HFO-1336mzz-Z AS A LOW GWP WORKING FLUID FOR TRANSCRITICAL RANKINE POWER CYCLES

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ABSTRACT

This paper briefly reviews basic properties of HFO-1336mzz-Z (cis-$CF_3CH{=}CHCF_3$), reports new data on the compatibility of HFO-1336mzz-Z with plastic and elastomeric materials and evaluates HFO-1336mzz-Z as a potential working fluid for Organic Rankine Cycles (ORC) driven by, relatively, high temperature heat (expander inlet at 175-250 ^{o}C). HFO-1336mzz-Z has a favorable toxicity profile (based on testing to date), it is non-flammable at 60 ^{o}C and 100 ^{o}C and offers a very low GWP of 2. It has a high critical temperature of 171.3 ºC and a low critical pressure of 2.9 MPa, relative to incumbent fluids. It remains chemically stable in sealed tube testing in the presence of common metals of equipment construction at temperatures at least up to 250 ^{o}C for two weeks. HFO-1336mzz-Z is compatible with several plastic and elastomeric materials commonly encountered in working fluid handling and use equipment. Maximum net thermal energy efficiencies of Rankine power cycles operated with HFO-1336mzz-Z are computed at high-side cycle pressures higher than about 4 MPa, i.e. under transcritical operation but under pressure levels not excessive for practical equipment. HFO-1336mzz-Z could enable more environmentally sustainable ORC platforms to generate power from available heat at higher temperatures and with higher energy efficiencies than incumbent working fluids.

Keywords: HFO-1336mzz-Z, Organic Rankine Cycle, Sustainability, Energy Efficiency, Power Generation, Climate Protection

INTRODUCTION

Generation of mechanical or electrical power from heat recovered from mobile or stationary internal combustion engines through Organic Rankine Cycles (ORCs) has been gaining attention. It can be realized with higher energy efficiencies than ORC applications driven by lower temperature heat.

It is widely recognized that the choice of working fluid (also referred to as the "refrigerant") plays a critical role in determining the attractiveness of an ORC application. Low Global Warming Potential (GWP) has been recently added to the list of specifications that a working fluid must meet, especially given that climate protection is a primary motivation for low temperature heat utilization. The availability of a suitable working fluid with a GWP sufficiently low so as to minimize business risk from climate protection regulations emerging around the globe is a prerequisite for substantial ORC research and development investments.

HFO-1336mzz-Z (cis-1,1,1,4,4,4-hexafluoro-2-butene), previously also referred to as DR-2, has been introduced as a developmental working fluid for various applications including ORCs [1-7] and high temperature heat pumps [5, 7, 8-14]. Figure 1 shows the molecular structure of HFO-1336mzz-Z.

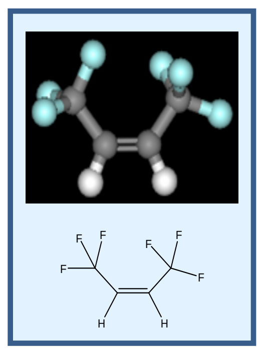

Figure 1: Molecular structure of HFO-1336mzz-Z.

Table 1 compares key safety, health, environmental and thermo-physical properties of HFO-1336mzz-Z to those of a familiar reference fluid that has been used for ORCs, HFC-245fa. The GWP of HFO-1336mzz-Z is 99.8 % lower than that of HFC-245fa.

Figure 2 shows a pressure-enthalphy diagram for HFO-1336mzz-Z. The slope of the saturated vapor line is, generally, higher than that of the isentropic lines in its vicinity, thus ensuring dry expansion for subcritical ORCs regardless of the degree of vapor superheat at the expander inlet.

Table 1: Basic properties of HFO-1336mzz-Z and HFC-245fa

	HFC-245fa	HFO-1336mzz-Z
	$CHF_2CH_2CF_3$	$CF_3CH{=}CHCF_3$(Z)
Mol. Weight	134.05	164.056
OEL [ppmv]	300(1)	500(2)
Flammability	Non-flam(1)	Non-flam(3)
Safety Class(4)	B1(1)	A1(5)
ALT [yr]	7.7(6)	0.060274(6) (22 days)
ODP	None	None
GWP	858(6)	2(6)
T_b [°C]	15.1(1)	33.4
T_{cr} [°C]	154(1)	171.3
P_{cr} [MPa]	3.65(1)	2.9
T_{fr} [°C]	-107(7)	-90.5(8)

(1) [15]; (2) DuPont AEL; (3) At 60 °C and 100 °C according to [16]; (4) [17]; (5) Not established, but meets criteria of A1; (6) [18]; (7) Honeywell product literature; (8) [19]

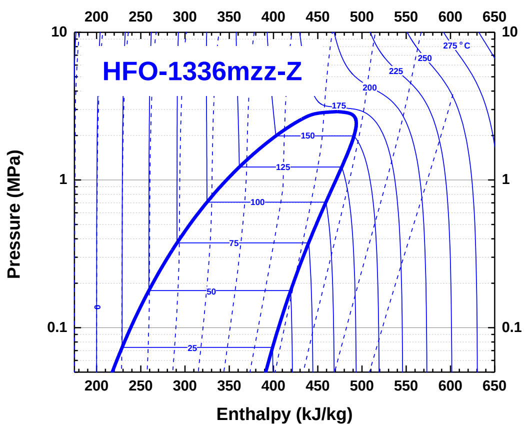

Figure 2: HFO-1336mzz-Z pressure-enthalpy diagram.

The remarkable chemical stability of HFO-1336mzz-Z, despite its unsaturated chemical nature, was first reported in a patent application by Kontomaris [20]. Subsequent evaluations of the stability of HFO-1336mzz-Z to various chemical transformations (e.g. thermal decomposition, dehydrofluorination, polymerization, oxidation, hydrolysis, structural isomerization and stereo-isomerization) and comparisons to the stability of other working fluids under consideration for ORCs was recently reviewed by Kontomaris [1].

The objectives of this paper are to: a) report measured interactions of HFO-1336mzz-Z with a representative selection of plastics and elastomers commonly found in ORC and other equipment; and b) evaluate the performance of HFO-1336mzz-Z in ORCs of a basic configuration (without a recuperator) driven by heat available at temperatures higher than the critical temperature of HFO-1336mzz-Z.

HFO-1336mzz-Z COMPATIBILITY WITH PLASTICS AND ELASTOMERS

Compatibility of HFO-1336mzz-Z with plastic and elastomeric materials of relevance to equipment construction was assessed through the familiar sealed glass tube methodology [21]. Material samples were immersed in glass tubes containing HFO-1336mzz-Z blended (in equal volumes) with a Polyolester (POE) ISO68 lubricant and were aged in an oven at 100 °C for two weeks. The specimen weight and hardness changes after aging are reported in Tables 2 and 3. They could be considered indicative of the degree to which additional material properties of interest, such as permeability or mechanical strength, would be expected to change as a result of exposure to HFO-1336mzz-Z.

The changes were, generally, small indicating only mild interactions between HFO-1336mzz-Z and the plastics and elastomers tested. The performance of plastics and elastomers could be affected by variations in molecular structure, compounding agents, fillers and forming processes. Therefore, it would be prudent before final material selection, to carry out compatibility testing with parts fabricated for actual use in equipment construction under test conditions representative of the intended end use.

ORC EFFICIENCY MAXIMIZATION

a) T_{exp_in}=225 °C

When heat is available at temperatures higher than the critical temperature of a working fluid, trasncritical operation of an ORC becomes feasible, provided that the working fluid remains chemically stable. It is assumed that a heat source is available to maintain the expander inlet at 225 °C. The high-side pressure, P_{high}, is varied to maximize the cycle net thermal energy efficiency, defined as the ratio of the net power produced over the power consumed by the pump as a percent of the heat input to the cycle. The following cycle parameters are kept constant:

Table 2: Weight changes of polymeric specimens after exposure to HFO-1336mzz-Z/POE ISO68 lubricant blends at 100 ^oC for 14 days

Material	Immediately after Aging %	24 Hours after Aging %
Neoprene	-0.55	-0.98
EPDM	2.39	0.84
Polyester Resin	10.04	4.94
Nylon Resin	-0.74	-0.79
Epoxy	0.66	0.56
Polyester PET	3.73	3.54
Polyester PBT	1.15	1.13
Polycarbonate	0.74	0.75
Polyimide	0.79	0.79
Teflon PTFE	3.05	2.72
Teflon FEP	3.29	3.09
Tefzel ETFE	6.25	5.61
Phenolic	-0.18	-0.31
PVC	0.68	0.70
PEEK	-0.06	0.01

Table 3: Hardness changes of polymeric specimens after exposure to HFO-1336mzz-Z/POE ISO68 lubricant blends at 100 ^oC for 14 days

Material	Immediately after Aging %	24 Hours after Aging %
Neoprene	7.10	2.58
EPDM	2.56	0.64
Polyester Resin	-1.01	-0.51
Nylon Resin	-1.00	-2.00
Epoxy	-1.01	-3.54
Polyester PET	0.00	0.00
Polyester PBT	-1.00	-1.00
Polycarbonate	-1.00	0.00
Polyimide	0.00	0.00
Teflon PTFE	-0.50	0.00
Teflon FEP	0.00	-0.51
Tefzel ETFE	0.00	0.00
Phenolic	0.00	0.00
PVC	0.00	0.00
PEEK	0.00	0.00

Condenser temperature: T_{cond}=75 ^oC. The condenser temperature of an ORC can be, relatively, low (e.g. 10-20 ^oC) when power maximization is the primary objective and a cold heat sink is available (e.g. river water). It can be, relatively, high (e.g. up to 90-100 ^oC) when maximization of combined heat and power is the primary objective (e.g. heat rejected from the ORC must supply a district heating network) or when heat rejection capability is limited (e.g. rejecting heat through the radiator of a truck to hot summer air).

Liquid sub-cooling at the condenser exit: ΔT_{subc}=5 K. A small degree of sub-cooling is specified to allow for protection of the liquid pump from cavitation.

Expander efficiency: η_{EXP}=0.75; Pump Efficiency: η_{PUMP}=0.50. Conservative values are specified for the expander and pump efficiencies. Assuming constant expander and pump efficiencies, regardless of operating conditions, is an oversimplification; it suffices for the purpose of demonstrating the thermodynamic properties of HFO-1336mzz-Z.

As the high-side pressure of an ORC with HFO-1336mzz-Z is increased above the HFO-1336mzz-Z critical pressure, for a given expander inlet temperature, the possibility of wet expansion (through or into the two-phase dome) emerges (Figure 2). When the expander inlet is kept at 225 ^oC, wet expansion becomes a risk only at high-side pressures approaching 10 MPa, probably impractical in most cases. Therefore, the maximum practical P_{high} value would be limited by availability and cost of equipment components, not wet expansion. Wet expansion would be, generally, undesirable (although some degree of misting may be acceptable for some expanders).

Figure 3 shows the power generated by the expander and the net power from the cycle (per kg of circulating HFO-1336mzz-Z fluid) as functions of the high-side pressure. As P_{high} increases from low values, the power generated by the expander increases faster than the power consumed by the pump. As a result, the net power generated increases. However, at higher P_{high} values, the power generated by the expander reaches a plateau while the power consumed by the pump continues to increase linearly and the cycle net power generation exhibits a peak. The maximum in the cycle net power per kg lies in the transcritical range of operation (P_{high}=3-4 MPa).

The cycle net thermal efficiency with HFO-1336mzz-Z, shown in Figure 4, reflects the maximum in the cycle net power, shown in Figure 3. Cycle net thermal efficiency becomes maximum at P_{high}=4-5

MPa. (The P_{high} value for maximum net thermal efficiency is somewhat higher than the value for maximum net power because heat input to the cycle continues to decrease with increasing P_{high} beyond the peak in net power.) The maximum cycle efficiency feasible in transcritical operation is 10-15% higher than subcritical cycle efficiencies. The absolute pressure (P_{high}=4-5 MPa) and pressure ratio (PR=10.7-13.3) in the vicinity of the maximum cycle efficiency remain at reasonable levels, feasible, possibly, with single-stage expanders (e.g. piston expanders).

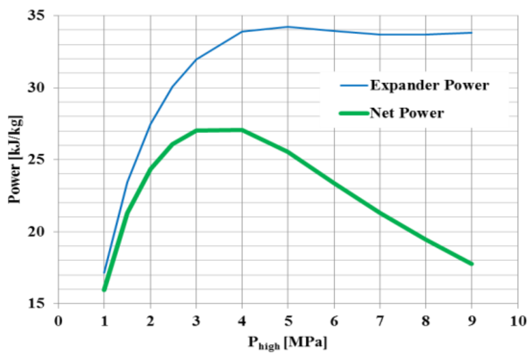

Figure 3: Expander and net power per kg from ORCs with HFO-1336mzz-Z as the working fluid (no recuperator; T_{exp_in}=225 ^oC; T_{cond}=75 ^oC; ΔT_{subc}=5 K; η_{EXP}=0.75; η_{PUMP}=0.50).

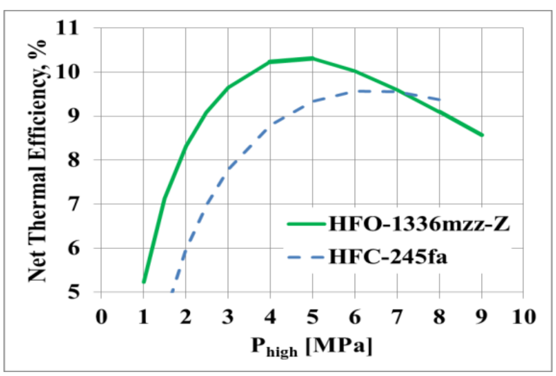

Figure 4: Net thermal efficiency (in %) of ORCs with HFO-1336mzz-Z as the working fluid compared to HFC-245fa (no recuperator; T_{exp_in}=225 ^oC; T_{cond}=75 ^oC; ΔT_{subc}=5 K; η_{EXP}=0.75; η_{PUMP}=0.50).

Figure 4 also compares the cycle net thermal efficiency with HFO-1336mzz-Z to that with HFC-245fa under the same conditions. The maximum feasible cycle efficiency with HFO-1336mz-Z (at P_{high} =4-5 MPa) is 16.5% higher than with HFC-245fa at the same pressure and 7.74% higher than the maximum efficiency feasible with HFC-245fa (at a significantly higher P_{high}=6.5 MPa). The cost of ORC equipment components increases when pressures exceed about 4 MPa.

b) T_{exp_in}=175-250 ^oC

For broader perspective, Figure 5 shows the variation of the net thermal energy efficiencies of representative transcritical Rankine cycles with HFO-1336mzz-Z over a range of supercritical temperatures at the expander inlet: T_{exp_in}=175-250 ^oC>T_{cr}=171.3 ^oC. Figure 5 is focused on supercritical high-side pressures only: P_{high}>P_{cr}=2.9 MPa. (Notice that the assumed degree of subcooling and expander and pump efficiency values in Figure 5 are somewhat different than those in Figures 3 and 4.) The cycles at various P_{high} values for T_{exp_in}=175 ^oC involve expansion into the two-phase zone. Cycle net efficiencies for T_{exp_in}=200, 225 and 250 ^oC exhibit increasing maxima at increasingly higher high-side pressures.

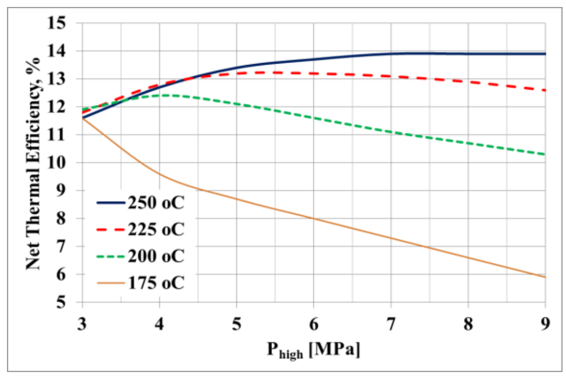

Figure 5: Net thermal efficiency (in %) of transcritical Rankine cycles with HFO-1336mzz-Z as the working fluid (no recuperator; T_{exp_in}=175-250 ^oC; T_{cond}=75 ^oC; ΔT_{subc}=0 K; η_{EXP}=0.85; η_{PUMP}=0.65).

SUMMARY-CONCLUSIONS

Data are reported in this paper on the compatibility of HFO-1336mzz-Z with plastics and elastomers. They indicate mostly mild interactions and reinforce the theme of a relatively low HFO-1336mzz-Z reactivity.

Higher temperatures at the inlet of the expander of an ORC, generally, enable higher cycle thermal energy efficiencies. HFO-1336mzz-Z remains chemically stable at temperatures at least up to about 250 ^oC, i.e. at temperatures higher than its critical temperature of 171.3 ^oC. This paper computes the performance of Rankine cycles (without recuperators) with HFO-1336mzz-Z as the working fluid for expander inlet temperatures in the supercritical range of 175-250 ^{o}C. It provides guidance for the optimum utilization of heat available at temperatures that can fully exploit the high thermal stability of HFO-1336mzz-Z (e.g. waste heat from stationary or mobile internal combustion engines). Maximum energy efficiency of Rankine power cycles operated with HFO-1336mzz-Z at a temperature of 225 ^{o}C at the expander inlet is predicted for a high-side pressure of about 4 MPa, easy to confine with common equipment. The predicted maximum efficiency with HFO-1336mzz-Z is 16.5% higher than the efficiency under the same conditions with HFC-245fa. At the same time the GWP of HFO-1336mzz-Z is 99.8% lower than that of HFC-245fa.

Use of a recuperator to desuperheat expanded vapor before entering the condenser and pass the heat to preheat liquid on its way to further heat extraction from the source could increase the thermal efficiency of ORCs with HFO-1336mzz-Z. However, it could reduce the amount of heat extracted from the source and add first cost. A recuperator was not considered in this paper.

The advantages of a transcritical Rankine cycle with a temperature profile of the heated working fluid closely matching that of the declining temperature of the heat source have been discussed in the literature [22]. Transcritical ORC operation with HFO-1336mzz-Z could allow a larger fraction of the heat available in a non-isothermal heat source to be extracted and a larger fraction of the extracted heat to be converted into power, leading to a higher power generation rate relative to subcritical operation.

The analysis in this paper suggests that a transcritical ORC with HFO-1336mzz-Z as the working fluid may be suitable for the utilization of heat at temperatures that enable expander inlet temperatures in the range of about 200-250 ^{o}C. However, the high-side pressure level and the nature of heat transfer under transcritical conditions are substantially different than under subcritical cycle operation. They have implications on equipment costs that must be considered before a definitive preference in favor of transcritical operation.

HFO-1336mzz-Z is currently under laboratory and field testing for various targeted applications. It is on a path to full-scale commercial production in the second half of 2016.

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NOMENCLATURE

ALT:	Atmospheric Life Time
GWP:	Global Warming Potential (one hundred year integrated time horizon)
HFO:	Hydro-Fluoro-Olefin
ODP:	Ozone Depletion Potential
OEL:	Occupational Exposure Limit
ORC:	Organic Rankine Cycle
P_{cr}:	Critical pressure
P_{high}:	High-side cycle pressure
T_b:	Boiling point at 1 atm
T_{cond}:	Condenser temperature
T_{cr}:	Critical temperature
T_{exp_in}:	Temperature at the expander inlet
T_{fr}:	Freezing temperature
ΔT_{subc}:	Liquid sub-cooling at the condenser exit
η_{EXP}:	Expander efficiency
η_{PUMP}:	Pump Efficiency

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