Effects of CO_2 on lubricating properties of polyolesters and polyalkylene glycols.

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SUMMARY

A major requirement for refrigeration oils is to provide effective lubrication for compressor bearings in a refrigerant atmosphere. Load-carrying capacity and anti-wear properties of synthetic lubricants have often been evaluated using standard methods like Falex Pin&Vee Block methods. However, this widely used standard test machine does not normally operate in artificial environments, such as pressurized gases. To characterise the behaviour of synthetic lubricants in a pressurized refrigerant-environment, extreme pressure method ASTM D-3233 has been adapted by bubbling gas through the lubricant during a test. However, the relevance of results obtained with this method with respect to CO_2 has been the topic of some discussion.
For a given application, the Extreme Pressure and Anti-wear behaviour of lubricants in a high-pressure CO_2-environment need to be evaluated. This paper evaluates the Pin&Vee Block method and describes a method more suitable to determine the influence of CO_2 environment on lubricants and additives. A Falex Block-on-Ring test machine with pressure chamber was used to investigate the effects of CO_2 on lubricating properties.

1. Introduction

A major requirement for refrigeration oils is that they provide effective lubrication for compressor bearings. Especially automotive air conditioning compressors have to work under hard conditions. Bearing loads vary and can be extremely high, in addition to this the oil film is often disturbed by refrigerant "flooding" or can be disrupted by vaporization of dissolved refrigerant. For proper bearing design viscosity data of lubricating oil with dissolved refrigerant is essential [1].

After the phase out of chlorinated HCFC refrigerants due to international regulations with respect to the protection of the ozone layer, now there is a tendency to use again natural refrigerants like ammonia and hydrocarbons. Also carbon dioxide (R 744) can be seen as one of the most interesting alternative working fluid for different applications [2]. First prototype systems for automotive air conditioning and heat pumps show increased efficiency in comparison to the state of the art systems using refrigerant R-134a [3].[4]. While the working fluid in conventional systems is in the sub-critical state, CO_2 is sub and- supercritical with respect to pressure and temperature. Experiences based on experimental and practical tests show lubricant behaviour to be one of the key issues in these systems, as the right choice of lubricant must also be considered to be part of the system construction.
The applications of future trans-critical CO_2 systems will require special synthetic lubricants due to the high pressure and the resulting high bearing loads. Therefore, lubrication properties need to be measured and compared to achieve high system performance and reliability [5]. Experimental solubility data of different synthetic lubricants show extremely high dilution of the oil by dissolved CO_2 significantly reduces the viscosity of the pure lubricant [6]. POE type oils show good miscibility, while PAG are less miscible with CO_2 [7] [8]. According to [9] an Almen-Wieland machine can be used to compare tribological properties of different refrigeration oils at 1 bar refrigerant atmosphere. First tests with CO_2 indicate different friction characteristics but do not confirm a drastic negative effect of CO_2 on lubricity. Wear test results obtained with Falex Pin&Vee Block saturated with CO_2 at room temperature and atmospheric pressure (gaseous CO_2 was

continuously bubbled through the lubricant sample during a five-hour test period) are reported in [10]. Ranking of four ISO VG 220 synthetic base stock lubricants from best to worst based on the results of those Falex tests is: PAG > POE > PAO >> AB. While it might be expected that higher solubility, and thus more CO_2 dissolved in the lubricant at a given temperature, would result in lower viscosity at that temperature, the experimental data did not confirm this expectation. This led to the conclusion that further tribological research at higher CO_2 pressures and more practical conditions is needed to develop an effective lubricant.
Clearly, the Pin&Vee Block and Almen-Wieland methods with bubbling of CO2 gas are not sufficient and do not predict field experience correctly. After all, a method that does not correlate with field behaviour has no use. The difficulty of predicting the field behaviour of newly developed products led to the definition of another simulation method, which is presented in this publication.

2. Materials tested and test geometry selection

Test method selection

The application of interest is a compressor bearing, typical working conditions and geometry of the application can be simplified to a sliding line contact (cylinder inside a larger cylinder) evolving into a conforming area contact because of run-in wear. Sliding occurs unidirectional and the load on the line contact is nominally constant. Utilizing the TAN-selection code[11,12] (Tribological Aspect Number), several geometries are proposed: Block-on-Ring, Timken, O-Ring or Pin&Vee Block test (similar to Almen-Wieland).

The Pin&Vee Block test in atmospheric condition was previously used but was found to be too limited. This test machine (Figure 1) uses a fixed and relatively low speed of 292 rpm. On a ¼" diameter journal pin, this leads to a sliding speed of 0,1 m/s. Maximum loading force is 13361 N (3000 lb) over four line contacts of ½" length, under a 42° angle. Thus, the normal loading is maximum 168 N/mm. Finally, it is not easy to perform tests with this equipment at elevated pressures unless the whole machine can be placed in a pressure chamber.

Figure 1 : Schematic of the Pin&Vee Block test method

It was found to be more appropriate to consider a Block-on-ring test machine, equipped with a pressure chamber (Figure 2).
In this test machine, unidirectional speed can be continuously varied between 0,01 rpm and 3000 rpm. On the 30 mm diameter standard rings, maximum speed is 5,5 m/s. With a maximum 1000 lb loading on a standard block of 6,35 mm width, line contact loading is 695 N/mm. The mechanical loading properties are therefore far more flexible than the Pin&Vee Block test equipment.

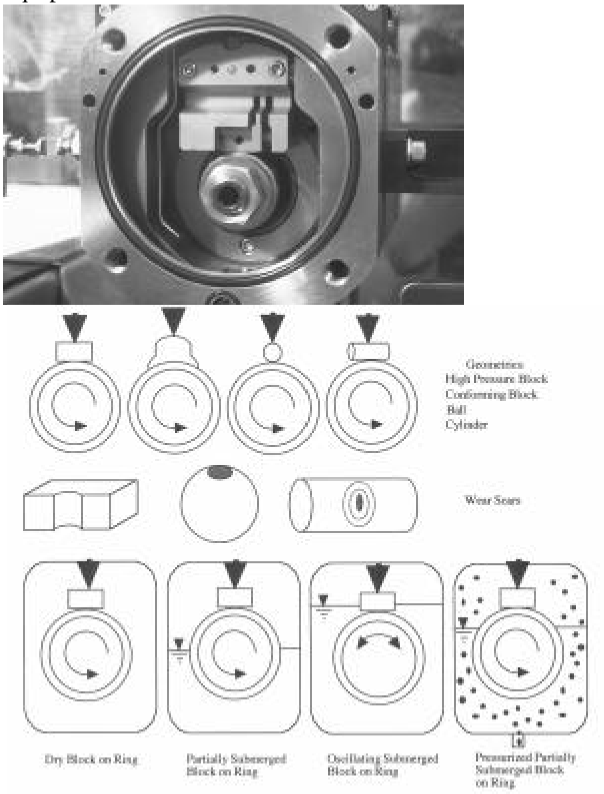

Figure 2: Block-on-ring test machine with pressure chamber. Contact geometry (above) – possible configurations (below)

The most important for this investigation, is that this test machine is equipped with a pressure chamber that allows CO_2 refrigerant to be introduced under pressure, so that the lubricant can be tested under more realistic conditions.

In this way, the effects of gas pressure on tribological relevant properties (solubility with lubricant, viscosity changes and change of AW- and EP- properties) and on the wear mechanism can be simultaneously evaluated.

Materials and lubricants
In this work, six synthetic lubricants of interest are evaluated in tribological sliding contact both against steel and aluminium to simulate the application.

POE-0	Polyol ester without additives
POE-1	Polyol ester with Additive pack A
POE-2	Polyol ester with Additive pack B
PAG-0	Polyalkyl glycol without additives
PAG-1'	Polyalkyl glycol with Additive pack C
PAG-2'	Polyalkyl glycol with Additive pack D

POE = Polyol ester without (0) or with (A, B) anti-wear additive packages. PAG = polyalkyl glycol with similar but not equal additive packages.

3. Comparison of Pin&Vee Block and Block-on-ring, extreme pressure methods.

3.1. Test methods

The target of the investigation is to develop a suitable wear test based on block-on-ring configuration, to evaluate the anti-wear properties of various lubricants. However, the loading levels of the Pin&Vee Block wear test cannot be directly transferred to the Block-on-ring test. Speed, entry angle, dynamic properties (vibrations) and the number of line contacts are all different. So it is required to firstly establish the load-carrying capacity or EP-properties of the lubricants in the selected method to compare at 10 bar CO_2 pressure. When the ultimate limiting load is known, a lower load can be selected for the –long term- wear tests.

Pin&Vee Block test data have been used to characterize lubricity properties of refrigeration oils since many years : [13,14,15]:. so a comparison of results between Pin&Vee Block and Block-on-ring is appropriate. With the Pin&Vee Block machine, the EP-test according to ASTM 3233-B was used in this test. A wear-in at 300 lbs is followed by a stepwise increase of the loading with 250 lbs per minute until failure is detected. CO_2 is bubbled through the lubricant during the test. Failure occurs when the friction suddenly increases when the lubricant film breaks down. Either breakage of the pin or the shear pin, overheating of the lubricant or excessive wear indicates this failure.

With the Block-on-ring machine, the test consists of a run-in wear period at 20 lbs load, and stepwise loading with 50 lbs until failure is detected. Failure of the lubricant film is indicated by sudden increase of the friction, seizure or excessive wear. A typical on-line result (Figure 3) shows the increase of friction at 200 lbs. Failure of the lubricant can also lead to incipient seizure rather than catastrophic failure. This is indicated by an increased variation of the friction force, as shown in Figure 4. Seizure can be confirmed after the test by microscopic evaluation of the wear track (Figure 5).

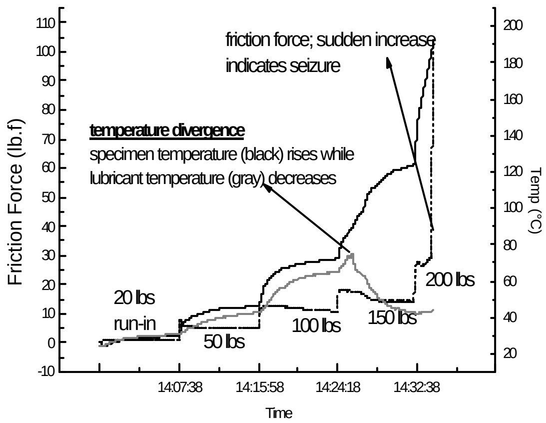

Figure 3 : On-line friction force in the extreme pressure Block-on-ring test, steel block. Immediate increase in friction force when lubricant film breaks down.

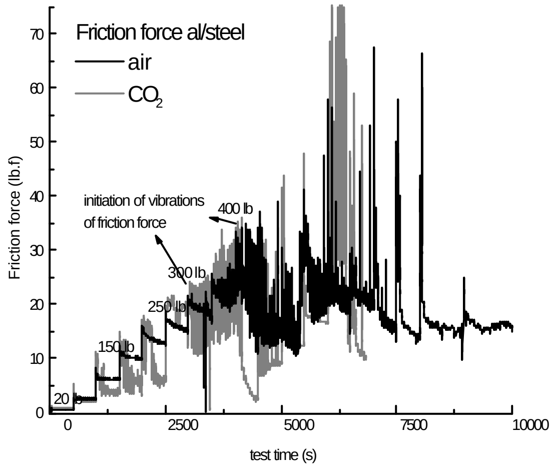

Figure 4 : On-line friction force in the extreme pressure Block-on-ring test, steel block. Breakdown of lubricant is indicated by incipient seizure (friction signal showing large variations)

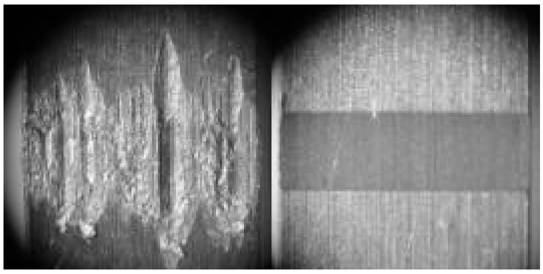

Figure 5 : Left : seizure of Aluminium test block in Block-on-ring E.P. test. Right : uniform wear of Steel test block.

3.2. Test results and discussion

The results of the Extreme Pressure tests are summarized below.

Pin&Vee Block test, CO_2 bubbling, steel-steel

Lubricant	Failure load ASTM 3233-B
POE-0	750
POE-2	750
PAG-2	1000

Table 1 : Pin&Vee Block EP tests of POE and PAG

Block-on-ring test, CO_2 pressure or air atmosphere Steel/Steel

Lubricant	Atmospheric (A) or CO_2	Failure load (seizure)
POE-0	A	>600
POE-0	CO_2	200
POE-2	A	>600
POE-2	CO_2	>300
PAG-2	A	> 300
PAG-2	CO_2	250

Table 2 : Block-on-ring EP tests of POE and PAG in air and CO_2, steel blocks against steel rings

The Pin&Vee E.P. method does not detect a difference between the Polyol esters with and without additive and indicates that the additized PAG 2 performs better than both POE's. However, the EP-test in the Block-on-ring machine, at pressurized CO_2 conditions, indicates that

there is a significant difference between POE with and without additives. Where both esters are equivalent in air, in the CO_2 atmosphere POE-0 without additive fails at a load of 150 lbs, while the additized POE-2 can carry the load up to 300 lbs or more. Furthermore, the testing of the additized PAG-2 in CO_2 indicates that the atmosphere also affects PAG.
These tests show that the Block-on-ring method in 10 bar CO_2 atmosphere produces contradictory results from the Pin&Vee Block method. Because the Block-on-ring method gives better simulation of the environmental conditions of the application (confirmed by first field experience), it must be concluded that the Pin&Vee Block method with CO_2 gas bubbling is not suitable to simulate the application correctly.

Because further results in Block-on-ring tests, including both steel and aluminium test blocks indicate a minimum seizure load of 150 lbs the anti-wear test will be executed at a constant load of 100 lbs.

Steel and aluminium blocks, steel rings, all in POE-0

Material combination	Atmospheric (A) or CO_2 (CO_2)	Failure load (seizure)
St/St	A	>600
St/St	CO_2	200
Al/St	A	400
Al/St	CO_2	300

Steel in PAG-2

Material combination	Atmospheric (A) or CO_2 (CO_2)	Failure load (seizure)
Al/St	CO_2	300

Table 3 : Block-on-ring EP tests of POE and PAG in air and CO_2, both steel blocks and aluminium blocks against steel rings.

4. Temperature effects

While EP tests were executed in the block-on-ring test machine, both the frictional force and the temperature of the block and of the test chamber (lubricant temperature) are continuously monitored. An example of the online data during a test on POE-0 in air is shown in

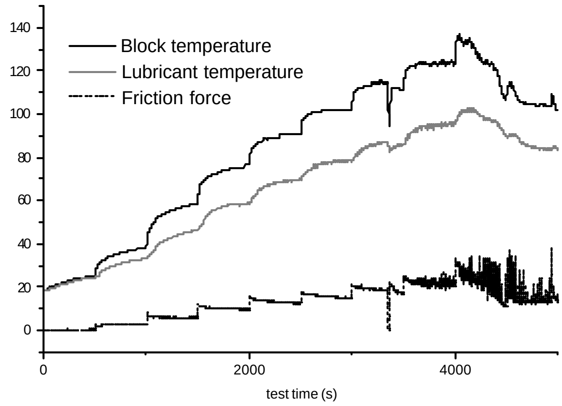

Figure 6. Every time the load on the contact is increased, the frictional force increases also leading to higher frictional heating. As the temperature of the block increases, so does the lubricant temperature because the lubricant absorbs the increasing frictional heat. However, something unexpected happens to this evolution when the test is executed in CO_2. Figure 7 shows that at a given point, the temperature of the test block increases rapidly while the temperature of the lubricant drops. Apparently, the lubricant no longer cools as well as before, so a lot of the frictional heat is no longer transferred from the block to the lubricant. It seems that this point is characterised by a certain threshold lubricant temperature of around 70°C.

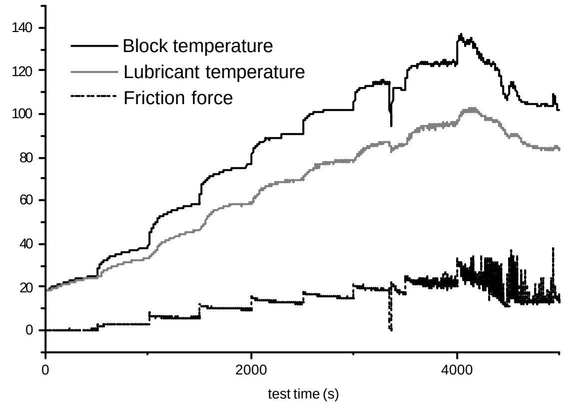

Figure 6 : Online data during Block-on-ring EP test in air, POE-0, steel block vs. steel ring

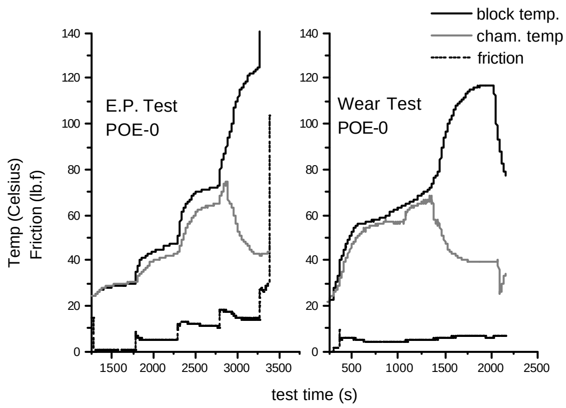

Figure 7 : Online data during Block-on-ring EP test (left) and Wear test (right) of POE in 10 bar CO2. Divergence of lubricant and block temperature
Some hypotheses can be put forward to explain this behaviour. It is possible that the viscosity of the lubricant changes dramatically, having an effect on the lubricant film thickness and that in turn may cause a difference in heat transfer. However, there is no indication in Figure 7 (right) that the friction changes dramatically, which would be expected from a sudden change in viscosity.
It is also conceivable that at the given temperature, the dissolved CO_2 expands out of the lubricant and gas bubbles are created that physically interfere with the heat transfer at the block.

In the EP test, this behaviour announces that the load carrying capacity is close to been reached. In the wear test, it is very likely that increased wear occurs from this point onwards.

This effect was not noticed for the PAG, but only for the POE-0 in 10 bar CO_2, confirming our thesis that reliable simulation tests can only be attempted when at least the high pressure CO_2 atmosphere can be recreated in the test machine.

5. Determination of Block-on-ring wear test

The Extreme Pressure tests indicated that wear tests must be done at a load level lower than 150 lbs. For comparison of anti-wear properties on synthetic lubricants at CO_2 atmosphere, a load level of 100 lbs was selected.

Test parameters

Parameter	Value	Remark
Speed	600 RPM	+/- 1 m/s
Load	100 lbs	69.5 N/mm
Temperature	'free'	online measured
Test duration	30-300 min	wear evolution
Materials	Ring : S10 standard	Block : H30 standard steel HP 380 standard die casting aluminium

The evolution of the wear volume is characterised by running the wear test for subsequent intervals of 30-90-150-210 and 300 minutes. After every interval, the test block is carefully removed together with the block holder (to retain alignment) and the wear scar width is measured. The wear volume can be calculated from this, assuming the wear scar forms a cylinder segment conforming with the ring. Observation in perpendicular direction confirms that this is indeed the case. Determining the evolution is essential to define the stages of wear : run-in, steady wear and/or accelerated wear. Earlier Pin&Vee Block test results suggest that a sudden increase in wear rate occurs after 5 hours of testing time. The wear evolution of unadditized POE-0 in air and in CO_2 is compared in Figure 8.

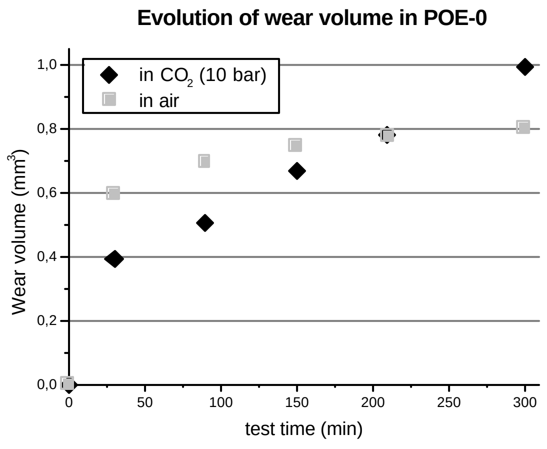

Figure 8 : Evolution of wear volume of POE-0 in air and in compressed CO_2

Whereas run-in wear in air is quite large, wear rate decreases with time. This is not the case in CO_2, at least not in the first 5 hours of testing. But also, an increase within 5 hours of testing is not noticed. But in Figure 7 it can be seen that temperature divergence effects already takes place in the first 30 minutes of the test. So any effects on reduced lubricity of the oil will already be active from the beginning of this evolution. Long term (+5 hours) wear in CO_2 will be larger than in air.

When the additized POE-2 is considered (Figure 9), the wear evolution is quite different. In this case, there is consistently lower wear of the steel blocks in CO_2 than in air, mainly because the run-in wear in air is much larger than in CO_2. A similar evolution is measured with the additized PAG-2 (Figure 10), but with lower wear values than POE-2.

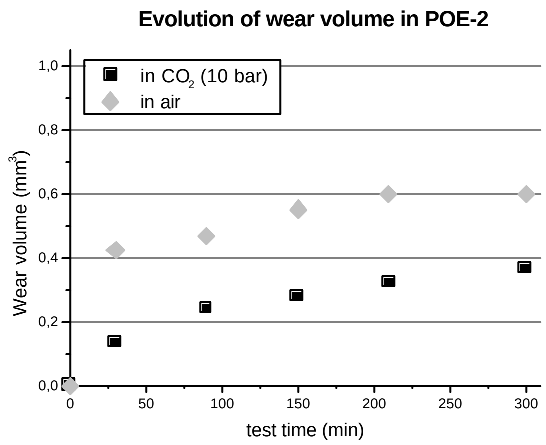

Figure 9 : Evolution of wear volume of POE-2 in air and in compressed CO_2

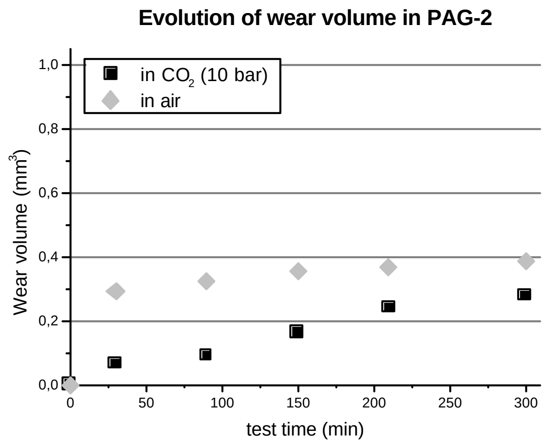

Figure 10 : Evolution of wear volume of PAG-2 in air and in compressed CO_2

However, there is a general indication that the wear rates in air tend to reduce in the long run, whereas the wear rate in CO_2 remains consistently higher. This means that the CO_2 environment may have some initial beneficial effects on wear reduction (seem to reduce the run-in wear) but that the wear in the long run may be larger than in air.

The wear volume after standard test duration of 5 hours in CO_2, is shown in Figure 11. Non aditized POE does not perform well in compressed CO_2. The special additives seem to have a large effect on AW- properties of POE,. Those effects for the PAG are much less pronounced.

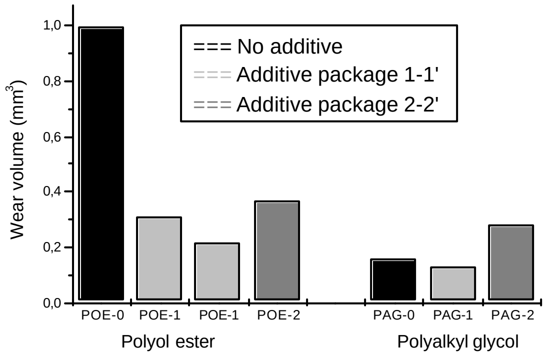

Figure 11 : Wear volume after 5 hour tests in CO_2 for different synthetic lubricants and additive packages.

6. Conclusions

1. Falex Pin&Vee Block method (ASTM 3233-B) using refrigerant gas bubbling through the lubricant is insufficient to simulate the effects of compressed CO_2 on load-carrying properties. In this case the conventional EP method (ASTM 3233-B) even leads to incorrect conclusions and gives no correlation with the practical experience of prototype testing. It is necessary to simulate under realistic conditions, and the actual presence of a high-pressurized CO_2 gas is relevant for the test results.

2. CO_2 has various effects on the EP and AW-wear properties of synthetic lubricating oils. The Falex Block-on-ring test machine can be used as the first screening test to simulate the behaviour of candidate lubricants used in future CO_2-air conditioning compressors. Additionally, the friction force, temperature of block and lubricant can be measured more accurately and the loading mechanism is more precise than with the Pin&Vee Block test machine. The variation on test data is expected to be lower, allowing a more precise comparison of different lubricant formulations.

3. Particularly in the investigated POE, a thermally induced effect appears, which is likely to affect the tribological properties. It is of the highest importance to be aware of effects like these to be able to prevent catastrophic compressor damage occurring in this special application, where solubility of CO_2 and lubricant is likely to play a main role.

4. The wear behaviour of synthetic lubricants at 10 bars CO_2 is clearly different from their behaviour in air. The 5-hour tests indicate that run-in wear is reduced but that the actual steady state wear-rate is larger. This conclusion has important consequences for lifetime predictions of the components.

5. It was clearly demonstrated that earlier test data obtained from conventional refrigeration oil applications cannot be adapted to CO_2 and have to be used with great care. It seems that only tests that were actually carried out in a high pressure CO_2 environment are likely to lead to correct conclusions.
Further research in this field is still necessary. Test duration must be extended to evaluate the long-term effects of CO_2 on wear.

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