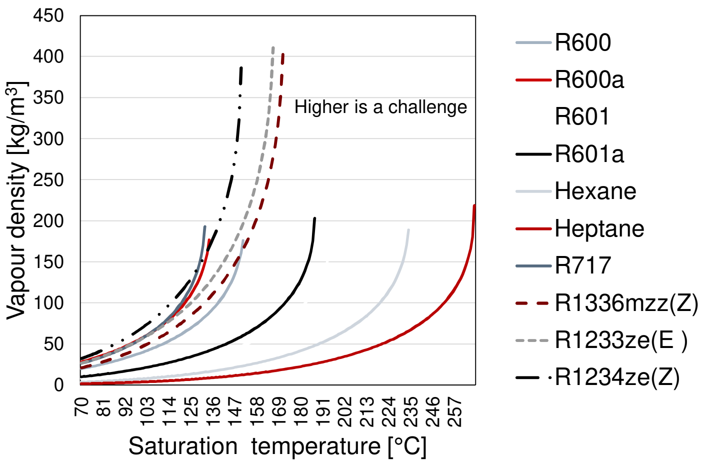






Assumptions:
500 kW cooling capacity
Temperature lift 60K
Superheat 20K and subcooling 20K

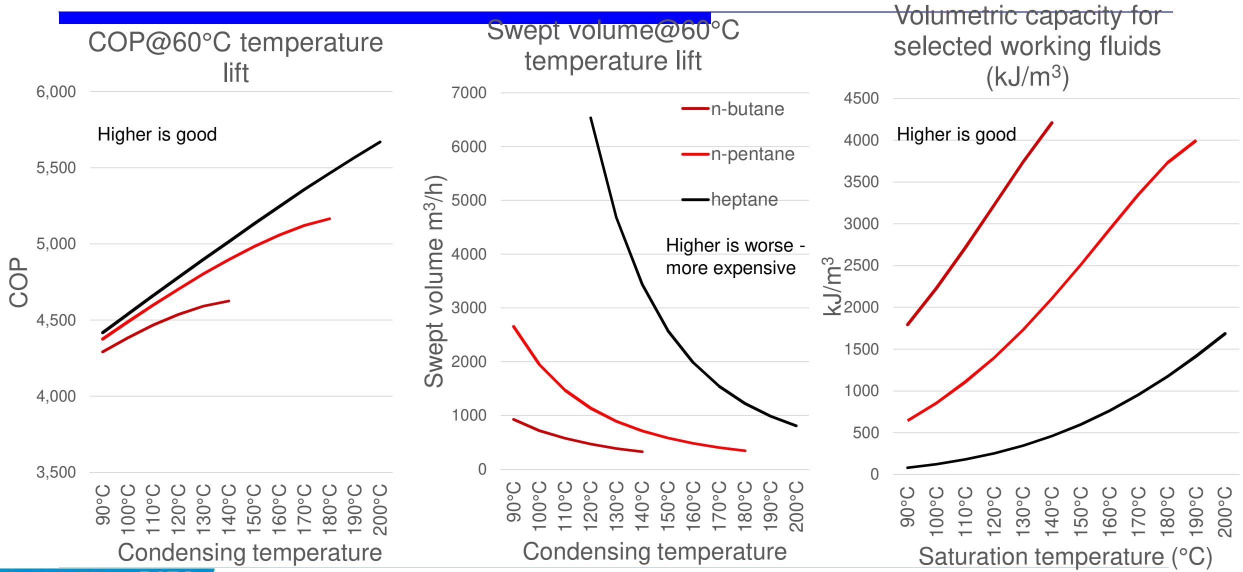
Fluorinated hydrocarbons are heavy



However,

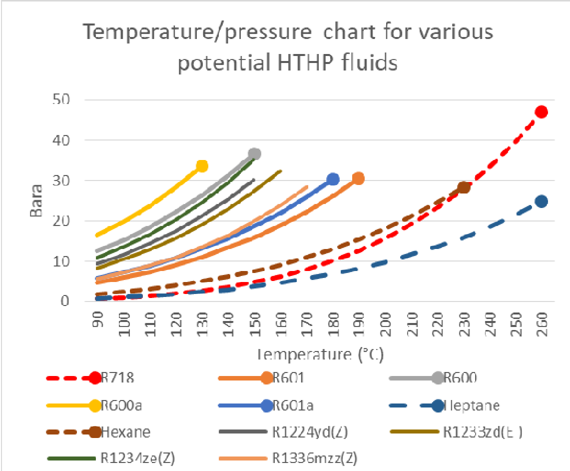
- A number of concerns about the new refrigerants and their long term stability is raised in some literature and is still being tested
- Questions about the true ambient impact of the break down products in sunlight and nature has been raised and is still not finally clarified
- It has therefore been decided not to proceed in this paper with these refrigerants

Properties of the selected candidate working fluids



System pressure

- System pressure is an important parameter to consider
- Vessel price tend to increase significantly when going over 40 bar
- For very high temperature well over 250°C the pressure in water vapor systems becomes very high



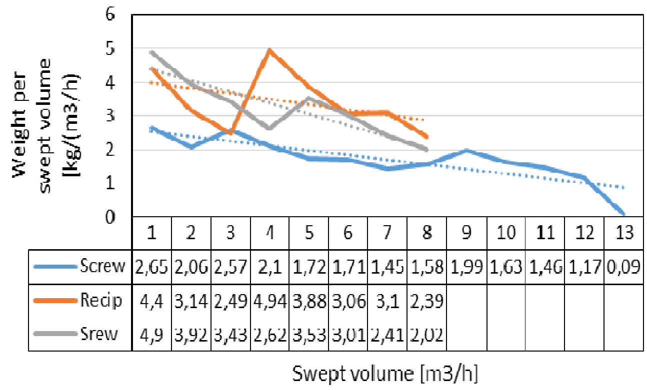
About flammability

Refrigerant	ASHRAE Class	LFL [%]	LFL (ISO817) [g/m3]	UFL [%]	UFL [g/m3]	Difference [%]	Stoichiometric concentration in air [%]	Stoichiometric concentration in air (ISO817) [g/m3]	Heat of combustion MJ/kg	Released Energy MJ/KG	Auto Ignition Temperature °C
R290	A3	2.1	37.8	10.0	179.9	7.9	4	72.0	46.3	3.3	470
R32	A2L	14.4	306.24	27.50	584.8	13.1	20	425.3	9.4	4.0	648
R1234yf	A2L	6.2	289.1	12.3	573.5	6.1	7.73	360.4	10.7	3.9	700
R1234ze(E)	A2L	7	303.0	12.0	559.5	5.0	7.73	360.4	10.7	3.9	368
R152a	A2L	4.8	129.7	17.3	467.3	12.5	5	135.1	16.5	2.2	440
R600a	A3	1.7	42.8	8.5	202.0	6.8	3.5	83.2	45.6	3.8	460
R717	B2L	16	139.0	30.0	208.2	14.0	20	139.0	22.48	3.1	651

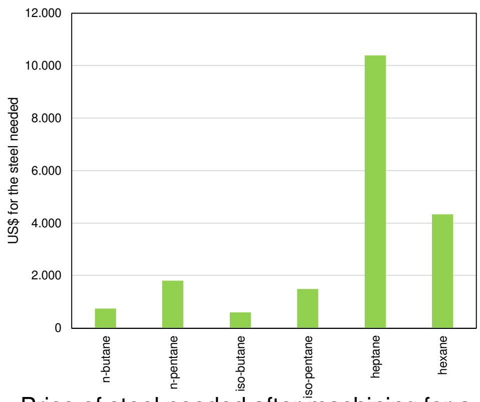
Stability of the working fluids at high temperatures

Type of working fluid		Experimental conditions			Cycle configuration	Objective of study	Optimisation objective function	Observation	Reference
	ASHRAE	Temperature (°C)	Pressure (Mpa)	Time (h)					
Cyclopentane	R-C601	220-350	3 - 7	80	Subcritical ORC	Decomposition rate	Vapor pressure	1.8% y^{-1}	Pasetti et al
Isopentane	R601a							1.2% y^{-1}	
n-Butane	R600							0.8% y^{-1}	
HFO-1234yf	R1234yf	200-250	3.7	80	Subcritical ORC	Maximum temperature	Vapor pressure	200°C	Invernizzi et al.
Cyclopentane	R-C601	240-300	4.3	309	Subcritical ORC	Decomposition products	Gas products concentration	65-270 ppm	Ginosar et al.
n-Pentan	R601	330-350	1	70	Subcritical ORC	Decomposition rate	n-pentane remaining concentraion	0.076% y-1	Dai et al.
R-245fa		140 - 400	4-5	24	SORC	Decompostion temperature	Fluoride ion concentration	320°C	Dai et al.
R-152a								180°C	
R-236fa								400°C	
R-134a								360°C	

Compressor size and rule of thumb price



The average value is 2.83 or rounded off 3 kg/(m³/h).



Price of steel needed after machining for a compressor at Tc=120°C and a cooling capacity of 500 kW

Conclusions

- Not all parameters can be calculated
- Not all components are identified or developed/selected yet
- Traffic light table can help to keep track of these topics
- For temperatures above 250°C, water (R-718) is the only viable way to produce superheated vapour

Components	Availability	Comments
Compressors	(green)	Not all brands and types
Refrigerants	(green)	Not all suppliers
Lubricants	(yellow)	Not all temperatures
Valves	(yellow)	Limits about 150 °C
Pipes	(green)	Be aware of documentation
Vessels	(yellow)	Low pressures, temp?
Filter driers	(red)	Not evaluated
Heat exchangers	(red)	Not all evaluated
Controls	(red)	Algorithms for new fluids
Sensors	(red)	Many sensors are limited to high temp.

Conclusions

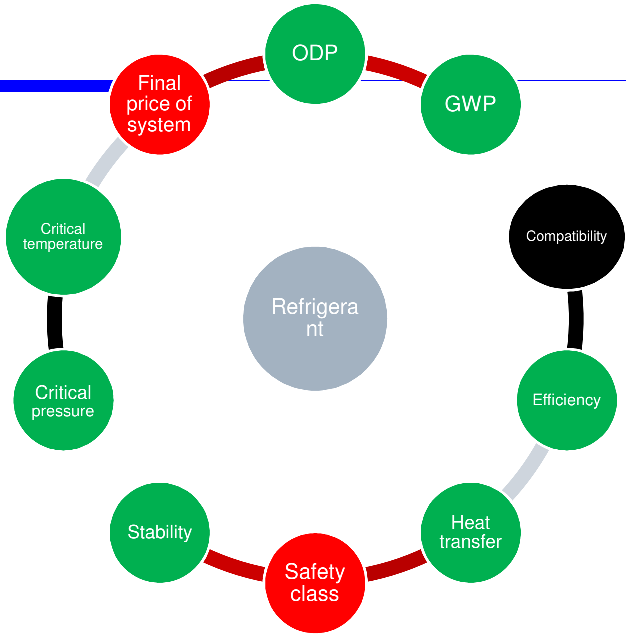
Selecting the best refrigerant includes a number og properties

All parameters are equally important

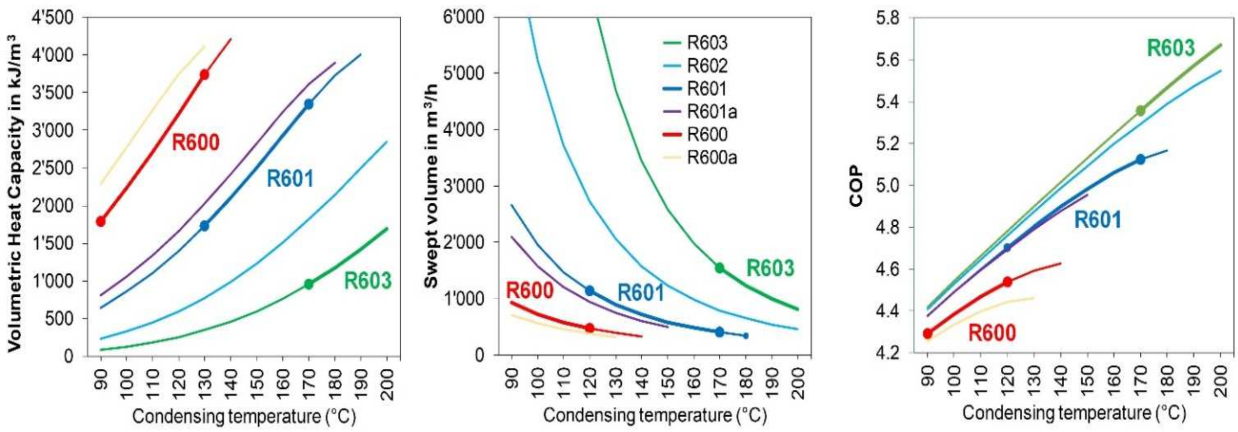
Some parameters can be calculated others need to be experimentally validated

When all parameters and design considerations have been done you can set up a field test

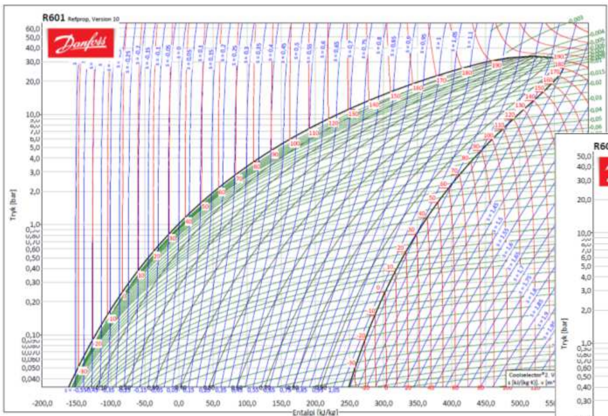
You can still be surprised

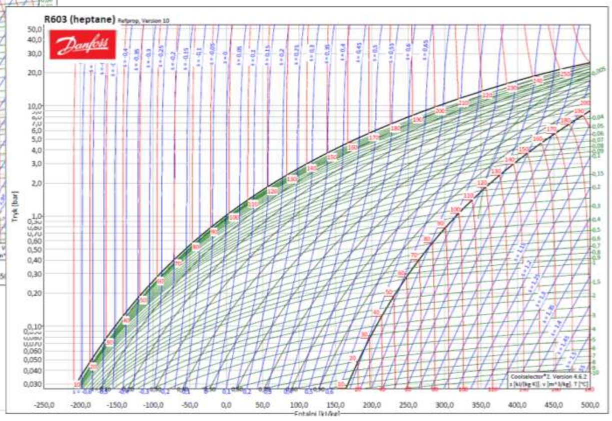


Conclusions

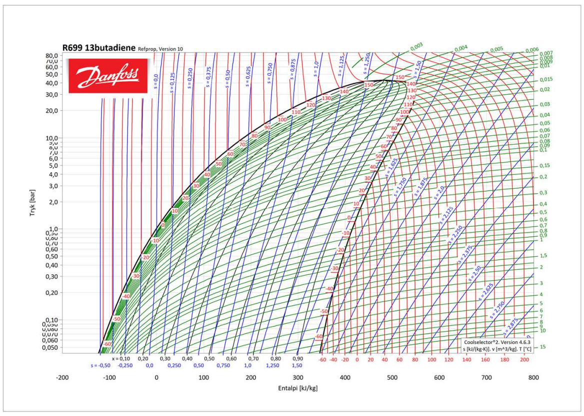


Some challenges ahead





Future work



Alkene	Formula
Ethene or ethylene	C2H4
Propene or Propylene	C3H6
Butene	C4H8
Pentene	C5H10
Hexene	C6H12
Heptene	C7H14
Octene	C8H18
Nonene	C9H18
Decene	C10H20

Alkanes	Formula
Metane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C4H10
Pentane	C5H12
Hexane	C5H14
Heptane	C7H16
Octane	C8H20
Nonane	C9H20
Decane	C10H22
Undecane	C11H24
Dodecane	C12H26
Cetane	C16H34
Eicosane	C20H42
Docosane	C22H46
Hexatriacontane	C36H74
Tetracontan	C10H82

Future work

- Diving in new solutions and exploring new technical options
- New gases will not emerge but have we looked at all options?
- Efficiency is of the essence and can we do better?
- The Industry has to learn with a new fact of life: flammable refrigerants
- Some of us have lived with it for years so why can other not?

Thank you for your kind attention