R1336mzz-Z - new generation nonflammable low GWP refrigerant

For new environmentally friendly refrigerants their low GWP values are usually at an expense of their flammability. R152a and R1234yf are the two of many examples of flammable low GWP synthetic refrigerants. Moreover, American Air Conditioning, Heating, and Refrigeration Institute, in its Low Global Warming Potential Alternative Refrigerants Evaluation Program, has identified no refrigerant, potentially applicable in future refrigeration systems, with GWP lower than 574 [1]. The above is strong evidence to a common believe that low GWP values compromise with flammability; until recently.

Properties of R1336mzz-Z

Non flammable single component fluid R1336mzz-Z with GWP of just 2 has been recently revealed by DuPont - American chemical manufacturer. The substance, previously known as development refrigerant DR-2, is in fact an olefin of butane (that is unsaturated molecule of butane containing a carbon–carbon double bond).

Boiling and critical temperatures of R1336mzz-Z are 33.5 and 171.3 °C respectively. Therefore, it can be potentially used as a working fluid for high temperature heat pump applications. For this range of temperatures, it can be considered as an alternative to refrigerants HFC-245fa and HCFC-123. Given that the later consist with chlorine and thus going to be completely phased out, R1336mzz-Z should be put into comparison with HFC-245fa (Table 1).

Refrigerant	HFC-245fa	HFO-1336mzz-Z
IUPAC name	1,1,1,3,3-pentafluoro-propane	(Z)-1,1,1,4,4,4-hexafluoro-2-
		butene
ASHRAE Std 34 Safety Class	B1	A1*
ODP	None	None
GWP ₁₀₀	1,030	9,4
Boiling temp., °C	15.1	33.4
Critical temp., °C	154	171.3
Critical pressure, MPa	3.65	2.9

Table 1 - Refrigerants comparison [2]

* expected

Given the comparison, presented in Table 1, R1336mzz-Z has lower GWP and potentially less toxic.

Figure 1 presents the plot of vapor pressures of new R1336mzz-Z compared to R245fa. From thermophysical point of view, it can cover greater condensing temperatures due to its high critical temperature at lower operating pressures (Figure 1). It is particularly important for designing a system with high condensing temperatures, as it is possible to keep operating temperatures reasonably low. For instance, setting the safety pressure limit to 2.5 MPa, new refrigerant gives possibility to design systems with condensing temperatures of up to around 160 °C.

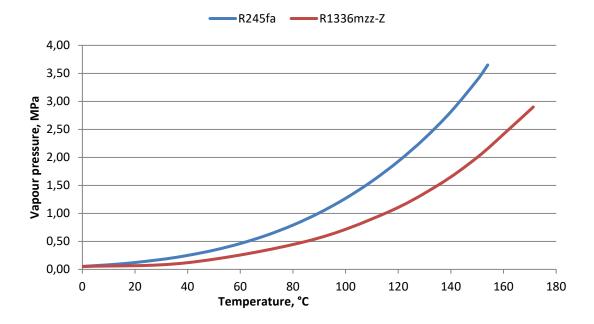


Figure 1 - Saturated vapor pressures of R245fa and R1336mzz-Z (adapted from [2])

R1336mzz-Z as a potential refrigerant

Pressure enthalpy diagram, as seen on the Figure 2, gives us further insight on thermodynamic properties of R1336mzz-Z and its applicability as refrigerant.

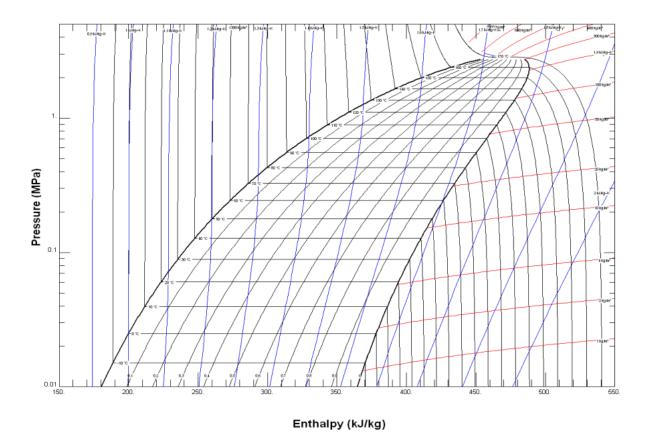


Figure 2 - Pressure-enthalpy diagram for R1336mzz-Z [2]

The saturated vapor line is greatly inclined to the right, towards the vapor region. Therefore, some superheat would be necessary to ensure dry compression. The required superheat is much dependent on the operation pressure/temperature range of compressor and can rich rather high values, as it is presented on the Figure 3.

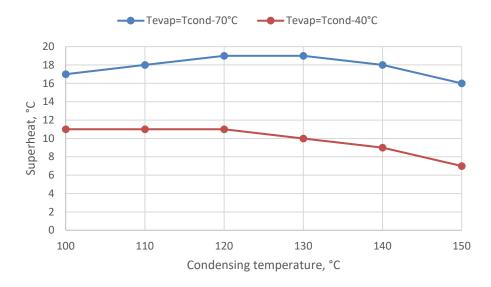


Figure 3 - Minimum suction vapor superheat for dry compression (adapted from [2]).

Heat pump system that is using R1336mzz-Z is expected to have greater performance compared to system operated with R245fa. At constant temperature lift of 40 °C and given the assumptions of 11K superheat and 5K subcooling, R1336mzzZ can reach COP of around 6.5 at wide range of condensing temperatures, whereas COP of R245fa is lower. Similar behavior is seen at other temperature lift values and condensing temperature ranges (Figure 4). R1336mzz-Z is also reported to have generally lower cooling and heating capacities [3] [4].

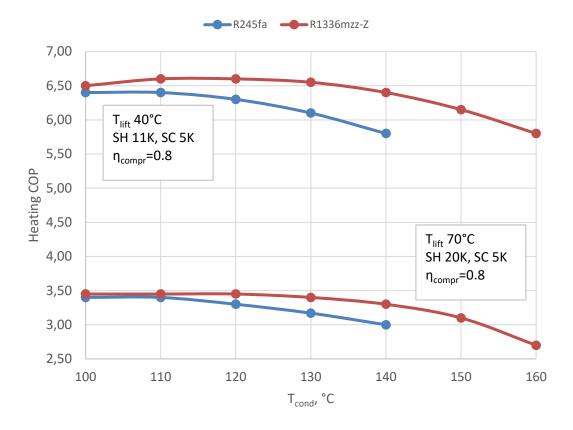


Figure 4 – Predicted simple cycle performance of R1336mzz-Z compared to R245fa (adapted from [4])

Safety and stability of the new refrigerant

Safety is an important refrigerant selection criterion. Knowledge on their flammability, toxicity, carcinogenicity and similar data is necessary in order to judge on safety of a refrigerant. For R1336mzz-Z the safety data is available from the manufacturer, that emphasizes it nonflammability and "favorable toxicity profile" [4]. However, it is early to draw any conclusions until independent safety data will be available publicly available. One can recall a number of safety issues raised by Daimler regarding R1234yf – refrigerant commercialized for mobile air conditioning application.

As reported by DuPont, R1336mzz-Z shows surprisingly good stability, despite its unsaturated chemical nature [4]. In the sealed tube stability tests (at the conditions when refrigerant is being aged for 14 days at elevated temperature of up to 250 °C) the refrigerant decomposition is very low and characterized with negligible formation of decomposition products [4].

Is R1336mzz-Z a new refrigerant of a choice?

R1336mz-Z is nonflammable HFO refrigerant that is close to commercialization. DuPont has promised to start the small-scale production of the refrigerant during this year. It was primarily designed as a foam

blowing agent [5], but could be potentially used in many applications, including Organic Rankine Cycles [6], high temperature heat pumps [3] and commercial chillers [4].

According to what presented above, this refrigerant has no competition and, perhaps, no weak point that can restrain it from being used at high temperature heat pumps category. It should be mentioned, however, that most of the presented above data has been demonstrated by representatives of refrigerant developer and manufacturer. Thus, data from independent research groups would be necessary to draw final conclusions.

Följ gärna våra publikationer och få vårt digitala nyhetsbrev. Anmäl dig genom att följa länken bit.ly/kth_ett.

References

- [1] X. Wang and K. Amrane, "AHRI Low Global Warming Potential Alternative Refrigerants Evaluation Program (Low-GWP AREP) – Summary of Phase I Testing Results," in *15th International Refrigeration and Air Conditioning Conference*, Purdue, 2014.
- [2] K. Kontomaris, Low GWP working fluid for high temperature heat pumps: DR-2, 2013.
- [3] K. Kontomaris, *Zero-ODP, low-GWP, nonflammable working fluids for high temperature heat pumps,* Seattle, WA: 2014 ASHRAE Annual Conference, 2014.
- [4] K. Kontomaris, "A low GWP replacement for HCFC-123 in centrifugal chillers: DR-2," DuPont, 2010.
- [5] DuPont, "Our Next-Generation Foam Expansion Agent," 2014. [Online]. Available: bit.ly/DuPontFormacel1100. [Accessed 22 Aug 2014].
- [6] F. Moles, J. Navarro-Esbrí, B. Peris, A. Mota-Babiloni, A. Barragan-Cervera and K. Kontomaris, "Low GWP alternatives to HFC-245fa in Organic Rankine Cycles for low temperature heat recovery: HCFO-1233zd-E and HFO-1336mzz-Z," *Applied Thermal Engineering*, no. 71, pp. 204-212, 2014.