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ABSTRACT

Refrigerants used in various air conditioning and refrigeration industries are going through changes today and continued changes into the near future. These changes are being driven by environmental and energy efficiency regulations and could result in the use of refrigerants that require the investigation of new lubricants. One such change is the use of refrigerants that carry a lower global warming potential (GWP) value then current refrigerants used in the market. Some of these refrigerants present certain challenges over current refrigerants such as changes in flammability requirements, higher pressures or stability of the refrigerant in system operation. These refrigerants and the changes they represent may require different lubricants in order to maintain system optimization ensuring that energy efficiency and reliable requirements are met.

The interaction between the refrigerant and the lubricant in any air conditioning or refrigeration system is a vital piece of information that is required to make certain optimal performance is achieved. The lubricant in a system is crucial to operation and needs to adequately lubricate the moving components in a system and return to the compressor when circulated. These conditions can drastically be affected by the refrigerant and lubricant interaction with improper choices resulting in consequences from lowering the overall performance to complete failure.

This paper will look at some of the current and proposed low GWP refrigerants and their interaction with various lubricants. Evaluations will be made and certain properties will be presented that are essential to system operation. Of particular interest will be the refrigerant solubility factor of low GWP refrigerant candidates that can affect system performance and reliability; the stability of newer low GWP refrigerant candidates that maintain comparable current refrigerant system requirements; the miscibility of low GWP refrigerants with lubricants that can affect oil circulation; and how chemistry changes to various lubricants can help increase energy efficiency in systems operated with low GWP refrigerants.

The information in this paper and the presentation will be a timely look at current and future needs for lubricants for various refrigerants that will help manufacturers in the air conditioning and refrigerant industry to evaluate the choices that need to be made in order to maintain the required system performance.

1. INTRODUCTION

Refrigerant gases have very low evaporation points, and can therefore be condensed under pressure to chill air. Through a process of repeatedly evaporating and condensing these gasses, heat is drawn from surrounding air and the temperature inside a given system or unit is reduced. These systems are refrigerators, freezers, air conditioners and heating, ventilating and air conditioning units (HVAC). Different types of refrigerant gases have historically included chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), hydrofluorocarbon (HFC), Ammonia, Hydrocarbons, Carbon Dioxide and many blends of these and other gases.

Refrigeration from the 1800's until the 1920's often used toxic gases such as Ammonia, Methyl Chloride and Sulphur Dioxide. Following the inevitable death and injury from leaks of these gases, safer gases were sought. The result was the discovery of chlorofluorocarbon (CFC) gas, which became the primarily refrigerant. It was colourless, odourless, nonflammable and non-toxic.

Scientists discovered in the 1970s, however, that when CFCs leaked into the atmosphere and exposed to the Sun's ultraviolet rays, a breakdown of the molecule resulted in chlorine ions which chemically attack the earth's Ozone layer. CFCs were banned in many countries in North America and Europe.

Some applications replaced CFCs with HCFCs – hydrochlorofluorocarbon. These have a shorter atmospheric life with less subsequent Ozone depletion. Better still, environmentally are HFCs Hydrofluorocarbon. These contain no chlorine and are thought to have zero negative effect on Ozone.
Many industrial applications have moved back to naturally occurring refrigerant gas such as Ammonia, Carbon Dioxide and Hydrocarbons in an effort to address the global warming effect that some refrigerants demonstrate. These and other alternative refrigerants which have low global warming potential are being evaluated today and each requiring investigation into the most optimized lubricant.

2. LOW GWP REFRIGERANTS

These 'alternative' refrigerants possess different characteristics that affect their suitability to be used, according to environmental, safety, cost and efficiency constraints but are considered as lower GWP options.

Refrigerant type	Safety and Other Considerations	GWP/ODP	Cost	Misc.
Hydrocarbon	Non-toxic with high flammability. Changes to system construction and reduced charge sizes are required. Easier to use in new systems.	3/0	Similar to R22	Miscible with mineral oils, but highly soluble.
Ammonia	High toxicity with low flammability. Mainly limited to indirect systems or direct systems in unoccupied spaces. Ammonia requires specialist design work.	0/0	Much less than R22	Incompatibility with copper materials, cannot be used as drop-in.
Carbon Dioxide	Non-toxic and non-flammable but has high operating pressures so entire construction must be capable of withstanding such pressures.	1/0	Less than R22	High operating pressures so cannot be used in existing systems; supercritical cycle demands expert design work
HFO	Non-toxic and low flammability. Has the potential to be a drop-in replacement in some systems.	4/0	Much more than R22	Very new products not commercially available yet, many unknown factors
R32	Non-toxic and non-flammable. Higher GWP values compared to other options.	675/0	Similar to R22	Popular candidate especially in regions that are currently converting away from R22.

2.1 Ammonia (NH_3) R-717

Ammonia has been highly effective in industrial refrigeration plants for over 130 years. It is deemed environmentally friendly, economical and energy efficient. Its boiling point of -33^{0}C makes it possible to have refrigeration temperatures below -20^{0}C without reduced pressure. It is a colourless gas, slightly flammable and in some mixtures with air can be explosive. Ammonia can endure moderate water levels and is ideal for large scale chilling. It must not be used with copper, brass or bronze and has a tendency for seal shrinkage.

2.2 Carbon Dioxide (CO_2) R-744

CO_2 has been used as a refrigerant since 1850 and is now regaining popularity due to its low environmental impact. It has excellent thermodynamic properties including a high cooling capacity and is therefore suitable for a large range of applications. Its ability to be in direct food contact makes it suitable for soft drinks chilling and ice-cream. It is non-flammable and non-toxic. Moisture can cause corrosion in the steel pipework and ice formation. Ice can block small capillary tubing which can lead to eventual system failure. R744 is also ideal as a secondary refrigerant.

The refrigerant operates at extremely high pressure in the trans-critical state and efficiency is reduced when operating in higher ambient temperatures.

2.3 Hydrocarbon (HC)

R290 Propane is used in Commercial and Process Refrigeration as a substitute for R22. Although Propane is non-toxic its mixture with air in certain proportions is explosive, trace levels of an odorant could be added to help identify a leak but most odorants are too reactive for refrigeration systems.
R1270 Propylene is a colourless, flammable, non-toxic gas and is part of the group of liquefied gases. It is used in high temperature chilling applications as a substitute for R22 and R502. Like Propane, Propylene is flammable so inventory must be small to reduce hazard.
Like R290 and R1270, R600a Isobutane is a colourless, easily liquefied flammable gas. It is commonly used in refrigeration applications, such as domestic refrigerators, drinks dispensers.

2.4 Hydrofluoro Olefin (HFO)

HFO-1234yf looks likely to become the refrigerant of choice for automotive air conditioning in Europe. However it is yet to become commercially available outside of automotive and only sample quantities are available for lubricant evaluation in stationary refrigeration and air conditioning.
HFO-1234ze is more commercially available as a foam blowing agent and testing is underway with refrigerant suppliers, lubricant suppliers and OEM compressor manufacturers for evaluation in some industrial and other refrigeration applications.
Both of these HFO refrigerants are considered mildly flammable.

2.5 Difluoromethane (R-32)

R-32 has a GWP of 675 and ODP of 0. It is mildly flammable but not toxic. It is more environmentally acceptable than other HFCs retaining the properties of the many common HFCs which can offer less disruption and cost for wholesale compressor and system changes that might be necessary for some non-HFC refrigerants.

3. LUBRICANT CHOICES

Refrigerant lubricants are required to possess many properties, from their base stock and / or additive content. They must be miscible with the refrigerant under the system conditions without becoming too solubilized as this may reduce viscosity to critically low levels and cause component wear. They must cool, lubricate and not interact with refrigerant, metalwork or seals. They must remain stable and transport additives and refrigerant uniformly around the refrigeration cycle. Unlike lubricants for industrial applications like gear oils, chain oils and hydraulics, refrigeration compressor manufacturers prefer minimal additive content, with low levels of antioxidant often being the only acceptable additive. Base oil quality and correct selection is therefore imperative.
Many other ‘practical’ and commercial factors determine lubricant choice – OEM approvals, price, availability, legislation, retrofit ability, multi-system adaptability, working life, environmental impact, energy efficiency, health and safety.
This paper will discuss current and potentially future lubricant options for low GWP refrigerants we have outlined and also provide some data on refrigerant lubricant interactions.

3.1 Ammonia

Ammonia requires oil with low solubility and very low carry-over. Oils that can counteract the seal shrinkage tendencies of R-717 are advised.

Naphthenic mineral oils (NMO) exhibit a low viscosity index and high solubility with R-717 which can result in poorer lubrication and more frequent oil changes. A natural low pour point and lower cost are benefits.
Paraffinic mineral oils (PMO) provide improved lubrication, low oil carry-over and good oil sealing. Less carbon build-up and good shear stability helps to extend drain intervals.
Polyalphaolefin oils (PAO) offer superior stability, viscosity index, wear performance and low seal swell over mineral oils, but at an increased cost.
Polyalkylene glycol oils (PAG) present a chemistry that can be modified to have miscibility with other oils or have solubility with NH_3 that can allow for the use of direct expansion evaporators and improve heat transfer in flooded evaporators. The overall higher cost of the oil can sometimes be overcome by improved performance and reliability.

3.2 Carbon Dioxide

R-744 requirements for lubricants can vary depending on the application. Sub-critical CO_2 refrigeration applications are served well by POE lubricant but could require an antiwear additive to protect the system from the heavy compressor demands of pressurized CO_2. In sub-critical systems with the proper oil separation less miscible lubricants can be used. For Trans-critical CO_2 systems however, even with antiwear additive, the resultant working viscosity of POE may not be adequate and could require an initial higher viscosity. PAG oil of similar viscosity grade but with superior viscosity index will maintain a satisfactory working viscosity at trans-critical conditions but may suffer on miscibility.

Polyalkylene glycol oils chemistry can be customized to control miscibility and solubility interaction. Higher viscosity index with or without additive introduction can provide superior lubrication. The product can be used for sub-critical and trans-critical applications. Higher cost and high water absorption are potential negatives.
Polyalphaolefin oils are very insoluble but this can be used with various components to have excellent separation from the refrigerant stream. This separation allows for the use in both sub-critical and trans-critical applications.
Polyol Ester oils (POE) can provide a wide range of adjustable chemistries that offer good miscibility which can eliminate the need for expensive separation techniques and offers utilization in lower cost direct expansion applications. The high solubility factor of the refrigerant into the lubricant could make some applications unachievable without the use of high viscosities and additives.

3.3 Hydrocarbons

Hydrocarbon refrigerants can be used in various domestic, commercial and industrial refrigeration and air conditioning applications and are attractive because of their low GWP values. Their highly flammable nature and limitations on charge size restricts there use. Most lubricants have good miscibility in hydrocarbon refrigerants which makes the choice of lubricants more dictated by other parameters. Isobutane and propane are two hydrocarbon refrigerants that are mainly used in refrigeration and air conditioning applications.

Naphthenic mineral oils lower cost makes them an attractive choice for a number of hydrocarbon applications but overall stability and performance can be lacking. The very high solubility of the refrigerant into the lubricant can result in viscosity reduction that can affect lubrication. Very low viscosities products might also be too volatile for certain applications and require additives to provide the needed wear performance.
Alkylbenzene oils (AB) at lower viscosities have been used in smaller system and provide less solubility and more stability than mineral oils. Lower viscosity grades still require additives for wear protection.
Polyol Ester oils offer a reduced solubility with the refrigerant and multiple varieties of chemistries can be created for various hydrocarbon products. Superior lubricating properties can allow the use of just the base stock without lubrication enhancing additives. Initial cost of the lubricant will be higher but can be offset by improved efficiency and reliability. The lubricants can be engineered to give good biodegradability which may be important for future sustainability parameters.
Polyakylene glycol oils can provide chemistries that limit the solubility of the refrigerant to very low levels which could be important in some applications. Overall cost and high moisture absorption may limit their use in certain applications.

3.4 HFO

Of the low GWP refrigerant systems being considered today, HFOs pose the most uncertainty with lubricant choice. All of the other refrigerant candidates have been used in the past for refrigeration, some have been continually used throughout the 20th Century and many have been lubricated in industrial compressor applications such as process gas manipulation. HFOs are new and despite good scientific knowledge existing, actual solubility, miscibility, viscosity / temperature analysis and compressor testing trials have been required.
Most HFO work has been done in the automotive air conditioning market where currently used polyakylene glycol lubricants with some modifications have been identified as candidates. Based on this information initially it looks like POE lubricants used currently for HFC refrigeration look suitable, but some lubricant and refrigerant interaction difference may require investigation into modifications.

3.5 R-32
As an HFC and being 50% of the composition of R-410A, R-32 is ideally lubricated by POE oils for a number of different applications. Based on initial studies, current products used with R410A will require some modifications to the lubricant-refrigerant properties for optimization with R-32.

4. EXPERIMENTAL PARAMETERS

There are a number of interactions between the refrigerant and the lubricant that need to be investigated in order to produce systems that are optimized for use. It is especially important when new refrigerants are developed that these interactions with lubricants are followed as a screening method to identify the correct candidates for additional system testing. A few of the more critical interaction parameters are listed below which will be supported later on with test results.

4.1 Miscibility
Miscibility is the property of substances to mix in all proportions, forming a homogeneous solution. In compressor systems, the refrigerant gas and the lubricant must be miscible to enable complete and efficient transport around the compressor system without dropping out or slugging. Improper miscibility will demand more energy to force the mixture through the system and can result in component wear and reduced energy efficiencies.

4.2 Solubility
Solubility is the property of a substance (the solute) to form a homogeneous solution in another substance (the solvent). Solubility depends on the chemistry, temperature and pressure. Despite the need for refrigerant gas and lubricant to be miscible, excessive solubility of the gas into lubricants can dramatically reduce the resultant oil viscosity and lead to wear and occasional system failure.

4.3 Energy consumption
The Energy Efficiency Ratio (EER) of a particular cooling device is the ratio of *output* cooling to *input* electrical power at a given operating point. EER is related to the coefficient of performance (COP) which is universal, unit-less and can be used in any system of units. EER = COP * 3.412.

4.4 Viscosity, Friction, Wear
Viscosity is a measure of the resistance or flow of a fluid to being deformed by stress. Viscosity is considered "thickness" or "internal friction". The less viscous the fluid, the greater its ease of movement. A fluid's relationship of viscosity to temperature is vital, this is Viscosity Index. High 'VI' fluids like PAGs and esters display less change in viscosity with temperature than low VI fluids, like mineral oils.
The 'coefficient of friction' (COF) is the ratio of the force of friction between two bodies and the force pressing them together. For refrigeration lubricants the interaction of the refrigerant with the lubricant needs to be taken into consideration and how it will affect these parameters.

4.5 Compatibility
Not only do lubricants and refrigerants need to be compatible with each other, but their chemical and physical interaction with the construction materials of the compressor system must remain inert. This includes a variety of materials used for seals, filters, rings, valves, wiring, insulation often involving several types of plastic and metal.

5. RESULTS AND DISCUSSION

Invention of new refrigerant molecules or expanded use of some current refrigerant chemistry has led to investigation of lubricants that work with new refrigerant chemistry or improve the performance of existing refrigerant chemistry. Presented below are test results of various refrigerant and lubricant interactions.

5.1 Lubricants for HFO-1234yf

HFO-1234yf as mentioned has a low GWP value which is due in part to the molecular structure having an unsaturated bond (double bond) but this has also questioned the stability of the molecule in application. Because of potential stability issues the choice of lubricant base stock and additives could be keys to a stable operating system. Table 1 shows the results of testing various POE lubricants and additives with HFO-1234yf at 175^{0}C for 14 days with moisture and air present. Changes to appearance of metal coupons in the test and the acid number are indications for reaction and instability. The results show that POE versions B and C indicate some stabilization of the HFO-1234yf and lubricant interaction at these conditions.

	Appearance				Acid No Change mgKOH/g Oil
	Oil	Cu	Fe	Al	
POE A	Amber	Dull	Dark	Dull	0.13
POE B	Clear	New	New	New	0.06
POE C	Clear	New	New	New	0.05
POE D	Slight Yellow	New	Dark	New	0.74
POE E	Yellow	Dull	Dark	New	0.16

Table 1: Stability tests of HFO-1234yf and POE lubricant formulations

5.2 Lubricants for R-32

Miscibility of the lubricant and refrigerant is an important parameter for optimal system operation. Lubricant and refrigerant combinations that are not miscible can effect compressor lubrication and overall system efficiencies. Synthetic lubricants like POE and PVE are currently used with R-410A refrigerant but investigation is needed to determine if they will be adequate for R-32. Table 2 shows miscibility results of two POE lubricants and one PVE lubricant currently used with R-410A and the miscibility results for these same lubricants in R-32. Miscibility was measured at two concentrations, 10% lubricant in refrigerant and 20% lubricant in refrigerant. The results indicate that the temperature at which R-32 and lubricant remain miscible is higher than what is seen with R-410A. This increase in miscibility temperature could have a negative effect on system performance. To counteract this potential decrease in performance changes to the chemistry of the lubricant can be investigated and this is illustrated in the table with POE 3 which indicates miscibility similar to what was found with lubricants and R-410A.

	Lubricant Concentration	
Lubricant/Refrigerant	10%	20%
POE 1/R-410A	-36^{0}C	-25^{0}C
POE 2/R-410A	-27^{0}C	-23^{0}C
PVE 1/R-410A	-32^{0}C	-29^{0}C
POE 1/R-32	-10^{0}C	5^{0}C
POE 2/R-32	5^{0}C	10^{0}C
PVE 1/R-32	0^{0}C	15^{0}C
POE 3/R-32	-35^{0}C	-30^{0}C

Table 2: Miscibility temperature comparisons of lubricants with R-32 and R-410A

5.3 Lubricants for R-600a

Approximately 70% of global refrigerator applications use R-600a as the refrigerant. A number of these applications use a naphthenic mineral oil of various viscosities as the compressor lubricant. Though the mineral oil can provide some cost benefits the overall cost of operation (reliability and performance) could be better served with other lubricant candidates. Stability of mineral oil in some applications can lead to deposits on valves and other compressor components that make the compressor less efficient. The high solubility of R-600a into mineral oils can lead to a viscosity of the lubricant at the bearing which is too low to maintain adequate lubrication which can lead to decrease in efficiency and potential compressor failure. The use of synthetic lubricants with R-600a can help provide a more reliable and efficient system. Because of solubility differences, synthetic lubricants can provide a greater capacity to a compressor when compared to a mineral oil of like viscosity. In addition, the superior lubricating properties of synthetic lubricants over mineral oils along with the potential to use a lower viscosity allows for an overall more efficient refrigerant-lubricant combination. Table 3 shows results of testing different synthetic lubricants with R-600a in a calorimeter at low back minimum conditions and comparing results to baseline tests with mineral oil. As can be seen variations to the synthetic lubricant composition, A1 though C1, results in higher EER values over mineral oil baseline test.

	Capacity	**Power**	**EER**
Baseline	849	159.5	5.32
A1	877	157.5	5.57
A3	884	158.5	5.57
A6	903	158.3	5.70
A8	908	159.3	5.70
B4	910	156.0	5.83
C1	914	155.0	5.90

Table 3: Calorimeter test comparisons of mineral oil and synthetic lubricants with R-600a

5.4 Lubricants for HFO-1234ze

Because of the potential near term availability of HFO-1234ze there has been an increased interest in using this refrigerant to replace R-134a in some applications. The low GWP value and potential similar efficiency make this refrigerant an attractive alternative to products that use a large amount of refrigerant like industrial chillers. A critical parameter to consider is the solubility or dilution factor of HFO-1234ze in current lubricants used in applications like screw compressors with R-134a. Figure 1 shows a comparison in solubility of an ISO 170 POE lubricant with both R134a and HFO-1234ze. The pressure is measured at refrigerant concentrations of 10, 20 and 30 percent in the lubricant. The lower the pressure is an indication that the refrigerant has more affinity to dissolve in the lubricant. As can be seen in the graph HFO-1234ze shows lower pressures for the same given concentration when compared to R-134a.

One of the big changes that is seen when a refrigerant is more soluble in a lubricant is the reduction in working viscosity (viscosity of the combination of lubricant and refrigerant). The working viscosity is critical in determining if this viscosity can support lubrication at the particular bearing. Figure 2 translates the solubility that was presented in Figure 1 into what the viscosity (cSt) would be of the same ISO 170 POE lubricant at given temperature and refrigerant concentrations for HFO-1234ze compared to R-134a. This work indicates there could be a need at certain conditions to increase the viscosity of the lubricant for products used with HFO-1234ze in order to maintain adequate bearing lubrication.

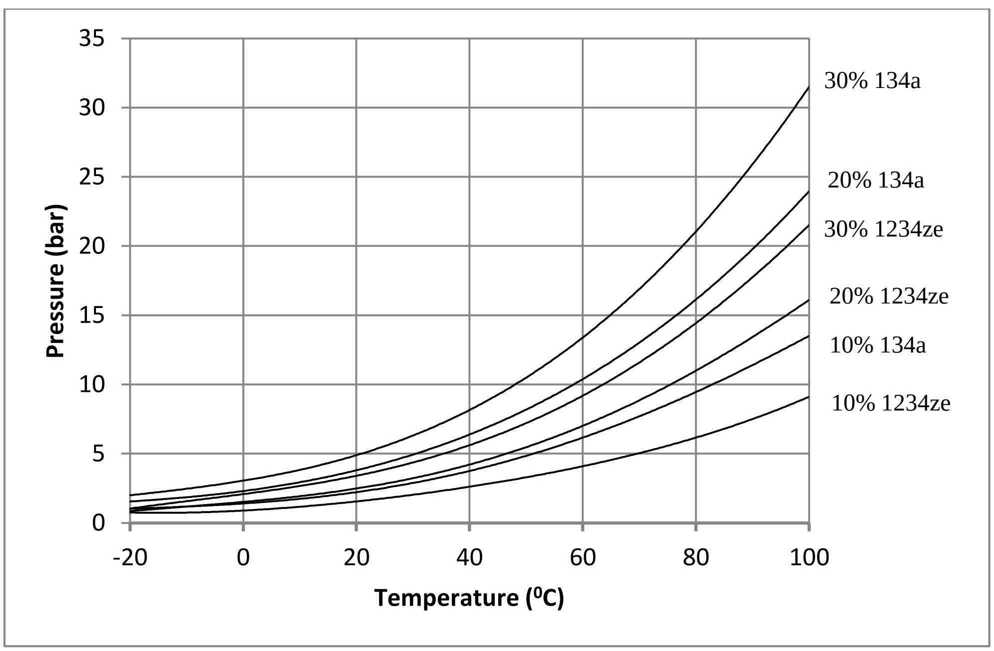

Figure 1: Solubility comparison of HFO-1234ze and R-134a in ISO 170 POE

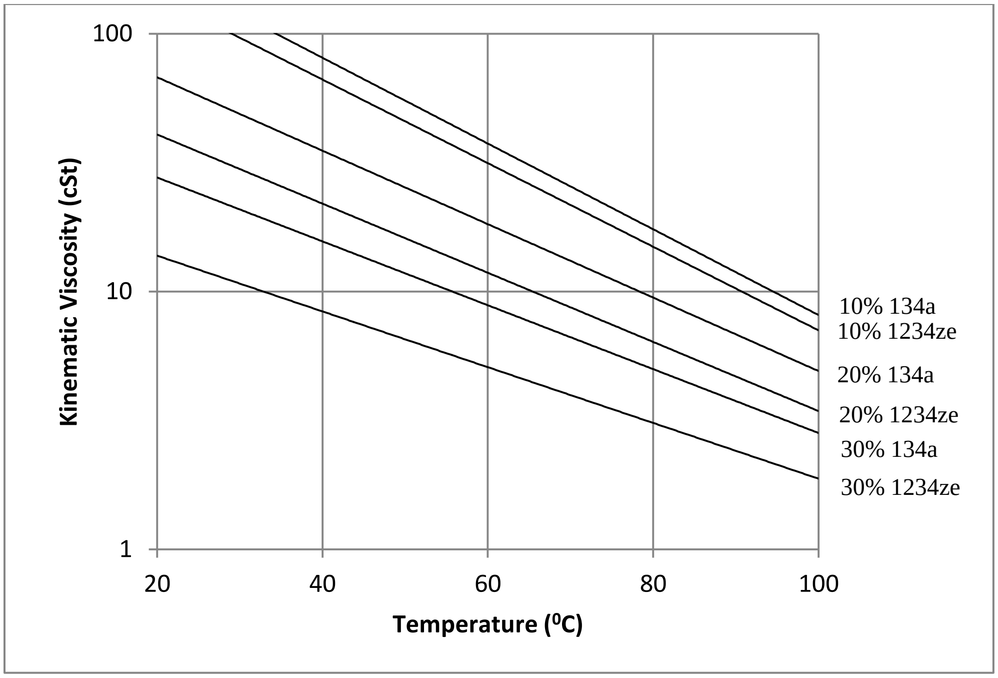

Figure 2: Working viscosity comparison of HFO-1234ze and R-134a in ISO 170 POE

6. Conclusion

Evaluating the interaction of refrigerants with lubricants is essential to providing a system that is stable and maintains the highest level of performance in operation. Parameters of stability, miscibility, solubility and energy consumption are part of the investigation into the compatibility of lubricants with refrigerants. It is important to consider these parameters along with others like environmental and safety aspects.

Lower GWP refrigerants like carbon dioxide and ammonia have been in use for a number of years in various applications and lubricant choices have been investigated for what benefits they can bring to the application.

R32 refrigerant even though its GWP value is higher than other refrigerants in this report it is being investigated as an R-22 replacement over R-410A in some regions. Initial evaluations indicate the need for further refrigerant and lubricant interaction tests.

Hydrocarbon refrigerants like R-600a and R-290 are currently being used in the field with mineral oils but synthetic lubricants have been identified that can provide benefits to overall system efficiency and reliability.

HFO refrigerants like HFO-1234yf and HFO-1234ze are new to the stationary refrigeration and air conditioning markets and require the same level of refrigerant and lubricant evaluation that has been conducted throughout the history of this industry. Further investigation could be needed into stability of the refrigerant, lubricant and system along with making correct lubricant choices to provide the needed lubrication and highest system performance.

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