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S. Bobbo
Consiglio Nazionale delle Ricerche

C. Zilio
Universita di Padova

G. Cortella
Universita di Udine

R. Camporese
Consiglio Nazionalle delle Ricerche

COMPOSITION SHIFT OF THE MIXTURES
R-125/236fa (49.4/50.6) AND R-509A

S. Bobbo*, C. Zilio**, G. Cortella***, R. Camporese*

* Istituto per la Tecnica del Freddo, Consiglio Nazionale delle Ricerche, Corso Stati Uniti, 4 – I-35127 Padova, Italy
** Istituto di Fisica Tecnica, Università di Padova, via Venezia, 1 – I-35131 Padova, Italy
*** Dipartimento di Energetica e Macchine, Università di Udine, via delle Scienze, 208 – I-33100 Udine, Italy

ABSTRACT

A shift in the composition of a refrigerant mixture in a refrigerating circuit is a phenomenon related to the thermophysical properties of the mixture and lubricating oil, the refrigerant/lubricant mass ratio in the circuit, and the features of the plant concerned. This phenomenon may also be accentuated by any leakage or by unsuitable charging procedures. This paper gives a detailed description of a method for measuring the circulating composition of a mixture. The method calls for the use of a gas chromatograph connected directly to the circuit so as to enable in-line analyses. Measurements were taken using two mixtures with different behavior, i.e. a zeotropic mixture with a wide glide, R-125/236fa (49.4/50.6), and an azeotropic mixture, R-509A (R-22/218 [44/56]). The mixtures were charged in a circuit with a dry evaporator and no receivers. The compressor was lubricated with POE oil. The composition of the mixture in the liquid phase was measured at the condenser outlet and the composition in the vapor phase was measured at the compressor discharge. The concentration of the low boiling component shifted at most from 49.4% to 54.5% in the case of the zeotropic mixture and from 44.0% to 37.8% in the case of the azeotropic mixture.

INTRODUCTION

Unlike the situation in the past, synthetic refrigerants will soon almost all be mixtures, with the sole certain exception of R-134a; the situation is very different for natural refrigerants, for which there is expected to be a prevalent use of pure fluids. The composition of the refrigerant mixtures, be they zeotropic or azeotropic, is a parameter of fundamental importance not only for the design of refrigeration systems, but also for their subsequent operation. In fact, the composition may undergo accidental or controlled change, the entity of which depends on the type of refrigerating circuit the mixtures are used in, the type of lubricating oil they are coupled with, the part of circuit being monitored, the operating conditions, the reliability of the circuit's seal and the type of charging procedure adopted.

For the sake of clarity, the following terms are defined: the rated composition is the composition of the mixture as declared by the manufacturer; the charged composition is the composition of the mixture actually charged in the circuit; the circulating composition is the composition of the mixture in the single-phase flow sections of the refrigerating circuit. Composition shift is used to mean the difference between the circulating composition and the charged composition.

What inevitably causes a composition shift is the glide (in the case of zeotropic mixtures) and the differential solubility of the mixture's components in the oil (for both zeotropic and azeotropic mixtures) [1, 2, 3, 4]. This composition shift could lead to more or less significant variations in the circuit's operating conditions. The performance of the plant could thus change considerably and critical conditions could develop if the mixture includes flammable components.

Since there is currently no general consensus as to the onset of an appreciable composition shift in circuits with a dry evaporator and no receivers, we investigated the behavior of two mixtures, R-125/236fa (49.4/50.6) and R-509A (R-22/218 [44/56]) in an experimental circuit with the above-outlined features.

The two mixtures were selected with a view to isolating the two aspects that contribute towards composition shift. Thanks to its wide glide, the first mixture emphasizes the effects of fractionation in the heat exchangers; because of the different solubility of its two components in POE oil, the second mixture facilitates the identification of the effects of the oil on the composition shift.

TEST RIG AND MEASURING METHODS

Test rig

The tests on the composition shift were performed on a compression system with a refrigerating circuit as schematically illustrated in Figure 1.

The compressor was of the open, single-cylinder, reciprocating type with a displacement of 169.5 cm^3 and a rotation speed of 900 rpm. Lubrication was ensured by polyol ester (POE) oil, with an oil charge in the compressor of 1 kg. The discharge line was fitted with a high-efficiency oil separator, pre-charged with about 0.7 kg of oil. The total oil charge was consequently 1.7 kg. The expansion valve was manual to ensure an accurate superheating control.

The heat exchangers were of the coaxial tube type. The refrigerant flowed in the inside tube and the configuration ensured a perfect counterflow. The two exchangers were the same size: the outside diameter of the inner tube was 16 mm, the outside diameter of the outer tube was 28 mm and each of them was 11 m long.
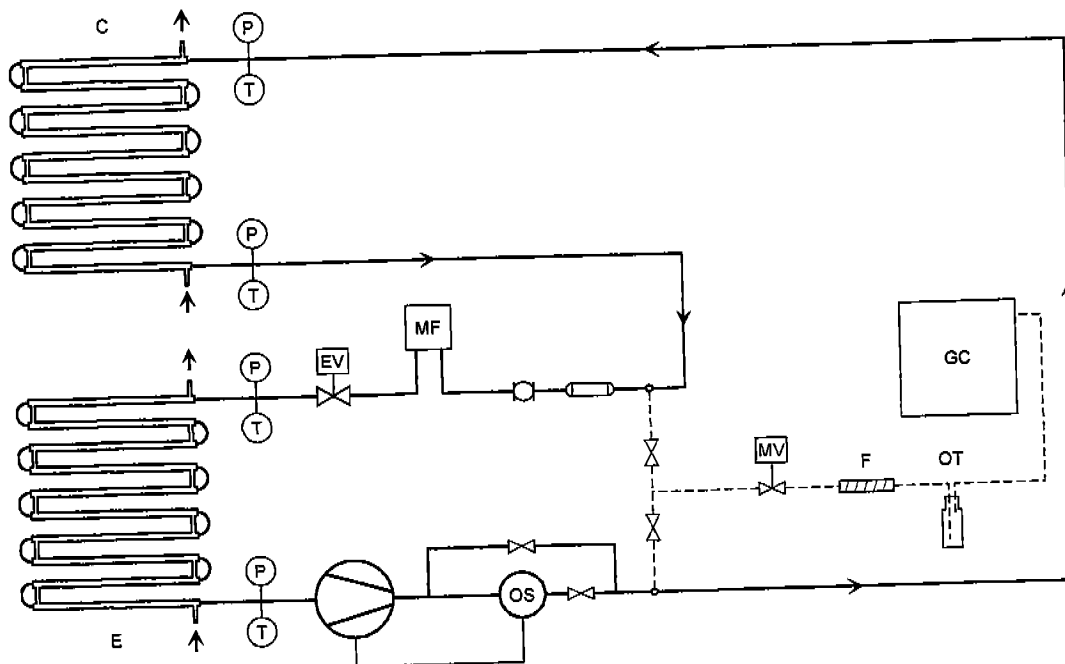

Fig. 1 - *Experimental set-up for the measurement of the circulating composition of refrigerant mixtures.*
OS *oil separator*   T *temperature*   P *pressure*   C *condenser*
MF *mass flow meter*   EV *expansion valve*   E *evaporator*   GC *gas chromatograph*
MV *metering valve*   F *filter*   OT *glass oil trap*

The condenser was water-cooled, whereas glycolated water was delivered to the evaporator. The inlet temperatures of the secondary fluid at the heat exchangers were kept stable to within a range of ± 0.05 °C.

The mixture's mass flow rate measurements were taken with a Coriolis-effect instrument connected immediately upstream from the expansion valve. The mass flow meter has an accuracy of ±0.4% of the reading. The temperature was measured with an accuracy of ± 0.05 °C by means of thermocouples. The pressure was measured using strain-gauge transducers installed at the inlet and outlet of both heat exchangers. The accuracy of the pressure measurement was ± 0.1% full scale (2500 kPa for the high-pressure transducers and 1000 kPa for the low-pressure transducers).

Each time the refrigerant was changed, the system was purged with nitrogen and left in a vacuum for at least 24 hours before it was recharged. The refrigerant charge was 2.711 kg in the case of R-125/236fa (49.4/50.6) and 2.549 kg for the R-509A. The mass ratio of refrigerant to oil was consequently 1.6 and 1.5, respectively.

For each mixture, we performed 5 tests at different evaporation and condensation temperatures suited to the specific applications of the mixtures involved. In all the tests, superheating at the evaporator outlet was maintained between 9 and 13 °C.

Method for sampling and measuring the circulating composition

From a theoretical standpoint, in order to satisfy the mass equilibria in stationary operating conditions, the circulating composition of the mixture should be the same in all the single-phase stretches of the circuit. To assess any departure from the charged composition, it would therefore suffice to measure it in any one of these stretches. However, in order to verify the reliability of our results, measurements were taken at two points on different single-phase stretches of the circuit.

Two sampling points were therefore prepared along the circuit: one was upstream from the expansion valve; the other was beyond the oil separator at the compressor discharge. Sampling was done by means of a pipe with an OD of 1/16", inserted at right angles to the flow and down to about half the inside diameter of the circuit's piping. An on-off valve, a metering valve for fine-adjusting the refrigerant flow, a filter and an oil trap were installed along the connection piping between the sampling point and the gas chromatograph, immediately downstream from the sampling point.

The need to use the filter stems from the fact that, since the sample flow was sent directly to the gas chromatograph, the traces of oil (which are inevitable despite the use of a high-efficiency separator) would be absorbed by the column filling, eventually interfering with its efficiency. In particular, because of the progressive pollution of the column, the retention times and areas of the peaks would vary with time, considerably affecting the reproducibility of the measurements. The oil trap (1 cm^3) was made of glass and enabled not only a further separation of the oil from the flow in the vapor phase, but also - and above all - a visual control over any residual presence of oil even beyond the filter.

The filter for separating the oil was made from a section of stainless steel pipe with an OD of 1/8", well packed with Chromosorb W. This material is capable of almost completely adsorbing the oil molecules, providing a sufficient amount of material is used to prevent the filter from becoming saturated before a series of analyses have been completed (a sequence of comparative tests demonstrated that a filter made with a 1/8" stainless steel pipe

Table 1 - Main gaschromatograph parameters.

Mixture	Column				Oven temp. (°C)	Detector
	Length (m)	Inside diameter (mm)	N$_2$ flow rate (cm^3·min^{-1})	Packing		
R125 + R236fa	1.5	2.1	40	Porapak T	140	FID
R22+ R218	2	2.1	50	Porapak T	140	FID

from 50 to 80 mm long has no effect on the measurements and ensures and excellent filtering action for several dozen analyses).

In steady state conditions, the on-off valve installed at the sampling point is open and the metering valve is used to establish a continuous flow of fluid towards the gas chromatograph. As a result of lamination with the metering valve, the liquid sample is also completely vaporized.

Table 1 shows the values of the main gas chromatograph operating parameters used during the measurements, which were selected so as to ensure an efficient separation of the mixture's components with the shortest possible retention times and also to ensure the reproducibility of the retention times and of the ratio between the areas of the peaks.

For the purposes of the composition measurements, the response of the Flame Ionization Detector (FID) was carefully calibrated using mixtures of known composition, specially prepared in vessels with an internal volume of about 240 cm^3. To weigh the components added to the containers, we used analytical scales with a resolution of 0.1 mg, obtaining an accuracy in the preparation of the sample mixtures of ± 0.01 of the percentage mass fraction. The accuracy of the composition measurement, taking into account all the errors made in the calibration of the gas chromatograph and in the performance of the measurements, was estimated to be ± 0.5 of the percentage mass fraction.

The calculation of the thermodynamic properties of the mixtures (particularly saturation temperatures and pressures), based on the experimental measurements, was performed by means of the Carnahan-Starling-De Santis equation of state. The coefficients of binary interaction are as follows:

$$R-125/236fa \qquad k_{12} = -0.00088$$
$$R-22/218 \qquad k_{12} = 0.09040$$

These were obtained from VLE measurements performed at our laboratory for the mixture R-125/236fa [5] and from data available in the literature on the mixture R-22/218 [6]. Figures 2 and 3 represent the VLE of the mixtures at a constant pressure.
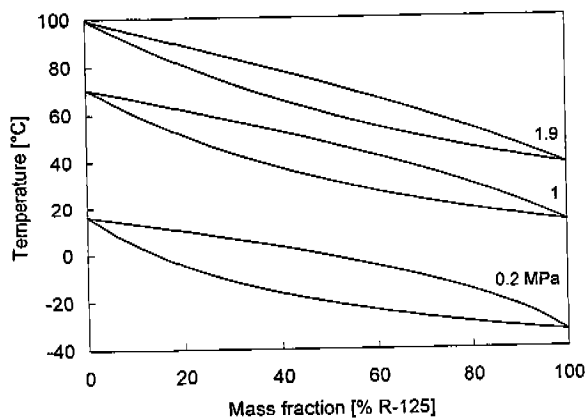

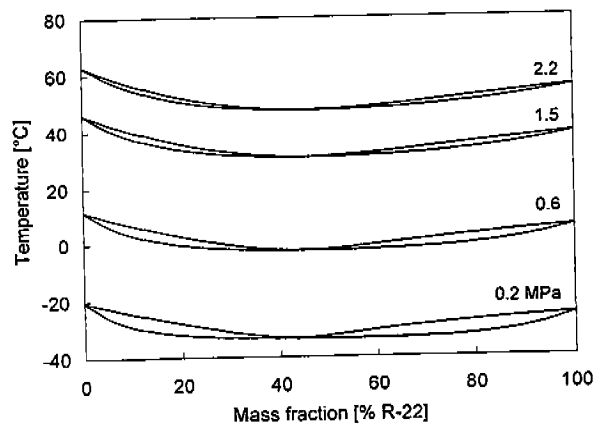*Fig. 2 - Vapor-liquid equilibria of R-125/236fa.*   *Fig. 3 - Vapor-liquid equilibria of R-22/218.*

RESULTS AND DISCUSSION

During the operation of the test rig, we found a marked difference in the behavior of the oil separator, which demonstrated a valid efficiency for R-509A, but seemed inadequate with the R-125/236fa (49.4/50.6). In the latter case we observed the presence of oil in the oil trap during the sample-taking phase, despite a high flow of oil being detected in the pipe from the oil separator to the compressor.

The composition shift detected during the tests is shown in Table 2, including the values measured in both the liquid and the vapor phase; for each operating condition, these two values come within the declared accuracy.

In the tests performed with R-125/236fa (49.4/50.6), the composition shift was in the sense of an enrichment of the mixture in the low-boiling component, despite the high solubility of R-125 in POE oil. This variation in composition is therefore mainly attributable to fractionation in the heat exchangers, as was to be expected considering the mixture's wide glide. It is also worth noting that the shift tends to be greater with higher evaporating pressures, whereas the condensing pressure is less influential.

In the case of R-509A, we found a decrease in the concentration of R-22 in the circulating mixture. Since the mixture is azeotropic and R-218 is not miscible in POE oil, we deduced that said shift is due almost exclusively to the different solubility of the two components in the oil. Here again, the composition shift varies mainly with evaporating pressures.

Although these results are strictly linked to the type of plant, the thermodynamic properties of the mixtures involved and the refrigerant/oil mass ratios, some conclusions can be drawn for systems with similar features, i.e.:

– composition shift could lead to significant variations in the performance of the system, although this observation depends heavily on the thermodynamic features of the mixture;

Table 2 - Test results on the circulating composition of the mixtures R-125/236fa (49.4/50.6) and R-509A.

Mixture	α	β		t_{ie}	t_{oc}	P_{ie}	P_{ic}
		liq	vap	(°C)	(°C)	(kPa)	(kPa)
R-125 / 236fa	49.4	51.6	50.9	-16.4	46.0	170	1523
		52.8	52.8	-1.6	45.4	326	1556
		54.3	54.5	9.6	45.2	505	1586
		51.7	52.0	0.0	28.3	382	1099
		53.9	53.4	11.7	55.6	508	1963
R-509A	44.0	41.9	41.5	-30.5	35.9	220	1833
		39.5	39.5	-15.4	34.1	380	1848
		38.2	37.8	-0.7	36.0	614	1866
		38.3	38.5	-1.2	27.0	604	1546
		37.7	37.8	0.9	46.7	645	2263

α *charged concentration of the low-boiling component (% mass fraction).*

β *circulating concentration of the low-boiling component (% mass fraction).*

t_{ie}, t_{oc} *temperature of the mixture at evaporator inlet and condenser outlet.*

P_{ie}, P_{ic} *pressure of the mixture at evaporator and condenser inlet.*

− composition shift could be a highly critical phenomenon in the case of one of the two components in the mixture being flammable and the rated composition of the mixture verging on the flammability region;

− composition shift can become particularly critical in systems which frequently need topping up because of refrigerant leakage.

ACKNOWLEDGEMENTS

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