HOW CHANGES IN LUBRICANT CAN ADDRESS CHALLENGES ASSOCIATED WITH HYDROCARBON REFRIGERANTS HIGH TEMPERATURE HEAT PUMPS (HTHP).

Manuel MUÑOZ-ALONSO^(a), Joe KARNAZ^(b), Liz DIXON^(a), Jun LIU^(c).

(a) Shrieve Products International Ltd. Kent, ME19 4YU UK, mmunoz@shrieve.com
 (b)Shrieve Chemical Products, LLC, The Woodlands, 77380 (TX), USA, jkarnaz@shrieve.com
 (c)Shrieve Chemical (Shanghai) Ltd, 3F, Bldg 2, JuXin HI-TECH PARK, No. 188 Ping Fu Road, Xuhui District Shanghai, CHINA, 200231

ABSTRACT

The knowledge of lubricant-refrigerant interactions is crucial to understand the behavior of a real working system. The greater the affinity between refrigerant and lubricant, the higher the temperature, or the greater the pressure, all of them reduce the working viscosity available during operation. An increase in the viscosity grade may compensate, but there are also operational high viscosity limits.

The behavior of lubricant-refrigerant pairs will be described in the oil sump in an alternative compressor, and the oil reservoir in a screw compressor. How different operational conditions influence differences in oil behavior and in oil selection, to provide the right viscosity at the right condition. All explanations will be illustrated with real products and working conditions, with data extracted from PVT charts obtained by direct measurement.

Keywords: Heat Pump, Hydrocarbons, Lubricant, Solubility.

1. INTRODUCTION.

A Heat Pump (HP) is a vapor compression refrigeration system but optimized on the warm side. The HP has all the elements of any Refrigeration / Air Conditioning unit: evaporator, condenser, compressor, and an expansion device. Its purpose is to take heat from a heat source through the evaporator and deliver it, at a higher temperature, through the condenser to a heat sink. The compressor work is then included in the heat delivered through the condenser.

The compressor requires lubricant for two main purposes: keeping a layer, cushion, between moving parts, in order to avoid wear and reduce friction, and sealing the high- and low-pressure sectors in positive displacement compressors. Due to the compressors' motion and the fluid circulation (refrigerant), some oil is expelled throughout the discharge port to the circuit, which has to be designed to recover that oil. This can be done with an oil separator.

The temperature lift achievable is not endless. There are technical limits depending on the fluid used. EN14825:2018 defines high temperature as over 65 °C, so delivering 70-130 °C can be called High Temperature Heat Pump (HTHP).

This delivery temperature has mainly two limits:

Critical Temperature of the refrigerant used: If the delivery temperature is higher than the fluid critical temperature, the High-Pressure side of the circuit will be transcritical, not a condenser but a gas cooler. This situation can be addressed, and it is workable if needed.

Discharge Temperature in the compressor: A lubricated compressor will have oil in the discharge port. The higher the delivery temperature, the higher the discharge temperature. It is very fluid dependent (oil and refrigerant), but the thermal resistance of the lubricant has a limit. The useful life of

the lubricant is reduced as the operational temperature increases.

The refrigerant has to be selected looking at the whole refrigeration cycle that has to perform, not only the temperatures. A higher molecular weight refrigerant can be used to reduce the working pressures. On the other hand, the saturation dome shape in the Pressure-Enthalpy diagram can impose a high superheating (SH) to avoid compressing into the saturated liquid region.

2. INFLUENCE OF THE FLUIDS TO BE USED.

The so called "natural refrigerants" have no environmental concern, so they are excluded from all the regulations like F-Gas and Montreal Protocol. On the other hand, each one has its particular concerns, so application in the field has to be made with care. Primary examples are as follows :

R-717. Ammonia. Toxic and flammable, very chemically active if in contact with several materials.

R-744. Carbon Dioxide. Low critical point, that means a transcritical operation in many situations. A high working pressure requires a high mechanical strength of the refrigeration system, that increase its cost and operational risks.

R-718. Water. Its low vapor pressure requires great swept volume in the compressor, and operation under vacuum.

Hydrocarbons (**HCs**): R-290, R-600, R-600a, R-601, R-601a. They are highly flammable, so special care has to be taken during operation. We will focus on this group.

3. REFRIGERANT CHEMISTRY, SOLUBILITY, AND INFLUENCE ON LUBRICANT WORKING VISCOSITY (LUBRICITY).

The most important property of a lubricant is the viscosity, that can be defined as the resistance to flow. The higher the viscosity, the higher the resistance to flow and hence the thicker the lubricant layer remaining on the surfaces. A properly selected lubricant will retain a minimum oil layer (cushion) between the mobile surfaces, to prevent wear and reduce friction. In volumetric displacement compressors, this layer also seals (separates) the high- and low-pressure sides of the circuit: compressor liners, orbiting and static scroll or as an interface between the two rotors of a scroll compressor.

In addition, sufficient chemical and thermal stability is needed to support the conditions inside a refrigeration circuit. The lubricant inside a refrigeration circuit always has a certain amount of gas dissolved, depending on their mutual affinity (gas-lubricant), the temperature, and the pressure.

There are two properties that condition the working viscosity inside the refrigeration system and have to be considered when selecting a refrigerant.

3.1. Solubility.

Solubility refers to the amount of gas dissolved inside the lubricant at specific conditions (temperature (T), pressure (P)). This dissolved gas greatly affects the resulting viscosity, since a gas has a much lower viscosity than the lubricant. The greater the dilution of the oil, the lower the resulting viscosity.

Solubility is affected by three factors:

<u>Chemical Affinity.</u> We will look at the polarity of the molecule. Chemicals of similar polarity will have a greater affinity, and hence a greater mutual solubility. Hydrocarbons are non-polar compounds. This means that they will have a greater affinity with hydrocarbon-based lubricants, no matter whether synthetic or mineral types (Mineral Oil, MO; Poly-Alpha-Olefins, PAO; AlkylBenzenes, AB). The dilution of the lubricant will be

important, the viscosity reduction will be also important, and even more important the amount of refrigerant permanently sequestered from the circuit. This last point is very important when there is a charge limit in the circuit.

Operational Pressure. The greater the pressure, the greater the amount of gas dissolved in the oil.

<u>Temperature</u>. In this case the effect is the opposite than the pressure. The higher the temperature, the lower the dilution.

In the Table 1 we can see how all these parameters affect the final working viscosity in a lubricant diluted with refrigerant. Progiline LPG WS 100 is more polar than Progiline RL WI 100, so the solubility of the R-290 is lower for the same conditions. The final viscosity is higher in this case. When looking at the pressure and temperature changes, in each one we see how the solubility is reduced when temperature increases, at constant pressure. And solubility is higher if the pressure is higher, at the same temperature.

Table 1: Effect of lubricant affinity, pressure and temperature in the solubility and final viscosity of propane.

P Bar a∖ T ⁰C	30	50	30	50	_
	53.7	37.15	85	50	cSt
4.06	4.9	3.2	3	2.2	% gas in oil
	12.3		35		cSt
8.36	15.8		10		% gas in oil
	Progiline RL WI 100		Progiline LPG	WS 100	-

3.2. Miscibility.

Miscibility refers to the capacity of two liquids to mix and remain in a single liquid phase. They are named immiscible if two liquid phases appear. It is very important to understand the behaviour of the lubricant-refrigerant pair used when designing a refrigerant circuit.

Miscibility is influenced by the chemical nature of the involved substances, the temperature, and the mass ratio. Figure 1 is an example of a typical miscibility chart that we can find in the technical information about a lubricant / refrigerant pair (Seeton, 2016).

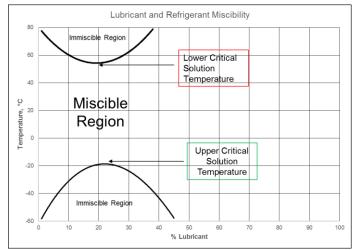


Figure 1. Typical Composition/Temperature chart for a lubricant/refrigerant pair (Seeton, 2016).

The lubricant selection criteria depend on the circuit characteristics, compressor type, and the refrigerant. Typically, the lubricant is selected to be miscible in a wide range of temperatures in order to improve the oil circulation throughout the circuit, yielding a better oil return to the compressor. There are also systems designed

to work with immiscible oil, and it is recovered in appropriate equipment purposely designed. This is the case with ammonia and hydrocarbon lubricants, where the density differential allows easier oil recovery in the bottom of liquid reservoirs.

4. HYDROCARBONS AND THEIR ROLE IN HIGH TEMPERATURE HEAT PUMPS.

The great affinity that hydrocarbon (HC) refrigerants have with also HC lubricants (MO, PAO, AB) can be an advantage for a good oil return, but it can also be a drawback when looking at the available viscosity in the oil sump. The amount of gas dissolved in the oil is reducing dramatically the available viscosity of the mixture and this gas is also permanently sequestered from the refrigeration/heating effect. This last point could be an issue when the system has a charge limit.

Looking at other lubricant chemistries, we could consider using Polyol Esters (POE), common with other refrigerant types, but this will not solve the dilution problem since the solubility of HCs in POEs is even greater than in HC-type lubricants.

We will compare two types of Poly-Alkylene-Glycols (PAG) with different grade of affinity for HCs. This Chemistry allows a grade of flexibility when formulating the lubricant, making the final polymer water insoluble (closer to the HCs, but less than HC type lubricants) or water soluble (less affinity with HCs). The higher polarity of the latter type reduces the affinity for HCs to a level sufficient to operate with a small refrigerant dilution, without being totally immiscible.

4.1. Oil sump in low pressure side of the circuit.

Reciprocating compressors and scroll compressors (for example) typically have the oil stored in the crankcase, oil sump, that is in the low-pressure side of the circuit. The crankcase condition (P,T) defines the available viscosity to work with.

Oil is taken from the oil sump by a pump or splashed to the mobile parts. Depending on model and make, there is always a minimum viscosity required to ensure a lubricant layer thick enough to protect mobile parts and sealing HP/LP sides of the circuit. For operational reasons there is also a maximum allowed viscosity to be considered. That could be the case of a HTHP start up procedure: if the operation temperatures are much higher than the ambient ones, our unit will need some time to warm up before start. Otherwise, the oil in the sump could be too thick to operate

Looking at keeping at least the minimum operational viscosity in harsh conditions (high T or P, high solubility), sometimes it could be enough to change the viscosity grade to a higher one. But there is also a limit, and a change of oil type could be needed.

Refrigerant: R-290		Zerol 150T/ISO VG 32		Zerol 350T/ISO VG 68		
SST (°C)	P sat Bar a	Oil sump ⁰C	Viscosity cSt	% gas in oil	Viscosity cSt	% gas in oil
-25	2.03	30	19	4	30	4
-5	4.06	30	9	9	12	9
20	8.36	30	1.75	25	1.5	30
30	10.79	40	1.25	30	<1	>30
40	13.69	50	<1	>30	<1	>30

Table 2. Effect of changing the viscosity grade in lubricants of the same type (SST: Saturated Suction Temperature).

Table 2 shows how useful lubricants in refrigeration applications became inadequate as evaporation temperature increases. A typical value for minimum working viscosity in a reciprocating crankcase is 12-15 cSt, of course very dependent on model, make, and oil distribution system. We can use this value as a minimum for our examples. Both lubricants in the Table 2 are Alkylbenzenes, ISO VG (ISO Viscosity Grade) 32 and 68. As can

be noted, in low evaporation temperature VG32 is enough. When the evaporation temperature increases (and hence the pressure in the oil sump), more gas is dissolved in the lubricant. For -5 °C SST we need to increase the VG to 68 since the available viscosity drops below the minimum for AB VG32.

Looking at Heat Pump applications, we see that these lubricants cannot be used. The effect of the pressure in the dilution can be clearly seen in the table. In addition, the crankcase has to maintain a temperature higher than SST, otherwise suction gas will condensate in the crankcase. The higher crankcase temperature, combined with the greater dilution by a higher pressure, make the resulting viscosity totally out of range.

A change in the Chemistry of the lubricant, looking for one with some polarity, will try to improve the available viscosity in the sump.

Refrigerant: R-290		Zerol 350T/ISO VG 68		Zerol RFL-68EP		
SST (°C)	P sat Bar a	Oil sump ⁰C	Viscosity cSt	% gas in oil	Viscosity cSt	% gas in oil
-25	2.03	30	30	4	62.3	2.3
-5	4.06	30	12	9	37	5.1
20	8.36	30	1.5	30	8.3	16.9
30	10.79	40	<1	>30	6	18.1
40	13.69	50	<1	>30	4.7	19

 Table 3. Effect of changing the lubricant chemistry.

The new lubricant added is a Water Insoluble PAG. Although it has some polarity in the molecule, it is still insoluble in water, and it is less miscible with propane than the AB. We noted that the dilution is almost half. This point, combined with a much higher Viscosity Index, gave us greater available viscosity values in the crankcase, but they are still useless for HP applications (positive SSTs). Viscosity Index is a parameter of the lubricant that measures how much the viscosity drops with the temperature. The higher the VI, the lower viscosity reduction for the same temperature increase.

If the change in the Chemistry is also combined with a change in VG, we could reach the viscosity values we need to operate the compressor in HP conditions.

Refrigerant:	frigerant: R-290		Zerol RFL-68EP		Progiline RL WI 100		Progiline LPG-WS 100	
SST (°C)	P sat Bar a	Oil sump ^o C	Viscosity cSt	% gas in oil	Viscosity cSt	% gas in oil	Viscosity cSt	% gas in oil
-25	2.03	30	62.3	2.3	88.0	2.3	115	1.25
-5	4.06	30	37	5.1	53.7	4.9	85	3
20	8.36	30	8.3	16.9	12.3	15.8	35	10
30	10.79	40	6	18.1	8.6	16.9	25	11
40	13.69	50	4.7	19	6.4	17.8	16	12

Table 4. Combined effect of a different lubricant chemistry with a higher viscosity grade.

All three lubricants listed in Table 4 are PAGs. The first two are WI type with different VG. The increase in viscosity results in a borderline available viscosity using RL WI 100 at 20 °C SST working conditions, compared to the ISO VG68 lubricant. Some advantage is reached with the same average dilution once we increased the VG. But this cannot last long. If our HP needs to work with a higher temperature heat source, we are again under the viscosity threshold.

The third lubricant in the table is a WS type PAG. Its maximum solubility for HC refrigerants is around 12-17% depending on grade and refrigerant. We reduced the "likeness" one step more, without becoming fully immiscible.

The dilution is now much reduced compared to the previous lubricants, and even at 40 °C SST with 50 °C in the crankcase the available viscosity is still over the minimum.

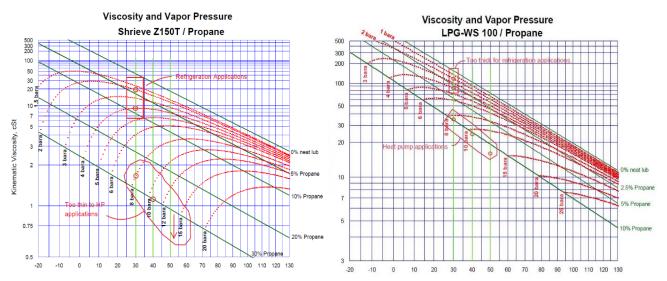


Figure 2. Pressure-Viscosity-Temperature charts for the first and last lubricant used in the Tables 2 to 4.

4.2. Oil sump/reservoir in the High-Pressure side of the circuit.

When looking at systems equipped with screw compressors, the oil reservoir is in the high-pressure side of the circuit. There are many possible configurations, with or without external oil separator, oil cooler, oil reservoir, fitting them internally in the compressor body... We will use as example a circuit with external oil separator and an oil cooler before reinjecting the lubricant into the compressor suction side.

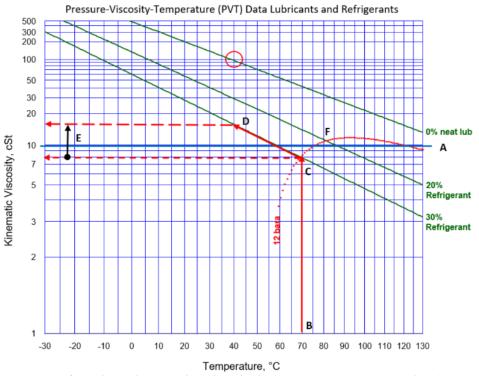


Figure 3. Example of manipulating working viscosity in screw compressor operation (Karnaz, 2021).

Figure 3 will help to understand the process experienced by the mixture oil + refrigerant. The oil dilution is fixed

IIR Compressors, Slovakia, 9-11 September 2024

at the oil separator condition (point C in the figure). Once out of the oil separator and in the oil cooler, since there is no gas to increase the dilution, the lubricant and its existing content are cooled down at constant composition, following the path C-D. Cooled lubricant is then injected in the suction side of the compressor, with an increased viscosity, at point D.

If the oil separator is thermally isolated to keep it hot, or the discharge temperature is increased for example 10 °C, the discharge point is F, after following the isobar to a 10 °C higher temperature. We find that the dilution has been reduced to a 10%, and there is where the cooling starts now. Cooling down 40 °C like before, the final viscosity at the injection point will be higher than point D.

The principles discussed during the reciprocating compressors application (mutual affinity, real working viscosity) are also valid here, and we will compare performances of two different types of PAGs. The refrigerant cycle used as example is described in Table 5, a typical one for a hot water production HP.

Refrigerant	SST (⁰C)	SSP (Bar a)	SH (K)	DT (°C)	SCT (°C)	SCP (Bar a)
R-290	-10	3.45	20	120	85	34.36
R-600	-10	0.70	20	100	85	11.26

Table 5. Heat Pump Cycle and Refrigerants Selected¹

	Discharge condition: 34.36 Bar a/ 120 °C				
	R-290 Discha	Cooled to			
	(34.36 Ba	r a/ 120 °C)	50 ºC		
Lubricant	Viscosity Dilution		Viscosity		
	cSt	(% gas in oil)	cSt		
Zerol RFL-68EP	2.7	12.5	8		
Zerol RFL-150X	5.5	12	20		
Progiline LPG-WS 100	5.5	9.5	20		

Table 6. R-290 in screw compressor. Lubricants' performance.

In Table 6 there is a summary of two lubricants' performance in the selected cycle with R-290. Generally speaking, a screw compressor needs a working viscosity over 10 cSt, ideally around 15 cSt, very dependent on model, make and working conditions. We will use these values in this example to compare lubricants performance.

When trying to use the Zerol RFL-68EP as done with the recips, we find that in those working conditions this lubricant is not adequate. We can then look to a higher viscosity grade in the same lubricant series, and RFL-150X provides a viscosity in the injection of 20 cSt, fully compliant with the needs of the compressor. These lubricants have the same range of refrigerant dilution.

The third lubricant listed is a WS PAG, already used in the recips paragraph for HP applications. This lubricant delivers also 20 cSt in the injection point but in this case, we are looking at an ISO VG 100 instead of the 150 of the previous one. The dilution is also 20% lower than the precedent. This means 20% less of sequestered refrigerant.

Table 7. R-600 in screw compressors. Lubricant's performance.

¹ SST: Saturated Suction Temperature. SSP: Saturated Suction Pressure. SH: Superheating. DT: Discharge Temperature. SCT: Saturated Condensing Temperature. SCP: Saturated Condensing Pressure.

	Discharge condition: 11.26 Bar a/ 100 °C				
	R-600 Discha	Cooled to			
	(11.26 Bar a/ 100 °C)				
Lubricant	Viscosity Dilution		Viscosity		
	cSt	(% gas in oil)	cSt		
Zerol RFL-68EP	2.65	20	<6		
Progiline LPG-WS 100	6.24	12.2	18		

Discharge condition: 11.26 Bar a/ 100 °C

When looking at R-600 (Table 7), we noted the higher solubility of this refrigerant compared to R-290. The dilution is higher even with a much lower pressure. Once more, in reducing the affinity of the lubricant for the refrigerant we do not need to increase greatly the VG to achieve a good working viscosity.

The effect of the refrigerant high solubility has been minimized manipulating the chemistry to reduce the mutual affinity, but not to a point of being fully immiscible and forcing any redesign of the system and its operation.

5. CONCLUSIONS.

The increasing need for Heat Pumps in modern days has driven the refrigeration Industry into uncharted territories , with temperatures and pressures never used before, with equipment working outside of its conventional boundaries.

Although the refrigerants and compressors can work in those exigent conditions, the compressor's lubricant thermal and chemical resistance can be compromised, together with the appropriate viscosity to protect the mobile parts and effectively seal high- and low-pressure sides of the circuit.

To properly select or validate an appropriate lubricant for these exigent conditions, the understanding of the interactions between lubricant and refrigerants are vital. Mapping them with adequate PVT charts (Pressure-Viscosity-Temperature), provide powerful tools to estimate the conditions in operation and the final viscosity in regime, allowing the system engineers to take the lubricant into account.

The procedures outlined in this work will help the refrigeration technicians to address the challenges, even changing the pre-selected lubricant if needed looking at the real working conditions, as illustrated in this work. A proper lubricant selection will expand the situations where to put the Heat Pumps at work.

REFERENCES

Karnaz, J, 2021. Lubricant Options for Screw Compressors Using Alternative Refrigerants. 12th International Conference on Compressors and their Systems 2021. Industry Talks 2 – Materials and Lubrication.

Karnaz, J., Muñoz-Alonso, M, 2022. Expanding Lubricant Options for Natural Refrigerants – What are the Limitations? 15th IIR-Gustav Lorentzen conference on Natural Refrigerants. June 13-15 2022. Trondheim, Norway

Muñoz-Alonso, M., Dixon, L., Seeton, C.J., Karnaz, J., 2021. The role of miscible PAG lubricants in ammonia refrigeration systems reduction and compactness. 9th IIR Conference: Ammonia and CO2 Refrigeration Technologies, Ohrid, 2021.

Seeton, C.J. 2006. Viscosity-temperature correlation for liquids. Tribology Letters, 2006, 22(1), 67-78

Seeton, CJ, Karnaz, J, 2016. Thermodynamic and Transport Properties of Lubricant and Refrigerant Mixtures. Oil Management in Compressors and Their Systems. Purdue University Short Course. July 10th, 2016.