Thermodynamic and Fluid-Dynamic Properties of Carbon Dioxide with Different Lubricants in Cooling Circuits for Automobile Application

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The application of carbon dioxide as the refrigerant in vehicle air conditioning requires the development of a suitable lubricant for the quickly rotating compressor. The phase behavior of different synthetic lubricants with carbon dioxide forms the basis for developing a CO_2^- cooling circuit. Furthermore, the influence of carbon dioxide upon the viscosity of the oil is essential for evaluating a lubricant. These data of the binary mixtures have been measured at temperatures between 5 and 100 °C under pressures of up to 150 bar. The qualitative observation of phase behavior took place in a high-pressure view cell, whose complete content is monitored. The phase equilibria have been determined in an autoclave based on a static-analytical method. The viscosity of the lubricant which is saturated with carbon dioxide has been measured with an integrated quartz viscosimeter. The phase behavior of oils with carbon dioxide can be divided into three different types: binary systems with closed miscibility gaps, systems with open miscibility gaps, and systems that show barotropic phenomena. Oils that show barotropic behavior in contact with compressed carbon dioxide are not recommended as lubricants. Oils with complete or limited miscibility with carbon dioxide may be used. The knowledge of phase behavior and the resulting viscosity of gas-saturated lubricants allow one to evaluate the applicability of lubricants in car-climatization systems.

Introduction

For about 50 years chlorofluorocarbons have been used as refrigerants for cooling systems. Manufacturing and utilization of these ozone-damaging refrigerants have been prohibited in Germany since Jan 1, 1995. Since then, R134a (fluorocarbon), which has no ozone-depletion potential but still contributes to the greenhouse effect, has been used.[1] Compared to R134a, carbon dioxide (CO_2) is a environmentally benign refrigerant and shall replace the common refrigerants in air-conditioning systems in the future. The small allowable size of climatization units in cars and the specific thermodynamic properties of CO_2 are challenges for designing the compressor and the whole cooling circuit. The oil has to lubricate the shaft and the bearings in the quickly rotating compressor, which provides the necessary cooling capacity.[2] On the one hand, the miscibility of the binary mixture consisting of lubricant and CO_2 influences the viscosity of the lubricant, and on the other hand, it causes a certain quantity of oil running through the circuit as ballast. The knowledge of thermodynamic and fluid-dynamic properties of the binary system is necessary for the development of a reliable cooling circuit.

Cooling Circuit with Carbon Dioxide

The introduction of the natural refrigerant CO_2 has effects on the design of each mechanical component in the cooling circuit, on the used material, and on the entire process. One reason is the relatively low critical
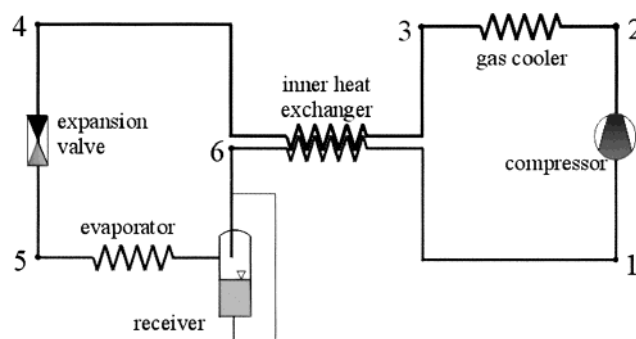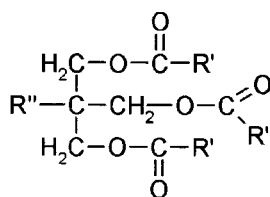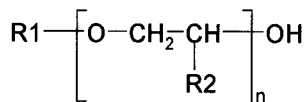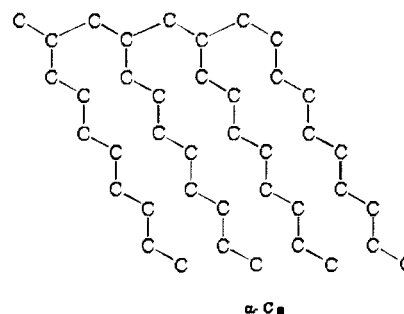
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Figure 1. Functional scheme of the CO_2 cooling circuit.

temperature of 31.04 °C, which is overshot by vehicle air conditioners on the hot side in most cases. The CO_2 process is consequently working supercritical on the high-pressure side, and the classical condenser is replaced by a gas cooler which works in the supercritical area.[3] For establishing a CO_2-refrigerating plant in cars, pressures between 30 and 140 bar and temperatures between −10 and +140 °C are necessary for a sufficient cooling efficiency. A cooling circuit (see Figure 1) consists of a compressor, gas cooler, inner heat exchanger, expansion valve, evaporator, and low-pressure receiver.[4]

It is necessary to raise the pressure at an increasing environmental temperature in order to produce a specific coldness. The reason for the insertion of the already mentioned inner heat exchanger is that the gradient of the isotherms increases at high pressure and without an inner heat exchanger the enthalpy after the gas cooler would be too high.[4] The "heart" of the refrigerant plant is the fast-rotating compressor. Without lubrication, the compressor would fail because of the large

Polyolester (POE) Polyalkylenglycol (PAG) Polyalphaolefin (PAO)

Figure 2. Structures of different synthetic lubricants.

mechanical stresses in the bearings and shaft. A minimum viscosity of the lubricant in contact with compressed CO_2 is necessary. The lubricant is withdrawn from the compressor in the circuit mechanically withdrawn and/or by the solubility in compressed supercritical CO_2. To avoid a lack of lubrication, the oil must be fed back from the circuit into the compressor. Therefore, the feedback of the oil from the cold components, especially from the evaporator, is important. Oils with a good miscibility with the refrigerant CO_2 are of advantage here.

Lubricants

Applicable lubricants have to show the following properties:[5] (a) good viscosity−temperature behavior and cryogenic flow behavior, (b) high thermical and chemical stability, and (c) high boiling point and low solidifying point.

Polyolester (POE), poly(alkylene glycol) (PAG), and poly(α-olefin) (PAO) are synthetic lubricants, which partly succeeded in application with common refrigerants. The basic structures of these lubricants are shown in Figure 2.[5]

In interaction with the refrigerant CO_2, the lubricant has to guarantee a sufficient lubrication of the compressor at high temperature. The lubricant also has to minimize the temperature in the hot parts of the compressor, i.e., shaft and bearings. A low viscosity of the oil is needed at low temperature for its reflux from the cold parts of the plant into the compressor.

Experimental Plants

High-Pressure Cell. For the observation of the phase behavior, a high-pressure cell (see Figure 3) applicable for temperatures between −20 and +150 °C and pressures of up to 200 bar is used. The interior volume is 25 cm^3 and can optically be observed by two opposite glass sight windows. The temperature is controlled by a heating jacket consisting of two semishells and a thermostat. The temperature is measured by a thermocouple, which is positioned in the upper third of the cell. Underneath the cell is fixed a stirrer, which propels a magnet for mixing the two substances in the cell.

Autoclave. The measurement of the phase equilibria and the determination of the viscosity of the CO_2 saturated oil take place in an autoclave (see Figure 4) with a volume of 1 L. It is designed for a temperature range of −20 up to +150 °C at pressures of up to 250
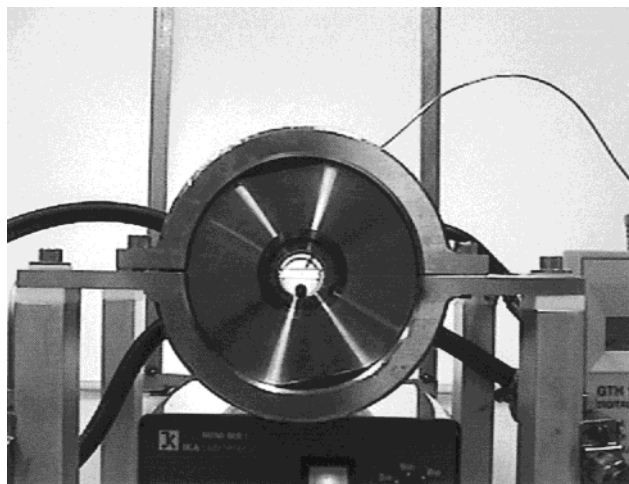
Figure 3. Photo of the high-pressure cell.
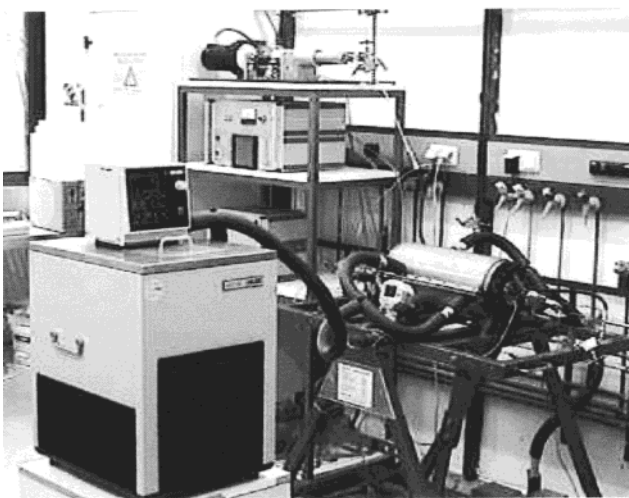
Figure 4. Photo of the autoclave with thermostat and pressure regulation.

bar. The autoclave is mounted on an oscillating device for mixing of the binary system.

The temperature is regulated by using a thermostat with two semishells around the autoclave. The phase equilibria are measured by the static-analytical method.[6] A sample is taken from the lower or upper phase, respectively. During the sampling, a bellow in the autoclave—controlled by a pump—compensates the pressure loss. The dynamic viscosity of the CO_2-saturated oil phase is determined with a quartz viscosimeter,
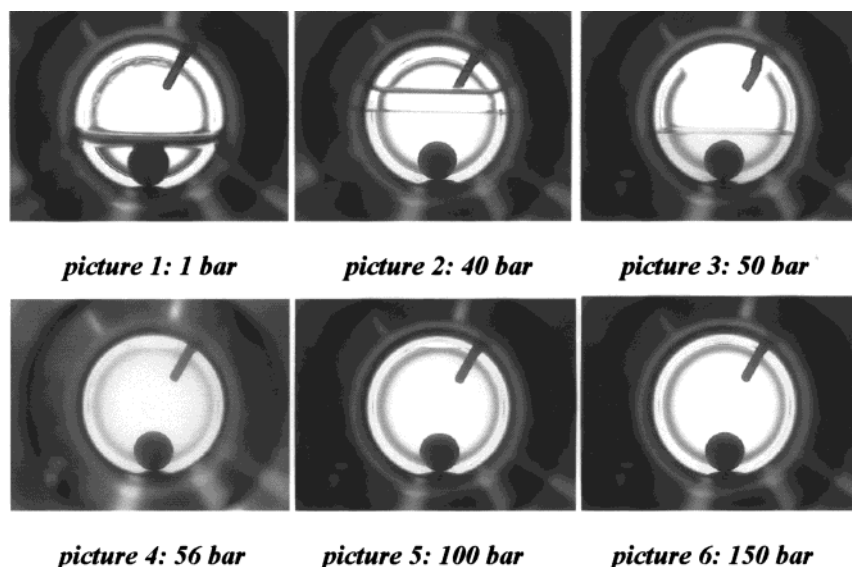
picture 1: 1 bar   picture 2: 40 bar   picture 3: 50 bar

picture 4: 56 bar   picture 5: 100 bar   picture 6: 150 bar

Figure 5. Phase behavior of the system POE−CO$_2$ (T = 5 °C).

picture 1: 1 bar   picture 2: 40 bar   picture 3: 50 bar   picture 4: 150 bar
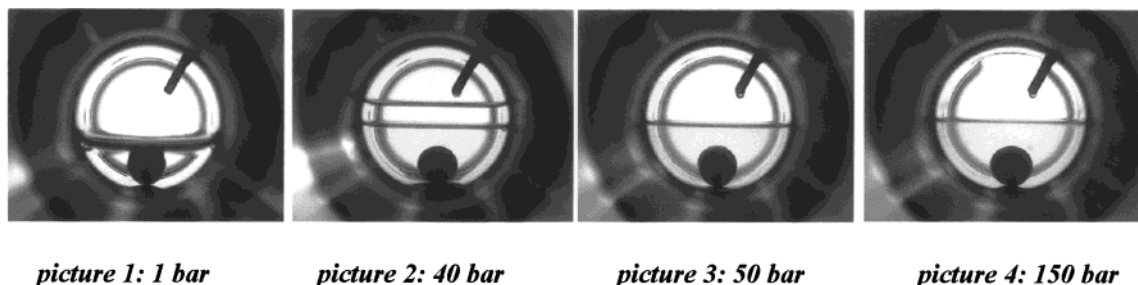
Figure 6. Phase behavior of the system PAG−CO$_2$ (T = 5 °C).

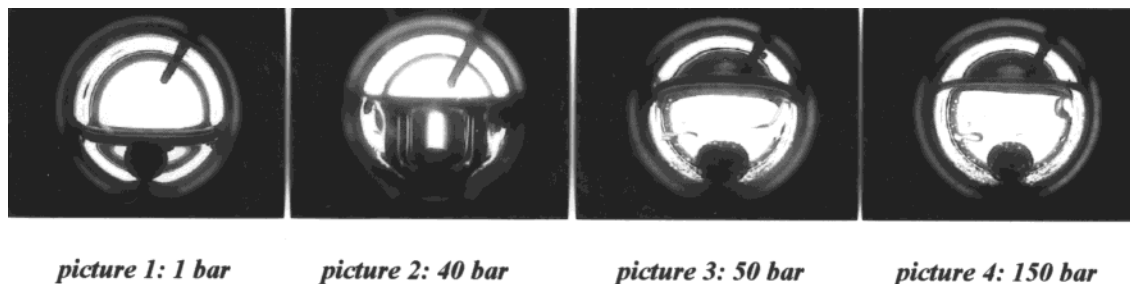picture 1: 1 bar   picture 2: 40 bar   picture 3: 50 bar   picture 4: 150 bar

Figure 7. Phase behavior of the system PAO−CO$_2$ (T = 5 °C).

which is integrated in the lower cover of the autoclave. The measurement range is between 1 and 10 000 mPa s.

Results and Discussion

Phase Behavior. (i) POE with CO$_2$. The pictures in Figure 5 show the phase behavior of the system POE−CO$_2$ at a temperature of 5 °C and pressures of up to 150 bar. Compared to the lubricant under atmospheric pressure (picture 1), the phase interface of the CO$_2$-saturated oil has increased at a pressure of 40 bar (picture 2). The increased volume of the lubricant phase is caused by the dissolved CO$_2$. The two phases above the lubricant phase consist of liquid and gaseous CO$_2$. At a pressure of 50 bar (picture 3), only one phase mainly consisting of liquid CO$_2$ exists above the lubricant. At that point the volume of the lower phase decreases because of the higher solubility of POE in liquid CO$_2$. The closing of the miscibility gap (one homogeneous phase) is observed at a pressure of about

56 bar (picture 4). The phase behavior does not change anymore (pictures 4−6) with rising pressure.

(ii) PAG with CO$_2$. A lubricant classified to a PAG basis displays a different phase behavior in a mixture with CO$_2$. A three-phase area also occurs in this binary system (picture 2, Figure 6). The increase of the volume of the lower phase is smaller compared to that of the binary system POE−CO$_2$ under the same conditions. The reason is that less CO$_2$ is dissolved in the lubricant PAG. At higher pressure of up to 150 bar, the lubricant is only partially miscible with liquid CO$_2$ (pictures 3 and 4).

(iii) PAO with CO$_2$. Barotropic behavior is observed with lubricants, which have a lower density than the liquid phase consisting of liquid CO$_2$ and dissolved lubricant. PAO with a density of about 840 kg/m^3 at 15 °C and 1 bar shows this phase behavior with compressed CO$_2$ at a temperature of 5 °C (see Figure 7). At a pressure of 40 bar, the CO$_2$-saturated lubricant PAO begins to "swim" on the liquid CO$_2$ phase (picture 2).
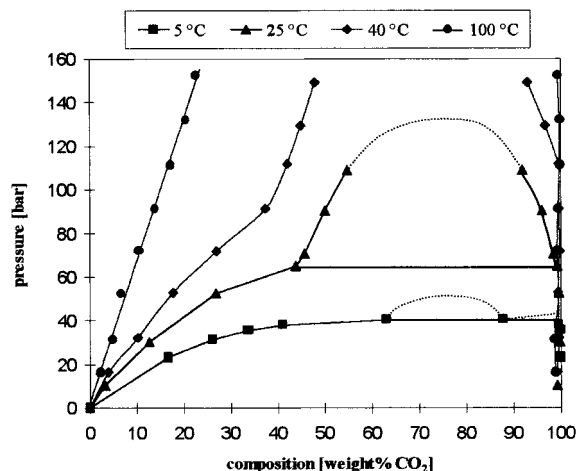
Figure 8. Pressure−composition diagram of the system POE−CO_2.

Figure 9. Pressure−composition diagram of the system PAG−CO_2.

Figure 10. Pressure−composition diagram of the system PAO−CO_2.

Gaseous CO_2 exists above these "mixed phases". The phase inversion can to be seen more distinctly in pictures 3 and 4 at pressures of 50−150 bar. The lower phase consists of liquid CO_2 saturated with lubricant. The upper phase consists of the lubricant PAO saturated with CO_2.

Phase Equilibria. (i) POE with CO_2. In Figure 8 the phase equilibrium of the system POE and CO_2 is presented. The curves on the left side of the diagram show the composition of the CO_2-saturated lubricant POE at different temperatures. On the right side of the diagram, the curves of the coexisting CO_2 phase are represented.

The solubility of CO_2 in the lubricant increases with decreasing temperature and rising pressure up to temperatures of 5 and 25 °C and pressures of about 55 and 135 bar. At these pressures the miscibility gap is closed, which means that POE and CO_2 are completely miscible. The 5 and 25 °C isotherms show an inflection point at about 40 and 65 bar. At these conditions, three phases coexist, as indicated by a horizontal line. Below these pressures, the CO_2 concentration in the oil increases considerably with rising pressures. There is an equilibrium between a liquid phase consisting of lubricant in which CO_2 is soluted and a gaseous CO_2 phase. Above the three-phase line, the lubricant is in equilibrium with liquid CO_2. A small area consisting of liquid and gaseous CO_2 exists at a temperature of 5 °C and a pressure of 40 bar (three-phase line) on the right side of the diagram. In the liquid CO_2 phase, more than 10 wt % of the lubricant POE is dissolved. At temperatures of 40 and 100 °C, the solubility of CO_2 in the lubricant POE increases also with rising pressure. The solubility of POE in liquid CO_2 decreases strongly with rising temperature.

(ii) PAG with CO_2. The phase equilibrium in the system PAG and CO_2 is shown in Figure 9. PAG and CO_2 are not completely miscible, which means that the system has open miscibility gaps at every temperature. The low solubility of PAG in CO_2 even at pressures of up to 150 bar is remarkable.

The solubility of CO_2 in the lubricant increases with decreasing temperatures and rising pressure. At subcritical temperatures (5 and 25 °C), the increase of the solubility is very strong until the three-phase line is reached. In the liquid−liquid miscibility gap, the solubility of CO_2 in PAG nearly stays constant. At high temperatures (100 °C), a constant increase of the solubility is measured.
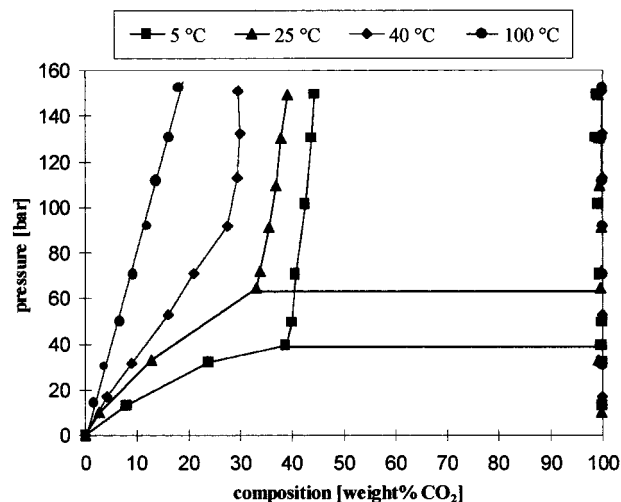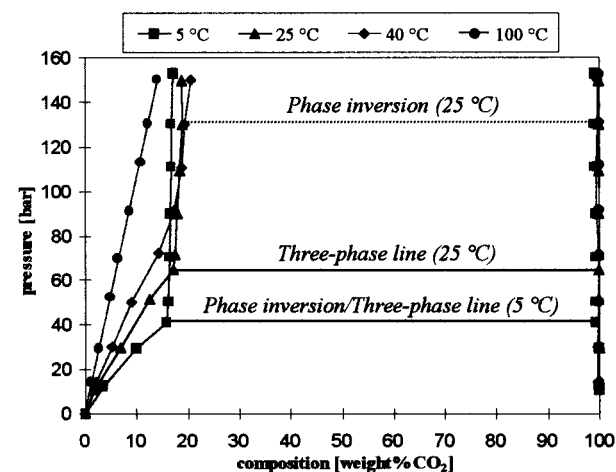
(iii) PAO with CO_2. The phase equilibrium of the system PAO and CO_2, presented in Figure 10, also displays open miscibility gaps in the complete pressure and temperature range. The solubility of PAO in CO_2 even at pressures of up to 150 bar is very low.

Compared to PAG, the solubility of CO_2 in PAO is lower. The barotropic behavior occurs at 5 °C at a pressure of 40 bar (almost on the three-phase line), and at 25 °C, it occurs at about 130 bar (approx. 65 bar higher than the three-phase line). At pressures of up to 60 bar at near-critical temperatures, the CO_2 solubility in the lubricant increases with decreasing temperature. This dependency changes at pressures of more than 60 bar. The isotherms 5, 25, and 40 °C have an intersection, which means that at higher pressure the CO_2 solubility in the lubricant decreases with increasing temperature. At a temperature of 100 °C, the solubility increases constantly with rising pressure.

Mixture Viscosity of the Lubricants. Phase behavior and thus the CO_2 solubility influence the viscosity of the lubricant. In Figure 11 the mixture viscosity of the lubricant PAG is shown as an example.

In the diagram on the left side, the viscosity is shown as dependent on the CO_2 pressure. The higher the temperature, the lower is the viscosity of the oil at low
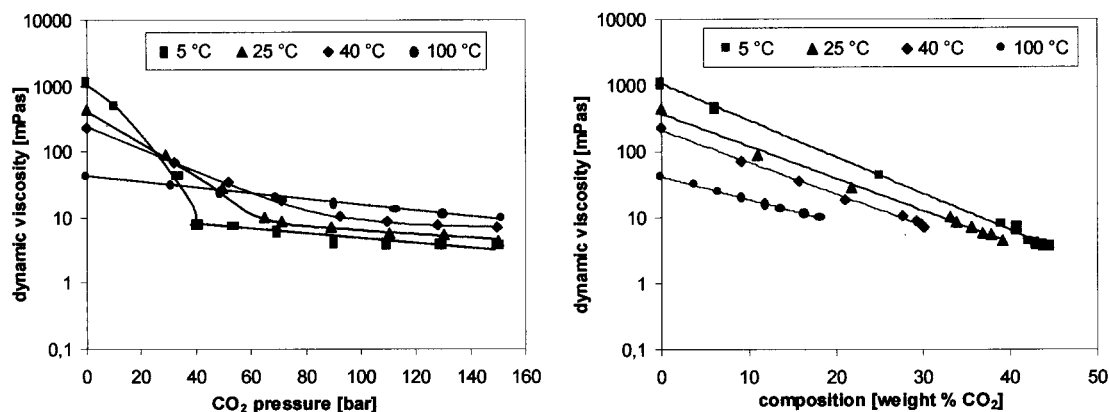
Figure 11. Dynamic viscosity of the lubricant PAG saturated with CO_2.
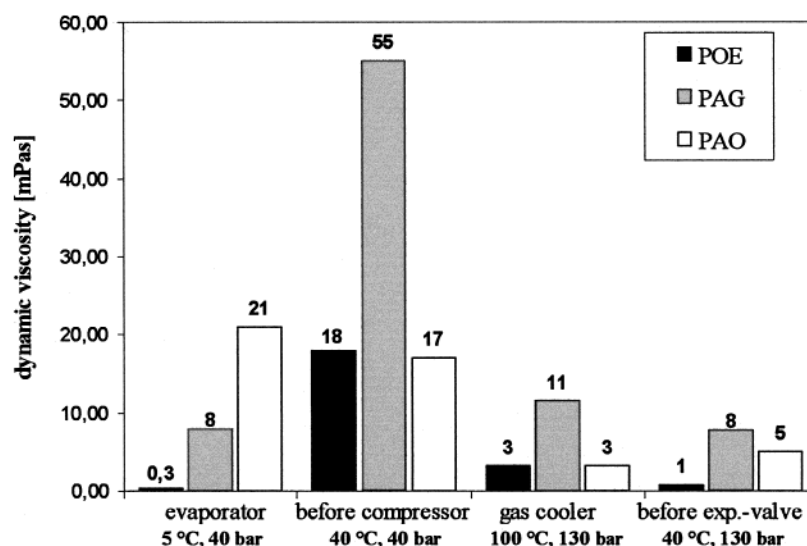

Figure 12. Mixture viscosity of the lubricants POE, PAG, and PAO.

pressures. At pressures of about 40 bar to 60 bar, this dependency changes: which means that with rising temperature the viscosity increases. This behavior is because of the solubility of CO_2 in the oil. The representation in a logarithmic viscosity—composition diagram on the right side of Figure 11 shows the influence of the dissolved CO_2 more clearly. At constant composition the viscosity is lowered with rising temperature.

The comparison of the viscosity of the CO_2-saturated oils POE, PAG, and PAO is presented at characteristic operating points[4] of the cooling circuit in Figure 12.

The viscosities of the pure oils are different. PAG has the highest viscosity followed by POE. The viscosity of PAO is clearly under the viscosities of PAG and POE by a factor of about 3. In the mixture POE possesses the lowest viscosity because of the very high CO_2 solubility in all operating points and indicates with 0.3 mPa s in the evaporator the most favorable flow behavior. PAG has a higher mixture viscosity in the whole cooling circuit because of its high viscosity and relatively low CO_2 solubility. It shows a better fluidity only in the evaporator with a viscosity of 8 mPa s compared to the lubricant PAO with 21 mPa s. PAO shows nearly the same mixture viscosity as POE before the compressor and in the gas cooler. In the cold parts of the circuit, especially in the evaporator, PAO has the highest viscosity of the investigated lubricants.

Conclusion

Phase behavior is a crucial size for the transport of the lubricant in the cooling circuit and for the feedback of the oil into the compressor. The solubility of CO_2 in the lubricant influences the flow behavior of the oil and thus the mixture viscosity in the entire cooling circuit substantially. A high fluidity is of advantage for the reflux of the oil from the evaporator into the compressor, particularly at low temperatures. A further criterion is a high solubility of the lubricant in the refrigerant. If the oil in the evaporator is completely dissolved in the refrigerant, the reflux into the compressor is ensured and the refrigerant may evaporate unhindered by layers of liquid lubricant.

PAG and PAO are not completely miscible with CO_2 and dissolve in the refrigerant only slightly. PAO shows barotropic behavior under certain conditions, which means that the lubricant floats on the liquid CO_2. This behavior may lead to difficulties in the starting procedure of the compressor. Furthermore, PAG and PAO can be trapped in unwanted places in the cooling circuit because of the low CO_2 solubilities. Furthermore low CO_2 solubility in the lubricant causes a high, perhaps unfavorable, viscosity of the mixture, especially in the cold parts of the cooling system. The consequence can be higher pressure losses in the plant. The completely miscible binary system POE—carbon dioxide shows good

flow characteristics and a high oil solubility in the refrigerant, particularly at low temperatures.

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