



Chemical stability of low-GWP refrigerants with polyol ester (POE) lubricants for high temperature heat pumps

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Abstract

High-temperature heat pumps (HTHPs) can play a significant role in reducing the internal waste heat and replace fossil fuel and electrically driven boilers in different industrial heat treatment and drying processes. The choice of low Global Warming Potential (GWP), zero Ozone Depletion Potential (ODP) and low trifluoroacetic acid yield (TFA) refrigerant for high temperature applications is of highest importance. Only chemically stable refrigerants can ensure long lifetime, safety and steady operation. The novelty of this work is the comparison of lab-controlled chemical stability tests of hydrochlorofluoroolefins (HCFOs) and hydrofluoroolefins (HFOs) alternatives in stainless steel gas reactors using latest ASHRAE guideline 38-2023 at high temperatures up to 150 °C and high pressures up to 31 bar for 21 days in combination with moisture and polyolester (POE) lubricants as well as in a pilot-scale HTHP installation, against the refrigerant samples from real industrial installations. The refrigerant decomposition products were analysed using Thermo Scientific Trace 1310 Gas Chromatograph with a thermal conductivity detector (TCD) and flame-ionization detector (FID) and compared with AHRI 700-2024 results. The results showed that both HCFO and HFO refrigerants undergo different polymerization processes in the presence of POE lubricants; water; or a mixture of POE lubricants and water. In contrast, the control refrigerant samples (with no water or oil contact) showed very little reactivity after 21-day tests but highly elevated water levels. Highly elevated water levels were found even in samples from real installations confirming that water is one of the degradation by-products. This study demonstrates that both HFO and HCFO refrigerants can be highly sensitive to POE lubricant composition, particularly to a high fraction of branched dipenta-esters, which are commonly selected for high-temperature applications. Key future work includes further Fourier Transform Infrared (FTIR) spectroscopy analysis of obtained polymers and degraded POE lubricants.

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1. Introduction

The European Commission has emphasized the urgent need to decarbonize energy-intensive industries, stabilize the EU energy market against excessive price increases, and achieve independence from fossil fuels by 2030 [1]. Moreover, improving energy efficiency across sectors and reducing overall energy usage are essential to protect the environment and reduce dependence on external oil and gas suppliers [2]. Heating accounts for over 60% of total energy use in the industrial sectors [3] and high-temperature heat pumps (HTHPs) could supply around 29 TWh of heat below 200°C while reducing the CO₂ emissions in EU industries by up to 67% [4]. About 37% of current industrial process heat demand is below 200 °C [5]. Industrial heat pumps offer high integration flexibility and can utilize various heat sources, whereas currently they are primarily deployed in low-temperature processes below 80 °C in sectors such as pulp and paper, food, and chemicals [3, 6]. Therefore, there is substantial potential for further development, particularly in improving

first-generation HTHP prototypes that can supply steam or hot air at temperatures up to 180 °C [5]. HTHPs up to these temperatures operate on the same fundamental principles as conventional heat pumps but may require modified components. Due to their strong potential for waste heat recovery, industrial HTHPs are expected to meet significant thermal demands in the temperature range between 100 and 200 °C across the European Union [7]. The design of HTHPs is highly dependent on the choice of refrigerant and the thermodynamic cycle configuration. To comply with recent and expected future legislation, suitable refrigerants for HTHPs must exhibit zero ozone depletion potential (ODP) and very low global warming potential (GWP). They should also have high critical temperatures, and favourable thermodynamic properties [8-10]. A key concern with hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) proposed for HTHP applications is their potential contribution to environmental pollution with persistent per- and polyfluoroalkyl substances (PFAS) [11]. Many synthetic HFO and HCFO refrigerants decompose in the atmosphere to trifluoroacetic acid (TFA), which contaminates drinking water and may have negative effects on the environment. PFAS, including TFA, have been linked to harmful health effects when consumed in significant quantities [12] and TFA yield during decomposition must be considered when selecting a high-temperature refrigerant.

The introduction of high-temperature refrigerants brings to the attention compressor lubricant compatibility and refrigerant chemical solubility aspects. Historically, compressor failures due to inadequate lubrication have been observed during the transition from CFCs) and hydrochlorofluorocarbons (HCFCs) to hydrofluorocarbons (HFCs) and even to propane-based systems. These issues were eventually mitigated through appropriate lubricant selection, crankcase heating strategies, and proper superheat control. Lubricants for HTHP applications must exhibit specific properties, including high thermal stability, appropriate volatility, chemical compatibility with system materials, sufficient lubricity, long-term stability throughout the compressor life, and environmental biodegradability [13]. Currently, mineral oils and semi-synthetic lubricants are generally not considered suitable for synthetic refrigerants. Instead, synthetic lubricants such as polyol esters (POEs), polyalkylene glycols (PAGs), and polyvinyl ethers (PVEs) are increasingly used in the refrigeration and heat pump industry (especially in Europe), as safer alternatives to mineral oils. POEs and PAGs are commonly applied not only with HFOs and HCFOs, but also with carbon dioxide, hydrocarbons, and HFCs [14].

The superiority of POE lubricants compared to mineral oils has been recognized since the late 1960s. During this time, the HVAC industry began focusing on ester-based lubricants derived from pentaerythritol (PE) and trimethylolpropane (TMP), which could be tailored to provide properties such as anti-oxidation (AO), anti-wear (AW), and anti-seize (AS). Early selection of POEs was influenced by the behaviour of CFC and HCFC refrigerants used with mineral oils. The miscibility, thermal stability, and fluid properties of the refrigerant-lubricant pair were primarily affected by alcohol and carboxylic acid composition. Alkyl branching of the carboxylic acid component improved miscibility, while linear acids tend to reduce it. Studies on HFC refrigerants indicated that linear acid esters perform better than branched or mixed esters in terms of miscibility. In hermetic systems, where good oil return is essential, tailoring the carboxylic acid structure in POEs enables an optimized balance between lubricant and refrigerant miscibility [15]. Commercial POE lubricants are typically composed of pentaerythritol esters (PECs), which can be categorized as linear, branched, or cyclic. Among them, linear PECs are often used as model compounds in lubricant-refrigerant interaction studies [16]. POE lubricants, being polar, can exhibit widely varying properties despite having the same viscosity index as mineral oils. Higher molecular weight POEs provide improved lubricity and, as their carbon content increases, their properties begin to be similar to non-polar mineral oils [15]. The thermal stability and water absorption characteristics of different lubricant are of high importance. Water can accelerate lubricant degradation, lead to acid formation and precipitation, and viscosity reduction. For these reasons, water content above 50 ppm should be strictly avoided [16]. Polar lubricants such as PAGs exhibit the highest water absorption among synthetic oils, whereas mineral oils, due to their non-polar nature, have the lowest water absorption capacity. Additionally, the viscosity index of POE lubricants plays a critical role in their water absorption behaviour and POE options with low viscosity index tend to have higher water absorptivity [17]. It is recommended that the water content in POE lubricants be kept very low, whereas fresh or unused POE lubricants should not exceed 100 ppm of water. Levels above 200 ppm can significantly damage system and lubricant performance [18]. According to Air-Conditioning, Heating, and Refrigeration Institute (AHRI) Standard 700-2024, the maximum allowable water content in both HFO and HCFO refrigerants is 20 ppm. This standard outlines the purity requirements and test methods for all refrigerants regardless of origin (new, reclaimed, or repackaged) for use in refrigeration and air conditioning systems [19].

There are several studies related to chemical stability of HFO and HCFO refrigerants using only older ANSI/ASHRAE standard 97-2007 “sealed glass tube” test method [20] but no updated ASHRAE Guideline 38-2023 (Guideline for Using Metal Pressure Vessels to Test Materials Used in Refrigeration Systems) [21].

There are ten different identified chemical degradation mechanisms of refrigerants such as: molecular rearrangement, polymerization (oligomerization), hydrodehalogenation, hydrogenation, elimination, oxidation, nucleophilic substitution, electrophilic addition, disproportionation, and pyrolysis [22]. As reported therein, the reaction rates for stereoisomer rearrangement (Z to E isomerization) for both HFOs and HCFOs were very low. However, it was underlined that R1336mzz(Z) and R1224yd(Z) may be more susceptible to isomerization due to their lower stability. [23] reported that R1233zd(E) with and without mineral oil is approximately 10 times more stable than R123 and 100 times more stable than R11 and the main degradation product was the stereoisomer R1233zd(Z) detected at levels below 1% after 14 days at 200 °C. Similar findings were reported in [22], where different refrigerants: R123, R514A, and R1233zd(E) (at temperature of 127 °C) and R1224yd(Z), R1336mzz(E) and R1336mzz(Z) (at temperature of 175 °C) were tested over 14 days with and without lubricants and different metals. In case of HCFOs (R1233zd(E) and R1224yd(Z)), tests were conducted using only mineral oil (naphthenic white mineral oil), while the other HFO refrigerants were evaluated with various synthetic lubricant alternatives, including PAG, POE, and PVE. In this study, R1233zd(E) decomposition was observed for case with zinc, where the reduction product 3,3,3-trifluoro-1-propyne (TFP) also known as R1243zf was observed. As reported, R1233zd(Z) stereoisomer can more easily form TFP compared to R1233zd(E) [22; 24 and 25]. [22] further suggests that higher than 130 °C operating temperatures can cause some isomerization even in the more stable E-type isomers, which can imply a significant high temperature application limitation. These findings are contradictory with [24; 26 and 27] results. [25] reported that the chemical stability of R1233zd(E) is lower than that of R1336mzz(Z) after aging tests in glass tubes at 175 °C and 200 °C during 14 days in the presence of various metals and a significant degree of stereo-isomerization from R1233zd(E) to R1233zd(Z) was observed. Moreover, [26] studied the chemical stability of R1233zd(E) with white mineral oil and three metal catalysts (cast aluminum, carbon steel, and copper) at 135 °C, 145 °C, and 155 °C for 7 days and confirmed the stability of R1233zd(E) and the primary degradation isomer product R1233zd(Z). [28] reported stereo-isomerization of R1233zd(E) by around 1.6% at 180 °C and 9% at 220 °C after 14 days under accelerated aging conditions. Moreover, the addition of stabilizers significantly reduced the rate of R1233zd(Z) formation at higher temperatures.

The 14-days chemical stability tests of R1224yd(Z) with 1000 ppm water and 1000 ppm air at 175 °C showed high stability. Additionally, it was reported that the presence of different lubricants can further enhance the stability of R1224yd(Z) [27]. Similar findings were reported for R1224yd(Z) with mineral oil [22; 25] except for low levels of TFP and R1243zf detected in presence of zinc. Moreover, it was found that R1224yd(Z) pristine refrigerant had elevated concentrations of R1224yd(E) [22]. The same study recommended using R1233zd(E) and R1224yd(Z) exclusively with mineral oil-based lubricants, rather than synthetic options such as POE, PAG, or PVE. The compatibility tests of R1234yf with POE VI32 lubricant under varying conditions of metal presence, polymer materials, air, and water were conducted [29]. As found, R1234yf exhibited significant degradation in the presence of air and water due to hydrolysis of the POE lubricant into carboxylic acids and alcohols, which then reacted with the refrigerant. Studies showed that HFO refrigerants such as R1234yf and R1234ze(E) in combination with POE lubricants under 14 days at 175 °C exhibit lower chemical reactivity compared to PVE lubricants [30]. Additionally, no TFP was detected in any of the R1234ze(E) and R1234yf exposures were reported by [25]. Instead, the controlled pristine R1224yd(Z) sample formed TFP in the presence of aluminum/iron/copper and zinc catalyst and in the presence of mineral oil with the three-metal catalyst combination. Only one document [31] reported isolated incidents of R1234yf polymerization during charging of mobile air conditioning (AC) systems, where silicone-like deposits caused irreversible system damage and indicated that probable causes included moisture and elevated temperatures during handling, leading to polymerization. To avoid polymerization, avoiding direct sunlight during transport and storage, slowly opening gas cylinders to prevent pressure changes, and avoiding rubber seals that contain peroxides (recommending PTFE materials) were recommended. Thermal stability and decomposition mechanism of R1336mzz(Z) were investigated by [22; 32 and 33]. Studies by [32] were conducted in the presence of RL68H POE lubricant over 24, 48, and 72 hours at 4 MPa and 250-270 °C. At 6.9 MPa, R1336mzz(Z) remained largely undecomposed, and the study concluded that the POE lubricant significantly influenced the thermal stability of refrigerant. Moreover, the study highlighted that temperature is a key factor in refrigerant oxidation and decomposition, where elevated temperatures significantly increase the decomposition rate and the formation of final products. R1336mzz(Z) and R1336mzz(E) were tested only with POE, PAG and PVE synthetic lubricants and thermal stability tests were carried out at 127 °C and 175 °C [28]. This study confirmed the stereoisomerization of the R1336mzz(Z) to the R1336mzz(E). Instead, [33] studied the thermal decomposition of R1336mzz(Z) using a tubular pyrolysis reactor connected to Gas Chromatography (GC) with Mass Spectroscopy (MS) over a temperature range of 100-800 °C. This work revealed the formation of the isomer R1336mzz(E) above temperature of 300 °C, but no R1234ze(E) formation

was detected. Moreover, at higher temperatures, C–H and C–F bonds broke generating $\bullet\text{H}$ and $\bullet\text{F}$ radicals, which triggered radical-induced decomposition.

Summing up, the literature review on the thermal and chemical stability of various HFO and HCFO refrigerants for high-temperature applications show no significant degradation products in HVAC and laboratory experiments nor signs of polymerization. Moreover, several studies have confirmed the high thermal stability of R1224yd(Z), R1336mzz(Z), and R1233zd(E) up to 175 °C. These experimental studies limited to maximum 14 days and older testing standard. However, no studies have examined the chemical stability of refrigerants in combination with different POE lubricants using the updated ASHRAE Guideline 38-2023 (Guideline for Using Metal Pressure Vessels to Test Materials Used in Refrigeration System) [21] Finally, no polymerization studies were conducted to better understand the instability of refrigerant nor the role of POE lubricant chemistry on chemical instability of refrigerant.

Therefore, the aim of this work is to investigate the chemical stability and material compatibility of lowGWP and low-ODP HFOs and HCFOs having different environmental TFA footprint with POE lubricants under high-temperature and high-pressure conditions representative for HTHP applications. The novelty of this work lies in longer test periods (21 day) while abiding to the updated ASHRAE Guideline 38-2023 (Guideline for Using Metal Pressure Vessels to Test Materials Used in Refrigeration Systems) [22], considering POE lubricant chemistry and the comparison of obtained degradation results with samples from real industrial installations.

2. Methodology

The compatibility and chemical stability of refrigerants and lubricants were evaluated using specially designed stainless-steel (SS) gas reactors. These tests followed the updated ASHRAE Guideline 38-2023 (Guideline for Using Metal Pressure Vessels to Test Materials Used in Refrigeration Systems). Each gas reactor consists of a cylindrical SS body, two SS ball valves and a four-screw closing mechanism (at the valve-cylinder connection interface), allowing for large sample volumes of approximately $99.98 \pm 0.1 \text{ cm}^3$. Fig. 1 shows the schematic and the first prototype of the SS gas reactor. Calibration of the gas reactor volume as well as the pressure sensors and performing refrigerant mass calculations were conducted following ASHRAE Standard 97-2007 (RA 2017) [21]. The reactors were designed to withstand pressures up to 68 bar.g (providing a safety margin of more than 30 bar) and temperatures up to 190 °C (a 40 K safety margin) compared to the experimental conditions. Additionally, the reactors used only SS and PTFE (Teflon) for sealing to ensure chemical inertness and avoid contamination. In total 21 SS gas reactors were built to enable parallel testing to assess the influence of different factors such as moisture content, lubricant type, and lubricant with elevated water content on the refrigerant stability.



Figure 1. Metal gas reactors with refrigerant samples during thermal stability tests in the lab oven (21 days).

To systematically investigate the effects of lubricant presence and moisture, four sample categories were prepared for each refrigerant:

- Control sample with pristine refrigerant (water content <20 ppm)

- Pristine refrigerant (water content <20 ppm) with additized POE lubricant (water content <50 ppm) – 1:1 mass ratio
- Pristine refrigerant (water content <20 ppm) with 5000 ppm added water
- Pristine refrigerant (water content <20 ppm) with additized POE lubricant (water content <50 ppm) and 5000 ppm added water

This matrix enables independent and combined assessment of lubricant-driven and moisture-driven degradation mechanisms. Since HFOs and HCFOs can undergo various chemical reactions when in contact with POE lubricants, refrigerants with different trifluoroacetic acid (TFA) yields were selected. The refrigerants tested included two HFO alternatives: R1234yf (100% TFA yield) and R1234ze(E) (10% TFA yield) and two HCFOs: R1224yd(Z) (97% TFA yield) and R1233zd(E) (2% TFA yield) [8-10].

Given that lubricant viscosity requirements can vary based on operating temperature, two different POE lubricants were tested with R1234yf and R1234ze(E). However, limitations were encountered with ASHRAE Standard 97-2007 when applying the refrigerant mass estimations for R1233zd(E). In the initial experiments, the refrigerant charge mass (≈ 5.7 g) was small relative to the reactor volume, resulting in complete refrigerant degradation at 150 °C after 21 days. This behaviour was attributed to an excessively high lubricant to refrigerant and surface-to-volume ratio, which likely accelerated chemical reactions. Even some aggressive gases (possibly hydrogen chloride, HCl) have seem to have been formed during testing, and signs of erosion-type corrosion along with permanent discoloration of stainless steel components were observed. Therefore, it was decided to increase the sample masses of R1233zd(E) and R1224yd(Z) to 35g in the succeeding tests to prevent complete decomposition into carbon, acids, and CO₂ at the test temperature of 150 °C. The aging and chemical stability experiments were carried out using a Termaks 4000 laboratory oven, which offers a temperature accuracy of ± 1 °C. The temperature during the 21-day tests was monitored using a Fluke 52II electronic thermometer connected to two calibrated T-type thermocouples, each with an accuracy of ± 0.2 °C. The testing temperature was always maintained below the critical temperature of the refrigerant to ensure that the testing conditions are matching the real applications. Pristine lubricant chemical composition was measured using special Gas Chromatograph (GC) with Flame Ionization Detection (FID) and Mass Spectrometry (MS) and Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS) for lubricants at project partner lab. Prior to the analysis, lubricant samples were diluted in toluene for GC, and in LC-MS grade acetonitrile for LC analysis. In addition, control tests of pristine POE lubricants in gas reactors were done in the oven at 150 °C for 21 days to assess their thermal stability and verify potential discoloration or physical degradation. These control tests did not reveal any significant colour change or alteration of physical properties.

As was found, POE VI85 lubricant is the same option for both HFO and HCFO refrigerants [13]. Table 2 summarizes the testing temperatures and compatible POE lubricants for the four refrigerants and sample compositions in metal gas reactors.

Table 2. Summary of the testing temperatures and compatible POE lubricants. (ref. refrigerant),

Refrigerant	R1234yf (21 days test, 90°C)	R1234ze(E) (21 days test, 100°C)	R1233zd(E) (21 days test, 150°C)	R1224yd(Z) (21 days test, 150°C)
Pristine ref. (20ppm water)	32.40g	20.67g	29.64g	34.57g
Pristine ref. and POE Lubricant (1:1 ratio)	34.25g ref. +30.1g POE VI32 30g ref. + 32.80g POE VI55	22.04g ref. + 20g POE VI55 19.96g ref. +20.42g POE VI85	27.59g ref. + 28.40g POE VI85	35.36g ref. + 33.54g POE VI85
Pristine ref. + water (about 5000ppm)	32.81g ref. +4.12g water	20.38g ref.+ 3.80g water	27.68g ref. +4.96g water	33.42g ref. +4.29g water
Pristine ref. + POE lubricant + water (5000ppm)	32.23g ref. + 32.44g POE VI32 + 5.12g water 30.78g ref. + 32.98g POE VI55 + 4.75g water	20.57g ref. +20.31g POE VI55 + 4.10g water 20.72g ref. + 20.20g POE VI85 + 4.23g water	34.71g ref. +32.83g POE VI85 + 5.34g water	34.85g ref. +33.43g POE VI85+ 5.71g water

Special care and attention were given to dosing the different components, which proved to be challenging, particularly due to the vacuuming steps required for all samples and hence multiple trials were necessary to

achieve values as close as possible to the target masses. After the 21-day chemical stability tests, the refrigerant samples were carefully separated from the other components and transferred to smaller SS gas cylinders for GC analysis, as well as to custom-built sealed glass tubes for visual inspection, as shown in Fig.2.

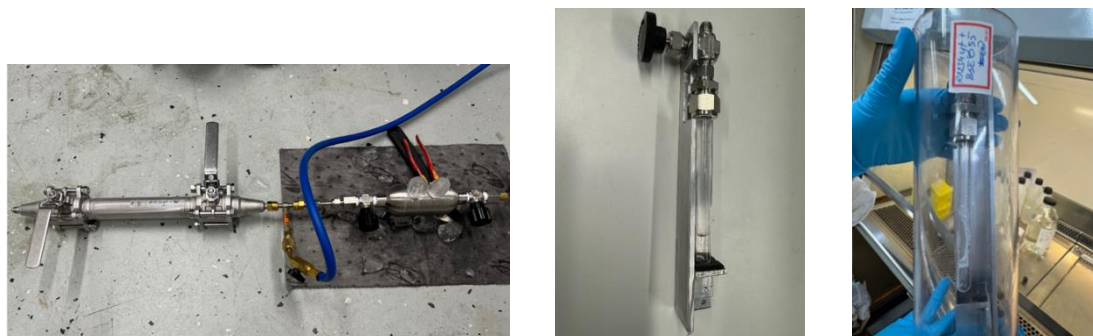


Figure 2. The transfer procedure of thermally treated refrigerant from the metal gas reactor to smaller gas bottle for GC analysis (a), sealed glass tube (b) and sealed glass tubes with polymer-like formations (c).

The small amounts of thermally treated refrigerant collected after the stability tests were afterward expanded, as shown in Fig.3 to another sealed glass and vacuumed sample container, to detect any signs of chemical reactions or polymerization, particularly in the presence of lubricant, water, or a combination of both. For the analysis of both pristine and thermally aged refrigerant samples, a Thermo Scientific Trace 1310 Gas Chromatograph (GC) was used and testing details can be found in [33]. The system was equipped with a porous polymer column (TG-Bond Q, 30 m length, 0.53 mm internal diameter, 20 μ m film thickness), a thermal conductivity detector (TCD), and a flame ionization detector (FID). Nitrogen (N_2 , 99.999% purity) was used as the carrier gas, while hydrogen (H_2 , 99.999%) and synthetic air (99.999%) were supplied for the FID. Measurements were conducted under isothermal conditions at 115 $^{\circ}C$, with a total run time of 10 minutes. As recommended by AHRI Standard 700-2024, the TCD detector is primarily used to characterize non-combustible gases such as R-744 (CO_2), water vapor, and air, while the FID detector is employed to analyze other refrigerants. The GC was calibrated using specially prepared calibration blends consisting of various mixtures of the relevant HFOs, HCFOs, HFCs and often CO_2 . An analytical balance (Mettler Toledo ME2002T/00) was used for all sample preparation and was calibrated using a 1000.00 g test weight, in accordance with the EURAMET calibration guideline (Stuart et al., 2015). The balance achieved a standard deviation of ± 0.01 g during calibration. For this study, only the TCD detector was used to track composition changes in the refrigerant samples. Because the gas chromatograph used in this study was not equipped with a mass spectrometer, compound identification was based on retention time comparison with calibrated reference mixtures, following guidance from AHRI Standard 700-2024 and reported degradation pathways in the literature. After operating the small HTHP system constructed with various standard metals for a continuous 21-day test period, both the POE VI85 lubricant and R1233zd(E) refrigerant were collected for analysis [13]. To ensure consistency across different experimental setups, the system test was conducted at a constant condensation temperature of 125 $^{\circ}C$ (17.2 bar,g) and a hot gas discharge temperature of about 150 $^{\circ}C$. Moreover, R1234ze(E) refrigerant samples that have been in use in industrial systems were also collected. The goal was to compare these results with those obtained from the controlled metal gas reactor tests, to detect possible degradation paths and likely reasons therein.

3. Results

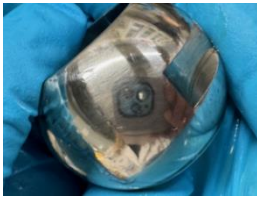
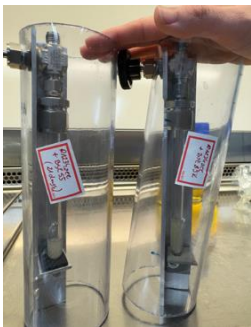
Firstly, pristine lubricant composition was analyzed using (LC-MS/MS) to quantify the relative fractions of linear and branched ester structures in the POE lubricants, as these structural features are known to influence miscibility and chemical interaction with refrigerants to understand the share of branched molecules in POE lubricants to evaluate possible risk of chemical interactions with refrigerant. As reported [15], branched molecules improve the miscibility of refrigerant and lubricant. Table 3 presents the results of pristine lubricant composition analysis. Notably, two lubricants exhibited low or absent levels of stabilizing additives, such as organophosphorus compounds (Table 3), which may reduce resistance to thermal or chemical degradation under high-temperature conditions.

Table 3. Commercial POE lubricants – pristine lubricant composition analysis.

Sample	Penta-esters			Dipenta-esters			Organo-phosphorus compounds
	Area [%]	Main acid	Other acids	Area [%]	Main acid	Other acids	
POE VI32	53	C5, C7	-	47	C5	C8, C10	No
POE VI55	4	C5	C8, C10	95	C5	C8, C10	Yes
POE VI85	32	C5	C7, iso-C9	67	iso-C9	C5, C7	Yes
POE VII170	8	iso-C9	C7, C8, C10	92	iso-C9	C7, C8, C10	No
POE VII170L	79	iso-C9	C5, C7	20	iso-C9	C5, C7	Yes

Notably, two lubricants exhibited low or absent levels of stabilizing additives, such as organophosphorus compounds (Table 3), which may reduce resistance to thermal or chemical degradation under high-temperature conditions. The possible effect of the additive (organophosphorous compound) will be discussed later (in Section Results). Tables 4 summarize the chemical stability results for different HFO refrigerants.

Table 4. Summary of chemical stability results for different HFO refrigerants. (Signs of instability after 21 days at 90 °C (R1234yf) and at 100 °C (R1234ze(E))

Refrigerant	Pristine refrigerant	Refrigerant with POE lubricant	Refrigerant with water	Refrigerant with POE lubricant and water
R1234yf	No reaction	No reaction with POE VI32 White porous polymer (foam type) with POE VI55 	White porous polymer (foam type) 	Transparent gel , smelly sample with both POE lubricants 
R1234ze(E)	No reaction	POE VI55: small white hard particle in gas reactor, whitish gel in glass tube, smelly sample  POE VI85: whitish gel in glass tube, smelly sample, no particle 	No reaction	Hard particles in whitish dense gel in both cases , smelly sample in both cases 

As seen in Table 4, both refrigerants seem to be very thermally stable when pristine samples with water content less than 20 ppm were analyzed. R1234yf was very stable with POE lubricant VI32 having less branched dipenta-esters. Instead, R1234yf with POE VI55 (deemed suitable for higher temperatures) was very unstable and polymerized after the 21-day test. Moreover, R1234yf exhibited pronounced instability in the presence of both water and POE lubricants, resulting in new liquid gel-type product was obtained at the end of the test. These findings are similar to earlier results reported for R1234yf and three different POE lubricants [34]. In this study, fluoride ions were detected in the aged, sealed glass tubes using GC analysis indicating the refrigerant decomposition, especially when there was air present. In the presence of air and high moisture, the highest fluoride ion concentration was recorded when R1234yf was aged in POE ISO32 branched dipenta-esters acid type lubricant and the lowest when it was aged in POE ISO32 mixed acid. Therefore, both studies suggest that the ratio between the branched dipenta-esters and penta-esters needs to be properly selected to reduce the risk of chemical degradation of R1234yf.

A similar pattern, as for R1234yf, was observed for R1234ze(E) in contact with POE oil and water, while the control thermally treated refrigerant sample did not show any signs of polymerization. Instead, tests conducted with two POE lubricants having a higher share of dipenta-esters showed very high chemical instability and new gel-type product in sealed glass tube expansion test (c.f. Table 4). Moreover, in the case of the test of R1234ze(E) and POE VI55 lubricant, small sharp white polymer type particles were obtained. Moreover, similar hard particles in a whitish dense gel were obtained in the test with POE lubricant and excess water. In this case, it was impossible to separate the lubricant or water from the gel., R1234ze(E) did not show any chemical instability when exposed to high water levels. Note that R1234ze(E) and POE VI32 lubricant tests were not conducted due to the compressor supplier recommendations. Nevertheless, it would be very interesting to test POE lubricant having a different chemical composition to understand the effect of dipenta-esters on the chemical stability of HFOs. Again, the results are similar to results published by [35]. As reported, the fluoride ion concentration was small (less than 65 ppm) in all cases, except for the R1234ze(E) and ISO32 branched acid mixture at 48 ppm moisture and 2000 ppm air. Moreover, authors pointed out the possibility of precipitation and accumulation of some decomposition products in the lubricant phase, supporting the observations of the present study. Consequently, both studies suggest that the ratio between the branched dipenta-esters and penta-esters needs to be properly selected to reduce the risk of chemical degradation of R1234ze(E). As seen in Tab.4, both HFOs showed a specific chemical instability that was never reported before. The observed polymeric formations are most likely derived from fluorinated refrigerant species [22, 25], as the POE lubricants themselves do not polymerize [35]. This interpretation is supported by previous observations of polymerization in pure refrigerant systems under rapid expansion conditions. This assumption is based on previous experience of polymerizing R513A and R1234yf refrigerant gas bottles obtained directly from suppliers in P2022-00477 project [36]. None of these refrigerants were used in a refrigeration system and all gas bottles were coming directly from the supplier. These refrigerants (both R513A and R1234yf) were polymerizing only when liquid refrigerant was expanded rapidly to ambient suggesting that R1234yf is unstable at some specific conditions. Since the polymerizing refrigerant can cause damage to the GC instrument, it was decided to only test the control refrigerant samples that were not showing any signs of polymerization. For the control thermally treated R1234yf sample, neither chemical degradation nor new unidentified peaks were detected using the TCD. The GC analysis (not shown in article) detected extremely low water levels at 1.812 min retention time, similar to the pristine R1234yf refrigerant. The GC analysis of R1234ze(E) revealed more unexpected results. The pristine R1234ze(E) tests confirmed lower purity refrigerant (about 96.64% pure) and some impurities such as R1234yf, water, 2 unknown substances (retention times 1.865 and 2.013min) and 2 non-combustible gases (oxygen and carbon dioxide) were detected. Instead, the thermally treated R1234ze(E) sample (shown in Fig.3) exhibited a substantial increase in water content, reaching approximately 852 ppm, which is roughly 26 times higher than in the pristine sample suggesting that water can be one of the by-products from R1234ze(E) degradation process. Moreover, a field R1234ze(E) sample from an industrial installation (the black graph) showed similar tendency and alarming water levels that confirms the chemical instability of R1234ze(E).

No degradation models for HFO refrigerants were found in open literature, except for one atmospheric degradation model for R1234ze(E) [36], which defines water as one of the final products. Table 5 summarizes the chemical stability results for different HCFO refrigerants analyzed. As seen in Table 5, R1233zd(E) refrigerant showed rather high chemical instability, and it was the only refrigerant that polymerized even in the control test without water or lubricant. R1233zd(E) was very instable with POE VI85 lubricant and produced a whitish gel and small particles after 21 days at 150 °C. Similar results were obtained in case of refrigerant and water. In contrast, R1233zd(E) in the presence of POE lubricant and water polymerized and formed a thin film polymer.

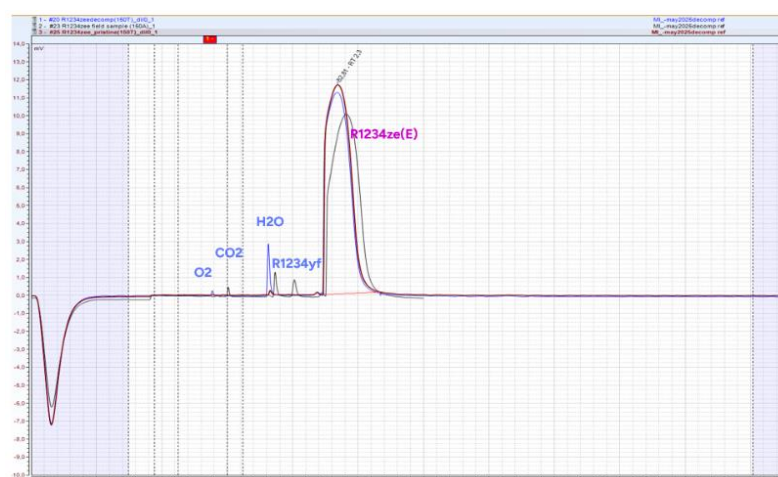


Figure 3. Comparison of GC results for three R1234ze(E) samples.

Table 5. Summary of chemical stability results for different HCFO refrigerants after 21 days at 150 °C.

Refrigerant	Pristine refrigerant	Refrigerant with POE lubricant	Refrigerant with water	Refrigerant with POE lubricant and water
R1233zd(E)	Small solid flakes (changing color to black after exposure to air)	very small drop of whitish gel (first test)	Small black particles, smelly sample (2nd test)	whitish polymer film (1st test, water not lost after 21 days)
		 Small solid flakes changing color to black (second test)	 Liquid refrigerant expansion test gives a dense liquid in glass tube	 One very small white particle, smelly sample (2nd test, all water lost)
R1224yd(Z)	No reaction	Small mm-size white particles in lubricant, brown lubricant, lower viscosity of lubricant	Refrigerant leakages (few unsuccessful trials)	Small mm-size plastic particles in lubricant, smelly sample, brown POE lubricant

Note that POE VI85 is mostly composed of dipenta-esters that can speed up the decomposing process of refrigerant. The GC analysis of pristine R1233zd(E) (not shown in article) revealed extremely low amounts of water and three very small other unknown peaks. Additionally, three R1233zd(E) samples were taken from the HTHP running for 21 days at 150 °C condensation temperature to analyze the compatibility of POE VI85 lubricant and one refrigerant sample (Nov.2024) analysis is shown in figure 4.

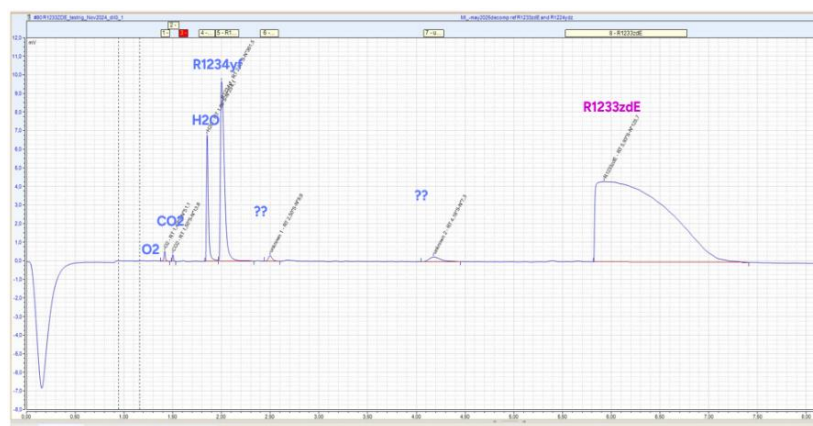


Figure 4. Comparison of GC results for two R1233zd(E) samples from HTHP system.

As seen, in all three cases extremely alarming levels of water up to 1600 ppm are detected. Moreover, a significant degradation of R1233zd(E) to R1234yf (up to 11%) was measured. The pristine R1233zd(E) GC tests showed just one extra unknown (Unknown 3, marked with '??'), which is found as well in gc analysis from Nov. 2024 indicating presence of one highly stable compound. Summing up, the results for R1233zd(E) show considerable instability due to different factors. The significant refrigerant decomposition rate in the HTHP system questions the possibility of using POE branched dipenta-esters based lubricants. Finally, a rather similar share of R1234yf was detected in the three samples. The aged POE VI85 lubricant analysis showed a dynamic viscosity reduction between 44.5% and 84%. Similar aging of POE VI85 lubricant with R1224yd(Z) refrigerant was observed and the viscosity reduction of 78.5% was measured. Fig.5 presents GC analysis results for pristine and thermally treated (21 days test) R1224yd(Z). The GC analysis of pristine R1224yd(Z) used in experiments (before thermal treatment) showed that its water content is slightly higher than pristine R1234yf, R1234ze(E), R1233zd(E) refrigerants. Moreover, two unknown peaks as well as R1233zd(E) or R1224yd(E) were detected. Note that these two unknown peaks do not have similar retention times compared to other cases. As seen, the water content is extremely much higher than for the pristine refrigerant case. Surprisingly, R1233zd(E) refrigerant peak and contaminant Unknown 1 (retention time 3.8 min) completely disappeared and some small amounts of R1234yf are measured.

The decomposition of R1233zd(E) and appearance of R1234yf in almost the same % is in line with the results for R1233zd(E) analysis. Moreover, the water content is increased more than 8 times compared to the pristine sample in presence of POE lubricant. As seen, R1233zd(E) as well R1224ydZ can easily degrade to R1234yf due to dichlorination reaction [38] reported that chlorotrifluoropropene isomers, R1233zd(Z), R1233zd(E) and R1233xf can react with alkali to produce the 3,3,3-trifluoropropyne (R1243zf), chloride salt and water in presence of alkali metals. In case of R1233zd(E), different isomerization reactions were reported at different temperatures to produce by-products of R1233zd(Z) or R1233xf (one of the synthesis precursors of R1234yf formation in presence of Cr-based catalyst) [39]. Unfortunately, the GC system was not calibrated for 3,3,3-trifluoro-1-propyne (TFP/ R1243zf) and 2-chloro-3,3,3-trifluoropropene (R1233xf) which are two of the possible decomposition products. The combination of elevated water formation and pronounced refrigerant instability, particularly for HCFOs, indicates that mineral oil-based lubricants may offer superior robustness compared with POEs under high-temperature conditions, owing to their lower sensitivity to moisture-induced degradation.

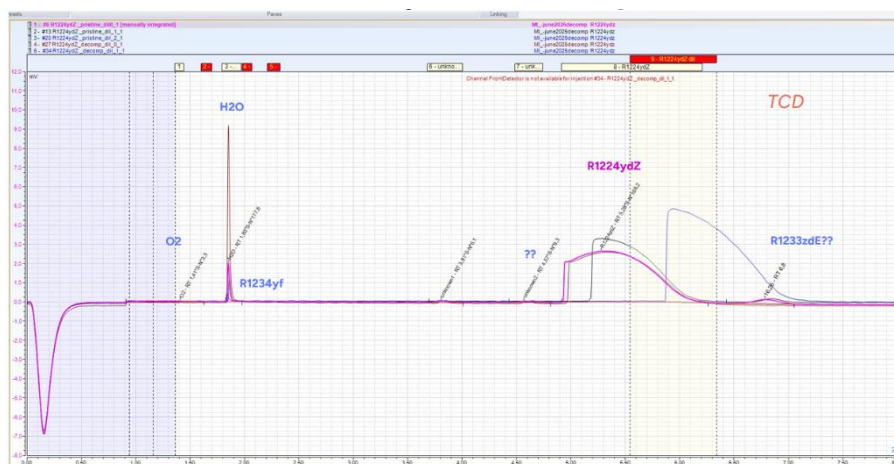


Figure 5. Comparison of GC results for R1224yd(Z) sample.

4. Conclusions

This study showed that some HFOs and HCFOs are very sensitive to POE lubricant composition and higher share of dipenta-esters that are more preferred for higher temperature applications. The key novelty of this work lies in the direct comparison between laboratory-controlled chemical stability tests, conducted in stainless-steel gas reactors according to ASHRAE Guideline 38-2023, and refrigerant samples obtained from pilot-scale HTHP operation and real industrial installations. As found, different parameters such as moisture content and lubricant can trigger polymerization processes that can lead to significant system failure. Each refrigerant seems to form different polymer structures and, in some cases, the polymerization might not be detected due to the accumulation of polymer particles in the lubricant phase. Moreover, the POE VI85 lubricant exhibited significant aging even after only 21 days in a pilot-scale HTHP test rig. Among all thermally treated refrigerants only R1234yf did not show elevated water content. Overall, the findings suggest that conventional POE lubricants may be inadequate for long term high-temperature operation, and that mineral oils or next generation, chemically stabilized POEs should be considered. Additionally, the unexpected degradation of R1233zd(E) into R1234yf highlights unresolved decomposition pathways that warrant further investigation before widespread deployment in HTHP systems.

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