Purdue University
Purdue e-Pubs

International Refrigeration and Air Conditioning Conference

School of Mechanical Engineering

2014

Low GWP Refrigerant and Partial Miscible Lubricant

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Review of Hydrocarbon Lubricants Behaviour

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ABSTRACT

Lubricant selection is based on several lubricant properties to satisfied compressor and system reliability, longevity and energy efficiency performances. The use of non-miscible or low soluble lubricant can bring some technical advantage for the compressor and the system. This paper presents investigations results on low GWP refrigerant alternatives for light commercial and commercial applications. This experimental data are compared to well non data for usual refrigerant HFC/oil pairs. The work also targets the reduction refrigerant charge associated with the compressor characteristics. Miscibility of propane in an AKB, POE and PAG oils has been measured as well as resulting viscosity for each pairs. With too low viscosity values, AKB oil is not suitable for the compressors. PAG oil exhibits a low solubility compared to POE oil, and a miscibility limit that can be used to reduce the refrigerant charge in circuits.

1. INTRODUCTION

Recent developments in regulations governing the use of refrigerants with respect to their global environmental impact (2006/842/EC "F-GAS" regulation recently voted in the EU with a new revision coming into force on January 1rst 2015, or 2009/125/EC Ecodesign directive about energy performance) implies the development of new refrigerants for which reliable lubricants must be proposed very soon. Refrigeration loops with R-290 as working fluid is one of the possible solutions. Indeed, R-290 has a GWP = 3 kg eq. CO_2/kg (Global Warming Potential) and 0 ODP(Ozone Depletion Potential) with high commercial availability and at much lower prices than HFC or HFO. Moreover, R-290 and R-22's saturation pressures are quite similar, but R-290's volumetric refrigerating capacity is higher and discharge temperatures are much lower, which are advantages for the refrigerant load in the circuit and the compressor's longevity. Continuous interest in hydrocarbons as natural refrigerants justifies the design of a propane compressor as well as the selection of suitable and efficient lubricants. The well-known problem with R-290 comes from its high solubility in current oils.

Thus, in this article we propose an overview of different couples of refrigerants (R-22, HFC, R-290) and lubricants (MO, PAG, AKB, POE, PVE). We compare these couples with our own measurements on different pairs R-290/oil. In a second step, some of the data is compared to measurements performed on a refrigeration loop by sampling from the carter of the compressor. Finally, tests related to compatibility with electrical motors are presented.

2. EXPERIMENTAL METHOD

2.1 Description of the experimental apparatus

Solubility, viscosity and miscibility measurements of oil / refrigerant mixtures are performed on a specific test bench, depicted in Figure 1 and Figure 2. The experimental procedure consists of introducing predefined masses of oil and refrigerant into a known volume cell. Required concentrations of each component are measured using a high accuracy bench scale (± 0.02g). The filled cell is then immersed in a liquid bath which automatically controls the temperature with a range from -20°C to +90°C. The cell is equipped with a pressure sensor with accuracies equal to ± 0.4% FS and a T type thermocouple (temperature measurement accuracy of ± 0.25 K for the global measurement chain). Each cell is also equipped with sight glasses providing the operator with a visual control of the mixture behavior and information to plot into the miscibility diagram of the mixture. The cells are designed for pressures less than 40 bar (4.10^6 Pa).

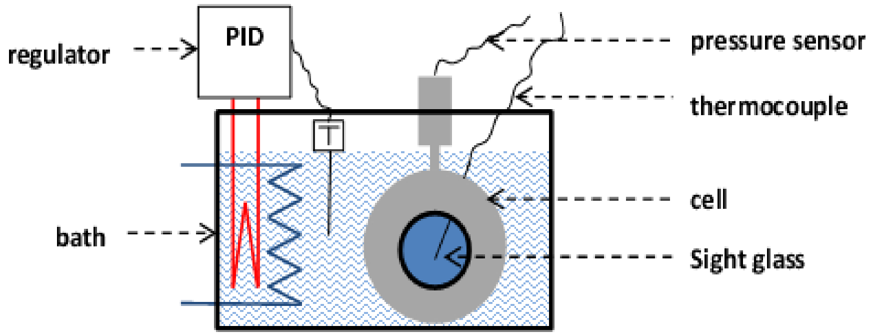

Figure **1**: Schematic representation of the test facility

Figure 2: Viscosity/solubility/miscibility cell (left) and miscibiliy/solubility cell (right)

Density of pure oil is measured using an oscillating U-tube density meter (range: 0-3000 kg.m^{-3}; accuracy: ± 0.5 kg.m^{-3}). The measurement principle of this instrument is based on the electronic measurement of the oscillation frequency from which the density value is calculated.

A specific cell has been designed to perform simultaneous miscibility/viscosity/solubility measurements. Besides a pressure sensor and thermocouple this cell is fitted to a vibrating rod viscometer (range: 0-100 mPa.s; accuracy: 0.1 mPa.s). A constant power source vibrates the rod immersed in the liquid phase and the amplitude variations are measured to determine the dynamic viscosity. The maximum service pressure is 100 bar (10^7 Pa).

2.2 Measurement procedure

Initially, the empty cells are pumped down to a pressure of 1 mbar in order to remove non-condensable gases and solvent residues resulting from the cell cleaning process. They are then weighed and filled with oil by pressure difference until the expected mass is achieved. Next, the cell is pumped down again to a pressure below 20 mbar so that any trace of moisture is eliminated and weighted again (it is to be noticed that the oil vapor pressure cannot exceed 1 mbar (Razzouk A. et al. (2007)), moreover the second weighting gives the mass of oil in the cell after pumping down). Finally, a predetermined mass of refrigerant is introduced within the cell which is once again weighed. At this moment, both oil and refrigerant masses contained in the capacity are known precisely. The total mass concentration of refrigerant in the cell C_{abs}, eq. 1, stays constant under any pressure and temperature conditions.

$$C_{abs} = \frac{M_{r,tot}}{M_{oil} + Mr,_{tot}} \tag{1}$$

Once the cell is immersed in the bath and stabilized at a given temperature, a certain period of time is required to reach steady state equilibrium. This time depends on the studied refrigerant-lubricant pair. From this moment, a data acquisition system is used to collect all the measured parameters during 10 minutes. This procedure is repeated from -20°C to 60°C (253.15 to 333.15K) with a temperature increment of 10 K.

The volume of vapor phase in the cell can easily be calculated from its total volume and liquid phase volume. Two assumptions are made: first, regarding the very low vapor pressure of oil, vapor phase only contains refrigerant; secondly, liquid phase behaves as a homogeneous mixture. Finally, for given pressure and temperature conditions, the mass of vapor refrigerant in the cell can be calculated from Equation (2).

$$V_{vap} = V_{tot} - V_{r,L} - V_{oil}$$

$$M_v = \frac{\left(V_{tot} - \frac{M_{oil}}{\rho_{oil,L}(T)} - \frac{M_r}{\rho_{r,L}(P,T)}\right)\rho_{r,v}(P,T)\rho_{r,L}(P,T)}{\rho_{r,L}(P,T) - \rho_{r,v}(P,T)} \tag{2}$$

Knowing the refrigerant vapor mass, it is possible to determine the solubility of refrigerant in oil by Equation (3):

$$x_r = \frac{M_{r,L}}{M_{oil} + M_{r,L}} \tag{3}$$

The performed experiments cover a wide range of solubility (from 0 % to 60 %) and the sight glasses were used to identify possible miscibility gap of mixtures.

2.3 Some Results and Discussion

The tables below contain the results of a measurement campaign on the couple R-290/POE ISO32. The results show the nonlinear nature of the solubility. According to the experimental procedure described in the previous paragraph, for each table the absolute concentration of refrigerant stays constant, but the mass of refrigerant dissolved in the oil (i.e. the solubility) varies with the cell's temperature. As expected, the refrigerant solubility decreases when pressure and temperature rise.

Different graphs can be drawn from these tables. The graphs of Figure 3 and Figure 4 show the variations of resulting pressure and viscosity according to temperature and absolute concentration for the couple R-1270/POE ISO68.

Table 1: Evolution of solubility and viscosity when superheat increases

Point	P [bar]	T [°C]	X_r [%]	SC [K]	µ [mPa.s^{-1}]
A	5	-2	29,86%	3	3
B	5	5	20,92%	10	5,5
C	5	19	10,51%	24	14
D	5	41	5,76%	46	18
E	5	50	4,80%	55	12

Table 1 resumes the evolutions of properties of this couple when it is heated under constant pressure. Points A to E are placed on the two graphs. When temperature increases under constant pressure:

- solubility of the liquid phase decreases;
- viscosity of the liquid phase of the mixture first increases (this is due to the refrigerant leaving the liquid phase) and then decreases (when the liquid phase becomes very poor in refrigerant, the viscosity decreases with temperature)

For mark legend see table 2

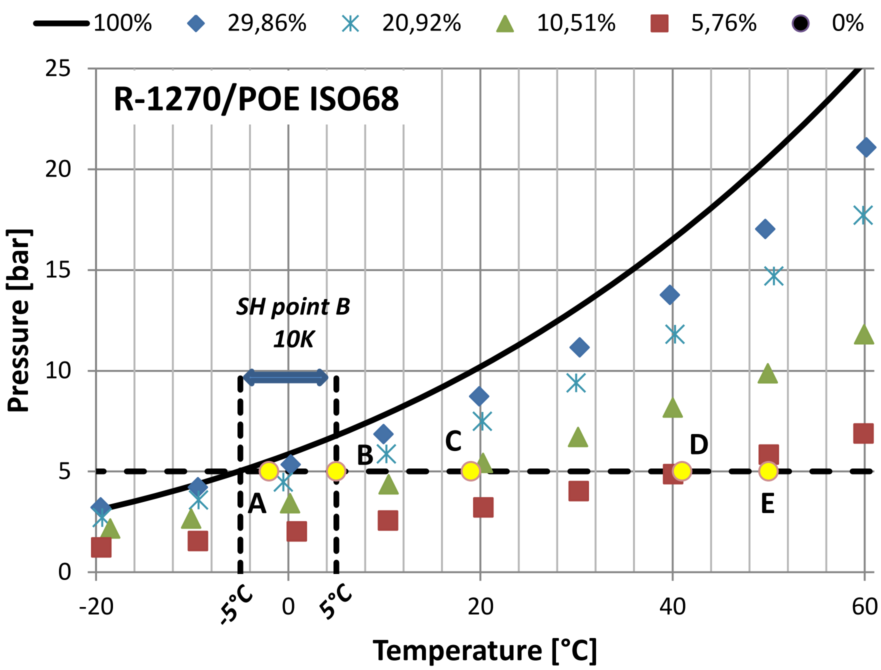

Figure 3: Pressure-temperature-concentration diagram

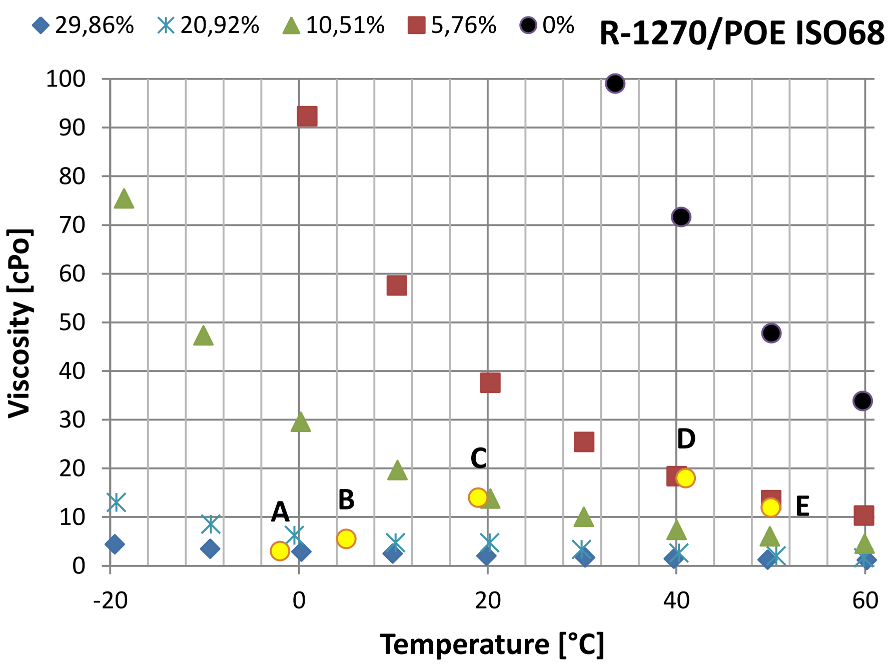

Figure 4: Viscosity-temperature-concentration diagram

Experimental data is used in thermo dynamical models in order to produce (P,x_r,T) graphs. Many of these models use activity factors (Martz W.L et al, Burton C.M .et al, Wahlström A,...). Indeed, this method allows to characterize liquid vapor equilibrium of a binary mixture with a limited number of variables and then to limit the number of measurement points. A brief description of the model used here has been described in previous papers (Charni and al ; Fleming J.S. and Yan Y).
Regarding the modelization of mixture viscosity, the effect of pressure on the dynamic viscosity is neglected here. As a result, a third order polynomial equation with temperature and refrigerant mass concentration as independent parameters was used to predict the dynamic viscosity.

2.3 Comparison and Discussion

The following graphs (Figure 5 and Figure 6) resume evolutions of solubility and viscosity when superheat varies, and for a saturation temperature T_{sat}=+10°C (283.15K). The eight studied couples are listed in Table 2; for each couple, the data source is indicated.

Table 2: Refrigerant/lubricant couples under the scope

Refrigerant	Lubricant	Grade	Data source
R-407C	POE	32	Oil supplier
R-410A	POE	32	Oil supplier
R-22	MO	32	Authors
R-22	POE	32	Oil supplier
R-290	AKB	68	Oil supplier
R-290	PAG1	68	Authors
R-290	PAG2	68	Authors
R-290	PAG3	68	Oil supplier

R-22/POE32 has the highest values of refrigerant solubility and logically the lowest values of resulting viscosity (these values are still acceptable for a correct lubrication of the compressor). R-22/MO32 has a much lower solubility and higher viscosity. This couple is also suitable and the lower solubility is an advantage regarding the total mass of refrigerant in a refrigeration loop. The two HFC based couples have intermediate solubilities and slightly higher viscosities. R-290/AKB68 has quite the same values of solubility as R-407C/POE32, but the resulting viscosity is much lower. When comparing R-290/AKB68 versus R-22/POE32, we find a solubility roughly divided by two and quite the same viscosity with very low values for small superheat: R-290/AKB ISO68 is not a good choice for compressor.

Figure 7 shows two non-miscible states for the couple R-290/PAG3_ISO68. This pair presents a maximum miscibility limit of about 12% all over the pressure/temperature range of measurements. This explains why the R-290/PAG3 has the lowest solubility. As a consequence, viscosity is too important for correct compressor operation, and this couple will be avoided.

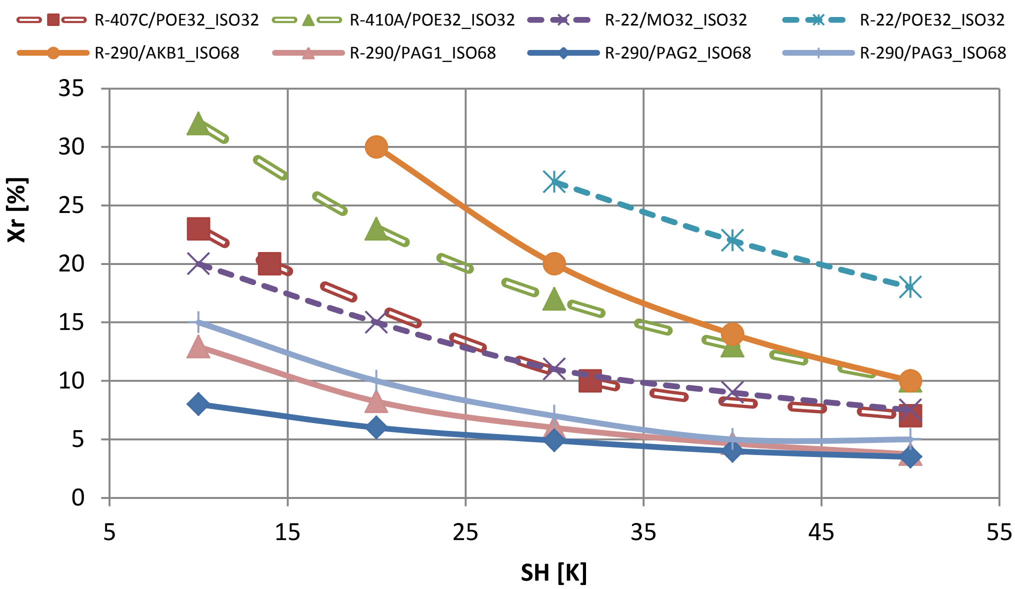

Figure 5: Evolution of solubility with superheat for T sat = 10°C (283.15K)

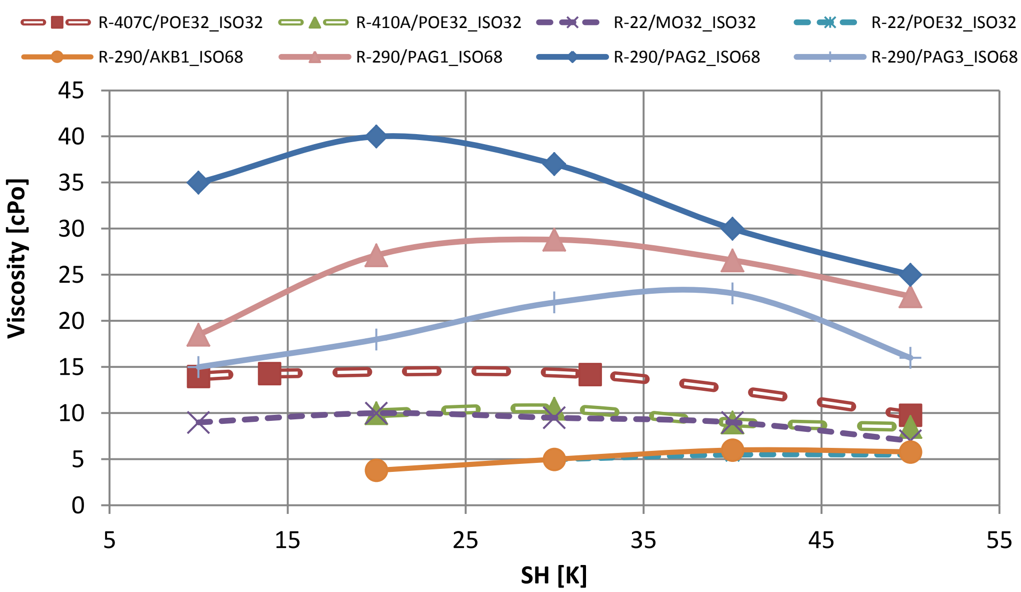

Figure 6: Evolution of viscosity with superheat for T sat = 10°C (283.15K)

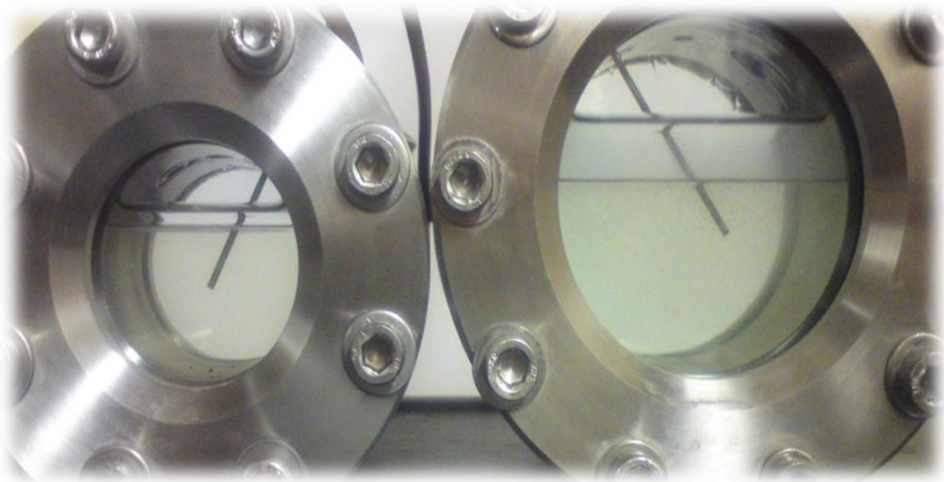

Figure 7: Partial miscibility of R-290/PAG3_ISO68 at 24°C (297.15 K), and absolute refrigerant concentration: 23% (left figure) and 31% (right figure)

3. SOLUBILITY TESTS PERFORMED IN THE CARTER OF THE COMPRESSOR

Suppliers provide Daniel plots, which, knowing the pressure and temperature, indicte the solubility of the refrigerant in the lubricant and the resulting viscosity. Unfortunately the data under low superheat conditions is not always very accurate. Furthermore, most of these plots do not give all lubricant ratio values (only 0% (pure refrigerant) and 70%, 80% and 90%). Yet, it remains a very good starting point to compare several lubricants for the same refrigerant. This is very valuable to compare existing pairs of refrigerant-lubricant with long field experience like R22-MO, R22-AKB or like HFC-POE or HFC-PVE. The characteristic measurements performed on a test bench are based on steady state values; they give a good idea of the behavior of the refrigerant and lubricant chemistry. However, the measurements don't ensure the behavior of the lubricant-refrigerant mixture in the compressor oil sump.

In order to check the actual behavior of refrigerant/oil mixtures in a compressor, tests have been run in a refrigeration loop with a scroll compressor. The compressor oil pump is connected at the lower end of the crank shaft (Figure 8).
An oil pickup tube is used for the oil pump inlet. The oil pickup tube rotation induces shear stress on the lubricant and the oil sump lubricant is stirred by this mechanical action. This could bring a better homogeneity of the oil sump lubricant-refrigerant mixture and bring lubricant outgassing process benefits.

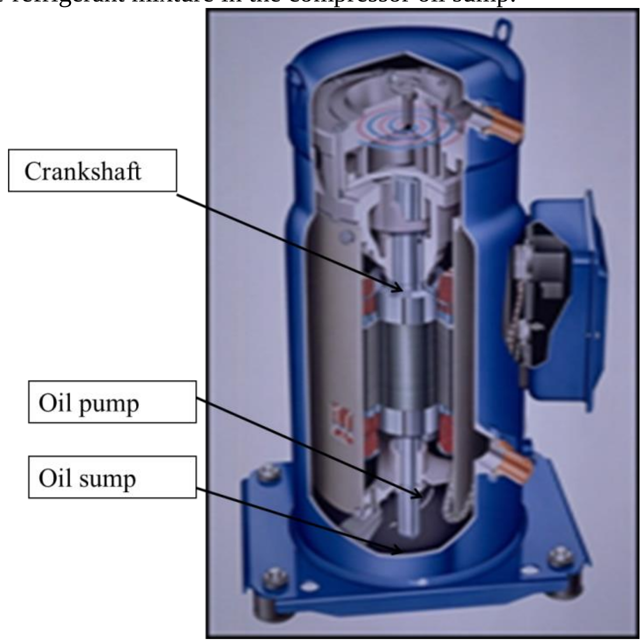

Figure 8: Compressor's crankshaft and oil pump

The compressor is a standard model with one extra fitting equipped with a valve in order to collect samples of oil/refrigerant mixture from the compressor oil sump. The process consists of running the compressor under steady state conditions and at controlled suction and discharge conditions. When the system conditions are stable, we sample a small quantity of lubricant mixture from the compressor oil sump. The sample vessel is weighed before sampling (w0) and after sampling (w1) in order to know the total mass sample (lubricant + refrigerant). Then the refrigerant is evacuated from the sample vessel, weighed again (w2) and the weight difference (w1-w2) gives the sample oil mass. The process is similar to oil circulation rate process measurement (ASHRAE standard 41.4-1996). With these 3 measurements, we obtain the refrigerant mass in the oil sump.

To check the suitability of the lubricant all over the application range of the compressor, we proceeded with tests at different superheat values and different saturated suction temperatures. Recorded parameters were oil sump temperature, oil behavior inside the oil sump, oil level, presence of foam and type of foamy situation.

For one saturated suction temperature (10°C/283.15K), the curves below (Figure 9) give the solubility versus superheat for different lubricants. For lower superheat values the measurement is repeated twice in order to have more consistent data. With a scroll compressor our measurements have demonstrated that impact of discharge pressure on Refrigerant/oil behavior in oil sump is negligible.

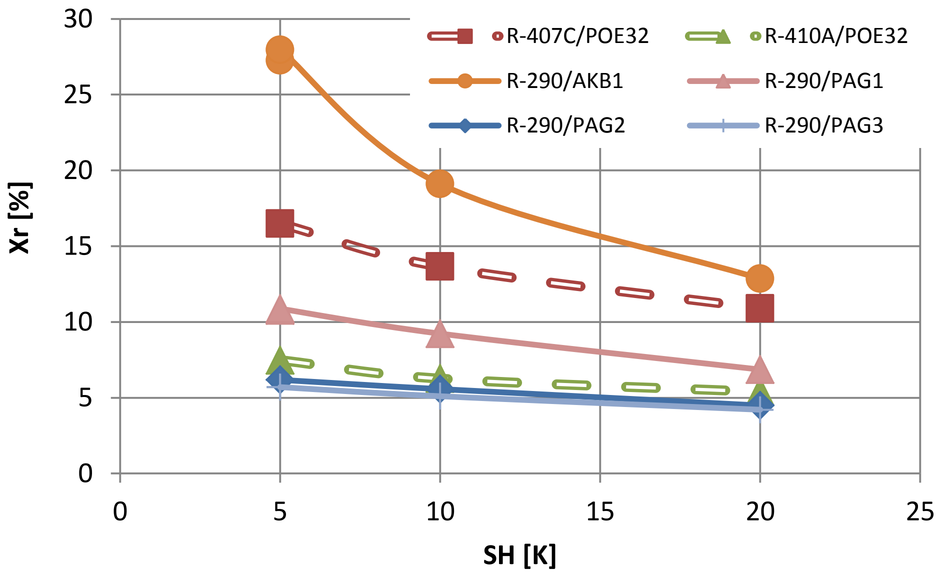

Figure 9: Lubricant % in oil sump versus superheat (K) for T sat = 10°C (283.15K)

4. COMPATIBILITY WITH COMPRESSOR MOTOR MATERIALS

Hermetic compressor motor materials can be affected by the new refrigerants/lubricants applications. For the screen process we evaluate several situations such as preliminary compatibility tests with plastic parts and motor insulation materials, or simple tests on compressors in order to see if the life testing indicates good chances of success.…

The compatibility test should be run with the lubricant and the refrigerant in bomb test. We evaluate magnet wire (twist pair), insulation material like Mylar, leads, cluster, varnish bonding stress, insulation sleeves, lacing tape, motor protection support,….

The objective of this work is to age parts inside a pressure vessel for 14 days at 150°C (423.15K)and then compare first with new material and also with other samples aged with experienced couples of lubricant/refrigerant (e.g: R-22MO, HFC/POE; HFC/PVE). First, compatibility tests are performed with lubricant and R-134a. At the end, the selected material will be checked with R-290 refrigerant including gaskets.

Dielectric and resistivity characteristic was not always available. In order to start the selection process we measured dielectric breakdown voltage and the sample PPM water content.

Table 3 below shows some of the results. We identified some impact on Mylar insulation material; it becomes very brittle on PAG2 lubricant.

Table 3: Lubricant investigation list

Lubricant	Lubricant Family	Viscosity (cSt)	Compatibility test	Dielectric test IEC 156/63
MO32	MO	32	OK (R22→ Reference 1)	> 25kV
MO2	MO	68	Not Done	Not Done
POE32	POE	32	OK (R410A-R134a →Reference 2)	> 25kV
POE1	POE	68	OK (R407C-R22 →Reference 3)	> 25kV
POE2	POE	85	OK	> 25kV
POE3	POE	68	OK (R407C→Reference 4)	> 25kV
AKB1	AKB	68	OK	> 25kV
AKB2	AKB	68	Not Done	Not Done
PAG1	PAG	68	OK	> 25kV
PAG2	PAG	68	NO OK	> 25kV
PAG3	PAG	68	OK	> 25kV
PAG4	PAG	68	To Be Done	> 25kV
PAG5	PAG	100	Not Done	To Be Done
PV1	PVE	100	Not Done	Not Done

Note: 'Reference 1 to 4' are present qualified lubricants for HCFC or HFC & used as baseline

5. CONCLUSION

Low refrigerant system charge is a key for R290 systems. The use of low R-290 solubility lubricants allows designing low charge units.
The work done shows two interesting candidates. One would be based on POE and the other on PAG base oil.
This study was done for lubricant selection. Subsequently, the compressor and system qualification work can start.
The reduction of refrigerant charge mass is a key for HC applications: less charge will allow using larger capacity units by end users while staying within the requirements of standards like EN378 or ISO 5149.
Based on 0.1 kg of R290/ kW of cooling capacity (F. Poggi, H. Macchi-Tejeda, D. Leducq, A. Bontemps), lubricant selection can reduce the R-290 mass in oil sump from 30 to 50%. In a classic system design based with 0.1 kg of R290/ kW, for 60kW capacity we estimate at least 18 to 30% refrigerant charge reduction.

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The present work has been supported by the FP7 European project 'Next Generation of Heat Pumps working with Natural fluids'(NxtHPG).

NOMENCLATURE

AKB	alkylbenzene	C	massic concentration	%
HC	hydrocarbon	cSt	cinematic viscosity	1cSt = 1 mm2/s
HFC	hydrofluorocarbon	M	mass	kg
HFO	hydrofluoroolefin	P	pressure	bar (10^5 Pa)
MO	mineral oil	T	temperature	°C (K-273.15)
PAG	polyalkylene glycol	V	volume	m^3
POE	polyolester			
PVE	polyvinyl ether			
POE	polyolester			

Greek

μ	dynamic viscosity	cP (10^{-3}Pa.s)
ρ	volumic mass	kg/m^3

Subscripts

Abs	absolute	Sat	saturation
L	liquid	Tot	total
Oil	lubricant	TBD	To Be Done
R	refrigerant	V	vapor

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