Novel Working Fluid, HFO-1336mzz(E), for Use in Waste Heat Recovery Application

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Abstract

HFO-1336mzz(E) is a novel, non-flammable, low global warming potential (GWP) working fluid which can be used in waste heat recovery applications such as high temperature heat pumps (HTHP) and Organic Rankine Cycle (ORC). The working fluid's performance in HTHP applications will be explored further. HFO-1336mzz(E) has a GWP of 18, a boiling point of 7.5ºC (45.5ºF) and a critical temperature of 137.7 ºC (279.9ºF). It has a zero Ozone Depletion Potential (ODP) and favorable toxicity profile based on testing to date. It remains chemically stable in glass sealed tube tests in the presence of commonly seen metals with temperatures up to 250ºC for 7 days. It has also shown good compatibility with many plastics and elastomers commonly encountered in equipment presently used with these types of working fluids. HFO-1336mzz(E) is a viable solution enabling both HTHP and ORC technology platforms to recover heat from various sources and reduce fossil fuel dependencies.

Keywords: Hight Temperature Heat Pumps; Organic Rankine Cycles; HTHP; ORC; Working Fluids; Low Global Warming; Waste Heat recovery; WHR, HFO-1336mzz(E), and E-1,1,1,4,4,4-hexafluoro-2-butene

1. Introduction

The need to improve energy efficiency has been a general topic of discussion for the last couple of decades, opportunities to integrate new heat recovery systems from geothermal, biomass and from various heat sources in the industrial sector are progressively being adopted to help address this concern. The potential of recovering waste heat and applying it in applications such as hot water supply (e.g. district heating), refrigeration/heating in the food industry, low pressure steam generation, process heating and drying/dehydration are some viable candidates. These applications would require a working fluid to meet the desired goals of recouping cost associated with the capital investment by providing energy savings versus an incumbent technology.

Presently, new heat pump technologies are being developed with an additional caveat of providing environmentally friendlier working fluids. As increased awareness on environmental impact and regulatory pressures for the reduction of greenhouse gases (GHG) emissions and elimination of ozone depletion potential (ODP) compounds becomes under scrutiny, more emphasis will be focused on alternatives that meet the new regulatory goals. The fundamentals of choosing a good working fluid are based on system optimization to maximize the thermodynamic performance characteristics, but significant portion of potential candidates are going to been removed as viable options based on climate protection initiatives. Even though these are the new realities, one should not have to sacrifice performance. These novel HFOs are being developed, like HFO-1336mzz(E) and R1336mzz(Z), to meet the more stringent regulations of low GWP and no ODP and they demonstrate the known characteristics of a good working fluids – stability, compatibility, favorable toxicity and performance even at high temperatures.

2. High Temperature Heat Pump Systems – Economic Evaluation

The feasibility of using a specific working fluid in a high temperature heat pump is based on many factors. The fluids need to demonstrate thermally stable, compatibility with metals, plastics and elastomers under the specified conditions, meet safety standards and provide the performance to economically justify their use. Determining whether a given solution can provide a reasonable payback on the upfront capital investment through verified energy savings is crucial component of the selecting a working fluid as is showing the long term reliability in operation. Since the hydrofluoro-olefins (HFO) based fluids are relatively new, the only means to show their potential reliability in these type of applications is to use similar methodology provided by ASHRAE which characterizes their behavior in a static system. Understanding the potential payback is a difficult assessment and one that seems to be the fundamentals in whether these systems will produce the desire effects as promoted. Using an example condition and comparing alternative energy seems to be the most constructive way to attempt to convey the benefits of these new working fluids in heat pumps as viable long term solution.

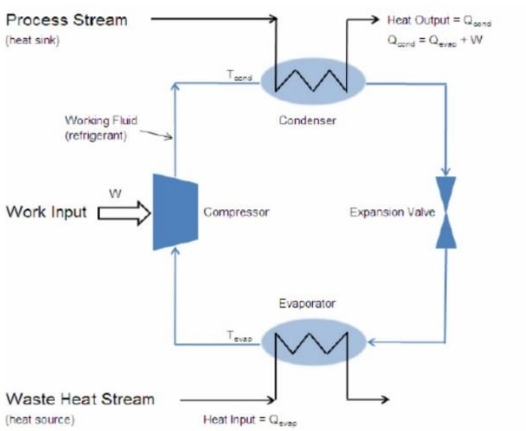

Figure 1. Closed-Cycle Vapor Compression Heat Pump System

As shown in Figure1, this is an example of a vapor compression heat pump system which is well-suited for use with refrigerant based working fluids and been shown to be reliable with the various components: evaporators, expansion valves, condenser and compressors. The efficiency of the heat pump system is typically reported by the coefficient of performance (COP) which is the ratio of heat output into the process stream divided by the work inputted by the heat pump. A simplified approach to determine payback time is provided below in Equations 1 through 3, the factors to consider whether or not to use a heat pump in a certain application reside on the economics. Several of the main variables needed to derive this are:

Variables (Input parameters):	**Example conditions:**
Q_{IN} = Heat Source	**(10 MMBtu/yr)**
O_T = Operating Time	**(95% uptime for 8736 h/yr)**
C_E = Electric Cost (Using HP)	**($0.045/kW-h)**
C_A = Alternative Energy Cost	**($5 MMBtu for Steam)**
Unit = HP System Cost	**($200,000/unit)**
COP_H = Coefficient of Performance	**(4.4, 3.4, 3.0)**

Determine: $\boldsymbol{W_{IN}}, \boldsymbol{Savings}$ & $\boldsymbol{Payback\ time}$

$$W_{IN} = \frac{Q_{IN}}{COP_H - 1} \tag{1}$$

$$Savings\left(\frac{\$}{\text{year}}\right) = \left[\left(Q_{IN} + W_{IN}\right)C_A - W_{IN}C_E\right]O_T \tag{2}$$

$$Payback\ time = \frac{Unit}{Savings} \tag{3}$$

Different facilities will have different input values and these should be understood before attempting to calculate payback time, but this approach gives the basis of how to determine the potential benefit of a heat pump system with a specified refrigerant. Several factors influence the size of the equipment set and its cost, but the COP_H is one variable's effect that has a direct correlation to the savings and time to recover the cost of the system. One thing to note in general about heat pumps, having a smaller lift temperature (difference between evaporator and condenser) is where they are most efficient with higher COPs. As this temperature difference increases, the COP_H decreases.

			Payback Time
Using	COP_H: 4.4	\$200,000 / \$213,372	= 0.9 *years*
	COP_H: 3.4	\$200,000 / \$153,924	= 1.3 *years*
	COP_H: 3.0	\$200,000 / \$75,165	= 2.7 *years*

3. Fluid Characteristics for HFO-1336mzz(E)

3.1. Chemical Structure and Physical Properties

The novel working fluid, HFO-1336mzz(E), is a hexafluoro-2-butene with an unsaturated bond similar to R1336mzz(Z). The main difference between the E and Z isomer is evident when looking at Table 1 and Figure 2 & 3 below as their differences are denoted by normal boiling point (NBP), critical temperature (T_c) and pressure (Pc), and vapor pressure. The HFO-1336mzz(E) has 7.5ºC boiling point, critical temperature of 137.7ºC and critical pressure of 3.15 MPa. Whereas R-1336mzz(Z) has slightly higher boiling point of 33.4ºC, critical temperature of 171.3ºC and lower critical pressure of 2.90 MPa. The P-H diagram for HFO-1336mzz(E) is also provided in Figure 5. Table 1 contains a list of potential refrigerants, both HFCs and HFOs, for use in high temperature heat pumps. The developmental refrigerant, DR-14a, is also included as a potential candidate. One trait not mentioned regarding R1234yf and R1234ze-E are their ASHRAE classifications of 2L, mild flammability. The critical temperature (T_c) is an important variable in heat pump applications as it represents the upper fluid temperature limit. These refrigerants in this list were assessed using two different lift temperatures to show their potential benefits with be HTHP applications. Benefits in heat pump systems for these new low GWP HFO working fluids are their higher critical temperatures and lower critical pressures which enable systems to be operated at higher temperatures with lower pressures.

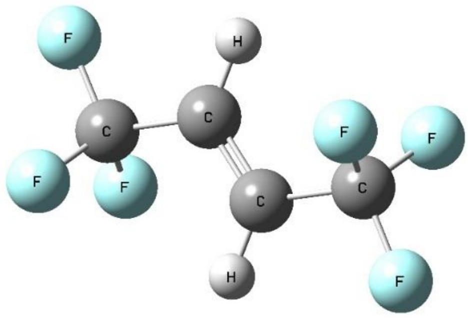

Figure 2. Chemical Structure of (E)-1,1,1,4,4,4-Hexafluoro-2-Butene (C4H2F6 or HFO-1336mzz(E))

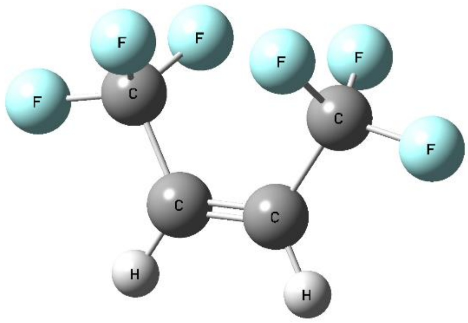

Figure 3. Chemical Structure of (Z)-1,1,1,4,4,4-Hexafluoro-2-Butene (C4H2F6 or HFO-1336mzz(Z))

Table 1. List of Common Refrigerants and their Properties and Characteristics

Refrigerant	GWP (AR5)	NBP (°C)	Tc (°C)	Pc (MPa)	Family	CAS#	Chemical name
R134a	1,300	-26.3	101.1	4.06	HFC	811-97-2	1,1,1,2-tetrafluoroethane
R245fa	858	15.1	154.0	3.65	HFC	460-73-1	1,1,3,3-pentafluoropropane
R1234ze-E	1	-19.0	109.4	3.63	HFO	29118-24-9	trans-1,3,3,3-tetrafluoropropene
R1234yf	1	-29.5	94.7	3.38	HFO	754-12-1	2,3,3,3-tetrafluoroprop-1-ene
DR-14A	415	-20.4	110.7	3.96	HFO, HFC	Proprietary Blend	Proprietary Blend
HFO-1336mzz-E	18	7.5	137.7	3.15	HFO	66711-86-2	trans-1,1,1,4,4,4-hexafluoro-2-butene
R1336mzz-Z	2	33.4	171.3	2.90	HFO	692-49-9	cis-1,1,1,4,4,4-hexafluoro-2-butene

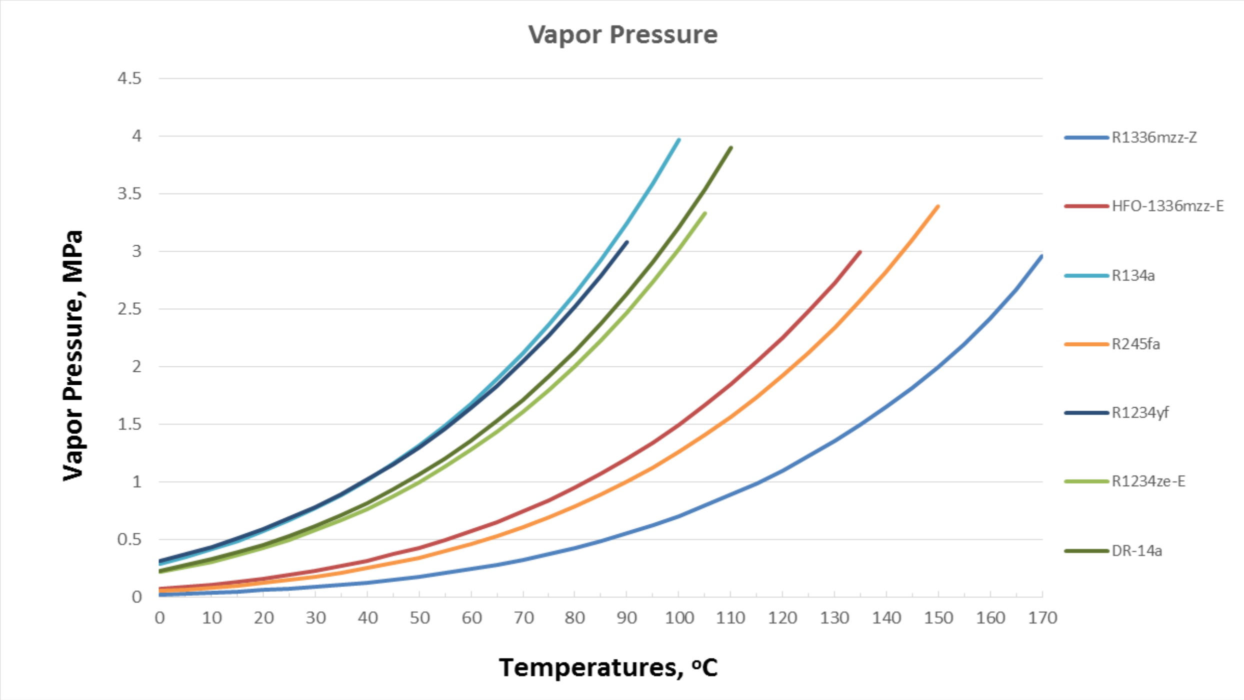

Figure 4. Vapor Pressure for Common Refrigerants and Newly Developed HFOs

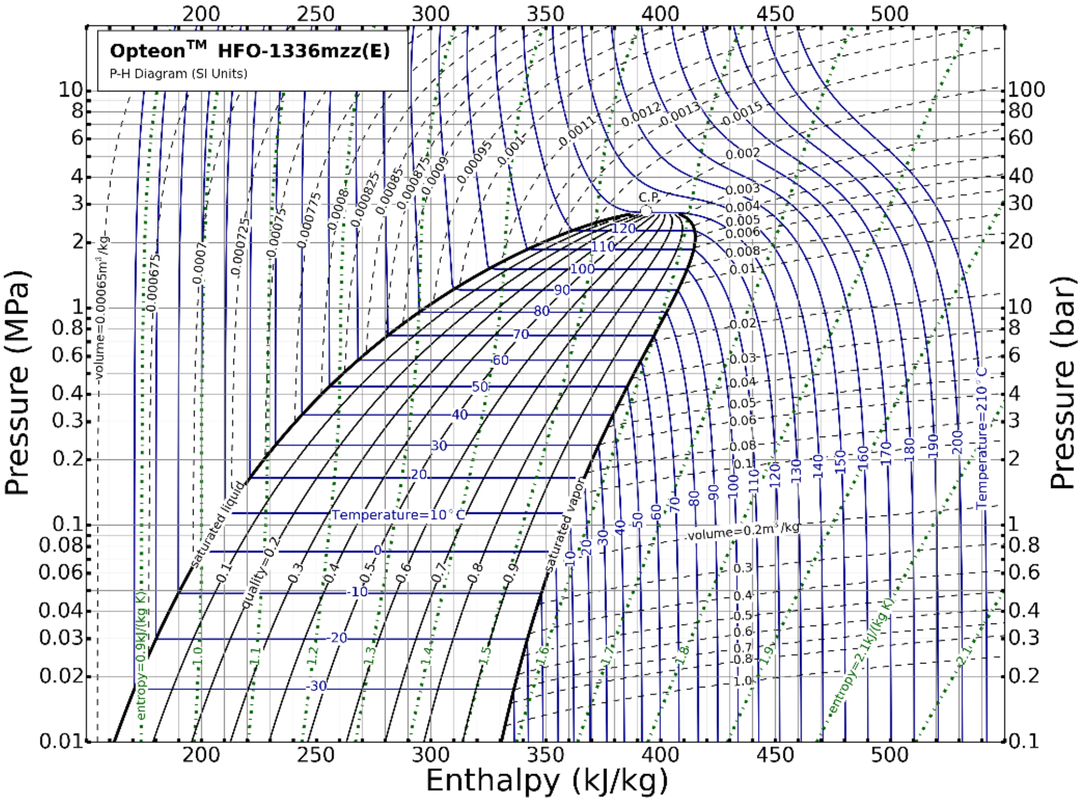

Figure 5. P-H Diagram for HFO-1336mzz(E)

3.2. Thermal Stability and Metal Compatibility

Two separate studies at elevated temperatures, 175ºC and 250ºC, were conducted to understand the stability of the HFO-1336mzz(E) molecule. At 175ºC for 14 days, the working fluid was mixed with a POE oil and placed in a sealed test tube with three metals – aluminum, copper and steel. The moisture of the fluid was measured at 7.5 ppm by weight. The analysis of the results at 175ºC showed that HFO-1336mzz(E) is very stable and compatible with both the POE oil and all three metals by exhibiting no visible or chemical of change to the fluid (by purity analysis). No corrosion was observed on the coupons as well. This indicates that this fluid would be extremely stable and viable candidate for both high temperature heat pumps and ORC applications. An additional study was performed at 250ºC (with no oil) with a variety of metal coupons and a standard with the fluid alone. The results in Table 3 show that fluid remains very stable even at these elevated temperatures. Minor surface tarnishing was observed by several of the metals which was believed to be a result of trace amounts of water, 25.7 ppm by weight. Nickel and aluminum coupons showed no evidence of corrosion.

Table 2. HFO-1336mzz(E) at 175ºC at 14 days with POE oil and Metal Coupons – Aluminum, Copper & Steel

Fluid	Temperature (ºC)	Duration	Oil	Coupon	IC - Anions (ppm wt%)		GC Results Purity (wt.%)	
					F-	Cl-	Before	After
HFO-1336mzz-E	175	14 days	POE	Aluminum, Steel, Copper	2.57	3.09	99.9986	99.9981

Table 3. HFO-1336mzz(E) at 250ºC at 7 days with and without Metal Coupons

Fluid	Temperature (ºC)	Duration	Oil	Coupon	IC - Anions (ppm wt%)		GC Results Purity (wt.%)	
					F-	Cl-	Before	After
HFO-1336mzz-E	250	7 days	N/A	Brass	0.54	3.31		
				Zinc	0.71	1.79		
				Nickel	1.17	0.77		
				Aluminum	0.91	2.6		
				Steel	0.41	1.23		
				Copper	0.99	0.57		
				N/A	2.66	1.04	99.998	99.976

A gas chromatography (GC) analysis was used in conjunction with a mass spectrometry and flame ionization detector were both quantitative and qualitative analysis were performed, respectively. The purity is reported in weight percentage above in Table 2 on the far right column, the HFO-1336mzz(E) concentration change at 175ºC was negligible at approximately 5 ppm. At the elevated temperature of 250ºC, weight concentration of HFO-1336mzz(E) decreased by approximately 220 ppm where the main product detected was R1336mzz(Z) at 59 ppm. Some isomerization between the E and Z isomers of 1,1,1,4,4,4-hexafluoro-2-butene molecule are known to occur at these elevated temperatures. However, an overall assessment can be made that the molecule is very stable even with various metal coupons and with POE oils as the fluoride ion concentrations were extremely low under these severe conditions. The chloride ions are contributed by known trace impurities that reside within the overall fluid composition and have been shown to be unstable at these elevated temperatures.

3.3. Material Compatibility – Plastics and Elastomers

A material compatibility study on HFO-1336mzz(E) with common plastics and elastomers in the presence of POE lubricant oil were elevated at a temperature of 100ºC for 14 days. Their individual weight and hardness changes were measured at the conclusion of the experiment and the results display mainly mild interactions between these plastics and elastomers as provided in Table 4. It is recommended that further evaluations be conducted for material and chemical compatibility not only with plastic and elastomers, but also covering various metals and lubricants typically found in a heat recovery system. This study only represents a subset of current experiments from our lab.

Table 4. Weight and Hardness Changes of Various Elastomers and Plastics with HFO-1336mzz(E) at 100ºC at 14 days with POE OIL

	Weight Changes		Hardness Changes	
Material	Immediately after Exposure %	24 hours after Exposure %	Immediately after Exposure %	24 hours after Exposure %
Neoprene C1276 -70	0.3	-0.3	0.47	-0.47
Epichlorohydrin	4.9	4.6	-5.58	-4.65
Butyl Rubber	13.0	12.3	-7.49	-4.28
EPDM	8.1	6.2	-8.37	-6.61
NBR	7.8	6.8	-6.98	-5.58
Neoprene C0873-70	5.9	5.4	-9.59	-6.39
Polyester	8.2	7.3	0.70	1.06
Nylon resin	-1.1	-1.1	-3.07	0.00
Polyamide-imide	-0.6	-0.6	0.00	0.00
Polyphenylene sulfide	0.0	0.0	0.00	0.00
PEEK	-0.1	-0.1	0.68	0.68
Nylon	-1.1	-1.1	-0.34	0.00
PTFE	3.4	2.9	-0.34	-0.68

3.4. Performance

Heat pump technology is believed to be an effective way to improve energy efficiency and reduce the environmental footprint in the industrial sector. The key points in introducing any new technology is demonstrating the advantages over an existing technique and/or the opportunity to increase savings. The payback calculation shown in section 2 specifically indicate how COP_H has a correlation and direct impact under given conditions. Higher-lift temperatures was briefly mentioned as they might affect the attractiveness of heat pumps as it decreases COP_H. In Figures 6 and 8 that follow, coefficient of performance (COP_H) for two classes of working fluids, HFCs and HFOs, was examined under two different lift temperatures (30ºC and 50ºC which is differences between condensing and evaporator temperatures) up to the critical temperatures. Figures 7 and 9, show the effect of the volumetric heating capacity (CAP_H) at these two different lift temperatures. The compressor efficiency, superheat (ΔT_{sh}), subcooling (ΔT_{sc}) and lift temperatures were fixed variables is this assessment, the condensing temperatures were adjusted so higher temperature effects could be evaluated for each working fluid. HFO-1336mzz isomers (E and Z) and R245fa had the highest COPs amongst the candidates selected and this suggests they would provide the best payback time.

One trend that become apparent is that volumetric heating capacity increases with temperature and this is an important factor as it affects the potential size of the compressor. The compressor is a critical and a costly component in the overall unit cost for the heat pump system. The COP_H generally has an optimal position which peaks and then rapidly decreases as the fluid approaches its critical temperature. The combination of these two variables are significant influencers in selecting a viable working fluid candidate for a specific operation. Obviously, performance is very distinguishable characteristic in determining the break-even point for installing a heat pump system and the financial aspect is just as critical as any other potential trade-off such as stability, reliability, toxicity, or flammability.

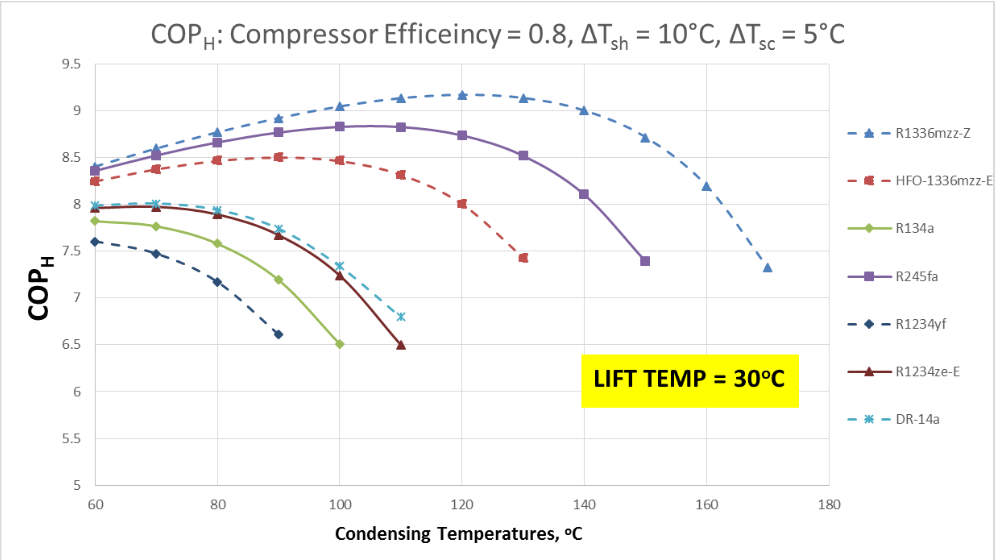

Figure 6. Temperature Lift of 30ºC Evaluated for its Effect on COP_H for Several Potential Working Fluids including HFO-1336mzz(E)

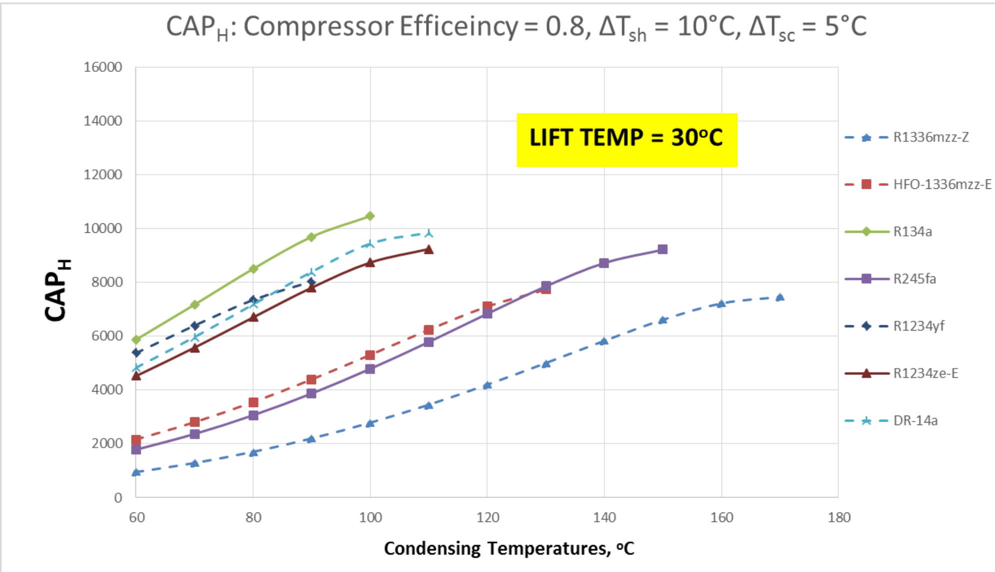

Figure 7. Temperature Lift of 30ºC Evaluated for its Effect on CAP_H for Several Potential Working Fluids including HFO-1336mzz(E)

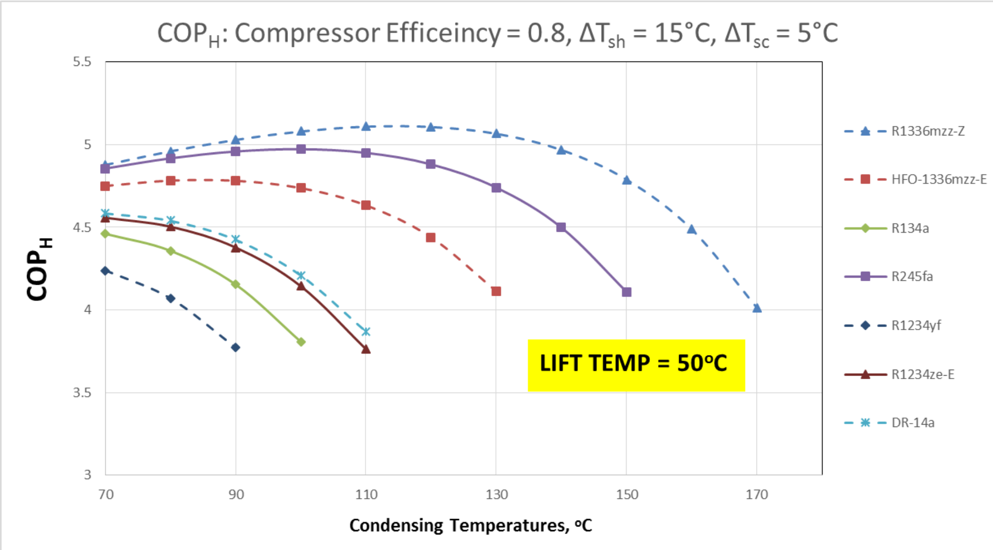

Figure 8. Temperature Lift of 50ºC Evaluated for its Effect on COP_H for Several Potential Working Fluids including HFO-1336mzz(E)

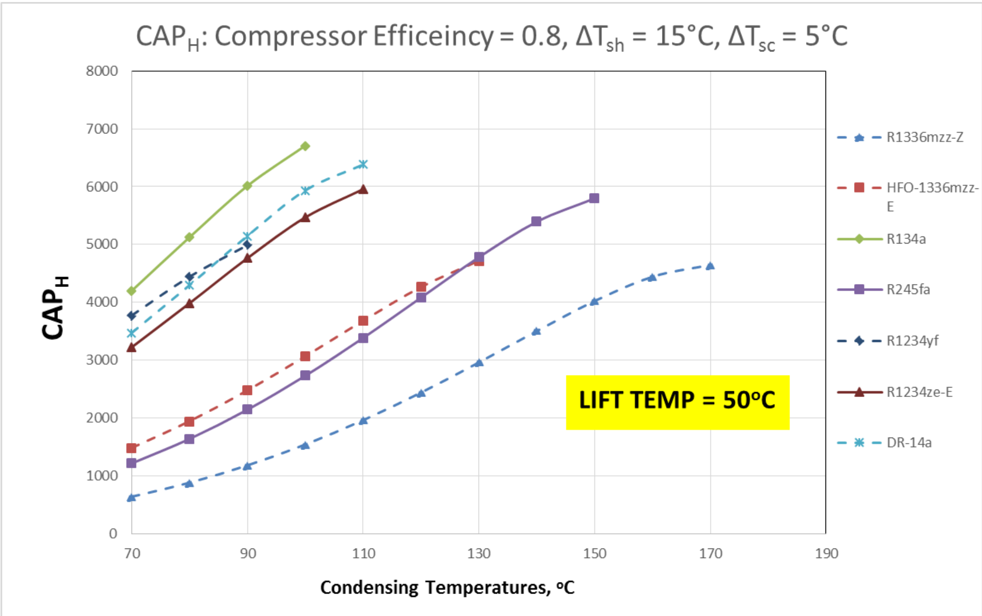

Figure 9. Temperature Lift of 50ºC Evaluated for its Effect on CAP_H for Several Potential Working Fluids including HFO-1336mzz(E)

3.5. Summary

Fluid characteristics are essential fundamentals in selecting a good working fluid which are based on system optimizing the thermodynamic performance, meeting upcoming regulations with low GWP and demonstrating both the stability and material compatibility at higher temperatures as well as being non-flammable and exhibiting favorable toxicity profile. As described in the paper, the HFO-1336mzz(E) has all of the characteristics to be a viable working fluid in waste heat recovery applications which include both high temperature heat pumps and low temperature ORC applications. Tests to date regarding the toxicity profile of the substance have been very favorable as compared to known substances, safety classification according to ASHRAE Standard 34 will be forth coming.

The E and Z isomers of 1,1,1,3,3,3-hexafluoro-2-butene allow for higher condensing temperatures than R134a, R1234yf and 1234ze(E) molecules and they have a lower GWP than R245fa. Two different lift temperature analyses show significantly high COP_H which helps the economic justification for their use in heat pump applications, several potential ones are:

- Low pressure steam generation
- High temperature drying
- Sterilization
- Process heating
- Food manufacturing industry

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