Lubricant Performance and Compatibility for New Low GWP HFO Refrigerant Blends

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ABSTRACT

The transition towards environmentally sustainable refrigerants is driving the development and adoption of new low Global Warming Potential (GWP) hydrofluoroolefin (HFO) blends. R-1132(E) blends have emerged as a promising next generation of refrigerants, due to their low GWP and favorable pressure characteristics. This study focused on developing a suitable polyolester (POE) lubricant for R-1132(E) blends, specifically R-474A and R-479A.

The research revealed that R-1132(E) blends exhibit dilution and stability challenges with POE lubricants compared to R-32. As a result, a new POE lubricant was developed to address these challenges and ensure compatibility with R-1132(E) blends. This presentation will discuss the properties of the new POE lubricant and highlight the potential of R-1132(E) blends to contribute to more environmentally friendly refrigeration and air conditioning solutions.

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Keywords: Lubricants, low GWP, HFO

INTRODUCTION

The imperative to mitigate climate change has intensified the need for environmentally sustainable solutions in the refrigeration and air conditioning sectors. A key focus has been the transition to refrigerants with lower Global Warming Potential (GWP) values. [1] With increasing regulatory pressure, including some local restrictions potentially pushing GWP limits to below 10, the industry is compelled to innovate and adopt alternative refrigerants that meet these stringent requirements. In this context, R-1132(E) hydrofluoroolefin (HFO) blends have emerged as promising next-generation refrigerants. [2]

However, the shift to low GWP refrigerants is not without challenges. The chemical stability of these refrigerants presents hurdles that must be overcome to ensure their practicality and reliability in real-world applications. [3, 4] This study addresses these challenges by focusing on the development of a suitable polyolester (POE) lubricant specifically designed for use with R-1132(E) blends, particularly R-474A and R-479A. Our research reveals the dilution and stability issues associated with POE lubricants in comparison to R-32, necessitating the formulation of a new lubricant to ensure compatibility and optimal performance.

The purpose of this paper is to elucidate the development and characterization of this novel POE lubricant. We demonstrate its effective working viscosity at compressor-relevant conditions and its chemical stability, which are crucial for the successful integration of R-1132(E) blends into environmentally friendly refrigeration and air conditioning systems. This paper will not only highlight the properties and benefits of the new lubricant but also underscore the potential of R-1132(E) blends in contributing to sustainable cooling solutions.

MAIN SECTION

REFRIGERANT DISCUSSION

Hydrofluoroolefin (HFO) refrigerants are widely recognized in the literature for having higher dilution potential and greater chemical instability compared to traditional hydrofluorocarbon (HFC) refrigerants such as R-134a and R-410A. [3] These characteristics are directly related to their lower global warming potential (GWP) values, which result from their shorter atmospheric lifespans. The increased reactivity of the carbon-carbon double bond in HFOs leads to faster decomposition in the environment. [2] Table 1 presents a selection of key physical properties of common refrigerants—including GWP and safety classification—that are critical factors in the selection process for air conditioning and refrigeration applications.

R-32 has gained traction as a replacement for R-410A, primarily due to its significantly reduced GWP. R-1132(E), also called trans-1,2-difluoroethene, offers an even lower GWP (<1). However, its adoption is limited by its higher flammability classification (2). Refrigerant blends such as R-474A (23 weight (wt) % R-1132(E) and 77 wt % R-1234yf) and R-479A (28 wt % R-1132(E), 21.5 wt% R-32, and 50.5 wt % R-1234yf) have the potential to mitigate flammability concerns while still offering substantially lower GWP values. [1, 2] Figure 1 depicts the chemical structure of R-1132(E).

Table 1 Key refrigerant characteristics [1, 2, 5, 6]

Refrigerant	R-410A	R-32	R-1132E	R-474A	R-479A
GWP	2090	675	<1	<1	<150
BP (°C)	-45.5	-52	-52. 6	-43. 7	-50.7
Crit. Temp. (°C)	71.4	78.1	75.6	87.8	79.5
Crit. Press. (mPa)	4.90	5.78	5.16	4.05	4.75
Flamm-ability	1	2L	2	2L	2L

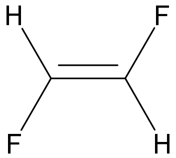


Figure 1 Chemical structure of R-1132(E)

POE DISCUSSION

Polyol esters (POEs) are a versatile class of lubricants that have been widely utilized in the refrigeration and air conditioning industry for many years, owing to their compatibility with a broad spectrum of refrigerant gases—including hydrofluorocarbons (HFCs), hydrofluoroolefins (HFOs), and others. [4] POEs are synthesized from polyols and acids, allowing their chemical structure to be tailored for specific refrigerant types and compressor systems. However, the selection of a suitable refrigerant-lubricant combination is critical, as the interaction between these components in a hermetically sealed compressor can significantly affect system performance. [4] Notably, the lubricant's working viscosity is influenced by temperature, pressure, and dilution with refrigerant gas. [7]

In this study, POE A was designed for optimal miscibility, solubility (working viscosity), and compatibility with R-32 refrigerant. However, when used with HFO blends such as R-474A or R-479A, POE A exhibited poor chemical stability. The subsequent sections will illustrate that by varying the polyol and acid constituents as well as the additive package, a new formulation—POE B—was developed to achieve enhanced chemical stability, even in the presence of more reactive refrigerants.

Table 2 summarizes the physical properties of POE A and POE B. The difference in polyol and acid composition between POE A and POE B is illustrated best by the difference in Kinematic Viscosity (KV) at 40 °C and the Viscosity Index (VI). Both lubricants have a KV of ~9.5 cSt at 100 °C, but a different KV at 40 °C, which contributes to the difference in VI. POE A has a viscosity index of 127, while POE B has a viscosity index of 91.

Table 2 Characteristics of POE A and POE B

ASTM Method	Test	Units	POE A	POE B
D445	Visc at 40 °C	cSt	65.8	82.1
D445	Visc at 100 °C	cSt	9.6	9.5
D2270	VI		127	91
D4052	Density at 20 °C	g/mL	1.024	0.957
D974	TAN	Mg KOH/g	0.035	0.01
D92	Flash Pt.	°C	277	269
D92	Fire Pt.	°C	321	305
D97	Pour Pt.	°C	-45	-39

Stability Overview

The chemical stability of HFO refrigerants was studied according to ASHRAE Standard 97, which involves charging and sealing a glass tube with a combination of refrigerant, lubricant, and metal coupons (representing the metallic components of a compressor which may catalyze any chemical instability experienced by refrigerant or lubricant at high temperature and pressure). [8] The test is conducted at 175 °C for 2 weeks. The purpose of this test is to approximate the compatibility of the refrigerant/lubricant pair over the lifetime of a compressor at relevant operating conditions (i.e. elevated temperature and pressure).

Additionally, ASHRAE Standard 97 was modified to include DI H_2O water (1000 ppm) or air (0.00015 bar) in addition to the refrigerant, lubricant, and metal coupons, according to the description in Table 3, to increase the severity of the test. Table 3 displays the analysis of the liquid post-test.

Table 3 Liquid analysis post ASHRAE 97 testing in R-479A. nc stands for no change.

Lubricant	Refrigerant	ΔTAN	ΔColor
POE A	R-479A	1.44	0.4
POE B	R-479A	0.06	1.3
POE B	R-474A	-0.04	0.1
POE A + H_2O	R-479A	1.6	0.2
POE B + H_2O	R-479A	0.08	0.2
POE A + Air	R-479A	0.33	0
POE B +Air	R-479A	0.02	1.3

As displayed in Table 3, ASHRAE Standard 97 testing results in POE A showed an increase in total acid number (TAN) of 1.44 mgKOH/g, which indicates chemical instability. No corresponding increase in TAN was observed for POE B in either R-479A or R-474A. Additionally in the tests conducted in the presence of air or water, POE A showed a significant increase in TAN (0.33 and 1.6 mgKOH/g respectively), but POE B did not. In a few cases, a change in the color of the lubricant was observed for POE B, but no corresponding change in the concentration of the metals was detected by Inductively Coupled Plasma Optical Emissions Spectroscopy (ICP-OES), which suggests that no significant reaction involving the metal coupon or the additive package took place. Finally, no change in clarity of the liquid was observed (i.e. no particulates, film or sediment). Overall, these results suggest that POE B is chemically stable in the presence of R-474A and R-479A, even under severe testing conditions.

Miscibility Overview

Miscibility in the HVACR industry is generally defined as how well the refrigerant and lubricant mix together in the liquid phase. This property is influenced by the chemical properties of both the refrigerant and the lubricant, such as polarity and molecule size. Single-phase miscibility of the lubricant with the refrigerant typically signifies suitable oil return from the evaporator in a compressor, which helps ensure adequate lubricant in the sump. [9]

Miscibility of lubricant/refrigerant pairs was measured according to ASHRAE Standard 218. [10] In this test, refrigerant and lubricant are charged and sealed in glass tubes. Lubricant/refrigerant mixtures are examined at a range of temperatures from -60 °C to +60 °C to determine the phase behavior (one phase, two phase, etc). Lubricant/refrigerant pairs that show one phase when combined at a wide variety of concentrations and temperatures are referred to as highly miscible.

HFO blends have been well established in the literature to have a high degree of miscibility with POE lubricants. [4, 11] POE A and POE B proved to be no exception. Both lubricants showed only one phase with R-479A and R-474A in the full range of the test, as displayed in Table 4, Table 5 and Table 6.

Table 4 Miscibility of POE A with R-479A. All temperatures are reported in °C

POE A with R-479A

Lubricant (wt%)	5	10	20	30	50
High Temp Boundary	>60	>60	>60	>60	>60
Low Temp Boundary	<-60	<-60	<-60	<-60	<-60

Table 5 Miscibility of POE B with R-479A. All temperatures are reported as °C

POE B with R-479A

Lubricant (wt%)	5	10	20	30	50
High Temp Boundary	>60	>60	>60	>60	>60
Low Temp Boundary	<-60	<-60	<-60	<-60	<-60

Table 6 Miscibility of POE B with R-474A. All temperatures are reported as °C)

POE B with R-474A

Lubricant (wt%)	5	10	20	30	50
High Temp Boundary	>60	>60	>60	>60	>60
Low Temp Boundary	<-60	<-60	<-60	<-60	<-60

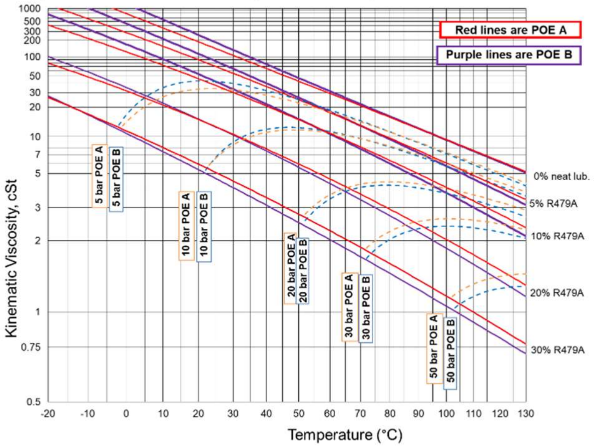
Refrigerant Dilution and Working Viscosity

As discussed in the Miscibility Overview, the refrigerant and lubricant exhibit complex mixing behavior, which can affect the lubricant's ability to perform its main function: preventing wear. Typically, if a lubricant shows full miscibility with a refrigerant over the whole temperature range, this indicates that the refrigerant and lubricant show good affinity and mix well. This same compatibility can lead to high dilution of the lubricant by the refrigerant, which leads to a lower effective working viscosity. Other reports in the literature indicate increased dilution of POE lubricants by HFO refrigerants [4, 12].

The dilution and viscosity data presented in this study were obtained using a PVT (pressure, viscosity, temperature) instrument. This testing approach has a longstanding history, with several standardized methods available for characterizing refrigerant/lubricant mixtures. The experimental setup employed here is adapted from the design described by Seeton and Hrnjak and constructed by The Lubrizol Corporation [13]. For each lubricant-refrigerant combination, pressure and viscosity measurements were collected across a range of temperatures, defined in Figure 2. The resulting data were analyzed and regressed to produce descriptive equations, which are applicable within the tested range of conditions. [14]

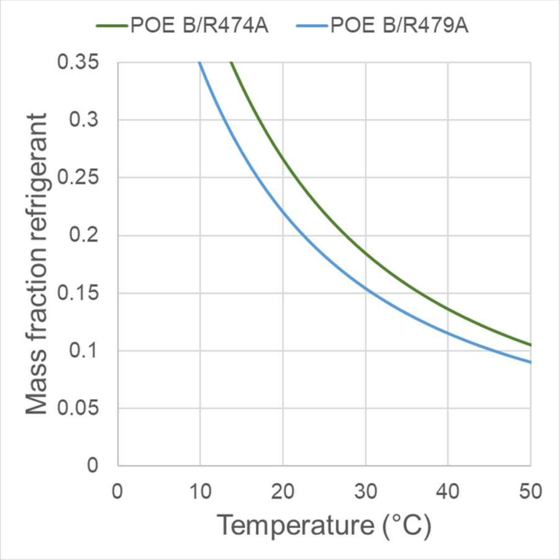
Figure 2 displays the data generated by PVT of POE A and B in R-479A as overlaid Daniel plots. As referenced earlier in Table 2, the difference in chemical structures between POE A and B results in different VIs, as measured at ambient pressure. Figure *2* shows that POE A and POE B have similar working viscosities at a variety of temperature and pressures in the presence of R-479A. The temperature-dependent behavior of POE B relative to POE A measured by PVT echoes the differences in VI of the two fluids. At the highest temperature and pressure working conditions, POE A shows a slightly higher working viscosity than POE B, but overall, the behavior of both fluids is remarkably similar.

Figure 2 Daniel Plots of POE A overlaid with POE B in the presence of R-479A generated by PVT.



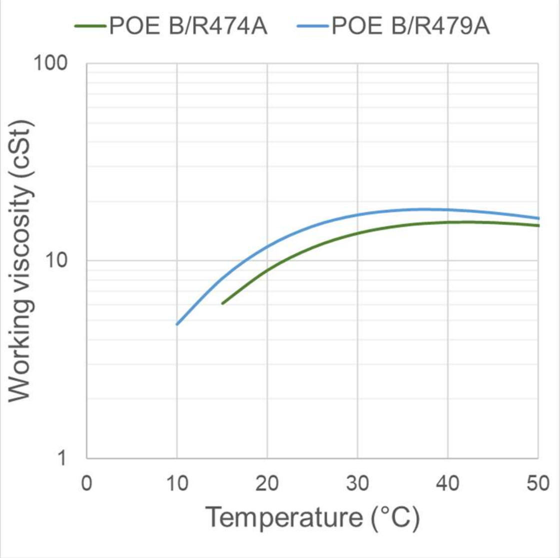
Next, the dilution of POE B was compared in both refrigerants, R-474A and R-479A. Table 1 lists some key characteristics of the refrigerants in question. Figure 3 displays the dilution of POE B in the presence of both refrigerants at 3 °C at saturated pressure (Tsat). This condition is used to allow for the relative comparison of refrigerants with different pressure characteristics. At any given temperature, POE B in R-479A shows a lower mass fraction of refrigerant, compared to R-474A, which can be contributed to the greater concentration of HFO in R-474A relative to R-479A.

Figure 3 Solubility at 3 °C Tsat. The pressure at this condition for R-479A is 7.93 bar and for R-474A is 5.79 bar. The concentration of refrigerant measured by mass faction vs temperature



The working viscosity of POE B in both refrigerants as a function of temperature is displayed in Figure 2. This data is presented in the same conditions as Figure 3, the saturated pressure at 3 °C. While the working viscosity of POE B in R-474A is slightly lower at lower temperatures than in R-479A, overall, the working viscosity is similar in both gases. The viscosity difference can be attributed to the slight difference in solubility shown in Figure 3.

Figure 4 Working viscosity vs Temperature at 3 °C Tsat. The pressure at this condition for R-479A is 7.93 bar and for R-474A is 5.79 bar.



CONCLUSION

With regulatory pressure potentially pushing GWP limits even lower, R-1132(E) blends such as R-474A and R-479A have emerged as a lower-GWP alternative to R-32. With the more reactive double bond, this type of HFO blend can cause chemical instability when paired with a lubricant at elevated temperature and pressure. A new POE lubricant was developed with improved chemical stability, as demonstrated by ASHRAE Standard 97 testing. Full miscibility was maintained, as well as a similar working viscosity as determined by PVT for both refrigerant blends.

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