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Konstantinos Kontomaris
*Chemours Fluorochemicals, Wilmington, Delaware, United States of America*, konstantinos.kontomaris@chemours.com

Luke D. Simoni
*Chemours Fluorochemicals, Wilmington, Delaware, United States of America*, luke.d.simoni@chemours.com

Mattias Nilsson
*Viking Heat Engines, Kristiansand, Norway*, mattias.nilsson@vikingheatengines.com

Tim Hamacher
*Viking Heat Engines, Remscheid, Germany*, tim.hamacher@vheg.de

Harald Nes Rislå
*Viking Development Group, Kristiansand, N*, hnr@vdg.no

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# Combined Heat and Power From Low Temperature Heat: HFO-1336mzz(Z) as a Working Fluid for Organic Rankine Cycles

Konstantinos (Kostas) Kontomaris[1*], Luke D. Simoni[2], Mattias Nilsson[3], Tim Hamacher[4], Harald Nes Rislå[5]

[1]Chemours Fluorochemicals, Wilmington, Delaware, USA
konstantinos.kontomaris@chemours.com

[2]Chemours Fluorochemicals, Wilmington, Delaware, USA
Luke.D.Simoni@chemours.com

[3]Viking Heat Engines, Kristiansand, Norway
mattias.nilsson@vikingheatengines.com

[4]Viking Heat Engines, Remscheid, Germany
tim.hamacher@vheg.de

[5]Viking Development Group, Kristiansand, Norway
hnr@vdg.no


* Corresponding Author

## ABSTRACT

HFO-1336mzz(Z) is evaluated as a working fluid for combined heat and power generation from low temperature natural or waste heat with reduced environmental impact. HFO-1336mzz(Z) safety, health, environmental, chemical and thermodynamic properties are reviewed and new data on the miscibility and viscosity of mixtures of HFO-1336mzz(Z) with ISO 220 and 320 polyol ester lubricants are reported. HFO-1336mzz(Z) Organic Rankine Cycle (ORC) performance was measured in an un-optimized prototype system at an expander inlet temperature of 196 °C and at condensing temperatures of 60 °C and 80 °C. Measured net thermal efficiency and net mechanical power capacity exceeded 10% and 10 kW$_{mech}$, respectively.

## 1. INTRODUCTION

Demand for heating and power continues grow as populations and living standards increase around the world. Increasing awareness of the environmental impacts associated with the extraction and combustion of fossil fuels, including urban air quality and climate change, and continued uncertainty in fossil fuel supplies and prices are motivating a renewed interest in the utilization of abundantly available low temperature heat. Waste heat (e.g. from industrial or commercial processes or from mobile or stationary internal combustion engines) or natural heat (e.g. geothermal or solar heat) are often available at temperatures in the range of 100 °C to 250 °C. Conversion of heat to mechanical (or electrical) power through Organic Rankine Cycles (ORCs) is one promising approach to low temperature heat utilization. It requires the use of working fluids that meet a demanding set of specifications.

HFO-1336mzz(Z) (cis-CF$_3$CH=CHCF$_3$; 1,1,1,4,4,4-hexafluoro-2-butene; CAS No. 692-49-9) was first developed as a low global warming potential (GWP) blowing agent for the expansion of thermosetting foam (e.g. Loh et al., 2015). It was later considered as a refrigerant for the replacement of HCFC-123 in low pressure centrifugal chillers (Kontomaris, 2010) and as a component (blended with trans-1,2-dichloro-ethyelene) of refrigerant R-514A (ASHRAE registration pending). HFO-1336mzz(Z) exhibited remarkable chemical stability at high temperatures that was first reported by Kontomaris (2011) and later more thoroughly documented by Kontomaris (2014b). It was then evaluated as a working fluid for high temperature heat pumps (e.g. Kontomaris, 2012, 2013 and 2014a;

Helminger et al. 2016) and ORCs (Kontomaris 2012, 2014b, 2014c, 2015; Molés et al. 2014; Molés et al. 2015). HFO-1336mzz(Z) is currently on a path to commercialization in 2017.

The emerging availability of HFO-1336mzz(Z), with a GWP sufficiently low so as to virtually eliminate business risk from increasingly restrictive climate protection regulations around the globe and with performance sufficiently high so as to reduce payback time for selected applications to attractive levels, is now motivating substantial ORC research and development investments. This paper examines the potential of an emerging ORC technology using HFO-1336mzz(Z) as the working fluid to provide heat and power from low temperature heat with reduced environmental impact. It reviews key HFO-1336mzz(Z) properties, reports newly measured properties and ORC system performance and identifies knowledge gaps for future work.

## 2. HFO-1336mzz(Z) PROPERTIES

### 2.1 Safety, Health and Environmental Properties

The basic safety, health and environmental properties of HFO-1336mzz(Z) are compared to those of a familiar reference fluid that has been extensively used in ORC applications, namely HFC-245fa, in Table 1. HFO-1336mzz(Z) is non-flammable at both 60 ºC and 100 ºC according to ASTM E681-2004. It has recently received a safety classification of A1 (lower toxicity; no flammability) according to ASHRAE Standard 34 with an Occupational Exposure Limit (OEL) of 500 ppm. HFO-1336mzz(Z) contains no chlorine, bromine or iodine and, therefore, has a zero Ozone Depletion Potential (ODP). The HFO-1336mzz(Z) atmospheric lifetime of 22 days and GWP with a hundred-year integrated time horizon of 2 compare favorably to those of HFC-245fa.

**Table 1:** Basic HFO-1336mzz(Z) safety, health and environmental properties compared to HFC-245fa

| | **HFC-245fa** | **HFO-1336mzz-Z** |
|---|---|---|
| | $CHF_2CH_2CF_3$ | $CF_3CH=CHCF_3(Z)$ |
| IUPAC name | 1,1,1,3,3-pentafluoro-propane | (Z)-1,1,1,4,4,4-hexafluoro-2-butene |
| Mol. w. (kg/kmol) | 134.05 | 164.056 |
| Flammability | Non-flammable[1] | Non-flammable[2] |
| Occupational Exposure Limit (ppmv) | 300[1] | 500[3] |
| Safety Class[3] | B1[1] | A1[3] |
| Atmospheric Lifetime (yr) | 7.7[4] | 0.060274 (22 days)[4] |
| Ozone Depletion Potential | None | None |
| Global Warming Potential (100 year Integrated Time Horizon) | 858[4] | 2[4] |

(1) Calm and Hourahan (2007); (2) At 60 ºC and 100 ºC according to ASTM E681-2004; (3) According to ASHRAE Standard 34; (4) Myhre et al. (2013)

Hydrocarbons, such as pentanes, are often used as working fluids in ORC systems. They are considered volatile organic compounds (VOCs) and are subject to regulation because they contribute to the formation of ground-level ozone, which is the primary contributor to urban "smog". HFO-1336mzz(Z) has a Maximum Incremental Reactivity (MIR) of only 0.04 $gO_3/g$ (Carter, 2011) or only 14% of that of ethane. HFO-1336mzz(Z) has a photochemical ozone creation potential (POCP), a measure of atmospheric reactivity to ground-level ozone favored in the European Union, of only 3.4 (Baasandorj, et al., 2011) or only 27.6 % of that of ethane (Federal Register, 2008). Therefore, despite its very short atmospheric lifetime, HFO-1336mzz(Z) is expected to be exempt from VOC regulations.

### 2.2 Thermodynamic Properties

Availability of accurate thermodynamic properties is key in the selection of a new working fluid and subsequent application development. Accurate thermodynamic properties in the vicinity of the working fluid critical point are particularly important for the ORC applications of interest in this paper.

HFO-1336mzz(Z) thermodynamic properties for early ideal cycle performance evaluations were estimated from limited measurements of liquid density, vapor pressure and critical temperature and pressure. They were derived through either cubic equations of state (EOS) or – for increased accuracy near the critical point – through an EOS based on an expression for the Helmholtz free energy with a number of terms limited by the available data.

Thermodynamic properties for equipment design must meet a higher standard of accuracy that requires measurements over a wide range of conditions including the region near (above and below) the critical point. Extensive HFO-1336mzz(Z) pressure-temperature-density measurements have recently been reported by Tanaka et al. (2016a) and Tanaka et al. (2016b). They covered a temperature range from 49.85°C to 229.85°C and pressures up to 10 MPa and they included measurements in the liquid, vapor, liquid-vapor and super-critical region. The reported temperatures and pressures were accurate within 0.028 K and 4 kPa, respectively. Densities lower than 100 kg·m$^{-3}$ were measured with a 0.6% accuracy and densities higher than 100 kg·m$^{-3}$ were measured with a 0.4% accuracy. Table 2 compares a few basic HFO-1336mzz(Z) thermodynamic properties to those of HFC-245fa. The HFO-1336mzz(Z) atmospheric boiling point, critical temperature and critical pressure reported by Tanaka et al. (2016a and 2016b) are in close agreement with the values reported earlier by Kontomaris (2010; 2014b).

**Table 2:** Basic thermodynamic properties of HFO-1336mzz(Z) compared to HFC-245fa

|  | **HFC-245fa** | **HFO-1336mzz(Z)[2]** |
|---|---|---|
| Normal Boiling Point °C | 15.1[1] | 33.47 |
| Critical Temperature °C | 154[1] | 171.27 |
| Critical Pressure MPa | 3.65[1] | 2.901 |
| Critical Density kg·m$^{-3}$ | 517[3] | 471 |

(1) Calm and Hourahan (2007); (2) Tanaka et al. (2016a and 2016b); (3) Honeywell literature

An equation of state explicit in the Helmholtz free energy was recently developed for HFO-1336mzz(Z) by Akasaka and Lemmon (2016). It was composed of an ideal-gas part and a residual part. In the absence of speed of sound measurements, the ideal-gas part was derived from an ideal-gas isobaric heat capacity expression based on Joback's group contribution method (Joback and Reid, 1987). In view of the limited available pressure-temperature-density data, the residual part was expressed in only polynomial and exponential terms (i.e. no Gaussian terms) that were regressed to represent the measurements by Tanaka et al. (2016a & 2016b) and the normal boiling point by Kontomaris (2014b). The Akasaka-Lemon equation of state represents the available vapor pressure and density data outside the critical region to within 0.2%; it deviates from the measured densities near the critical point by up to 2%.

## 2.3 Chemical Stability and Compatibility with Plastics and Elastomers
The remarkable chemical stability of HFO-1336mzz-Z at high temperatures, despite its unsaturated chemical nature has been documented by Kontomaris (2014b). In summary, HFO-1336mzz-Z is comparably stable to HFC-245fa at temperatures up to 250 °C in the presence of metals commonly used in equipment construction and small levels of air and oxygen that could occasionally infiltrate power generation equipment. HFO-1336mzz(Z) has been found to be compatible with a wide range of plastics and elastomers (Kontomaris, 2014a).

## 2.4 Lubricant Selection
Although oil-free expanders are, in principle, feasible, a suitable lubricant would be required for most practical ORC applications with HFO-1336mzz(Z). A preferred lubricant must balance several, potentially, conflicting requirements. It would, generally, be <u>miscible</u> with HFO-1336mzz(Z), it would form sufficiently <u>viscous</u> blends with HFO-1336mzz(Z) to meet expander specifications and it would remain <u>chemically stable</u> over the intended use conditions. Although other classes of lubricant may be suitable, only polyol ester (POE) type lubricants are considered in this paper. Only HFO-1336mzz(Z)/POE blend miscibility and viscosity are partially addressed in this section.

### 2.4.1 Miscibility

A lubricant selected for the ORC applications in this paper must form, preferably, homogenous mixtures with HFO-1336mzz(Z) at the expected operating conditions. Commercially available POE lubricants of, relatively, low ISO viscosity grades (32 and 68) were tested for miscibility with HFO-1336mzz(Z) in blends containing up to 70 wt% lubricant by Kontomaris (2010). They were found to be miscible at temperatures higher than -15 °C up to the highest temperature tested, namely 85 °C.

Lubricants of ISO grades 170-220 or higher could be needed for ORC applications with HFO-1336mzz(Z) to meet minimum viscosity requirements at temperatures that would typically exceed 100 °C. Blends of a commercially

available ISO 220 POE lubricant with HFO-1336mzz(Z) containing up to 70 wt% lubricant were tested for miscibility. The lowest test temperature was -25 °C, i.e. well below the condenser temperature for most ORC applications. The highest test temperature was 150 °C, i.e. significantly higher than the usual miscibility test temperatures for air conditioning and refrigeration applications. In principle, separation of lubricant/refrigerant blends to lubricant-rich and refrigerant-rich phases is possible at high temperatures such as those expected in the evaporator of an ORC application with HFO-1336mzz(Z).

Sealed glass tubes containing the selected ISO 220 POE lubricant and HFO-1336mzz-Z in various proportions were prepared and immersed sequentially first in a cold and then in a warm agitated constant temperature bath controlled at the targeted temperature levels. The miscibility characteristics of each HFO-1336mzz-Z/lubricant blend were visually observed and recorded, after temperature equilibration, at temperature increments of 5 °C. Blends with a homogeneous, translucent solution appearance were qualified as miscible, "M", at the observation temperature. Blends separating into distinct phases divided by a meniscus or exhibiting turbidity (i.e. cloudiness or haziness) indicative of the formation of individual droplets were designated as non-miscible, "N". Test results, summarized in Table 3, showed that blends of the selected ISO 220 POE with HFO-1336mzz(Z) were miscible throughout the range of conditions tested.

**Table 3:** Miscibility of HFO-1336mzz(Z) with an ISO 220 POE lubricant

Temperature, °C

| refrigerant/oil [wt%] | -25 | -20 | -15 | -10 | -5 | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 | 105 | 110 | 115 | 120 | 125 | 130 | 135 | 140 | 145 | 150 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 95 / 5% | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | (*) | |
| 90 / 10% | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | (*) |
| 85 / 15% | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M |
| 80 / 20 % | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M |
| 70 / 30% | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M |
| 40 / 60% | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M |
| 30 / 70% | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M | M |

(*) These conditions were not tested because the HFO-1336mzz(Z)/POE blend could have expanded to fill the glass test tube.

2.4.2 Working Viscosity

ORC applications can generate large differentials between the high- and low-side system pressures that lead to strong thrust forces and heavily loaded bearings. The lubricant must provide adequate lubricity to protect against frictional wear to and ensure long-term reliability and extended useful life of moving parts. It must also seal passages to minimize leakage of the working fluid from high to low pressure regions. It must form mixtures with HFO-1336mzz(Z) at the points of lubrication sufficiently viscous at the high typical operating temperatures to meet (but not greatly exceed) the minimum required viscosity specified by the expander manufacturer. Blends of a selected lubricant with HFO-1336mzz(Z) must have, for adequate lubrication, kinematic viscosities under working conditions of at least a few to several cSt. Lubricant/HFO-1336mzz(Z) blend viscosity at a given temperature and pressure can be significantly lower than the viscosity of the neat lubricant at the same temperature as a result of HFO-1336mzz(Z) solubility in the selected lubricant.

The Daniel plot (Daniel, 1983) for blends of a commercially available ISO 220 POE lubricant with HFO-1336mzz(Z) is shown in Figure 1. It provides estimated values of the kinematic viscosity and liquid-phase composition of HFO-1336mzz(Z)/lubricant blends over a range of temperatures and pressures. The relationships between temperature, pressure, liquid-phase composition and blend viscosity were determined from saturated pressure and viscosity measurements over a range of temperatures and liquid-phase compositions. It was assumed that the oil was effectively nonvolatile and the vapor phase consisted of pure HFO-1336mzz(Z), the fugacity of which was calculated through a Helmholtz-explicit EOS (Akasaka and Lemmon, 2016). The non-ideality of the liquid phase was described through the NRTL activity coefficient model (Renon and Prausnitz, 1968) with binary interaction parameters regressed to the measured Vapor-Liquid Equilibrium (VLE) data. With the relationship between temperature, pressure and liquid-phase composition determined, the liquid-phase mixture viscosity as a function of temperature and lubricant wt% content was correlated with a two-parameter version of the mixing rules proposed by Yokozeki (1994). Figure 1 was constructed from experimental viscosity and VLE data over the temperature range of 20 to 100 °C that were regressed within 3.9% and 0.28%, respectively. The mixture viscosity values at high temperatures, estimated through distant extrapolation from data at temperatures at or below 100 °C,

are more uncertain than at lower temperatures within the experimental range. <u>Figure 1</u> suggests that the viscosity of blends of HFO-1336mzz(Z) with the selected ISO 220 POE lubricant would be adequate for a wide range of applications except, possibly, those involving the high temperature and pressure region of <u>Figure 1</u>.
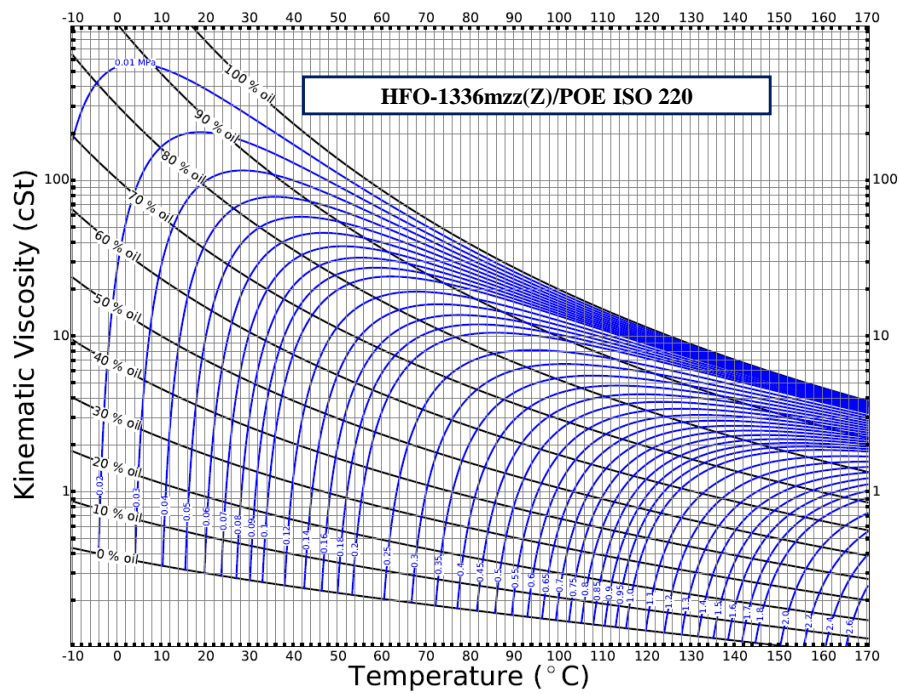


**Figure 1:** Daniel plot for HFO-1336mzz(Z) with an ISO 220 POE lubricant
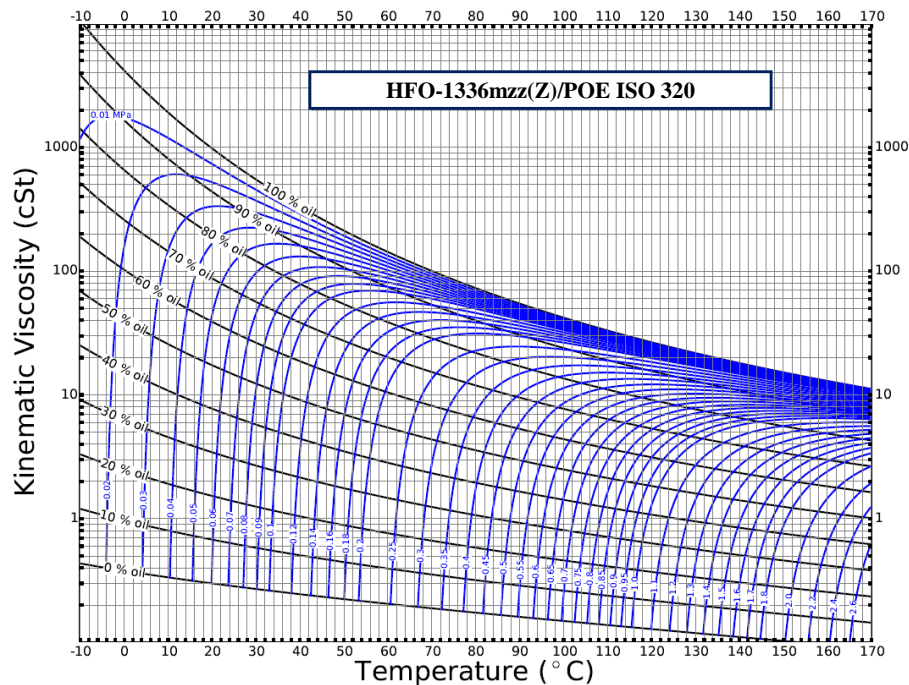


**Figure 2:** Daniel plot for HFO-1336mzz(Z) with an ISO 320 POE lubricant

The liquid-phase equilibrium composition and kinematic viscosity of blends of a commercially available ISO 320 POE lubricant with HFO-1336mzz(Z) are shown in Figure 2.   Figure 2 was constructed from experimental viscosity and VLE data over the temperature range of 20 to 80 °C that were regressed within 0.4% and 0.3%, respectively. Figure 2, shows that higher working viscosities become feasible (particularly at high temperatures and pressures) with the ISO 320 POE lubricant than with the ISO 220 POE lubricant of Figure 1.

## 3. HFO-1336mzz(Z) PERFORMANCE IN A PROTOTYPE ORC SYSTEM

HFO-1336mzz(Z) has been evaluated as an ORC working fluid through computational modeling by Kontomaris (2012, 2014b, 2014c, 2015), Molés et al. (2014), Molés et al. (2015) and Sakaue et al. (2016).  In addition to its attractive safety, health, environmental and chemical properties, HFO-1336mzz(Z) was predicted to enable attractive ORC performance.

A prototype ORC system for distributed power generation from renewable and waste heat sources has been developed by Viking Heat Engines of Norway in collaboration with AVL Schrick of Germany.  It is based on a novel, relatively small reciprocating piston expander capable of generating up to about 12-14 $kW_{mech}$ of mechanical power at a maximum speed of 1,500 rpm.  A new active expander valve train with variable opening timing (including brief opening durations) was developed to realize a wide range of expansion/pressure ratios. As a result, the system operates efficiently over wide ranges of source heat temperatures (from about 90 °C to 200-220 °C), output heat temperatures (from about 20 °C to 90 °C) and part loads (as low as 30% of full load). The system is capable of handling, typically, evaporating pressures from about 2 MPa to 3 MPa and condensing pressures from 0.1 to 0.9 MPa.

The main prototype ORC system components are shown in Figure 3. The evaporator is a plate-type heat exchanger including liquid preheating and vapor superheating sections.  A plate-type recuperator is included to desuperheat the expanded vapor and transfer heat to preheat the liquid working fluid leaving the pump on its way to the evaporator. The recuperator is significantly smaller than the evaporator. The recuperator heat flux and efficiency are increased with higher expanded vapor superheat and lower condensing temperature, which lead to higher heat transfer driving temperature differences in the recuperator. The condenser is, typically, also a plate-type heat exchanger.  However, dry air coolers external to the ORC system are installed when ORC heat is rejected to the ambient. The condenser slightly sub-cools the liquid to protect the pump from cavitation. It discharges into a liquid accumulator which supplies the pump.  The prototype ORC system generator/inverter can provide electrical power (e.g. to the grid) at a fixed frequency even when the expander is operated at a variable speed. Therefore, the variable expander speed can be optimized, in addition to the variable expander inlet valve opening time, to maximize energy efficiency.
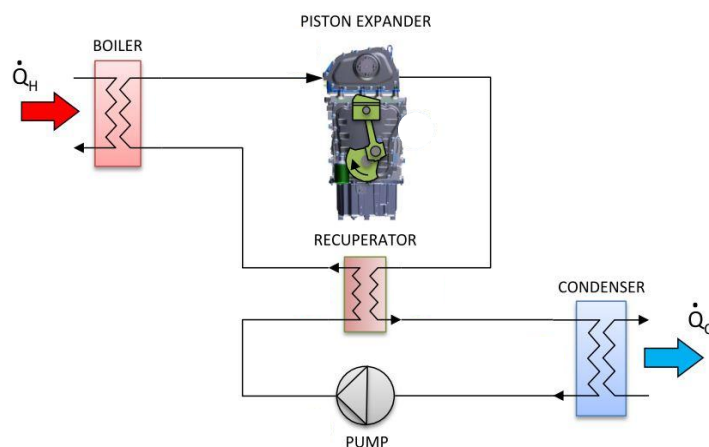


**Figure 3:** Main prototype ORC system components and simplified flow diagram

The performance of the prototype ORC system was tested with HFO-1336mzz(Z) as the working fluid and an ISO 220 POE lubricant over a range of conditions representative of potential small-scale Combined Heat and Power applications (micro-CHP). The prototype had been designed for a working fluid with substantially higher vapor pressure than HFO-1336mzz(Z) and was not optimized or adapted for testing with HFO-1336mzz(Z).

Stable operation was established at an evaporating temperature of $T_{evap}$ = 170 ºC and a vapor superheat at the expander inlet of $\Delta T_{superh\_exp\_in}$ = 26 K, i.e. at an expander inlet temperature of $T_{exp\_in}$ = 196 ºC. A commercially available thermal oil was used to carry heat to the evaporator. System performance was measured at two, relatively, high condensing temperatures at which the heat released could be used to meet some heating duty (e.g. heat a nearby building or supply a local district heating network): 60 ºC and 80 ºC (with corresponding liquid sub-cooling at the condenser of 14 and 11 K, respectively). The work generated by the expander was measured with a high-precision torque flange. System net thermal efficiency and net mechanical power generating capacity were measured at each pair of expander inlet and condensing temperatures, ($T_{exp\_in}$, $T_{cond}$), at three levels of the expander speed, nominally 900, 1,250 and 1,500 rpm. At each expander speed, the expander inlet valve opening duration was varied to vary the fluid volumetric flow rate, so as to observe the resulting efficiency/capacity relationship. It should be noted that the maximum liquid flow rate feasible with the prototype system pump limited performance under some test conditions.

Figure 4 shows system net thermal efficiency and net mechanical power generation capacity combinations that were realized in the above series of tests. Gross mechanical power generation was measured as delivered at the expander shaft. The net mechanical power was calculated by subtracting the power consumed by the pump (about 15% and 17% of gross power at the 60 ºC and 80 ºC condensing temperatures, respectively). It can be used directly, e.g. to drive a compressor, or it can be converted to electrical power through a generator. The net thermal efficiency was defined as the system net power output as a per cent of the rate at which heat was supplied at the evaporator.
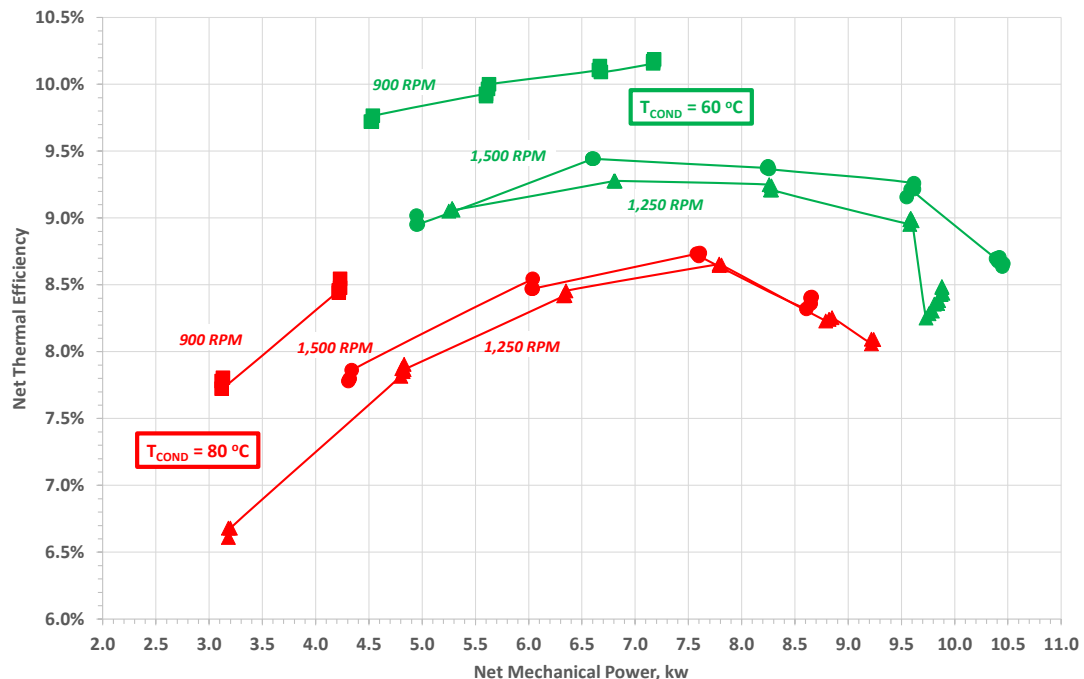


**Figure 4:** Measured performance map for a prototype ORC system with HFO-1336mzz(Z) as the working fluid at $T_{evap}$ = 170 ºC and $\Delta T_{superh\_exp\_in}$ = 26 K, (i.e. $T_{exp\_in}$ = 196 ºC); $\Delta T_{subc}$ = 14 K at $T_{cond}$=60 ºC and $\Delta T_{subc}$ = 11 K at $T_{cond}$=80 ºC

Figure 4 shows that, generally, the larger the difference between the expander inlet temperature and the condensing temperature (i.e. between the heat input and output temperatures) the higher the system thermal efficiency. For a given pair of expander inlet and condensing temperatures, higher thermal efficiency (over a limited power capacity

range) was achieved at the lowest expander speed of 900 rpm. Higher working fluid flow rates and, therefore, higher capacities were achieved with higher expander speeds. At a given expander speed, higher flow rates and higher capacities were realized with longer admission valve opening durations. Maximum thermal efficiency was achieved at intermediate values of valve opening durations. The highest capacities, at the longest valve opening durations tested, were realized with suboptimal efficiencies.

# 4. SUMMARY-DISCUSSION

Climate protection, improved air quality and energy security are motivating the utilization of low temperature (natural or waste) heat to increase energy efficiency and reduce dependence on fossil fuels. HFO-133mzz(Z) was evaluated as a working fluid for combined heat and power generation through organic Rankine cycles driven by heat at temperatures of about 200 ºC. HFO-1336mzz(Z) has been recently classified as an A1 (lower toxicity; no flammability) refrigerant according to ASHRAE standard 34 and it has a GWP of only 2. It has demonstrated in past studies (Kontomaris, 2014b) chemical stability comparable to that of HFC-245fa, a working fluid that has been used extensively in ORC applications. 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 2017.

A fundamental <u>equation of state</u> for HFO-1336mzz(Z) based on the Helmholtz free energy has been developed by Akasaka and Lemmon (2016) based on extensive measurements by Tanaka et. al (2016a and 2016b). It would allow a more accurate estimation of HFO-1336mzz(Z) thermodynamic properties (including at conditions near the critical point) required for power generation equipment design. It could, possibly, be further improved through more extensive measurements, including vapor and/or liquid speed of sound.

A commercially available POE <u>lubricant</u> with an ISO viscosity grade of 220 was evaluated for use with HFO-1336mzz(Z) in ORC applications. The ISO 220 POE lubricant was found to be miscible with HFO-1336mzz(Z) over a wide range of conditions. It is projected to maintain a kinematic viscosity of about 4 cSt at 170 ºC and to form mixtures with HFO-1336mzz(Z) of adequate working viscosities for a wide range of conditions. It was used in ORC system tests at evaporator temperatures up to 170 ºC and expander inlet temperatures up to 215 ºC without any observed issues. For applications that may require higher working viscosity values than those feasible with the ISO 220 POE, a commercially available ISO 320 POE lubricant was evaluated. The ISO 320 POE lubricant is projected to maintain a viscosity of over 10 cSt at 170 ºC.

The <u>chemical stability</u> at high temperatures of a POE lubricant and of its 50/50 wt% mixture with HFO-1336mzz(Z) was examined by Kontomaris et al. (2013). It was evaluated according to the sealed glass tube testing procedure of ASHRAE 97 in the presence of metals and small levels of air and moisture, representative of air infiltration into power generation and other equipment. The neat lubricant and its mixture with HFO-1336mzz(Z) were found to generate Total Acid Number (TAN) values of 1.6 and 2.3 mg KOH/g oil, respectively, under continuous exposure to 250 ºC for seven days. The measured TAN values indicate a non-negligible degree of lubricant degradation. However, the test temperature and continuous exposure conditions were more severe than the actual intermittent exposure to lower temperatures that would be encountered in many ORC applications. Further work is required to establish whether the chemical stability of currently available POE lubricants would be adequate or stabilization additives, periodic lubricant replacement or other lubricant types must be considered.

HFO-1336mzz(Z) <u>Organic Rankine Cycle (ORC) performance</u> was measured in an un-optimized prototype system designed for working fluids with vapor pressures significantly higher than HFO-1336mzz(Z). The prototype expander operated stably with HFO-1336mzz(Z). The evaporator operated with a sufficiently uniform distribution of the entering and evaporating HFO-1336mzz(Z), as indicated by infrared thermography, to make effective use of the available heat exchange surface area. The power output in some tests with HFO-1336mzz(Z) was limited by the pump capacity; a larger pump will be considered in future tests. The liquid sub-cooling could be reduced without undue pump cavitation risk to further increase thermal efficiency (by about 0.4%). Measured net thermal efficiency and net mechanical power capacity exceeded 10% and 10 $kW_{mech}$, respectively.

The performance map of <u>Figure 4</u> can be used to evaluate the potential of the prototype ORC system with HFO-1336mzz(Z) in prospective applications, including small-scale <u>Combined Heat and Power</u>. In view of the efficiency/capacity trade-off observed at high capacities, optimum system operation would be determined by the relative value of the output power and heat (and the cost of the input heat, if any). Higher power generation would,

probably, outweigh higher efficiency in most applications, especially when the source heat is provided free of charge.

The prototype ORC system that was tested in this paper has been designed for minimal mechanical and flow frictional losses. As a result, it achieves high isentropic efficiency despite its relatively small size which, generally, magnifies the proportion of frictional losses relative to useful power output. However, relatively higher flow rates required with HFO-1336mzz(Z) for a given power generating capacity lead to (quadratically) higher frictional flow losses. Experience with other working fluids has shown that, with system optimization, efficiency can be significantly improved. Further optimization of the ORC system for HFO-1336mzz(Z) would focus on further minimization of frictional flow losses in restricted vapor flow passages (e.g. expander valves, small-diameter piping sections, pipe steep diameter and flow direction changes, heat exchanger flow restrictions).

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