LOW GWP REFRIGERANTS FOR HIGH TEMPERATURE HEAT PUMPS

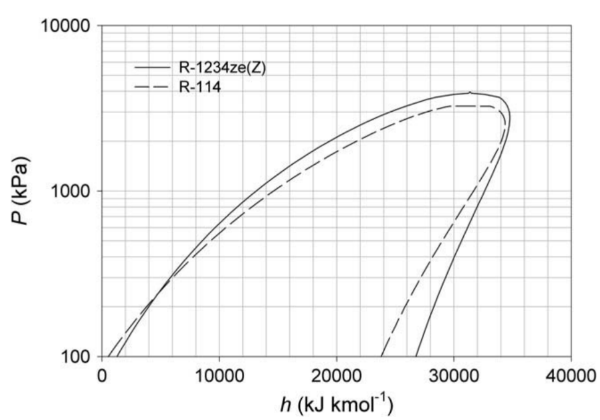
Heat pumps are seen as a great opportunity to reach the EU target for a reliable, affordable and sustainable energy supply. The technology is capable of delivering heat from low temperature sources at useful temperature levels. The higher the temperature, the greater the amount of applications the heat can be used. Various industrial processes can utilize the heat at temperatures of around 75 °C and higher. However, the use of heat pumps in these applications is limited by absence of reliable refrigerants suitable for high temperature applications.

High temperature heat pumps today

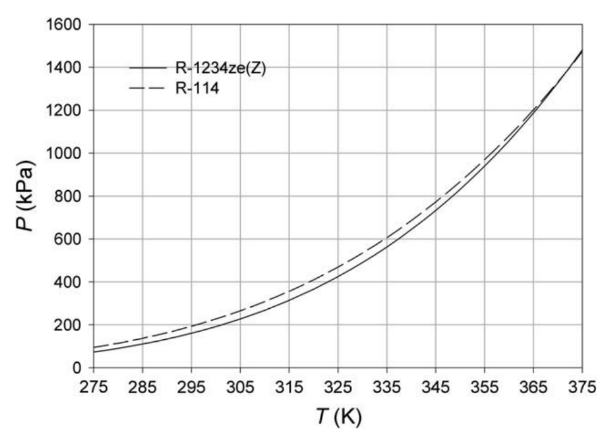
R500 and R114 has been refrigerants used in medium and high temperature heat pumps. Since the production of these ozone-depleting refrigerants has discontinued, other substances are used in new equipment these days. For instance, R134a is a commonly used refrigerant in medium temperature heat pumps. Natural substances as propane and carbon dioxide are used as well. However, many industrial applications would benefit from refrigerants, capable of reaching higher temperatures, than can be provided with R134a. For this reason, the applicability of R245fa as a refrigerant for high temperature heat pumps for industrial applications has been investigated. With critical temperature of 154 °C this refrigerant can be effectively used at condenser temperature levels of around 125°C [1]. However, it is mildly toxic and its GWP is relatively high. Therefore, there is a need for environmentally friendly substances for high temperature applications.

HFOs as low GWP refrigerants for high temperature applications

Applicability of different hydrofluororolefins (HFOs) for high temperature applications has been investigated in a number of studies. It was shown that out of the number of propene isomers, R1234ze(Z) deserves consideration as a possible R114 replacement as have similar thermodynamic properties.



a) Ph diagram



b) Saturation pressure curves

Figure 1 – Predicted thermodynamic properties of R1234ze(Z), compared to that of R114 [2]

R1234ze(Z) has critical temperature of 150 °C, high heat transfer coefficients [3] and comparable to R114 theoretic cycle performance [2]. Figure 2 presents the comparison of theoretical cycle performance and volumetric capacity of R1234ze(Z) to that of a number of other refrigerants [4].

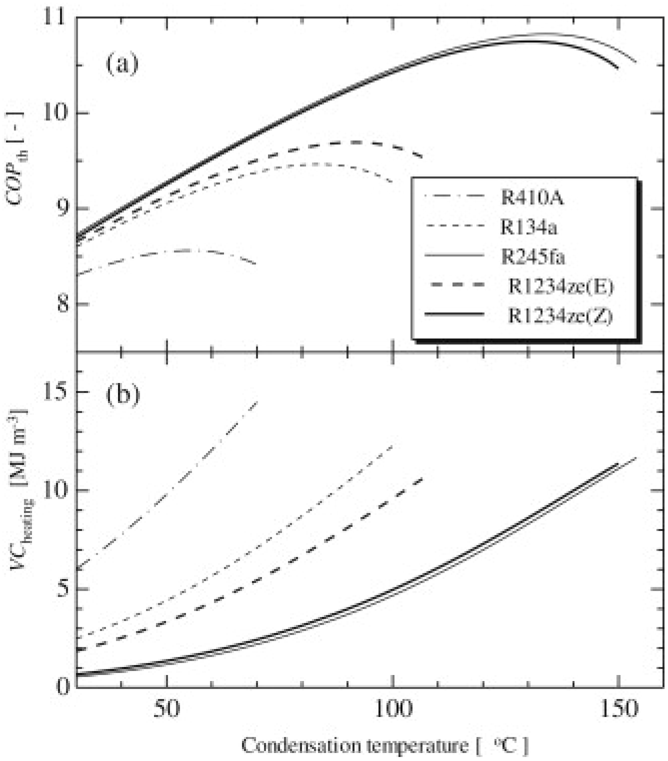


Figure 2 - (a) Theoretical COP (b) volumetric capacity (isentropic compression, 35K temperature lift, 3K superheat and 20K subcool) [4]**.**

It can be seen that in terms of heating COP and volumetric capacity, R1234ze(Z) is comparable to R245fa. The COP of every refrigerant reaches its maximum point at condensing temperatures at levels, approximately 20K below the critical temperature. For R1234ze(Z) the theoretical COP is quite high and therefore there is a potential to design efficient heat pump system based on this refrigerant.

New high temperature refrigerants under development

R1234ze(Z) is an example of potential refrigerant for high temperature applications. However, it cannot solely cover a wide range of desired condensing temperatures. Development is therefore ongoing to create a wider amount of refrigerants and refrigerant blends with properties suitable for a wider range of operating conditions.

DuPont has been developing a number of refrigerants with critical temperatures up to 171 °C [5]. The composition of most of the refrigerants under development is undisclosed and they are therefore referred as development refrigerants (DR). The fundamental property data for some of the development refrigerants is summarized in Table 1. The table is complemented with properties of other refrigerants, suitable for high temperature applications (R1234ze(Z), R134a and R234fa).

Table1 – Fundamental information for selected high temperature refrigerants [5] [6]

Refrigerant	R134a	DR-14A	DR-12	R1234ze(Z)	R245fa	DR-40A	DR-2
GWP_{100}	1300	~415	32	<1	858	<170	2
T_{cr} [°C]	101.1	110.7	137.7	150.1	154.0	166.5	171.3
P_{cr} [MPa]	4.06	3.96	3.15	3.53	3.65	3.50	2.90
T_b [°C]	-26.1	-20.5	7.5	9.8	15.1	25.5	33.4
Temp Glide [K] (@P=1 atm)	-	0.04	-	-	-	0.86	-

Among a number of the development refrigerants, DR-14A is the azeotropic blend with properties closest to R134a. It is non flammable and can be seen as an alternative to R134a widely used today in the medium temperature applications. DR-12 and DR-40a are covering similar to R245fa range of temperatures, but less toxic and have lower GWP values. DR-2 is the refrigerant with the highest critical temperature and can be potentially used in very high temperature heat pumps.

The vapour pressures comparison for the selected refrigerants is presented in the Figure 3. Comparing to the reference refrigerants R134a and R245fa, condensing temperatures of some of the development refrigerants are higher at similar pressure levels. This is advantageous in order to keep the pressure in the system below the practical value of, for example, 2.5 MPa.

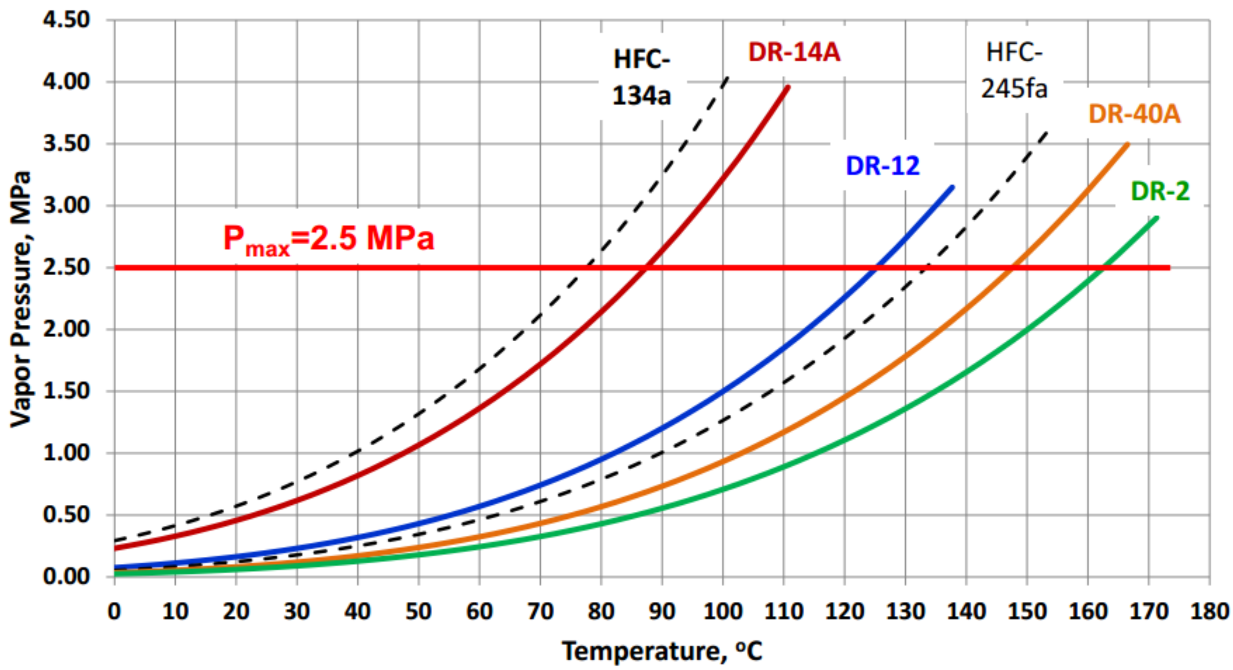


Figure 3 – Vapour pressures of selected high temperature refrigerants [5]

Theoretical heating COP values of the development refrigerants are promising (Figure 4) with refrigerants DR-40A and DR-2 expected to have better performance over a wide range of condensing temperatures.

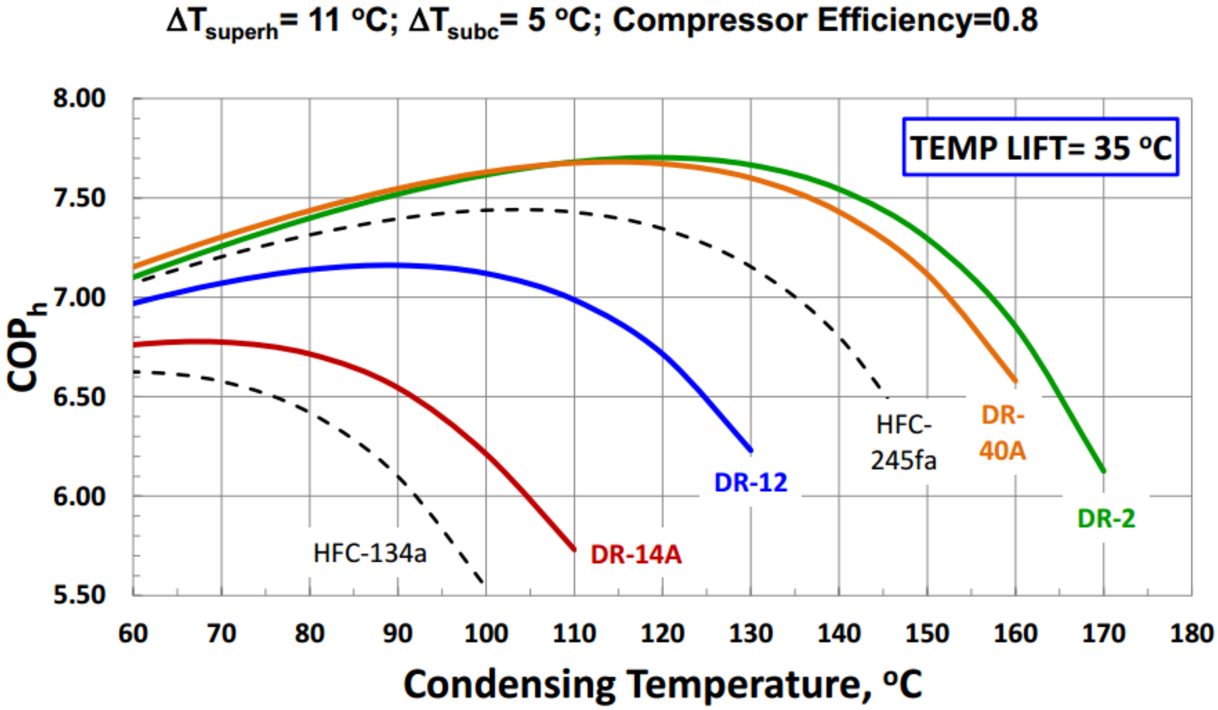


Figure 4 – predicted cycle performance of selected high temperature refrigerants [5]

Composition of DR-2 has been revealed

Recently, DuPont has revealed the composition of refrigerant DR-2, discussed above. The refrigerant, known as the "hydrofluoro-olefin-based fluid" [7], is in fact pure substance – R1336mzz(Z). Similarly to the group of propene isomers, DR-2 is an isomer of butane. Its chemical structure is shown on Figure 5.

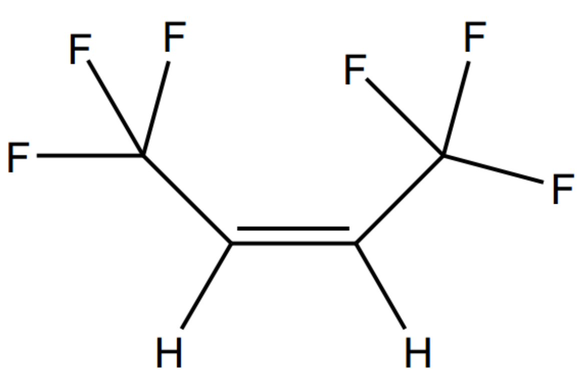


Figure 5 – chemical structure of (Z)-1,1,1,4,4,4-Hexafluoro-2-Butene ($C_4H_2F_6$ or R1336mzz(Z))

Given the properties of R1336mzz(Z) it can become a breakthrough in low GWP refrigerants for high temperature heat pumps. Unlike many other low GWP refrigerants, R1336mzz(Z) is non-flammable and thus requires no compromise between low GWP value and flammability. In our next article, we will make a closer look on this refrigerant, its thermodynamic properties, safety and other important properties.

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