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Research Paper

Selection of lubricant oils for high temperature heat pumps: A review and selection methodology guidelines☆

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ABSTRACT

Lubrication is key to the performance and reliability of high-temperature heat pump systems. The primary function of the oil is to lubricate and protect the compressor. In addition, it also provides cooling of the parts heated by friction, a seal against working medium gas leakage, removes impurities, and reduces the noise produced by the moving parts. To fulfil these tasks the lubricant oil must have the required properties, in particular viscosity, which is temperature and pressure dependent and is impacted by the solubility and miscibility between oil and working medium. There is limited literature dedicated to a concrete selection methodology of appropriate lubricant oils for high temperature heat pumps operating with different working media. The objective of this work is to fill this gap and provide a guiding methodology for the selection of appropriate lubricant oils for these applications. A systematic selection methodology is proposed which involves tribology and chemistry studies, along with wear tests to determine the lubricity properties of oils and their mixtures with working media. In addition, based on an extensive literature review, an overview is given of the most suitable lubricant oils for a given working medium.

1. Introduction

Heat pump technology is a promising option to decarbonise industrial heat demand and to help achieve the worldwide goal of net zero emissions by 2050 [1–5]. Heat pumps will upgrade waste heat to usable temperature levels and therewith reduce the energy input to industry. For industrial applications, it is essential to develop heat pumps capable of achieving high temperatures (> 100 °C) [6,7]. Compression heat pumps (CHP) are a common technology based on reverse Rankine cycle and are widely used in domestic and industrial refrigeration applications, as well as heat pump applications [6–9]. CHP use a working medium that upgrades heat from a low temperature heat source to a high temperature heat sink. This working medium changes phase during the thermodynamic (reverse Rankine) cycle. A schematic and a pressure-enthalpy diagram describing the thermodynamic cycle of a CHP are shown in Fig. 1.

A basic CHP consists of four components: evaporator, condenser, expansion valve, and a compressor. The condenser and evaporator are heat exchangers where heat is exchanged between the heat pump system and the external heat sink and heat source, respectively. The compressor uses electrical power (Pe) to compress the low temperature working medium vapor leaving the evaporator to high pressure and temperature (step 1–2). The high temperature working medium vapor enters the condenser where it rejects heat Q_{out} by condensation to the heat sink at high temperature T_H (step 2–3). The working medium then leaves the condenser as high temperature and pressure liquid and enters the expansion valve where its temperature and pressure drop (step 3–4). At low-temperature and pressure the liquid working medium enters the evaporator where it absorbs heat Q_{in} from the heat source at low temperature T_L by evaporation at low pressure and leaves as a low-temperature vapour. The result of the cycle is that waste heat is pumped from the heat source to the high-temperature heat sink using electrical power. The operating temperature range is primarily determined by the selection of the working medium, the cycle design, and the choice of the compressor type.

A CHP is a proven technology for temperatures up to 100 °C, and

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ongoing research aims to increase the sink temperature to 150 °C for what are considered high temperature heat pumps (HTHP) [2]. However, for much higher temperatures, beyond 150℃, this technology starts to suffer from limitations due to the lack of appropriate working media [2] and appropriate compressors for high temperatures [10]. These limitations include unstable working fluids at high temperatures or working fluids with Global Warming Potential [4], and the challenge of designing compressors for high temperatures with correct tolerances. The major limitations are the critical point of the working media and the compressor operating constraints at high temperature levels and pressures [10–15]. Lubrication of the compressor at high temperatures is one of the critical issues and requires specific demands on the lubricant oils. It is pointed out that the safety limit to avoid oil degradation is 180 °C for most of the commonly used lubrication oils in compressors [13].

Lubrication is crucial for proper operation of the compressor and for the efficiency and the performance of the heat pump. Lubricant oil is required for the lubrication of the compressor, expansion valve, and other moving parts. It must have the required characteristics, particularly in terms of viscosity, which is temperature and pressure dependent. Additionally, the solubility of the working medium in the oil significantly affects its lubricating properties (viscosity) and heat pump capacity, as the dissolved working medium will remain in the liquid state and will not be available for the thermodynamic cycle. The result is a reduction of the heat pump's thermal capacity and the Coefficient of Performance (COP). The main function of the oil is to reduce frictional wear of moving surfaces, including bearings and other moving parts of the compressor. In addition, oil also provides cooling of the compressor, removes debris, and provides a seal against working medium gas leakage. The oil also reduces corrosion, deposits, and the noise produced by the moving parts. Poor lubrication can lead to the compressor damage [16].

There are several interdependent variables to be considered with the heat pump design: compressors, bearings, working media and lubricant oils. The aim during the heat pump design and working media/oil selection is to evaluate and select the optimal combination for a given application. Briefly stated, the choice of the working medium is dictated by the operating conditions of the CHP, and the lubricant oil is chosen to meet the interaction requirements of stability, compatibility, miscibility, and solubility with the working medium. This is supported by a tribology study which determines the required lubrication for the moving parts, bearings, materials, and surface finish used in the compressor design to realize the required minimum oil film thickness [10,17].

A wide variety of lubrication oils exists. In addition to the traditional mineral oils (MO), synthetic oils like Polyolester (POE), polyalkylene glycol (PAG) and polyalphaolefin (PAO) are important for different CHP applications. The chemistry of the oil/working medium mixtures determines the influence of viscosity, solubility and miscibility on the operational suitability of a lubricant oil. For example, a highly soluble refrigerant in the oil decreases the working viscosity for the compressor and a low solubility or partial immiscibility (liquid–liquid separation) results in oil accumulation in the system components. Ultimately, this results in not enough oil returning to the compressor and thus a risk of mechanical damage. Moreover, accumulation of oil in heat exchangers degrades the thermal performance [18,19]. An optimum solubility and miscibility of oil and working medium mixture is therefore necessary to prevent oil accumulation and to guarantee the return of oil to the compressor [18].

Despite the growing interest in HTHP, there is a notable lack of literature addressing systematic methodologies for selecting suitable lubricant oils for specific working media. Existing studies typically explore individual lubricant-working media combinations, but to our knowledge, no comprehensive review provides guidelines for selecting appropriate lubricants across various working media for HTHP applications. Although Bock [20] offers an overview of lubricants for refrigeration systems with different working media and compressors, a dedicated discussion on HTHPs remains absent. In general, the compressors supplier's choice the oil for a given compressor by considering the viscosity, viscosity index, oxidation and rust issues, and foaming problems with less attention to the solubility and miscibility issues and their effects on lubricity and performance.

This paper aims to address this gap by proposing a concrete guiding methodology for selecting suitable lubricant oils for HTHPs based on their compatibility with different working media. Additionally, an overview of relevant literature concerning lubricant selection for compression heat pumps will be provided to support the proposed methodology.

The remainder of this paper is organized as follows: Section 2 gives an overview of the heat pump system. Section 3 discusses the functions and types of lubricant oils. Tribology is discussed in section 4. Section 5 is dedicated to the characteristics of the lubricant oil and the chemistry study. Section 6 is concerned with lubricity tests. The selection methodology is presented in section 7. Lubricant oils additives are discussed in Section 8. An overview of appropriate lubrication oils for working media for HTHP is presented in section 9. Conclusions are drawn in section 10.

2. Heat pump system

This section discusses the working media, the compressor, and the oil management system, using the basic premise of a heat pump cycle shown in Fig. 1.

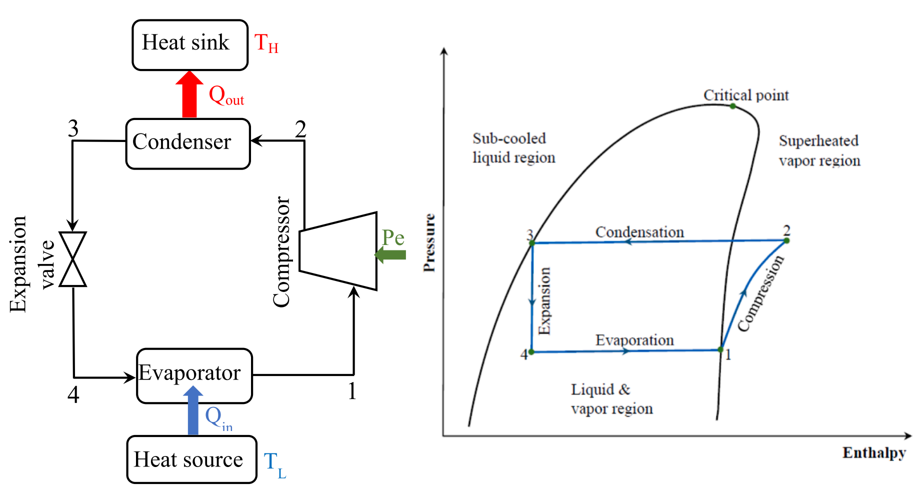


Fig. 1. Schematic of a compression heat pump (left), p-h diagram of the compression cycle (right).

2.1. Working media for high temperature heat pump

In principle, any chemical substance which can undergo a liquid–gas phase change at acceptable pressure and temperature conditions can operate as working medium for a CHP [21–25]. Several working media can be used for HTHPs, and many theoretical and experimental studies have been carried out to help select which is the most appropriate [21–26]. It is concluded that from a theoretical point of view an adequate HTHP working fluid for a subcritical cycle would have a critical temperature significantly higher than the targeted condensation temperature. It would also have a low boiling point, consequently ensuring a small volumetric flow after the evaporator to keep the compressor size reasonable. The working media can be divided into three categories: natural working media and synthetic working media (Hydrofluoroolefins (HFOs)/Hydrochlorofluoroolefins (HCFOs)), or a mixture of the two [25–27]. Mixtures can be used to improve the COP of the HTHP if large temperature changes (glides) in the heat source and/or heat sink exist [27–33]. A detailed historical review on the evolution of working media, from early uses to the present, and the potential future working media considering the existing and future regulations is given in [32]. It is worth noticing that the choice of the working medium sets the conditions on the design of the compressor and the oil selection. Thermodynamic properties of the working medium determine the load on the bearings in the compressors via the pressure difference and compression ratio between high and low side of the compressor. The solubility of the working medium in the lubricant oil will affect the working viscosity which influences the choice of the type of bearing and required viscosity of the lubricant oil [17].

2.1.1. Natural working media

HTHPs using natural working media as working fluid have gained particular interest in recent years due to their low Global Warming Potential (GWP). The usual natural working media are hydrocarbons (HCs), CO_2, ammonia, and water.

- Hydrocarbons

The most applied HCs for HTHP are Butane (R600), Isobutane (R600a), Pentane (R601), and their mixtures. The HCs have good thermodynamic properties and are less harmful for the environment (Ozone Depletion Potential (ODP) = 0, GWP < 10) but are flammable and thus introduce safety concerns.

- Ammonia (R717)

Ammonia is widely used since the 1920′s. It has good thermodynamic properties and an ODP of 0 and GWP < 1, but is toxic and flammable. It is especially applied in large industrial refrigeration plants where it often outperforms synthetic working media. It is also the common working medium for sink temperatures below 90 °C.

- Water (R718)

Water is the most natural, safe, and the least expensive working medium. It has good thermodynamic properties and offers a high potential for applications in HTHP given its high critical temperature of 374.15 °C and its high latent heat. Being a dry compression medium, high superheat is obtained after compression, which can be counteracted by water injection. Its atmospheric boiling point is 100℃, requiring evaporation at under vacuum in case of heat source temperatures above 100℃.

- Carbon dioxide (R744)

Carbon dioxide is an inert, non-toxic, non-flammable, safe, and chemically stable gas. Regarding its thermodynamic properties, it has high conductivity, high specific heat at a constant pressure, and considerable density in a gaseous form (a high volumetric heat capacity). This results in compact systems, reducing investment costs. Carbon dioxide is an appropriate working medium for applications for HTHP [34–37]. However, carbon dioxide has much higher operating pressures than other working media which results in high mechanical stress and load on moving parts and bearings [38–42]. The solubility of CO_2 in oil is another problem related to the high operating pressures and temperatures [38]. The temperatures in condenser and compressor exceed the critical temperature of CO_2 (31 °C) so that the cycle becomes a *trans*-critical cycle. This affects the CO_2/oil solubility at high working pressure in CO_2-systems. The low critical temperature introduces several technical challenges [38–42].

2.1.2. Synthetic working media

Synthetic working media (HFOs and HCFOs) have low GWP (< 20) and are a replacement for HFCs which are prohibited by F-gas regulation and the Kigali Amendment to the Montreal Protocol [43,44]. The tetrafluoropropene series (R1234yf, R1234ze(Z), and R1234ze(E)), and exafluorobutene working media (R1336mzz(Z) and R1336mzz(E)) are the most studied HFOs for applications in HTHPs. HCFOs like R1233zd (E) and R1224yd(Z) contain chlorine and thus have a non-zero ODP, but their short life results in a negligible impact on the ozone layer. Although synthetic working media are still widely used today, their degradation products (e.g., PFAS) have a global warming and/or carcinogenic potential and will possibly be banned in the future according to [34–39]. The use of HFOs has been steadily growing, increasing from 6 % to 24 % of total fluorinated gas volumes between 2016 and 2019 [45].

Several countries are now exploring the possibility of banning HFOs. French Senate recently passed a law to ban products which contain PFAS by 2026 [46]. A proposal is prepared by authorities in Denmark, Germany, the Netherlands, Norway and Sweden and submitted to ECHA [46]. It aims to reduce PFAS emissions into the environment and make products and processes safer for people. EU could ban the production and use of PFAS in the next years to reduce the risks to humans and the environment [47].

2.1.3. Working medium mixtures

A mixture can behave either as a pure working medium (azeotropic mixtures), or differently (non-azeotropic, or zeotropic) [48]. These mixtures can have higher COP than pure working media if there is a temperature glide at the source and/or sink [49,50].

- *Azeotropic mixtures*

Azeotropic mixtures are a mixture of two or more working media which evaporates and condenses at a constant temperature and given pressure [51]. In this sense, azeotropic mixtures behave like pure working media in all practical aspects.

- *Zeotropic mixtures*

Zeotropic mixtures are mixtures of working media with different boiling points [52–54]. During evaporation, the most volatile component will boil off first and the least volatile component will boil off last. The opposite happens during condensation. This leads to a temperature glide during evaporation and condensation. In practice, the saturation temperature at the inlet of the evaporator will be lower than at the outlet. In the condenser, the saturation temperature at the inlet will be higher than at the outlet.

This temperature glide occurring in these mixtures can be beneficial. Due to the limited volumetric heat capacity of the waste heat streams like air, water and gases, temperature glides do exist in the evaporator. Pure working media have a constant temperature during evaporation which results in a loss of exergy and a degradation of the COP caused by large temperature differences between the working medium and waste heat stream. This can be avoided by using zeotropic mixtures with a temperature glide due to the different boiling points of each mixture component. The perfect glide matching will significantly reduce the exergy degradation in the heat exchange process [54]. This is represented by the Lorenz-based cycle, the ideal cycle for zeotropic mixtures that can achieve improved performance compared to the Carnot cycle. The same phenomenon occurs at the condenser side if the process sink shows a temperature glide.

2.1.4. Working medium selection for HTHP

The properties of working media that are fundamental for the selection of appropriate working media for HTHP applications are:

- *Coefficient of performance*: The amount of heat that is produced at the high-temperature sink side related to the amount of compressor work needed.
- *Volumetric heating capacity*: This is basic for the compressor design to achieve the aimed COP. This determines the volume flow for a given capacity and therewith the size of the compressor.
- *Critical temperature*: For HTHP, the critical temperature must be significantly (20–30 K) higher than the aimed condensation temperature [55] for subcritical cycles.
- *Pressure ratio*: The pressure ratio should be as low as possible to minimize the compressor power. This is determined by the desired temperature lift and the working medium.
- *Pressure level*: The absolute pressure level is essential as high pressure requires higher structural strength and hence high costs. While low pressure level (i.e., below atmospheric) can result in air ingress from the environment.
- *Environmental requirements:* Due to the regulations, the working media must have as low ODP and GWP as possible.
- *Safety:* Toxicity and flammability are safety issues which must be considered.

The choice of working fluid impacts the compressor design, and it is a compromise between maximum system performance and minimum volumetric flow rate [13]. Zini et al. conduct a theoretical analysis to evaluate potential fluids with suitable thermodynamic properties for HTHP's [56]. They concluded from their analysis that maintaining a constant HTHP lift (at 40 K) results in having the highest COP across all fluids when the condensing temperature ranges between 85 % and 90 % of their respective critical temperatures. Another result from their analysis is that natural fluids, including water and alcohols like ethanol or methanol, emerge as promising potential candidates.

The properties of potential high-temperature working media are summarized in Table 1 [57,58]. More details concerning potential working medium for HTHP can be found in literature [2,26].

Table 1
Properties of potential working media for HTHP [57,58].

Working medium	*Type*	P_{crit} *(kPa)*	T_{crit} *(°C)*	*GWP*	*ODP*	*Safety Group*
R1224yd(Z)	HCFO	3337	155.5	1	minimal	A1
R1233zd(E)	HCFO	3624	166.5	1	minimal	A1
R1234yf	HFO	3382	94.7	<1	0	A1
R1234ze(E)	HFO	3635	109.4	6	0	A2L
R1234ze(Z)	HFO	3531	150.1	<1	0	A2L
R1243zf	HFO	3518	103.8	<1	0	A2
R1336mzz(Z)	HFO	2903	171.4	2	0	A1
Ammonia	Natural	11,363	132.4	0	0	B2L
CO_2	Natural	7377.3	31.0	1	0	A1
Water	Natural	22,064	374.0	0	0	A1
Propane	Natural	4251.2	96.7	3	0	A3
Isobutane	Natural	3629	134.7	4	0	A3
Butane	Natural	3796	152.0	4	0	A3
Isopentane	Natural	3378	187.2	5	0	A3
Pentane	Natural	3368	196.6	5	0	A3
R245fa	HFC	3651	153.9	1030	0	B1
R365mfc	HFC	3266	186.9	794	0	A1
R410A	HFC	5782	78.1	6750	0	A1
R134a	HFC	4059.2	101.1	1430	0	A1
R227ea	HFC	2925	101.8	3220	0	A1

2.2. Compressors

The compressor compresses and transports gaseous working medium around the heat pump circuit. The different types of compressors are classified as dynamic or positive displacement compressors [14,59–61], as depicted in Fig. 2. The displacement compressors increase the pressure of the working medium by compressing it to a small volume, whereas the dynamic compressors increase the pressure by accelerating the working medium. The most used types of compressors in HTHP systems are scroll, screw, and piston compressors [14]. All three types are positive displacement compressors. However, the piston compressor is a reciprocating type, and the other two are rotary compressors. These types of compressors can be oil-free, oil-injected, or oil-flooded.

There are other types of compressors that can potentially be used for a HTHP. Centrifugal compressors have been used for HTHP and are now continuously being developed for this application [14]. Another possibility are twin rotary compressors which can be used for sink temperatures in the order of 75 °C. In this report the focus is on compressors that need an oil lubrication system. A comprehensive review addressing compressors for HTHP is given in [14]. Ma et el. addresses the research status of high-temperature and high-pressure compressors with focus on their design and strategies for reducing the discharge temperature of scroll, piston, and screw compressors [6].

Table 2 shows an overview of the normally used refrigeration oils for the different types of compressors. The aim is that in the future a similar table can be made for compressors for HTHPs.

2.3. Oil management system

It is unavoidable that a small fraction of the lubricant oil is discharged with the working medium and circulates through the other components of the heat pump. It is vital that the lubricant oil returns to the compressor by mechanical means (oil separator) or by the working medium flow (solubility) under all operating conditions. The compressor is usually provided with an oil management system [62–66]. The purpose of this system is to confine the lubrication oil inside the compressor and to minimise oil presence in other system components. For example, the presence of oil in the evaporator and condenser would form a thin film of oil which will degrade the heat transfer and consequently the heat pump performance [12]. The oil management system is usually mounted at the discharge line of the compressor to avoid the oil from leaving the compressor. It consists of the following components [62], see Fig. 3:

Oil injector and pump supply the oil pressure needed for the lubrication of the compressor.

Sump is a reservoir which contains the bulk of the compressor oil. The sump is provided with an oil level indicator.

Oil separator separates the oil from the working medium, and the filter function is to remove debris present in the oil.

Oil temperature regulator adjusts the temperature so that the oil has the required temperature and hence viscosity.

There are different types of oil separators based on gas–liquid separation methods which, in turn, depend on the liquid droplets' size distribution in the gas. Oil separators are classified based on the separating mechanisms used. Two types are proposed by Seon et al. [64]: porous and inertial. This classification is based on the collecting method of oil. Porous-type oil separators collect the oil droplets by coalescence via a filter or mesh. The inertial type is based on the density difference between the droplets and the working medium vapour. The selection of a separator is based on a trade-off between separation efficiency,

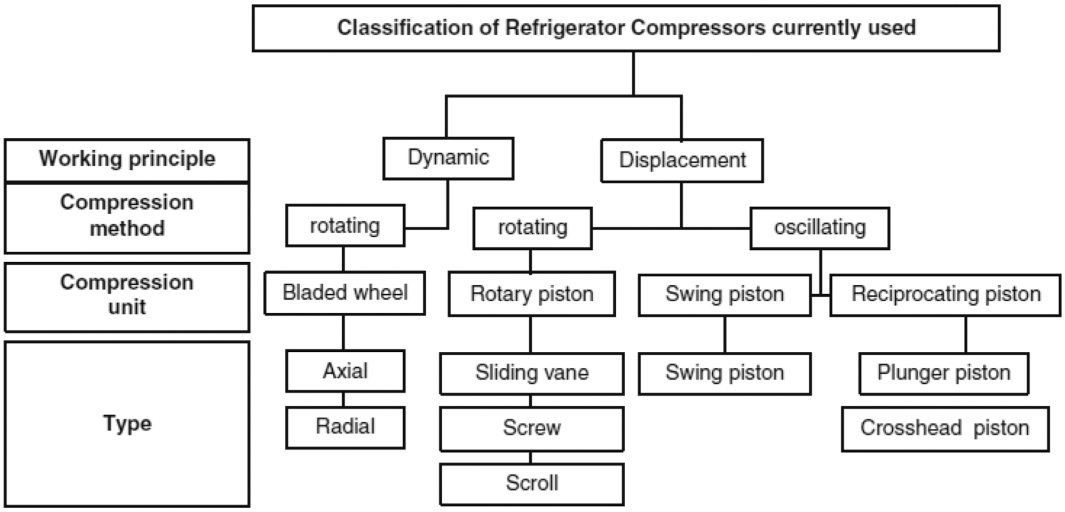


Fig. 2. Classification of refrigeration compressors according to their operation mode [20].

Table 2
Overview of usually used refrigeration oils for different types of compressors [20].

Refrigerant Compressor type	Hydrocarbons (e.g., R290, R600a)	Ammonia (NH3)	FCKW, HFCKW (e.g., R12, R22)	FKW, HFKW (e.g., R134a, R404a)	Drop-In (e.g., R402A, R403A)
Hermetic (e. g., piston)	MO, AB, ISO VG 15–32	–	MO, AB, (MO/AB), ISO VG 15–32	POE, ISO VG 10–32	MO/AB, ISO VG 32
Open piston	MO, AB, PAO, ISO VG 46–100	MO, AB, PAO, PAG, ISO VG 32–68	MO, AB, MO/AB, ISO VG 32–68	POE, ISO VG 32–68	MO/AB, ISO VG 32–68
Semi-hermetic	MO, AB, PAO, ISO VG 46–100	–	MO, AB, (MO/AB), ISO VG 32–68	POE, ISO VG 32–68	MO/AB, ISO VG 32–68
Scroll	MO, AB, ISO VG 46–100	–	MO, AB, ISO VG 32–68	POE, ISO VG 32–68	MO/AB, ISO VG 32–68
Screw	MO, AB, PAO, PAG, ISO VG 68–220	MO, PAO, PAG, ISO VG 32–68	MO, AB, ISO VG 68–150	POE, ISO VG 100–150	MO/AB, ISO VG 68
Turbo	MO, PAO, PAG, ISO VG 68–100		MO, ISO VG 68–100	POE, ISO VG 68–150	MO/AB, ISO VG 68

volume, cost, and pressure drop [65]. The three most used types of separator mechanisms are: impingement (inertial collision), coalescence (filtration separation), and centrifugal. Centrifugal separators are most used due to their simple design while providing acceptable efficiency- most commonly, the centrifugal cyclone separator. More detailed information on the oil separators can be found in [64–66].

As the oil separation efficiency is never 100 %, there is always a small fraction of the oil which will circulate with the working medium through the system. This possibly leads to a reduction in the heat transfer and performance of the system [67,68]. In general, the performance of a heat pump system increases with decreasing amount of unseparated lubricant oil that circulates through the system. The study by Kim et al. showed experimentally the efficiency and the pressure drop of a cyclone oil separator in a heat pump system where PVE oil is used in combination with R410A [67]. They measured five different cyclone oil separators with different heights and diameters and developed empirical equations to predict the efficiencies and pressure drops.

It is worthwhile to notice that enough oil should be used to establish the required lubricant film thickness in the compressor. However, an excess of oil is also detrimental; it can result in slug and damage to the compressor. Kim et al. show that the proper amount of lubricant oil charge in the compressor can be predicted by calculating the amount of oil retention in each component of the heat pump system, for which purpose the mass flow rate of the lubricant is required [67]. That is, to simulate the performance of a heat pump system and to charge the proper amount of lubricant in the compressor, it is necessary to predict the efficiency and pressure drop in the oil separator under various operating conditions.

Based on current and possible future applicability of HTHP's, Table 3 provides potential separation technologies (including non-mechanical separations technologies) for oil-refrigerant separation in a CHP. Relevant Key Performance Indicators (KPIs) of these technologies are given. These separation technologies have a specific distinctive application range, (dis)advantages, and maturity levels.

3. Functions and types of lubricant oils

In this section, the main functions and types of lubricant oils are discussed.

3.1. Functions of lubricant oil

The functions of the lubricant oil are described in the following.

Lubrication: The primary function of the oil is to lubricate and protect the compressor. The oil forms a thin lubricant film to prevent moving mechanical parts from wearing fast [10,69]. The viscosity of the lubricant is a decisive parameter for this process, for which the thickness of the layer is a function. If the viscosity decreases, the layer will be thinner. Decreasing the oil's viscosity reduces the power consumption of the compressor [69,70]. However, to ensure hydrodynamic lubrication, a specific layer thickness is required. Eventually, boundary lubrication will occur as will be explained in Section 4. At this point, the friction is affected by both the oil and the surface of the materials, increasing the risk of wear in the compressor[71,72].

Cooling: The second function of lubricant oil is cooling. During compression, the temperature of the working medium increases and becomes superheated. Part of this superheating is prevented by cooling by the oil, helping the compression process to be an isentropic process and reducing thermodynamic losses [73]. The oil must be cooled down in the oil management system to ensure proper lubricating performance

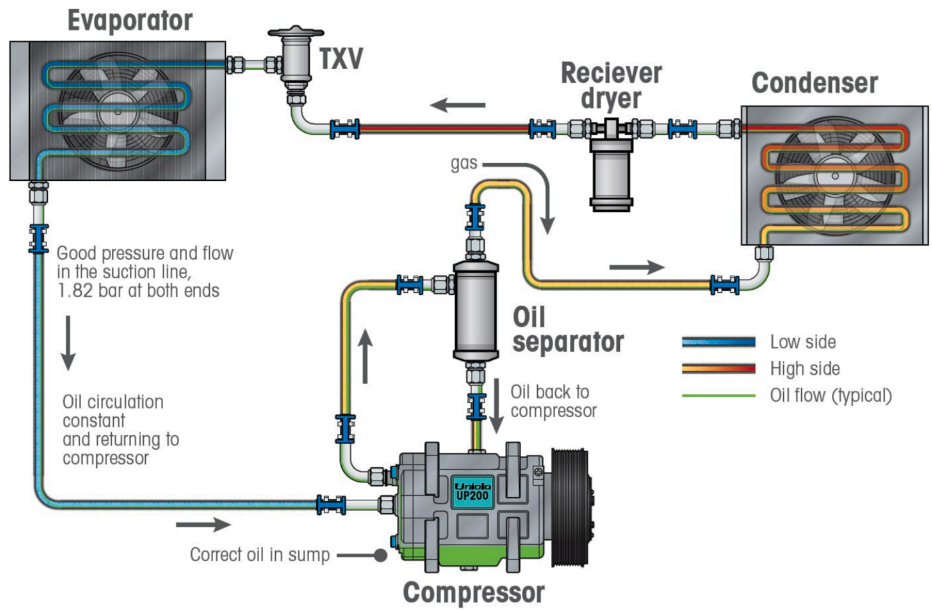


Fig. 3. Illustration of a heat pump system where an oil separation system is used[63].

Table 3
Overview of KPI for gas–liquid separation technologies.

Oil-gas Separation Method	Dropletsizes [μm]	Separation Efficiency [%]	Pressuredrop [-]	Capex [-]	TRL [-]
Mechanical separation • Impingement • Coalescence • Centrifugal	–3000 Down to 0.1 4–1000	> 99 70–99	−/o+	oo	99
Non-mechanical separation • Electrostatic Precipitation • Ultrasound • Membrane Separation • Micro filtration • Ultra filtration • Nano filtration • Adsorption	< 2-?? 0.1–10 0.01–0.1 <0.01 0.1–1	–99.9 < 90 > 95 > 95 > 90 > 90	+ooo -	− + − − -o	3 9* 9* 9* 9*

+ = positive, o = neutral, − = negative
* Membrane separation and adsorption are not used for oil separation from gas. KPIs are given for the use of these separation technologies for oil–water separation.

when reinjecting. The mechanical components of the compressor, such as the bearings, are also cooled by the oil, reducing the risk of failures [69]. The lubricant oil can absorb about 5–10 % of the generated heat during the operation of the compressor [74].

Sealing: There are small cavities between stationary and moving parts in compressors. Back flow occurs through these cavities from high-pressure to low-pressure areas. This phenomenon strongly reduces volumetric efficiency resulting in a loss of work. The oil can fill and seal these cavities, increasing the volumetric efficiency [75].

Purification of the system: The final benefit of the oil is the removal of impurities from the system. In the oil sump, an oil filter is often present to remove impurities that are dissolved and transported by the oil [76].

The HTHP designers need to understand the interaction of the oil with the working medium and its effect on the operation and performance of the system [77]. Depending on the heat pump design, compressor type, and the oil separator efficiency, the oil content in the system can be in the range of 1–5 % mass based [78].

Usually, the oil is selected by the compressor manufacturer. Aspects addressed before need to be considered by the compressor manufacturers during the selection of the appropriate lubricant oil for a given application. These include viscosity, solubility, miscibility, compressibility and density, chemical and thermal stability, low hygroscopicity, thermal conductivity, Dielectric strength, neutralisation number, flash and fire point, compatibility with materials, electrical resistivity, non-deposit forming, and environmental acceptability. Note the parameters dielectric strength and electrical properties of the oil are only relevant in specific cases. Some compressor designs allow the fluids to get in direct contact with the electric motor of the compressor. In this case, a higher electric resistivity of the oil is preferred to insulate the electric motor [79].

3.2. Type of lubricant oils

The basic requirements for the lubrication oil of refrigeration systems for a given working medium are well defined by the standard DIN 51 503-1 [20].

Before the ban of CFC working media in 1990, most heat pump compressors used mineral oils for lubrication. Since then, new synthetic oils have been developed and are now the best choice for most heat pump applications [80–83]. Polyolester, polyalkylene glycol, and polyalphaolefin oils are used for different heat pump applications. Mineral oil and Polyolester are the most used lubricant oils in the refrigeration and air conditioning systems due to their chemical stability, lubricity, and low cost. Oil manufacturers use additives to enhance the oil performance for lubricity improvement, pour point depression, anti-foaming, and for increasing thermal and chemical stability. By balancing a lubricant's formulation, it is possible to specifically design appropriate oils to be used with specific working media for a given application [78]. The following type of oils are distinguished [20,78,80–83]:

- Mineral oils (MO): Dewaxed Naphthenic oils and Paraffinic oils
- Semi-synthetic oils: Mixtures of Mineral Oils and Alkylbenzenes (MO/AB)

- Fully synthetic oils: Alkyl benzene oil (AB), Polyalphaolefin oil (PAO), Polyalkylene glycol oil (PAG), Polyvinyl ether oil (PVE), and Polyolester oil (POE)

MO are dewaxed naphthenic or paraffinic lubricant oils [69,78,81] which are derived from the refining of crude oil. These oils are suitable lubricants for heat pumps for low-temperature ranges as they provide good viscosity and high compressor efficiency. Due to their low cost and availability, they are the traditional lubricants used in refrigeration. Mineral Dewaxed Naphthenic oils are compatible with CFCs, HCFCs, and ammonia [20,80–83]. MO oils have low pourpoints, good cold flowing as well as high thermal and chemical stability. However, due to the low-temperature range and their tendency to have poorer thermal and oxidative stability compared to synthetic oils, mineral oils show limited potential for applications in HTHP.

MO/AB are mixtures of highly refined naphthenic mineral and highly stable alkylbenzenes oils. The presence of alkylbenzenes greatly improves the solubility and thermal stability of the naphthenic components. The proportion of synthetic components is usually between 30 % and 60 %. Semi-synthetic oils are recommended for CFC/HCFC systems [20].

AB oils are based on chemically and thermally stable alkylbenzenes. They show excellent solubility in CFC (HCFC) working media and mixtures thereof. They are especially suitable for heavy-duty ammonia compressors with very high outlet temperatures [20]. AB oils are also suitable for hydrocarbons and their mixtures (propane/isobutane).

PAO oils are suitable for ammonia compressors due to their good thermal stability. The formation of oxidation products (coke) is avoided even at high compressor outlet temperatures. Compared to mineral oils and particularly in the case of screw compressors, the use of PAO can reduce the amount of oil mist and oil vapor which collects in oil separators. The amount of oil in the working medium vapour can also be minimized. PAO display good viscosity-temperature behaviour and thus good low temperature flowing characteristics. The low pourpoint and low viscosity of these oils guarantee satisfactory oil return [20].

POE oils have good thermal and chemical stability. They are suitable for systems with CFC, HCFC, HFC, or HFC due to their miscibility. However, POE oils are hygroscopic, thus absorbing water vapour quickly.

PAG oils are polar which makes them very hygroscopic (c.f. Fig. 10). They are compatible with natural working media.

Each type of synthetic oil has a given specific characteristic tailored for specific applications, making them suitable for use in different applications [78]. In general, synthetic oils are typically more expensive than their mineral counterparts. Some synthetic oils are more environmentally friendly due to better biodegradability and less toxicity.

4. Tribology

As discussed in section 2.1, the selection of the working medium for a given application will set conditions on the design of the compressor via temperature conditions and compression ratio [17]. This will lead to the choice of the required type of bearing, choice of materials, surface finish, and the required viscosity of the lubricant to achieve sufficient lubrication films. Tribology, the study of rubbing between surfaces in contact with relative motion is used to reduce friction, improve the efficiency, and extend the life span of mechanical systems. Friction is the resistance to relative motion, wear is the loss of material due to that motion, and lubrication is the use of a fluid to minimize friction and wear. There are different types of friction: static friction, rolling friction, kinetic friction, sliding friction, etc [10,79,84–93]. Similarly, there are different types of wear, such as abrasive wear which appears when a hard, rough surface slides over a softer surface or adhesive wear, which is caused by debris between surfaces. Erosive wear occurs when solid or liquid particles impinge against a surface. Surface fatigue occurs as a surface is weakened by cyclic loading. Tribology therefore illustrates how wear evolves in time under operational conditions, under known surface roughness.

The first step for the choice of the lubrication oil is to determine the type of surface contacts, type of material, friction type, and potential wear which might occur [84–86]. There are several techniques which are used to characterize the surfaces depending on the need for tribological applications. Techniques like light microscopy, SEM, SIM, Auger, XPS, and AFM and other methods are used [85]. The ratio of the lubricant film thickness to the surface roughness is called λ. The wear regimes are based on this ratio [10,84]:

- $\lambda < 1.2$ is boundary lubrication,
- $4.1 < \lambda < 3$ is thin (or mixed) film lubrication,
- $\lambda > 3$ is full film hydrodynamic lubrication,

A Stribeck curve is a plot illustrating the frictional characteristics of a lubricant oil, under conditions such as boundary, mixed and hydrodynamic regimes as shown in Fig. 4. Each of the regimes is defined by the λ ratio as discussed before. The Stribeck curve plays a firm role in evaluating the effect of a change of the lubricant's viscosity due to working media, or due to lubricant's additives, and the effect of surface roughness. The Stribeck curve shows the friction coefficient as a function of speed, viscosity and load. The lubrication regimes for the different bearing types are also indicated in the Fig. 4.

The optimal lubrication is essential for long-term operation and efficiency of the compressor. Fast running machines require lower oil viscosities than slower running machines, while high bearing loads require higher viscosities than those with lower loads [20]. Operating experience has shown that refrigerator compressors require much lower viscosities than those calculated from the hydrodynamic lubrication theory [20]. It is important to recognize that the working medium will dissolve in the oil, and it will influence the working viscosity.

A tribometer (or wear tester) is generally used to generate the Stribeck curve [10,84]. There are different types of tribometers [38,84,92–98] which can be used for the determination of the lubricity characteristics of oil/working medium mixtures like pin-on-disc [94–96] and block-on-ring [95–97]. The choice of the type of tribometer depends on the type of compressor, type of bearing and wear in the system. These tribometers simulate the normal working conditions of the compressor parts by setting the temperatures, the contact pressures, and contact speeds. The elements used in the tribometer are made of materials used in compressors (i.e., aluminium, cast iron). Most of the tribological studies concern oils/HFCs mixtures and there are few studies related to oils/HCs mixtures.

An illustration of a block-on-ring tester is shown in Fig. 5. Gorny et al. used a block-on-ring setup under the operation conditions of the compressor to determine the lubricity properties of POE/R134a and MO/R290 mixtures [99,100]. The tribological wear tests help to determine the best oil/working medium mixture with the best lubrication properties (viscosity) among the tested oils/working media combinations. The mixture with the best lubrication properties leads to the least amount of wear caused by the same load and operating conditions [100]. It is worth noticing that most of the wear in the compressor occurs during the start and stop phases.

As an example, Fig. 6 shows the wear volume for three different POE oils with the same viscosity grade but from different suppliers. POE1 is the superior lubricant as the wear volume is the lowest. When mixtures of these oils with R134a are used as lubricant the viscosity decreases resulting in higher wear for the same operating conditions [98]. This shows the importance of the wear tests for the mixtures oil//working medium to effectively determine the effect of the working medium on the lubricant oil properties.

Drees et al. also used a standard block-on-ring method like the one shown in Fig. 5, but with an added pressure chamber to evaluate the effect of CO_2 on the lubrication properties of POE and PAG oils at high pressures [38]. These tests are of interest as systems using CO_2 are in a *trans*-critical state at high pressures. This requires special synthetic oils

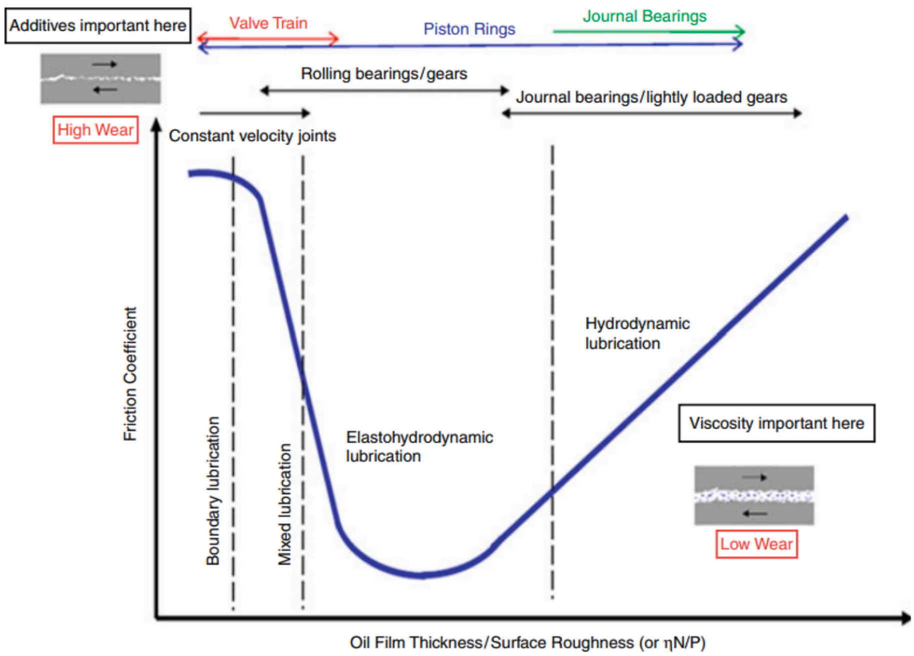


Fig. 4. Stribeck curve [79].

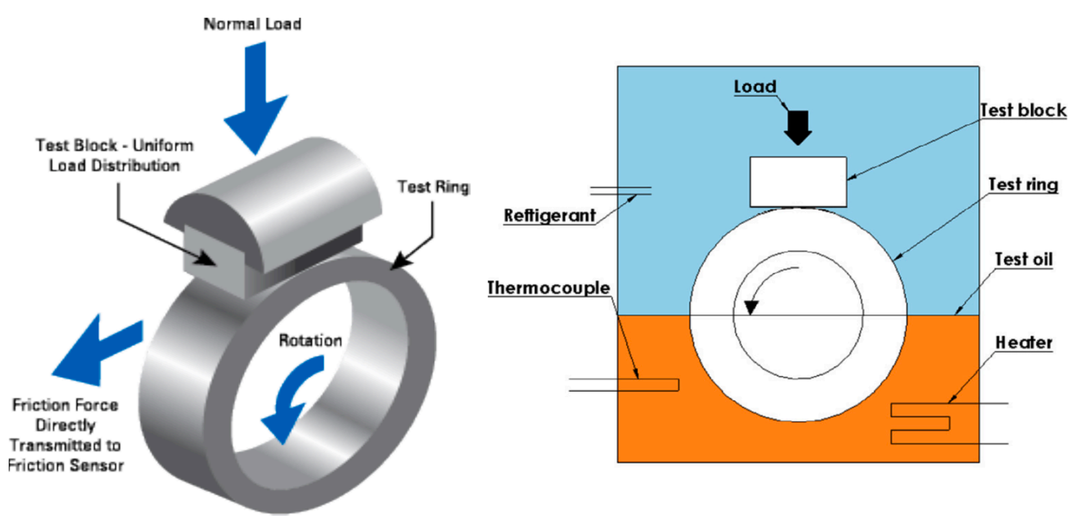


Fig. 5. A CAD-illustration of a block-on-ring wear tester (left) [101] and an illustration of the one used by Gorny et al. (right) [100].

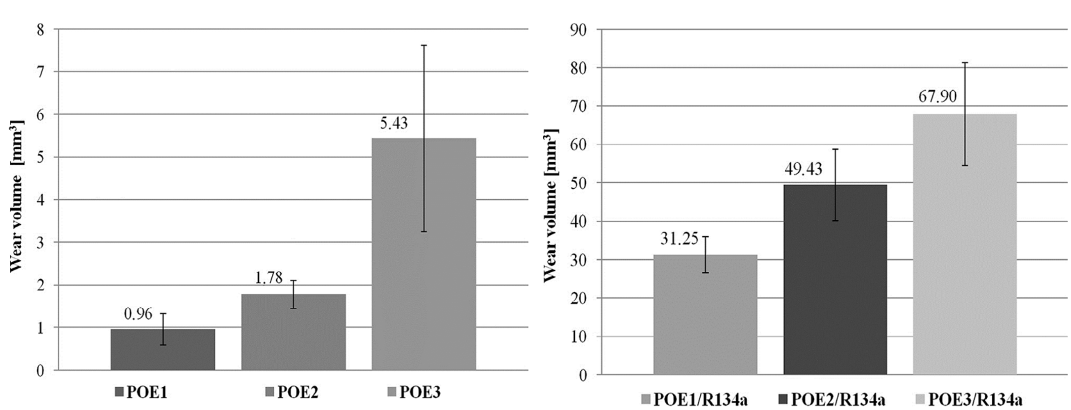


Fig. 6. Wear volume results after the tests with only POE oil and with POE/R134a mixtures [98].

due to high bearing loads. It is known from solubility experiments that the dissolution of CO_2 in synthetic oils significantly decreases the viscosity of the pure oil. POE oils show good miscibility while PAG oils are less miscible with CO_2 (c.f. Section 9).

5. Characteristics of the lubricant oil and chemistry study

As indicated previously, the following parameters must be considered when selecting the correct lubricating oil for a high-temperature heat pump compressor.

5.1. Viscosity

As discussed in Section 4 Tribology, the thickness of the oil film is the major factor which characterizes the load-bearing ability of the lubricant oil. The viscosity of the lubricant determines the thickness of the oil film. The oil viscosity is a measure of the resistance to flow and depends on temperature and pressure. At lower temperatures, oils become thicker and thus gain viscosity which impacts the compressor performance and reliability [88]. High viscosity leads to degradation of the compressor efficiency as the oil cannot flow adequately to provide effective lubrication, and wear can occur due to lubricant starvation in the bearing system. An adequate viscosity is therefore necessary to maintain a sufficient lubricant film thickness for hydrodynamic lubrication [69,70] and avoid wearing out the compressor. Lubricant oils are classified as a function of their viscosity into ISO viscosity classes. DIN 51519 defines 18 different viscosity classes from 2 to 1000 mm^2/s at 40 °C [78].

5.2. Solubility

Solubility is the capability of working media to dissolve in an oil by the interaction between the liquid oil and the vapour working medium. It is generally described as the mass fraction of working medium in oil. The working medium is an effective solvent and provides various levels of solubility in the lubricant oil that changes the viscosity of the lubricant more than the temperature alone. Ammonia, as an example, has very low solubility in nearly all oils, except POE [82]. Furthermore, when it is highly soluble, the working medium can migrate to the oil sump which increases the risk of foam forming. The working medium dissolved in the oil significantly reduces the viscosity, improving oil fluidity and minimizing the negative influence on heat transfer in heat exchangers [102].

Both the change of viscosity (or the working viscosity) and the pressure associated with the solubility need to be considered when designing the bearings in a compressor. These variables are also the most significant parameters to consider between each lubricant/working medium combination when changing the chemistry of the working medium, lubricant, or viscosity grade of the lubricant oil [103–108].

The high pressure and temperature in the compressor will cause a decrease in oil viscosity (linked to the solubility of the working medium in the lubricant), which would affect wear protection if the viscosity at the application conditions is not adequate. The effect of the viscosity decrease can be mitigated by selection of the appropriate lubricant oil [78,109]. The selected oil must be viscous enough to provide good lubrication at the highest temperature but not so viscous that it will not flow at the lowest temperature: this is referred to as its 'pour point' which is the lowest temperature at which an oil will pour or flow, as measured using the standard ASTM D-97 test [78,81].

Oil evaporation and dissolving in the working medium fluid can cause problems such as clogging and reduction of heat transfer [110]. The solubility of the oil in the working medium can significantly impact the performance of the condenser and evaporator via the increase of the resistance of the heat transfer, the change of the thermodynamic equilibrium between the vapour and liquid phases, the flow field pattern, and the increase of the pressure drop [111–113]. Ribeiro et al reported a decrease of the capacity and an increase of the power input with increasing oil circulation ratio (OCR) [112]. Several studies have confirmed that the oil level in sump strongly affects the oil supply in high-back-pressure compressors [113–117]. The oil discharged from the compressor with the working medium will affect the oil level resulting in an insufficient oil supply. It is also demonstrated that oil in heat exchangers affects the pressure drop, flow pattern, and coefficient of heat transfer [118–125]. Excessive solubility decreases the oil viscosity and causes lubricant oil carry-over and foaming [126,127].

5.3. Miscibility

The miscibility is the ability of two liquid substances to mix and form a homogeneous mixture, independent of the conditions and concentrations [79]. The miscibility in this case concerns the interaction between liquid oil and liquid working medium. When there is good miscibility between the working medium and the oil, any oil that is carried into the cycle will come back easily with the working medium. In Fig. 7, a miscibility gap diagram illustrates under which conditions of temperature and concentration the two fluids are miscible. These characteristics are experimentally determined in glass tubes where different concentrations of oil-working medium are mixed and evaluated at different temperatures, as shown at the right-hand side of Fig. 7.

The miscibility is key for the oil transportation throughout the system. If the two fluids are immiscible, the transportation of oil deteriorates. Phase separation can cause deterioration of performance of the evaporator and condenser [89]. The result is that oil can accumulate in the system, and the compressor can run out of oil [80]. Phase separation can also lead to malfunctions in oil separators and decrease the performance thereof [89]. For any given working medium, the percentage that can be dissolved into the lubricant oil depends on the degree of miscibility of the working medium, the pressure of the working medium vapor, the temperature of the lubricating oil, and the duration of contact.

Fig. 7 shows the miscibility diagram of R134a and a POE oil [78]. In this example, glass tubes are filled with mixtures with different concentrations of the working medium (2–48 %) and they are tested over a temperature range (−60 to120 °C). Tubes with phase separation are in the shaded region and the tube with one phase (full miscibility) are in the unshaded region. Another example of miscibility test is shown in Fig. 8.

Miscibility is the most difficult parameter to evaluate due to the large range of operational conditions. However, heat pump manufacturers use the miscibility to determine the effect on the system performance via proper heat transfer in the heat exchangers [77,81]. The poor flow of the oil through the heat exchangers can degrade the system performance [71,77]. The presence of liquid or two-phase working fluid at the compressor suction should be avoided to prevent reliability issues and mechanical damage, such as liquid hammer, oil dilution leading to wear and erosion. Still, some heat pump systems operate with wet compression, though they are still far from commercial availability. For this reason, miscibility requirements are defined based on the evaporator temperature and distance between the compressor and heat exchangers.

The lubricant/working medium concentration is the dominant parameter for the miscibility required to achieve the required compressor and system performance. Lubricant concentration in the range of 10–20 % in the working medium is in some sense the rule [79]. This is based on the criteria that when a lubricant/working medium mixture is cooled, the highest point temperature between one phase (miscible) and two phases (immiscible) can usually be found in that range. This point is called the upper critical solution temperature (UCST), indicated with the red dot in Fig. 7. The lower critical solution temperature (LCST) can also be defined within this concentration range when moving from lower temperature to higher temperature as given by the green dot in Fig. 7. The LCST is usually not as important in operation as the UCST because UCST is usually the high temperature/pressure side

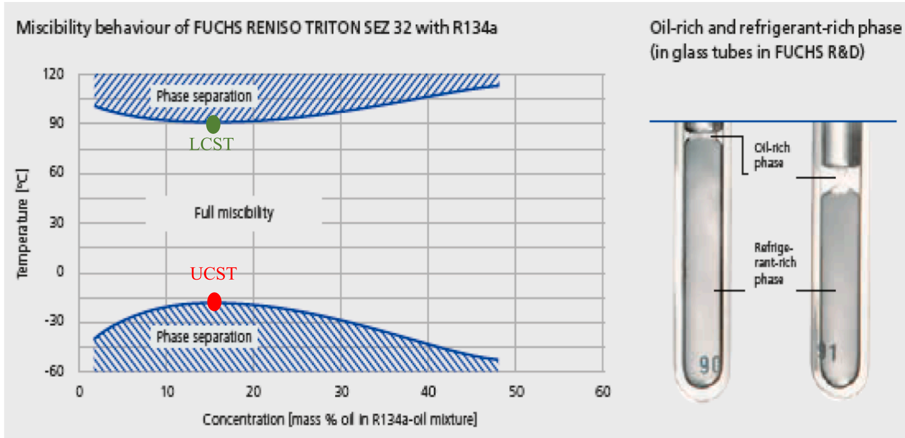


Fig. 7. Miscibility of R134a and POE oil [78].

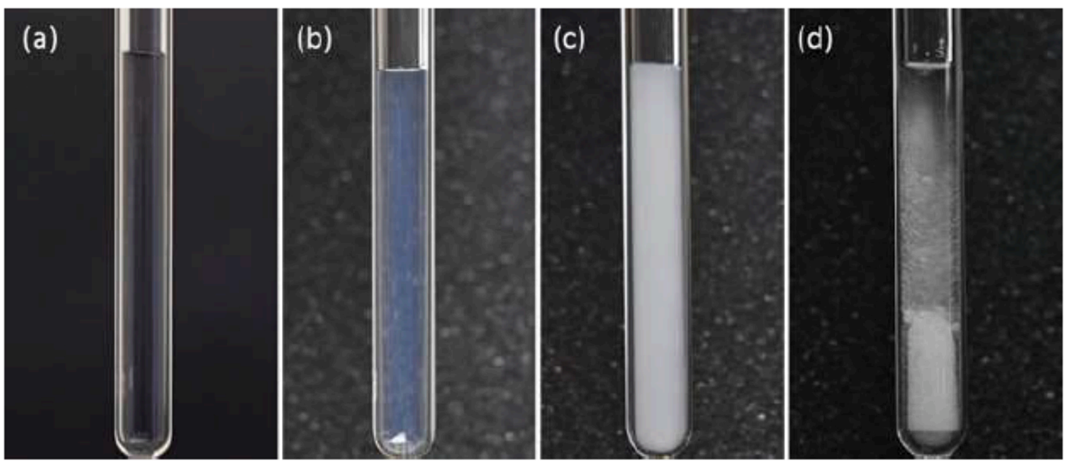


Fig. 8. Different miscibility behaviours of an oil/working medium mixtures in glass tubes [129].

of the system with higher temperatures that lower the viscosity of the lubricant in the system, thus allowing it to flow more easily.

There is always a need to measure the miscibility of each lubricant and working medium. Popovic showed how system capacity and efficiency are affected by miscibility and solubility by considering different combinations of lubricants and working media [104]. It is concluded that the lubricant miscibility's influence on the system performance is mainly due to its effect on the evaporator performance, rather than the compressor performance. Oil lubricant forming a one-phase solution with the working medium facilitates the control of the oil circulation rate and minimizes the negative effect on the heat transfer [73,128].

Barthel et al. study the miscibility behaviour of different oil/working medium mixtures, and they generate Daniel plots [129]. Fig. 8 shows an example of their study which illustrates different miscibility behaviours of the oil/working medium mixtures in glass tubes. The mixture spectrum varies from excellent miscibility (a) through to poor miscibility (b-c) to separation into two phases (d). The aim is to have a one stable phase as shown on the left-hand side of Fig. 8.

Takaki et al. [130] experimentally evaluated the chemical stability of two POE's and one MO oil in combination with R290. The study consists

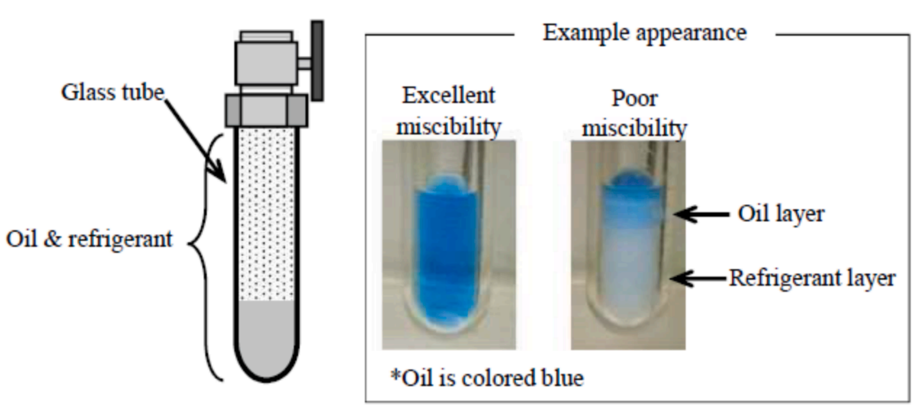


Fig. 9. Illustration (left) and picture (right) of the determination of the phase separation temperature [130].

of determining the miscibility, solubility and viscosity of the oil/R290 mixtures, phase separation temperature, the stability, and a tribology test using a block-on-ring test setup like that shown Fig. 5. The results of the study indicate that one of the POE-oils shows excellent practical performance in combination with R290. Fig. 9 shows an illustration of the test used for the determination of the phase separation temperature.

In summary, the working medium and the oil are miscible if only one phase exists in a glass tube (Fig. 8a). Immiscibility means phase separation into oil phase and working medium phase (Fig. 8c), which negatively impacts oil transport as oil will accumulate in the system and the compressor may run dry. Poor miscibility also has a negative effect on the heat transfer as oil in the heat exchangers can form an insulating oil film which increases the thermal resistance and hence decreases the system performance.

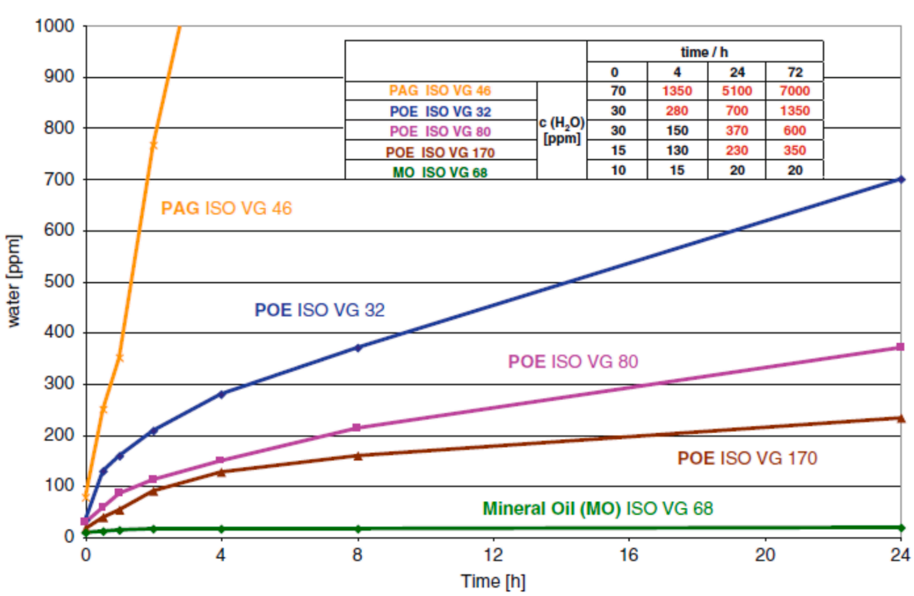
5.4. Stability and compatibility

The thermal and chemical stability of the oil and its material compatibility are essential. It is required that oil is thermally and chemically stable including additives at the heat pump operating conditions. The thermal stability of the lubricant oil has to do with its exposure to high temperatures over a longer period. This can lead to a complex decomposition reaction with undesired reaction products. This reaction can be activated by metals like copper, iron, and aluminium. For applications in HTHPs, the high temperatures can cause thermal decomposition of the oil and the formation of undesirable products. Ageing stability is also a selection criterion. To accelerate these kinds of tests, an increase in temperature of 10 K will double the speed of ageing [20,78]. An increase in the acid number and of the copper plating is an indication of oil ageing. Copper plating is the process that copper from the heat pump circuit (if applied) is dissolved in the lubricant oil and transported around the system where it is deposited on hot metal surfaces. Copper plating can occur due to oil instability, moisture in the system, impurities, oil acidification by the working medium, and aging due to contact with oxygen. In some cases, acids are formed by mixing oil and working medium. The formed acid can work as a catalyst and accelerate the breakdown process of oil and the working medium.

Oil should also not cause any degradation of materials within a HTHP system and any potential interaction between oil and system components needs to be considered. This is especially important for elastomeric seals [10]. Often tests are performed regarding thermal, hydrolytic, and oxidative stability [79]. The water content in the oil is a parameter of interest for chemical stability and it must be limited to a given value (ppm) depending on the oil type. Water can cause formation of decomposition products. Fig. 10 shows the water absorption of different oils. Non-polar oils like mineral and PAO oils absorb less water than polar ones like PAG and POE, which are more hygroscopic [20,78]. As an example, Ma et al. note that water vapor compressors face problems of corrosion and water vapor intrusion of lubricating oil. The promotion of the application of water vapor compressors in high-temperature heat pump steam systems requires urgent solutions for the problems of corrosion, sealing, high-temperature control, and long-term operational safety [6].

The chemical stability of lubricants, additives and working media is affected by heat (thermal), water (hydrolysis) and air (oxidation). Tests have been developed to evaluate combinations of lubricant, working media and materials like metals, polymers, and thermoplastics. Severe test temperatures are usually used to accelerate reactivity to simulate reaction stability over several years of operation in a short time. Stability tests are performed within sealed glass tubes as outlined in ASHRAE Standard 97. This helps to quickly screen candidates at various conditions for visual and chemical changes. Typically, colour, acid content, dissolved metals in solution, precipitation formation, and copper plating are key parameters in the investigation. This procedure has been used over the years to test numerous combinations of working media and lubricants. For example, working media like R12 usually show some reactivity when tested with mineral oils at temperatures above 150 °C. This is observed with the breakdown of the working medium, formation of acids, and attack of the oil through acid catalysed reaction from working medium breakdown and thermal stresses on the oil [131]. On the other hand, HFC working media are more stable and show little breakdown when tested with lubricants. Huttenlocher et al. tested several lubricant oils with various HFC working media and found little decomposition of the HFC working media in glass sealed tube testing at high temperatures 150 °C-200 °C [132]. It is noticed that some of the synthetic lubricants that are commonly used with HFC working media show some instability. POE oils showed an increase in acidity at temperatures between 175 °C and 200 °C while certain PAG oils showed minor structural changes.

The stability testing performed on lubricants and working media is effective and it is an acceptable method for future testing of potential new lubricants and working media. While HFC working media showed higher levels of stability over the years, newer working media with lower GWP based on HFO have less potential stability due to their



		time / h			
		0	4	24	72
PAG ISO VG 46	c (H_2O) [ppm]	70	1350	5100	7000
POE ISO VG 32		30	280	700	1350
POE ISO VG 80		30	150	370	600
POE ISO VG 170		15	130	230	350
MO ISO VG 68		10	15	20	20

Fig. 10. Water absorption of different lubricant oils [20,78].

chemical structure. It is important to understand the stability aspects of some of the new lower GWP working media given the less stable aspect over HFC working media.

Rohatgi et al. performed chemical and thermal stability studies on HFO working media [133]. Results show that compared to HFC working media, HFO working media and HFO/HFC blends showed more instability especially in the presence of air and moisture. Analysis of sealed tubes after heat ageing with HFO-based working media and lubricants showed increased levels of fluoride ion and acidity, especially with air contamination. When higher levels of air (1000–2000 ppm) are introduced during glass sealed tube testing at 175 °C for 14 days with R-1234yf and lubricant, hydrogen fluoride was detected as a reaction product in the tube, and darkening of the lubricant-working medium solution and corrosion of the metal coupons was observed [133]. Other authors also confirmed the instability of HFO working media in the presence of contaminants such as air and moisture along with instability with certain additives used in lubricants or material processes [79]. Fig. 11 shows a picture of a sealed tube experiments [133].

Material compatibility analysis is required for working media and lubricants to avoid degradation of system materials during operation, which could result in system failure. Material compatibility tests are performed prior to lubricity tests. Strips of materials used in the compressor such as steel, copper, aluminium, stainless steel, and polymers, are immersed in Pyrex glass tubes filled with a working medium/oil mixture. The test consists of observing the presence of microscopic reactants, corrosion or degradation of the strips as shown in Fig. 11.

Below, some studies are reported that were carried out for the chemical and material compatibility of the system fluids and various system components. Doerr et al. evaluated the compatibility of lubricants and working media with materials used in construction of internal hermetic motors, such as the insulation materials [134]. The study measured changes in strength and elongation of polymeric motor materials with various lubricant chemistries. Results indicate only slight changes amongst different lubricants (with working medium and temperature) where exposure to heat is more detrimental to the integrity of the material. Majurin et al. evaluated compatibility of motor materials with tests in combination of HFO and HFC working media with POE and PVE lubricants and identified potential materials of concern [135]. Eyerer et al. reported an experimental study of material computability of R1233zd-E, R1234yf and R1234ze-E with different polymers in combination with POE lubricant oil [136]. Tangri et al. studied interaction of R1234ze-E blends in combination with POE oil with different thermoplastics and elastomers [137]. Other forms of compatibility concern electrical properties, particularly within a compressor and motor.

5.5. Daniel plots

The concentration of the dissolved working medium in oil depends on temperature and pressure. The dissolution significantly decreases the viscosity of the pure oil. This is due to the lower viscosity of the pure working medium [70,71]. To accurately predict the behaviour and viscosity of the mixture, the composition of the mixture must be known. Research indicates that for lighter working media, 3–5 wt% dilutes in the oil but for heavier working media, this percentage can be between 5–40 wt% [89]. For some oil-working medium combinations no lubricant film will be sustained if the fraction of working medium in the oil exceeds the 25 wt% [89].

Seeton et al. developed a method for testing working medium/lubricant mixtures circulating in a closed looped system [108]. This method has become a standard for generating pressure-viscosity-temperature (pVT) relationship plots, known as Daniel plots. Daniel plot gives the viscosity (μ) of the mixture oil dissolved in working medium for the operating conditions (p, T). The optimum operating viscosity of the oil under the influence of the working medium is a compromise between minimum viscosity required for reliable compressor lubrication and the necessary low-temperature flowing properties needed to maintain sufficient oil circulation in the circuit.

The dissolution of the working medium vapor into the lubricant oil is of importance in the compressor sump as it affects the viscosity appreciably. As mentioned already, the interaction between the solubility and viscosity is illustrated by the Daniel plots [78,137,138]. These plots are deduced from solubility measurements and provide valuable information on the amount of a working medium that dissolves in the lubricant oil under given pressure and temperature conditions and how the kinematic viscosity changes. Daniel plots, shown in Fig. 12, show the solubility as curved lines of constant pressure (isobars) and lines of constant composition (isopleths) as a function of temperature. These plots are generated by models based on measurements and are used to

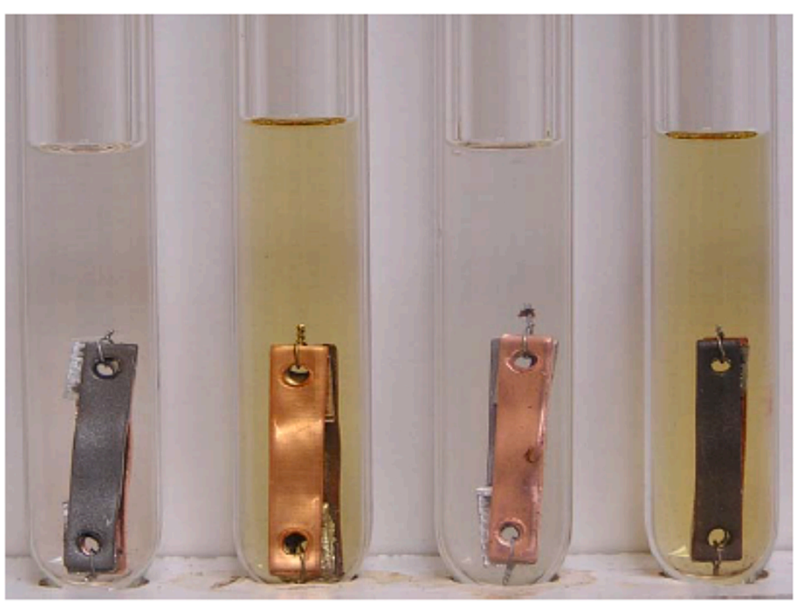


Fig. 11. Picture of sealed tubes containing HFO-1234yf/POE mixture with copper, steel, and aluminium strips [133].

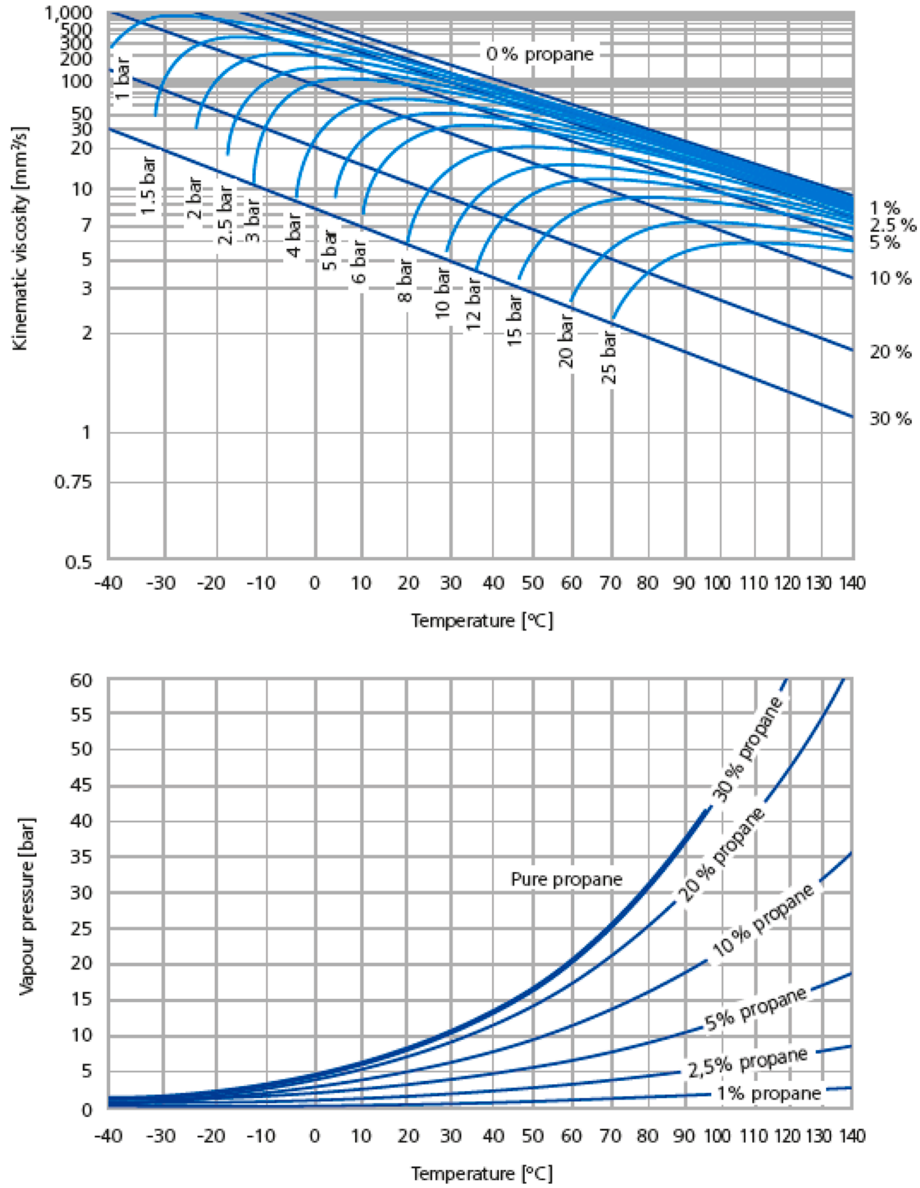


Fig. 12. Daniel plot for a PAG/R290 mixture [78].

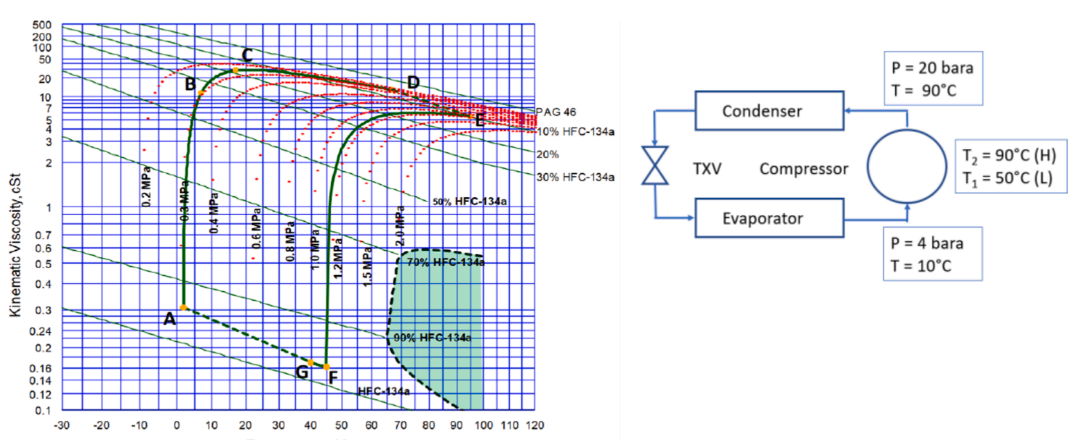


Fig. 13. Daniel plot for HFC-134a/PAG 46 mixture (left) and compression cycle (right) [79].

determine the solubility and viscosity for a given mixture [129,139]. The plots are also used to evaluate the working viscosity of the lubrication oil under operating conditions.

The pVT charts are very specific for a given oil/working medium combination [78]. An example of the Daniel plot for a mixture PAG/propane (R290) is shown in Fig. 12. This shows the viscosity of the mixture oil/dissolved working medium under operating conditions (p, T). In general, the higher the pressure and lower the temperature, the higher the working medium content. The viscosity decreases with increasing content of working medium as can be seen from Fig. 12.

Daniel plots are used to accurately determine the working viscosity of the mixture oil/working medium so that the required viscosity can be obtained. Fig. 13 shows the Daniel plot, and the cycle used for a given heat pump [79]. This example shows how a heat pump cycle can be combined with a Daniel plot to assess the working viscosity at different locations in the heat pump for different operating conditions- most importantly in the compressor. In the chart at the left-hand side of Fig. 13, B to C is the suction phase and C to D represents low side compressor operation at various oil sump temperatures. D to E is the discharge stage associated with high side compressor operation. This plot also shows the lower Critical Solution Temperature (CST) miscibility of this working medium and lubricant combination, showing that the data for the pVT plot must be cut off in the immiscible green area. From the cycle conditions, it can be shown how the viscosity for different operating conditions can be determined. For this example, at the low side conditions of 0.4 MPa and using oil temperature of 50 °C, the solubility is approximately 12 % with working viscosity of 1.5 10^{-2} Pa.s. If we evaluate this same combination at the high side condition of 2 MPa and 90 °C oil temperature, then we obtain a solubility of 20 % and working viscosity of 4 10^{-3} Pa.s. This means that depending on the application and compressor, this lubricant may be adequate for operation in low side condition but may not have enough viscosity to maintain sufficient bearing protection at hot side operation. It is worthwhile noticing that high solubility means low working viscosity and vice-versa. For any operating point, the viscosity can be estimated for comparison of different lubricant types and viscosity grades.

The interplay between appropriate miscibility, solubility, and working viscosity for an oil/working medium mixture is important for the choice of the appropriate combination. These properties are interrelated, and a compromise must be found. Barthel et al. studies the miscibility behaviour of different oil/working medium mixtures [129]. The study of the behaviour of the oil/working medium mixtures through the whole system helps in the design of an optimal system. To generate these graphs glass tubes tests are prepared. They show the impact of the type of oil and the tuning of the chemistry of a given oil on the performance. They demonstrate the interaction between the solubility and the viscosity by using Daniel plots. Two examples from their study are discussed here. The first example concerns the study of two mixtures of two different 68 Pa.s POE oils with R454B, A and B. Fig. 14 shows the miscibility graphs for the two mixtures. Although the two POE oils are of the same chemical family and they have the same neat viscosity, their miscibility graphs are different. POE(A) shows a narrow region of miscibility with immiscibility behaviour at low and high temperature. POE(B) shows perfect miscibility over approximately the whole tested range. This difference in miscibility behaviour disappears when considering the solubility and viscosity.

Fig. 15 shows the Daniel plots for the two oils with R454B. The two graphs are nearly identical even though the miscibility is different. For examples, at 70 °C and 2 MPa, POE(A) shows a viscosity of 5.1 Pa.s for 14.3 % R554B and for POE(B) the viscosity is 5 Pa.s for 14.2 % R454B.

The second example concerns the mixtures of two different 220 Pa.s POE oils (C and D) with R1234ze(E). Fig. 16 shows the miscibility graphs for these mixtures. The two graphs are practically similar, with large region of immiscibility. POE(D) has a region of immiscibility at high temperatures which is small.

Although the miscibility of the two oils POE (C) and POE (D) are similar, the solubility and viscosity are different, as can be seen from Fig. 17. The Daniel plots for the two oils mixture with R1234ze(E) do not overlap as in Fig. 15. The isobars for the two oils are different over the tested range. For examples, at 20 °C and 0.2 MPa, POE(C) shows a working viscosity of 110 Pa.s for 13.3 % R1234ze(E) and for POE(D) the viscosity is 54.7 Pa.s for 19.9 % R1234ze(E). At 100 °C, the mixtures show a similar behaviour. POE(C) shows a working viscosity of 3.4 Pa.s for 23.4 % R1234ze(E), and for POE(D) the working viscosity is 3.9 Pa.s for 25.1 % R1234ze(E). Other examples can be found in reference [129].

These examples illustrate how the properties of the lubricant oil affects the mixture properties. Chemical properties of the oil like chain length, degree of branching, polarity will influence the miscibility and solubility with a working medium [140]. The mixture properties depend on the heat pump operating conditions and the chemistry of both the lubricant oil and working medium. The complex molecular interaction between oil and working medium makes the prediction of miscibility and solubility difficult and experimental data is required to optimize the system. It is important to optimise both the miscibility and solubility simultaneously for a given lubricant oil and working medium for given operation conditions.

The last example concerns a study done by Tangri et al [137]. They studied experimentally the solubility and miscibility of R515B and R471A with a POE-based oil over a temperature range of −20 °C to 120 °C and −30 °C to 75 °C, respectively. Fig. 18 shows the Daniel plot for R515B with POE32. A comparison of R515B and R410A working viscosities at the state points of the compressor are shown in the plot. The plot illustrates similar working viscosities for R515B and R410A at the outlet of evaporator (A), inlet of compressor (B) and outlet of compressor (D). However, there is a slight increase in viscosity of R515B at the inlet of the compressor (3.6 % increase at state point B) and in the compressor sump (19.6 % increase at state point C). The viscosity change in the region from state point B (inlet of compressor) to state point C (highest temperature in compressor sump) is due to a decrease in solubility at sump temperature range 20 to 70 °C.

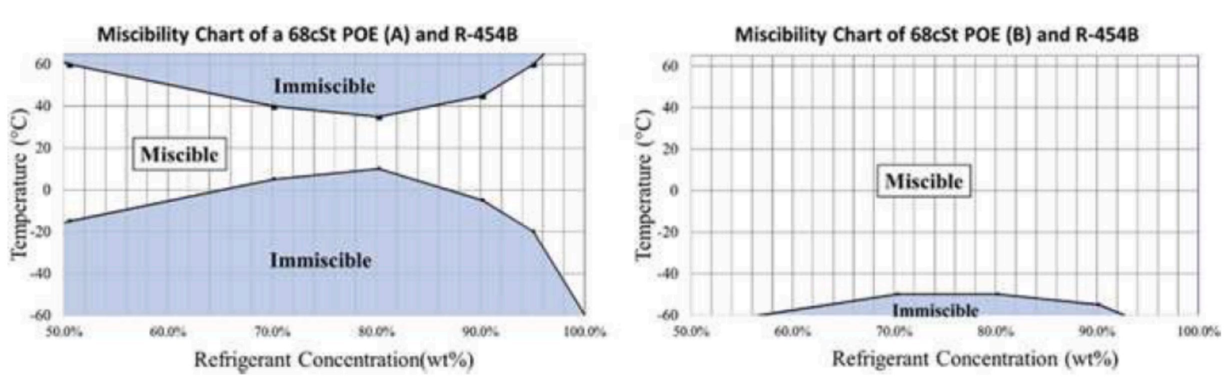


Fig. 14. Miscibility graphs for two different POE oils with R 454B [129].

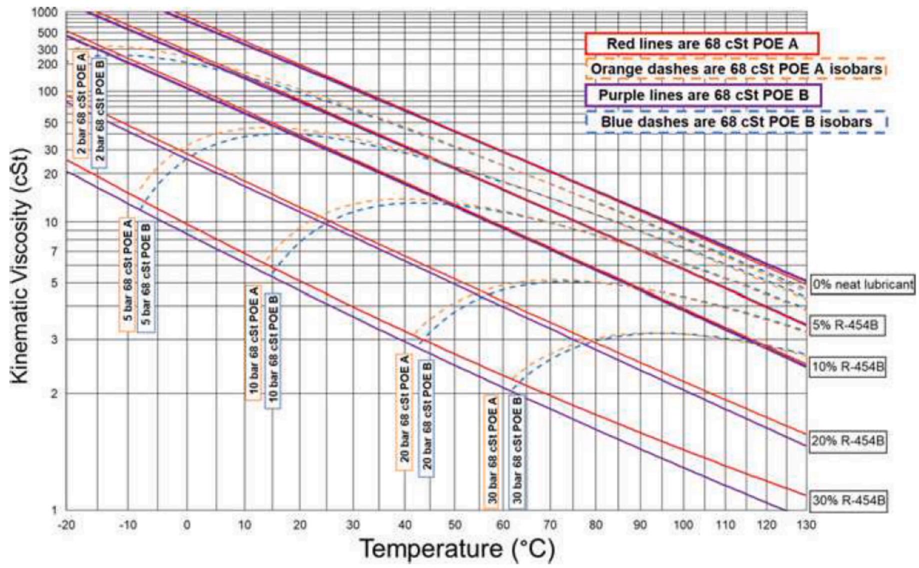


Fig. 15. Daniel plot for the two POE oils mixtures with R454B [129].

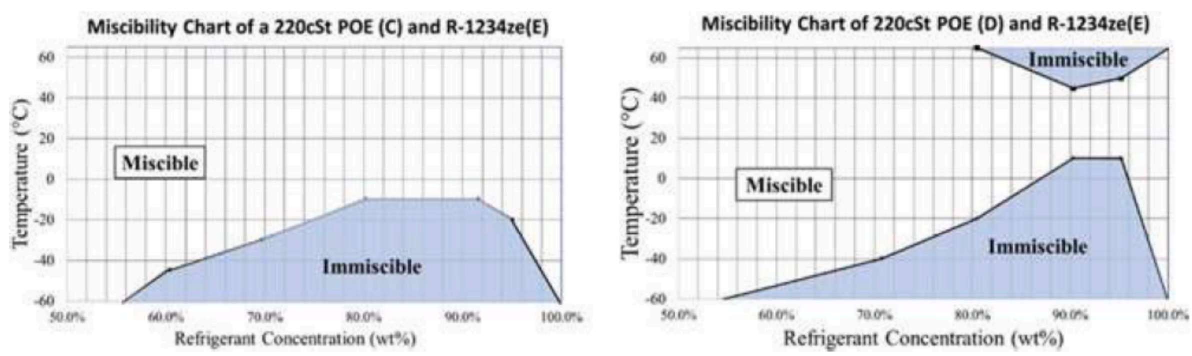


Fig. 16. Miscibility graphs for two different POE oils with R 454 [129].

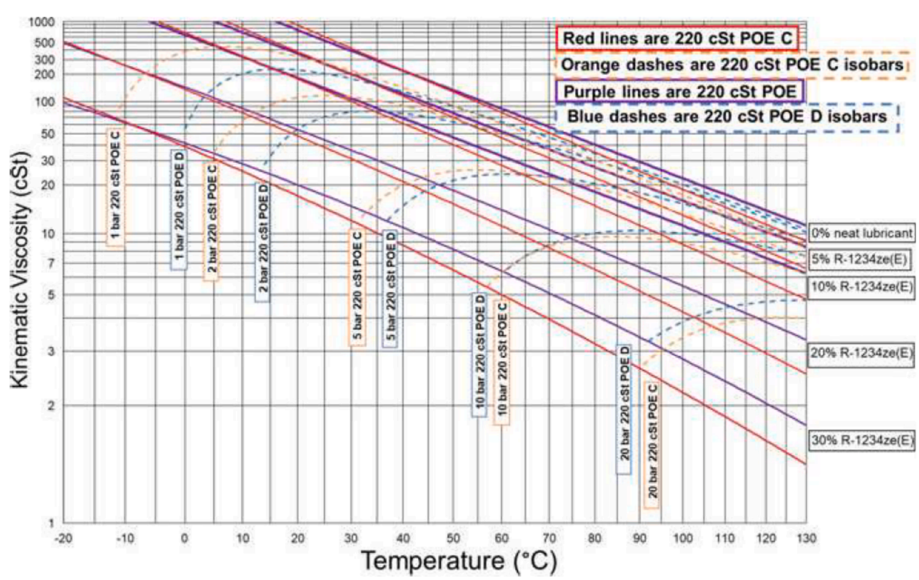


Fig. 17. Daniel plots for the two POE oils mixtures with R1234ze(E) [129].

6. Lubricity tests

After the selection of the appropriate oil for a given working medium, lubricity tests must be done using a wear tester, a test bench, and/or in a compressor test loop [10,17,100,141]. These tests will help to assess in real compressor operating conditions the chemical stability

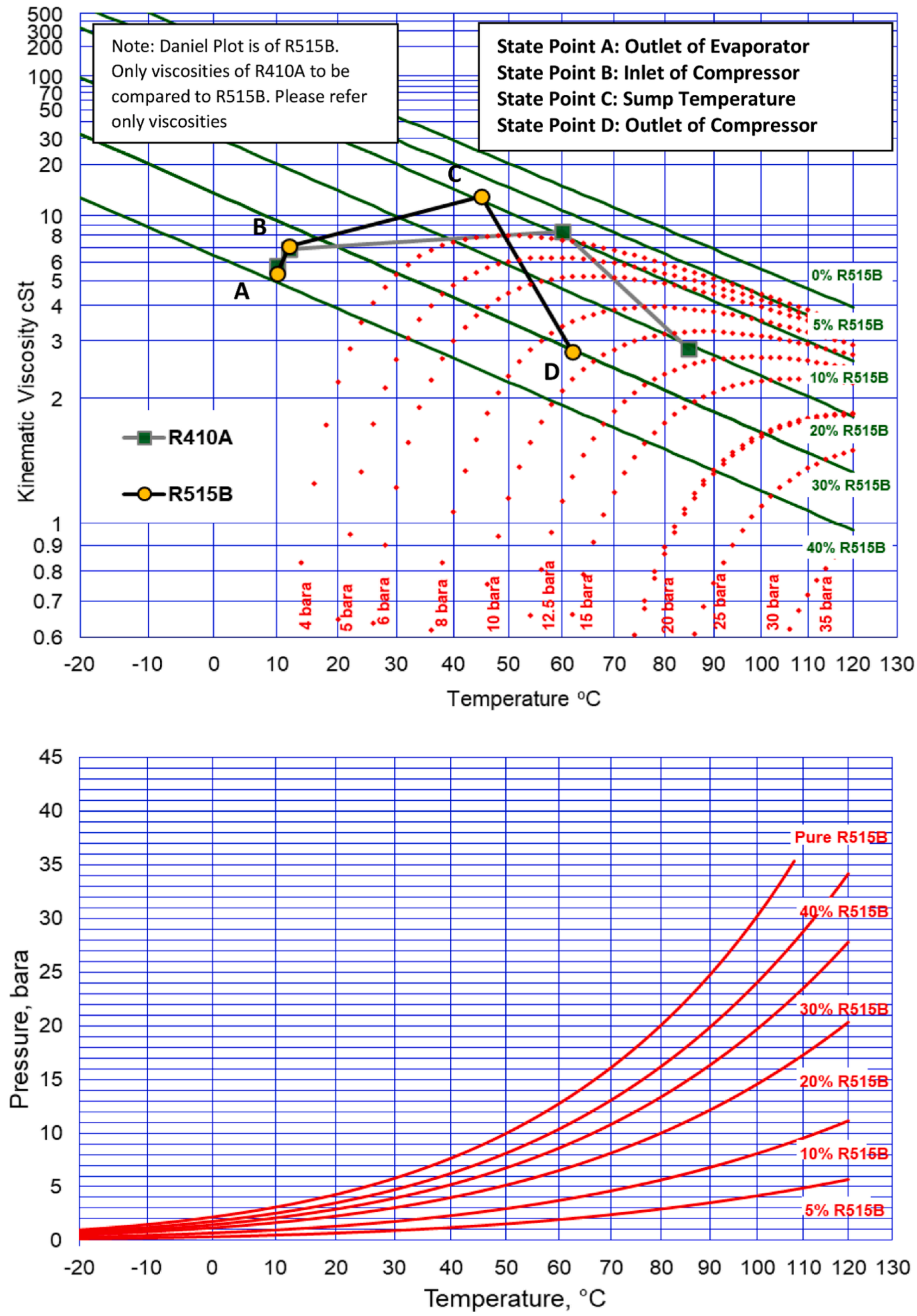


Fig. 18. Daniel plot for R515B with POE32 over the temperature range −20–120 °C [137].

and compatibility with materials. Examples of lubricity tests can be found in [38,94–100]. Seong et al. used a heat pump test loop to assess in real operating conditions the chemical stability and compatibility with materials of R466A with POE oil [141]. The tests are done using an accelerated test protocol and the oil is sampled periodically during the test and analysed.

7. Selection methodology

In this section, a selection procedure for lubricant oil for a given working medium is proposed based on the characteristics discussed in the foregoing sections. Once the working medium is chosen for a HTHP application based on the criteria discussed in Section 2.1, then follows the selection of an appropriate compressor. The choice of the working medium and the required capacity set the conditions for the design of the compressor and the oil selection. After that, a tribology study is required to determine the required lubricant oil for the moving parts, bearings, materials, and surface finish used in the compressor design to realize the required minimum oil film thickness. Then follows a chemistry study as the dissolution of the working medium in the lubricant oil (solubility) will affect the working viscosity, thus influencing the type of bearing and the required viscosity of the lubricant oil. Once the adequate oil/working medium combination is selected, lubricity tests must be done using a wear tester, test bench, and in a compressor test loop. The test must be done under the operating conditions of the HTHP.

The selection methodology consists of the steps: selection of working medium and compressor based on application, tribology and chemistry analysis, and finally lubricity tests. These steps are summarized in the following.

7.1. Tribology study

The tribology study is the evaluation of the contact surfaces using appropriate surface analysis techniques and identifying the type of wear mode. This is usually done by the compressor supplier. Stribeck plots are used for the evaluation. The required viscosity is determined and related to the results from chemistry study (Daniel plots) as discussed in Section 5. A tribometer is then chosen to simulate the normal working conditions of the compressor parts by setting the temperatures, the contact pressures, and contact speeds. In the final stage, the test can be done in a compressor test loop.

7.2. Chemistry study

The chemistry analysis consists of the screening of potential working medium/oil combinations to optimise for optimum miscibility and solubility under operating conditions. Each of these parameters are strongly influenced by temperature and pressure revealing regions of both good and poor mixing. The thermal and chemical stability along with material compatibility are also evaluated. The chemistry analysis will also guide the selection of appropriate lubricant additives.

In addition to the viscosity, the working medium miscibility and solubility are determinant factors in the lubricant oil selection. Typically, Daniel plots are used to determine the lubricant viscosity required for a given compressor design. Miscibility of the lubricant and the refrigerator liquid phase often plays a key role in the return of lubricant to the compressor. This affects the compressor reliability and performance. Good miscibility and solubility facilitate the return of oil to the compressor, which is important for its reliable operation and for the system performance. The chemistry analysis therefore consists of the following steps:

- Determination of solubility, miscibility, and stability & material computability
- Determination of the working viscosity of the mixture oil/working medium via Daniel Plots, which must be experimentally determined under the operating conditions of the HTHP.

7.3. Lubricant additives

Lubricant additives can be considered for use to improve the properties and performance of the base oil. The Stribeck curve helps also to optimize surface finish, lubricant viscosity, and lubricity additive for boundary lubrication. This is discussed in Section 8.

8. Lubricity tests

The selected oil lubricant candidate should be validated in a bench test for lubricant oils. In this test the performance characteristics of the oil can be evaluated, such as oxidation, corrosion, aeration, shear stability, friction and material compatibility. This is done by accelerating the conditions causing the performance characteristics. After that the wear tests in the compressor can be performed. Endurance tests in the compressor can be done by increasing stresses on the compressor bearings by using high pressure differential and compression ratios. During the tests, lubricant oil can be periodically removed from the compressor and evaluated for the presence of iron dissolved in the oil [17,141].

It is worth noting that there are strategies which can be used for the selection considering the tribology study, economics and other factors and they are discussed in the literature [99]. These methods can, for example, be used to determine the lubricant oil for a given working medium with the best lubricity properties for lowest cost.

9. Lubricant oils additives

Normally all lubricant oils consist of a basis oil with additives which are added to improve the properties and performance of the base oil. Most additives are designed to specifically improve one property, but some additives are multifunctional and improve several properties. Lubricant additives are usually used to ensure high aging, thermal stability, increase wear protection, and reduce foam formation. Additives are chemical components or blends used at a specific treat rate to provide one or more functions to the oil. Ideally, additive components are multifunctional and soluble in lubrication oil. The design of additives must consider the chemical and physical properties of the base oils, especially their polarity. On average, lubricating oils consist of 93 % base oil(s) and 7 % additives [142]. Additives help with a wide variety of functions, such as:

- *Boundary lubricity additives* enhance fluid lubricity by adsorbing on the metal surface to form a film, limiting metal-to-metal contact.
- *Extreme Pressure Additives* are a special type of boundary lubricity additive that form a metal salt layer between mating surfaces that limit friction, wear and damage.
- *Corrosion Inhibitors* prevent the fluid from corroding system surfaces. These comprise of benzotriazole and its aryl derivatives which are the most widely used copper metal deactivators [143–145]
- *Alkalinity Additives* essentially serve as a buffer, neutralizing acidic contaminants to preserve the fluid's corrosion protection and maintain the pH in a suitable range. Examples include alkanolamines like: Monoethanolamine (MEA), Triethanolamine (TEA), Aminomethylpropanol (AMP), 2-(2-aminoethoxy) ethanol.
- *Metal Deactivators* reduce corrosion when dissimilar metals contact each other. They act by forming a protective coating on the metal surface. Examples include: Mercaptobenzothiazole, Tolyltriazole, Benzotriazole.
- *Antioxidant (AO) additives:* Lubricant oils can absorb water and oxygen to form hydroperoxy oxidation products. There are many AO-additives which are effective at high temperatures in the absence of any iron catalyst [146,147].
- *Antiwear additives*: These additives are used to improve lubricity of the oil. These are different linear, branched or substituted aryl and alkyl chain forms of phosphorous that may contain sulfur or halogen heteroatoms [147]. Detergents stabilize dirt and wear debris in oil formulations.

10. Appropriate lubrication oils for working media for HTHP

This section discusses the selection of appropriate lubricant oils for the HTHP working media outlined in Section 2.1, based on an extensive literature search. It is worthwhile to note that the most references in this section are from reference [78], as less information concerning the development of lubricants can be found for other oil suppliers.

A summary of the parameters which are important to evaluate

Table 4
Parameters used for the selection of a lubricant oil for a given working medium.

Parameter	Description
Miscibility	Ability of the lubricant and working medium to maintain a single phase over a range of operating conditions
Solubility	Mixing rate of working medium into the oil which affects the compressor efficiency and viscosity through refrigerant leakage
Working viscosity	Viscosity based on the mixing of the lubricant and working medium which affects bearing lubrication and compressor efficiency
Stability	Ability of the working medium, lubricant, and additives to maintain an acceptable level of reactivity
Compatibility	Interaction of lubricant and working medium with materials of construction and other physical parameters found within the heat pump

during the selection of a lubricant for a given working medium are listed in Table 4.

- *Oils for HFOs:*

Rohatgi et al. [133] conducted tests with motor materials and the low GWP working medium HFO-1234ze in combination with two POE oils and one PVE oil. These tests determined the thermal and chemical stability, and the long-term material compatibility. Sealed tubes were prepared according to ASHRAE Standard 97–2007. The sealed tubes are aged at 175 °C for 14 days. After aging, the tube contents were visually examined for change in lubricant colour, cloudiness in the lubricant, floc or particulate formation, film formation on tube walls, changes in appearance of the metal coupons, surface corrosion and/or copper plating on the steel surface. Digital pictures of the tubes before and after aging were taken for the record. The tube contents were also analysed by gas chromatography, for Total Acid Number (TAN) and by Ion Chromatography to determine total halide, total organic and total inorganic anion concentrations. The tests are summarized in Table 5.

Using the fluoride ion concentrations after aging as indicators of working medium decomposition and TAN as indicators of lubricant decomposition, the following conclusions are drawn:

- With 2000 ppm air, ISO 32 Branched Acid lubricant decomposition was small in HFO-1234ze at both moisture levels.
- HFO-1234ze was more stable than other tested HFO's.
- HFO-1234ze showed a small amount of working medium decomposition when compared to other HFO's used in the test.

Lee et al. reported miscibility measurements of R1234ze(E) with POE68 and PVE68 oils in the temperature range of −35 °C to 80 °C [148]. The miscibility test results show that POE68 and PVE68 oils are completely miscible with the refrigerant R-1234ze(E) at the mass fraction below 20 % and 10 %, respectively. Other studies also report the solubility of R1234ze(E) with POE oil [149,150].

The use of POE lubricant in combination with HFO's is also discussed by other authors [23,151–156,158]. Arpagaus [23] investigates the HFOs R1336mzz(Z) and R1234ze(Z) and the HCFOs R1233zd(E) and R1224yd(Z). A POE oil with a viscosity of 170 mm^2/s (at 40 °C) is used to achieve sufficient lubrication at high operating temperatures. Fukuda et al. studies working media R1234ze(E) and R1234ze(Z) for high temperature heat pumps [151]. The lubricant oil applied in the compressor was POE VG68 for both working media. Bock [153] measured the vapor–liquid-equilibria data (P-T-x) and liquid densities of binary mixtures of R1234ze(E) with a POE oil. It is concluded that the measurements agree with existing mixture models. Gasservei [157] also mentioned that R1234ze working medium is miscible with POE and PAG oils, so it should always be used with these types of oils. Shah et al. [90] used POE oil in combination with R1233zd(E) and the experiments showed the necessity for oil cooling due to high condensing temperatures. Majurin et al. [155] and Suemitsu et al [156] suggest the use of MO with R1233zd(E). Kostantinos [103] mentions that based on the chemical composition of HFOs, it would be expected to be compatible and miscible with POE type lubricants.

Table 5
Test of the thermal and chemical stability experiments done by Rohatgi et al. [133].

Working medium	*Lubricant Type*	*Contaminant Condition*	*Test Condition*
HFO-1234ze	Mixed Acid POE	No contaminant Air Water Both air and water	175 °C / 14 days
	Branched Acid POE	No contaminant Air Water Both air and water	175 °C / 14 days
	PVE Oil	No contaminant Air Water Both air and water	175 °C / 14 days

Hewitt [39,90] studies a heat pump which uses R1233zd(E) as working medium in combination with POE 68 oil, the working viscosity could be maintained above 10^{-3} Pa.s over the range of operation of the heat pump, a minimum viscosity to ensure safe operation of the compressor.

Jessberger [158] studies the upscaling effect of a HTHP using R1233zd(E) as working medium. Two similar heat pumps with a scale difference in capacity of 3.2 are used for the study. Both heat pumps use POE oil as lubricant at 40 °C but with different viscosities; the small capacity heat pump (A) uses POE with a kinematic viscosity 173 mm^2/s and the larger heat pump (B) uses POE with a viscosity of 80 mm^2/s. Both heat pumps use an oil separator which efficiently separates the oil from the working medium vapour. It is found out that compressor B operates more efficiently than compressor A, which is due to a higher viscosity of the oil for HTHP A and relatively lower friction losses compared to the total power draw for HTHP B. It is concluded that the COP for both HTHPs shows a similar trend as a function of the temperature lift.

As an example, RENISO TRITON CE 500, is a fully synthetic refrigeration oil based on saturated, synthetic ester (POE), specially designed for high temperature heat pumps for the working media R1234ze and R1336mzz [78]. The miscibility of RENISO TRITON SE 170 with R1234ze(E) is shown in Fig. 19. The Daniel plot for RENISO TRITON SE 170 and R1234ze(E) mixture is given in Fig. 20.

- *Oils for Ammonia (R-717)*

Ammonia is applied as working medium in many industrial refrigeration systems, such as in breweries, food factories and large cold stores. MO is the classic lubricant used with R-717 at low temperatures. It has good compatibility and miscibility. It also has good compatibility with seal elastomers. The use of MO lubricant in combination with ammonia is also discussed by many authors [2,78,103,143,153–166]. However, PAO oils are superior to MO, especially at high temperature as there is no deposit formation and there is a good stability as can be seen from the sealed tubes tests at 120 °C shown in Fig. 21 [159]. On the other hand, synthetic PAO oils have lower evaporation losses than MO oils and hence less oil refilling quantities in the compressor as shown in Fig. 22. PAO-oils provide high lubricating film thickness and still provide reliable lubrication at high temperatures which is very suitable for HTHP.

In a study by Mobil [81], it is claimed that PAO or PAO/AB (Alkylbenzene) blends are the preferred lubricants for R-717. Feja et al. [87] measured the solubility, vapour pressure and viscosity of four different oils mixed with ammonia up to 5 MPa and 140 °C. They used two hydrotreated MOs and two PAO's. PAO oils show better solubility with ammonia than mineral oils. The use of POE lubricant in combination with Ammonia is also discussed by many other authors [2,31,78,103–110,131,152–157].

The Daniel plot for RENISO SYNTH 68 and R717 mixtures is shown in Fig. 23. RENISO SYNTH 68 is a thermally stable PAO with excellent cold flowing properties for NH_3 systems with highly stressed compressors and low evaporation temperatures. Due to its outstanding cold flow properties RENISO SYNTH 68 is also recommended for use in plate evaporators with narrow tubing diameters [78].

- *Oils for Hydrocarbons*

The purity of hydrocarbons is critical when used as working media, because if there are any impurities present (sulphur, water, etc.) it could cause the oil lubricants in the system to degrade and damage the

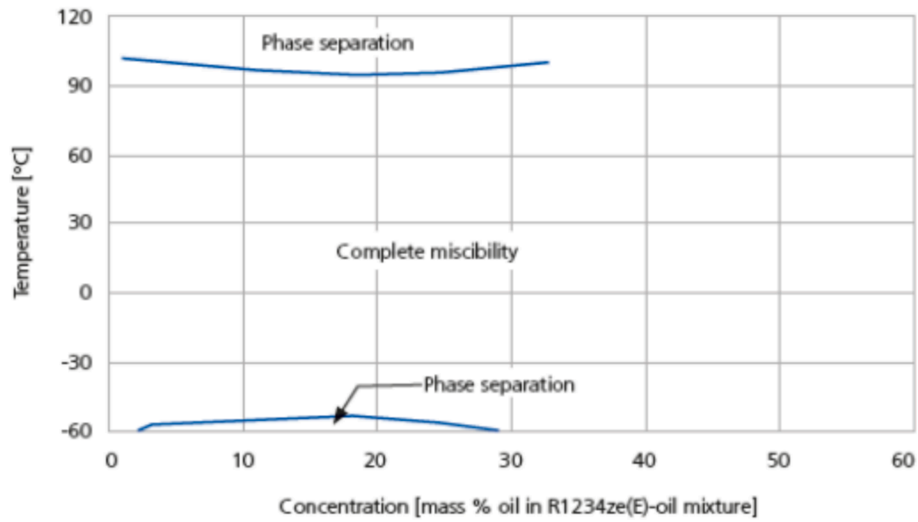


Fig. 19. Miscibility of RENISO TRITON SE 170 (POE) and R1234ze(E) [78].

compressor. Furthermore, if the hydrocarbon is not of high purity (> 99 %), it can sometimes be mixed with other hydrocarbons, which can drastically alter the physical and thermodynamic properties of the original hydrocarbon [157].

As is the case with all other kinds of hydrocarbon working media, isobutane is highly miscible with all types of lubricants. As MOs and these working media are highly soluble together, it may be necessary with some systems to use more viscous oils to compensate for this increased solubility. Lubricants that contain silicone or silicates are not recommended. Table 6 shows compatible lubricant oils with isobutane.

Kubo et al [160] carried out a study of various families of Freon and Hydrocarbon working media, including evaluation of thermal stability, cost, and durability testing (Sealed tube test) of combinations of promising working media and lubricating oils. A normal pentane was selected as the best working medium and a PAG as the most suitable lubricating oil.

Babarinde et al. [161] studied the effect of the use of graphene nano-lubricant to enhance the performance of isobutane in a vapour compression system. The results show that isobutane performed better with graphene nano-lubricant compared to the base lubricant. However, this is still at low TRL.

Dorine uses POE and PAG as lubricant for their HEX-compressors for working media R600 and R601 [162].

It is claimed that the REINSO LPG oil series is used successfully with hydrocarbon working media. The following quotes are from reference [78]:

- RENISO TRITON SE/SEZ series (POE): Synthetic refrigeration oils based on chemically and thermally extremely stable polyol esters (POE). Their polar structure also reduces the working medium dissolution and thus the decrease in viscosity compared to mineral oils.
- RENISO SYNTH 68 (PAO): Highly pure polyalphaolefins (PAO) as base oils for very good cold flow properties and a favourable viscosity-temperature behaviour (high VI). RENISO Synth 68 has been firmly established in hydrocarbon working media for over 10 years and has good practical experience.
- RENISO WF series (MO) for R600a applications RENISO WF refrigeration oils based on selected hydrogenated mineral oils, so-called isodewaxed base oils, with an effective additive system for increased wear protection. Low-viscosity RENISO WF oils have been used by well-known manufacturers for over 20 years to increase efficiency in fully hermetic R600a refrigerator compressors.

The Daniel plot for RENISO LPG 185 (PAG)- R601a (i-pentane) mixture is shown in Fig. 24.

- *Oils for R718*

Water is an appropriate working medium for high temperature heat pumps. However, the density of water vapour is relatively low compared to other working media at temperatures < 100 °C. This requires large compressors or high-speed compressors to transfer equivalent mass flows compared to what a smaller compressor would do with other working fluids [163,164]. There is little literature on the lubrication oil for water, and most literature concerning water as a working medium uses oil-free compressors [167–169]. Kobelco [166] developed an oil-free R718 turbo-compressor. Husseini et al. [164] indicated that water is used as the lubricant for bearings and gap-sealing. Shoyama et al [165] developed a heat pump which uses a turbo compressor where water is used as working medium and as lubricant.

- *Oils for R744*

As discussed in section 2, carbon dioxide is an appropriate working medium for applications in HTHP [35–37] when used under supercritical conditions. It has a very low GWP, good heat transfer characteristics, non-flammable, and good materials compatibility. Carbon dioxide has much higher operating pressures than other working media, which results in high mechanical stress and load on moving parts and bearings [38,41,42,81]. The solubility is another problem related to the high operating pressures and temperatures [38]. There are POE specifically designed for CO_2 [58,78,159]. POE oils have a good miscibility with carbon dioxide, PAG oils show a limited miscibility, and PAO oils are not miscible with CO_2 as illustrated in Fig. 25. Experimental solubility studies are done for several mixture CO_2/PAG and POE lubricant oils have been published in the literature [42,170–172]. In general, at the same temperature and pressure, CO_2 is most easily dissolved in POE oils and the least in MO oils (POE > PAG > AB > MO). CO_2 causes a different degree of viscosity drops of viscosity depending on the type of oil. In terms of mass %, viscosity decreases in the order AB > MO > POE > PAG [20].

- *Oils for Zeotropic working media*

There is little literature concerning the oils used for zeotropic mixtures at high temperatures. Stockel et al used a POE for a mixture of propane (R290) and dimethylether (DME) [173]. Zuhlsdorf indicates

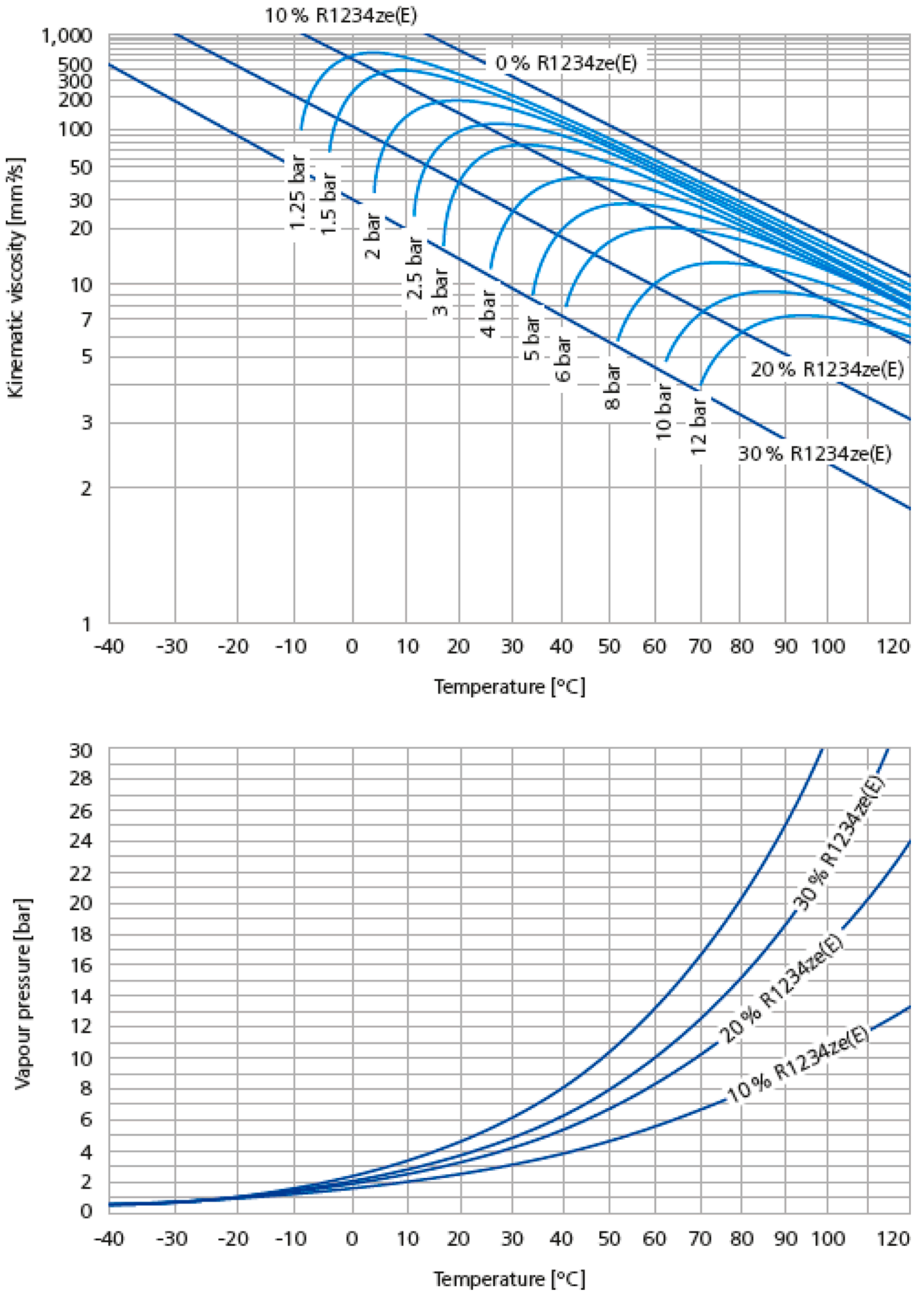


Fig. 20. Daniel plot of RENISO TRITON SE 170 (POE) with R1234ze(E) [78].

that mixtures of hydrocarbons can operate with both MO and synthetic oil [174]. Quenel et al. developed a heat pump that uses a mixture of R290 and isobutane (R600a) where PAO oil is used for the maximum outlet temperature of the compressor of 120 °C [175]. Venzik et al. investigated the performance of a CHP with three working media R290, R600a, and a zeotropic mixture thereof. They used a PAO oil for the heat pump [176]. They observed a general improvement of the COP with the zeotropic mixture, although this was lower than expected from theory. This is due to a reduced superheating of the working fluid entering the compressor, which causes different solubility in the lubricant oil consequently increasing friction. Another contributing factor is the likely increased leakage between the cylinder and the piston resulting in a decrease of the efficiency of the compressor.

In the literature it is indicated that synthetic oils based on PAG are also appropriate for hydrocarbon working media (propane, propylene, butane, etc.) and their blends [78].

- *Lubricants for future working media*

The HFO/HFC blends include many new working media, although not all of these are available commercially, and not all these working media are classified by ASHRAE. Evaluation of miscibility behaviour, stability tests and solubility/viscosity measurements are required to characterize these new working media with existing oils or new oils to be developed.

However, in all cases it is always possible to find the appropriate lubricant oil for a chosen working medium by applying the selection and test methods discussed in the foregoing sections. To evaluate and carefully select a compressor oil for a given working medium, the lubricating properties should be tested in a mixture with the working medium under the prevailing conditions.

A summary of the literature concerning appropriate lubricant oils for different working media is given in Table 7.

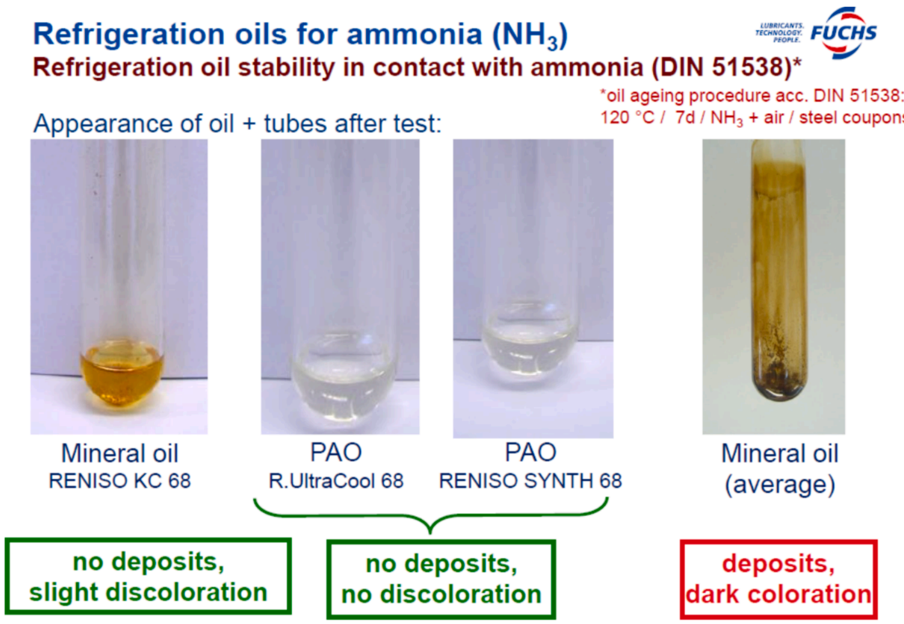


Fig. 21. Sealed tubes tests done at 120 °C for MO and PAO in combination with Ammonia [159].

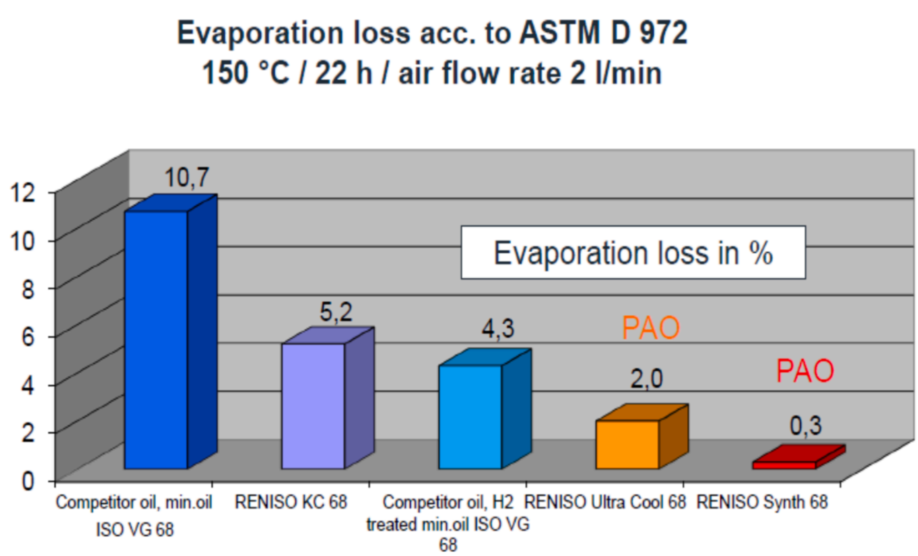


Fig. 22. Comparison of the evaporation losses for MO and PAO [159].

- *Oil suppliers*

The lubricant oils the oil suppliers can deliver depend on the application, as summarized in Table 8. Extended information concerning appropriate oils for given working media and compressors can be found in references [78,81–83,157,182].

From all the information gathered through literature search and consulting the oil suppliers' brochures, the most appropriate lubricant oils for the different types of working media appropriate for HTHP are summarized in the following:

- HFO's: POE, PAG, PVE.
- Ammonia (R717): POE, MO, PAO, AB, PAG
- Hydrocarbons (R600, R601, etc): PAO, POE, PAG, AB
- Carbon dioxide (R744): PAO, PAG.
- Zeotropic mixtures: PAO is mentioned as appropriate for zeotropic mixtures of hydrocarbon working media.
- Future working media: As future working media most probably will consist of natural working media and their mixtures; the existing synthetic oils can be optimized for the chosen mixtures under the prevailing conditions.

11. Conclusions

Lubricant oils are required for the lubrication, sealing and cooling of compressors. High-temperature heat pumps require specially designed lubricants, suitable for extreme working conditions. High temperatures and pressures decrease the working viscosity of the lubricant and working medium mixture. The lubricant must be miscible with the working medium and must be chemically stable. The oil must be separated properly from the working medium to avoid degradation of the heat pump's performance as it increases the pressure drop and affects the heat transfer in the heat exchangers. Also, the working medium dissolves in the oil, which changes its thermophysical properties and affects the heat pump performance. There are diverse types of

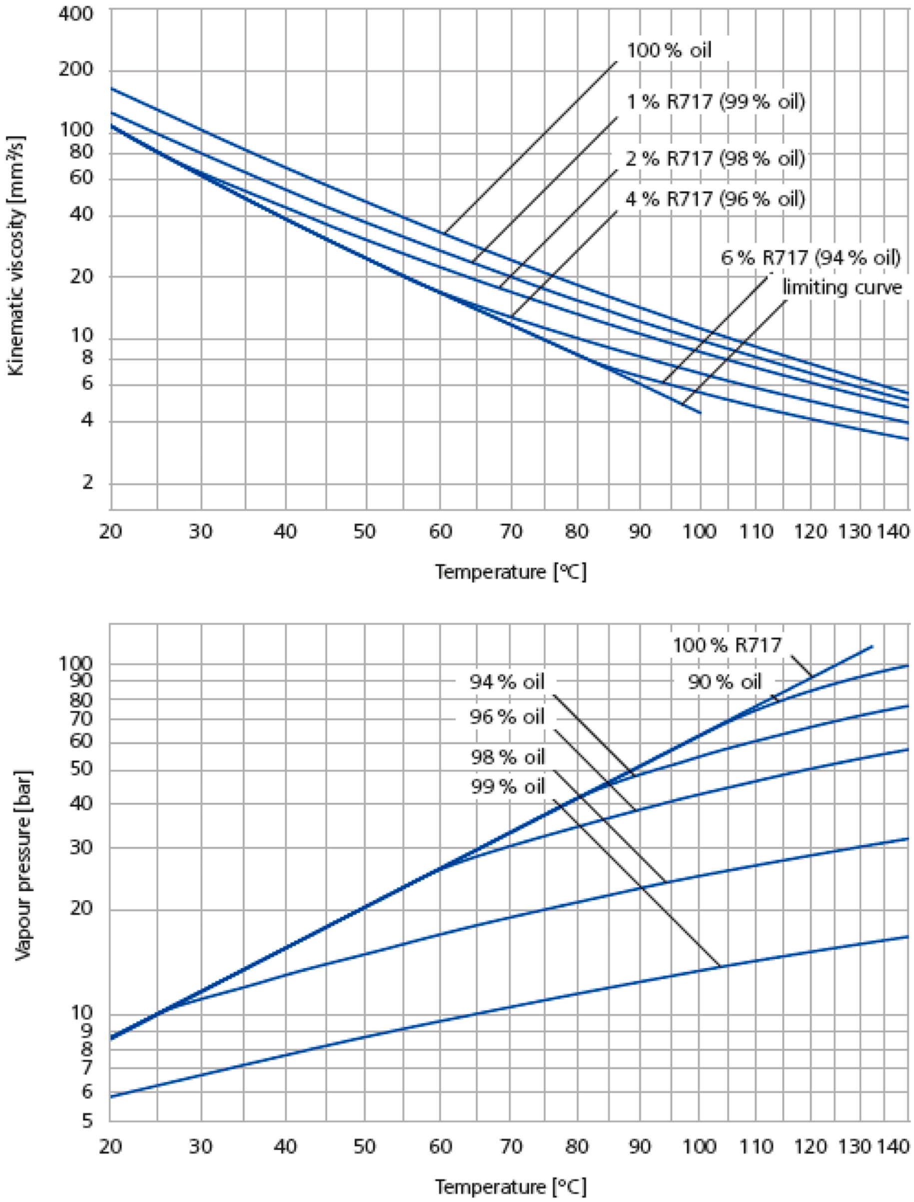


Fig. 23. Daniel plot for RENISO SYNTH 68 and R717 mixture [78].

Table 6
GS Technical datasheet for isobutane [157].

Lubricant	Compatibility
Mineral (M)	Compatible with hydrocarbon type refrigerants. They have excessive solubility in high temperature applications. This situation can be compensated by using higher viscosity mineral oils.
Alkybenzenic (AB)	Fully compatible.
Semi-synthetic (MO/AB)	The mixture of mineral and alkybenzene oil is the most appropriate to work with this type of refrigerant.
Polyolester (POE)	Too much solubility with hydrocarbons. May require using POE of higher viscosities.
Polyalkyleneglycols (PAG)	Soluble, depending on working conditions.
Polyalphaolefines (PAO)	Soluble, recommended for low temperature applications.

lubricating oils, mineral, semi-synthetic or fully synthetic oils. The most important criteria used during the selection of an appropriate lubricant oil for a given working medium are: thermal and chemical stability, miscibility, solubility and working viscosity.

To evaluate and carefully select a lubricant oil for a given working medium, the lubricating properties should be tested in a mixture with the working medium under the prevailing conditions. The first step in the selection of the lubricant oil is based on fundamentals of tribology, which is done by the compressor supplier to determine the required working viscosity. Then follows the analysis of the lubricant viscosity considering the working medium solubility (Daniel plots). The selection methodology can be summarized in three steps as follows:

1. Tribology study by evaluating the contact surfaces using appropriate surface analysis techniques and identifying the type of wear mode. Stribeck curves are used to determine required viscosity and then related to the results from chemistry study (Daniel plots). A tribometer is then used for lubricity tests to simulate the normal working conditions of the compressor parts by setting the temperatures, contact pressures, contact speeds.
2. The chemistry study consisting of the screening of potential working medium/oil combinations establishes the optimum miscibility and solubility under operating conditions. The thermal and chemical

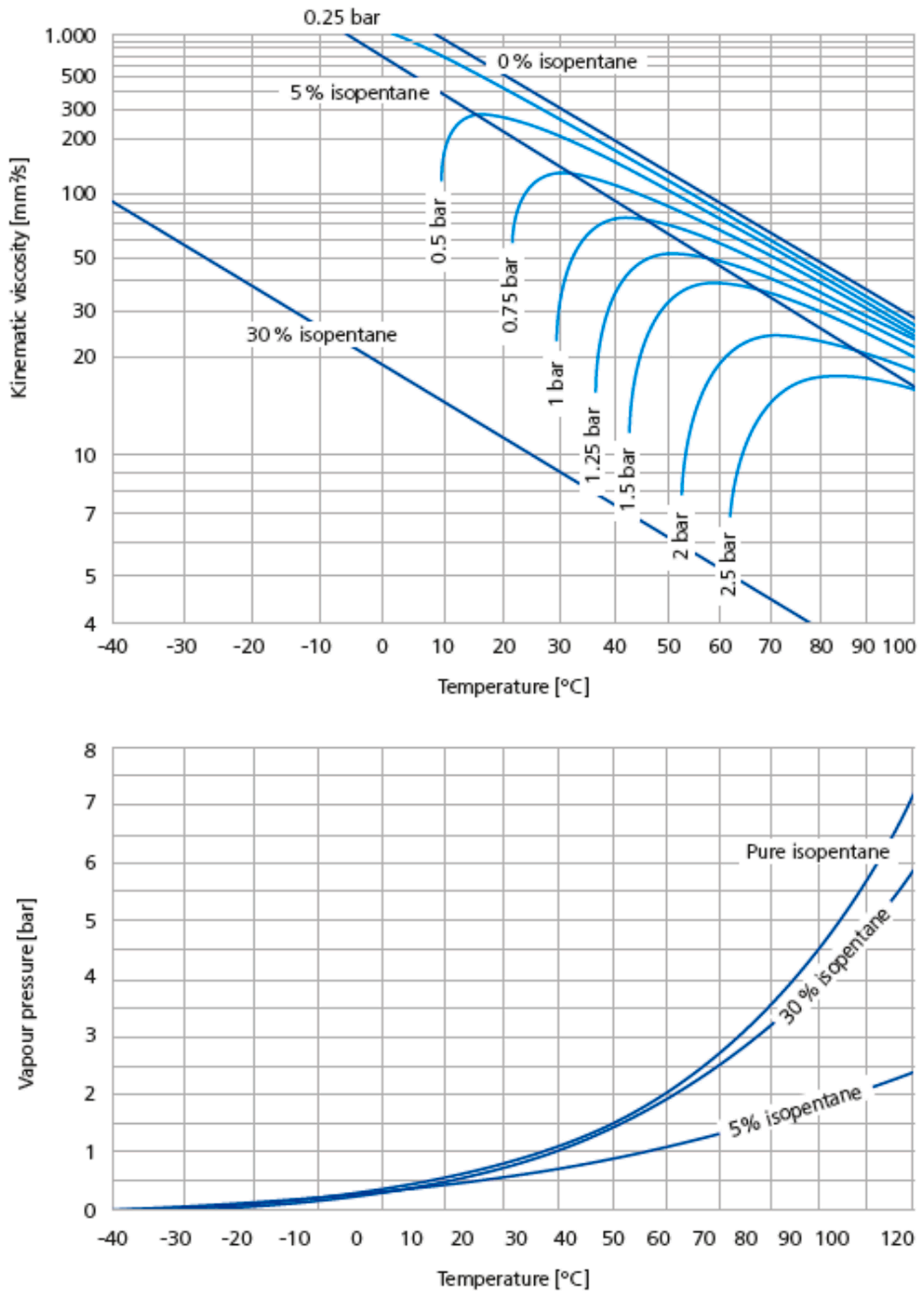


Fig. 24. Daniel plot for RENISO LPG 185 (PAG)- R601a (i-pentane) mixture [78].

Fig. 25. Illustration of miscibility of CO2 with different oils [159].

stability along with material compatibility are also evaluated. The chemistry analysis will also guide the selection of appropriate lubricant additives. Working viscosity of the oil/working medium mixture must be determined via Daniel Plots which must be experimentally determined under the operating conditions of the HTHP. Lubricant additives can be considered for use to improve the properties and performance of the base oil.

3. The selected oil lubricant candidate should be validated in wear tests in a bench test for lubricant oils. In this test, the performance characteristics of the oil like oxidation, corrosion, aeration, shear stability, friction and material compatibility can be evaluated. This is done by accelerating the conditions causing the performance characteristics. During the tests lubricant oil is periodically sampled from the compressor and evaluated for the presence of materials dissolved in the oil.

Table 7
Summary of the literature concerning appropriate lubricant oils for different working media.

	MO	POE	PAO	PAG	AB	Water	Oil-free
R717	[2,20,78–83,87,159]	[78,87,159]	[20,81,82]	[2,20,78,159]	[2,20,75,78,81,87]		
R600	[20,151,157,161,177]	[78]	[20,78,178]	[20,78]	[20,157]		
R601		[78]	[78]	[160,162,179]	[20]		
R1233zd(E)	[89,135,155,156,181]	[2,23,39,78,79,89,90,136,151,158,178,181]		[79,154,181]			
R1234ze(E)		[2,23,78,89,129,133,136,137,148–151,157,184]		[157]			
R1336mzz(Z)		[2,78,103,152]					
R718						[164,165]	[14,166–169,180,183,185]
R744	[169]	[38,42,78,79,143,170,171]	[79]	[42,79,170,173]	[79,169]		

Table 8
Oil suppliers.

Supplier	Lubricant
Fuchs	Lubricant oils for different working media and type compressors (HC, NH_3, CO_2, HFC&HFO) [78]
Exxon-Mobile	Lubricant oils for different working media [81]
Bitzer	Various types of compressors for different applications for several working media with the appropriate lubricant [82]
Kluber	Variety of lubricants [83]
Gasservei	Supplier of working media, database for the appropriate lubricant oils for the working media [157]
CPI	Specialty gas compressor lubricants [182]

Selection of a suitable oil for compressors operating in high-temperature heat pump applications requires careful attention to ensure reliable and efficient operation of these heat pumps. This is a prerequisite for industrial heat pump technology to deliver the promise to decarbonise industrial heat demand.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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