Comprehensive approach to predicting the circulation composition of zeotropic refrigerants

Chen Jiufa

(Department of Power Engineering, Southeast University, Nanjing 210096, China)

Abstract: The problem of composition shift in zeotropic fluid circulation, which is encountered in modern air conditioning and refrigeration systems, is studied. It reveals that the composition shift phenomena is contributed by fractionation related to four mechanisms. This paper concentrates on the modeling of component fractionation in heat exchangers. Element approach is employed, and the amount of each component holdup is calculated element by element with a proper void fraction model. The circulation concentration is determined from the refrigerant differential holdup in heat exchangers. Simulations have been carried out to prove the validity. The results can improve the reliability and efficiency in zeotropic refrigerant applications.

Key words: zeotropic refrigerant; composition shift; circulation composition

Zeotropic refrigerant mixtures have been considered as environmentally benign refrigerants for refrigeration and air conditioning systems. But investigations find that in zeotropic refrigerant systems the measured circulation composition differs from the nominal composition, which is the so-called problem of composition shift[1-7].

Composition shift can cause changes in system pressures, temperatures, capacities, flammability, efficiency, etc. To achieve reliable performance in zeotropic refrigerant systems it is necessary to understand the mechanisms, hence to model and predict the composition shift in refrigerant circulation.

This paper studies the circulation composition characteristic for zeotropic refrigerant mixtures. The composition migration mechanism is analyzed. Detailed mathematical models for determining the circulation composition are developed.

1 Modeling Composition Shift

The composition shift behavior of zeotropic refrigerants can be analyzed from their vapour-liquid equilibrium characteristics. Differing from azeotropic mixtures, a zeotropic mixture will have different compositions between the vapor and liquid phase in equilibrium. Since each component will have different chemical potential—volatility, each component will have a different composition in the vapor phase compared with the liquid phase. For the more volatile

components, their vapor compositions will be higher than their compositions in the liquid phase. For the less volatile components, their compositions in the vapor phase will be less than their compositions in the liquid phase. Tab.1 shows the calculated equilibrium compositions for zeotropic refrigerant R407C under a pressure of 2 200 kPa.

Tab.1 R407C vapor and liquid equilibrium data at the pressure of 2 200 kPa

$T/℃$	Vapor quality	Liquid mass composition			Vapor mass composition		
		R32	R125	R134a	R32	R125	R134a
49.9	0.0	0.230	0.250	0.520	0.306	0.302	0.392
51.7	0.319	0.201	0.229	0.570	0.274	0.283	0.443
53.6	0.799	0.175	0.207	0.618	0.244	0.261	0.495
54.4	1.000	0.164	0.196	0.640	0.230	0.250	0.520

R407C has three components, with R32 and R125 being more volatile than R134a. Shown in Tab.1, the compositions of R32 and R125 in the vapor phase are higher than their compositions in the liquid phase. For the less volatile component R134a, its vapor composition is lower than that in the liquid phase.

The fractionation behavior originates from the vapor liquid composition differentiation in the two phase region, and can be analyzed into four mechanisms:

● Differential holdup in the heat exchangers;

● Differential holdup in the receivers and accumulators;

● Differential holdup in the lubricant oil;

● Differential leakage.

In the two phase region of heat exchangers, slip flow will happen. Vapor flow concentrated with more volatile components will have a higher speed than the liquid flow. Since the liquid will count for more than

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90% of mass, the two phase region will have a differential holdup of refrigerant components with higher compositions of less-volatile-components. As a result the compositions of the more volatile components will be pushed upwards in the refrigerant circulation.

The contribution to circulation composition shift caused by the receivers and accumulators is also associated with the two phase composition differentiation. In most cases those vessels will be concentrated with less volatile components, hence upsetting the circulation compositions with more volatile components.

The lubricant oil will have a similar effect as that of the receivers and accumulators.

The refrigerant leakage in the two phase region will result in refrigerant circulation composition change. If vapor leaks, the system will be left with the compositions of less volatile components going up. If leakage occurs in the liquid phase, the system will be concentrated with more volatile components. Since leakage is unpredictable, it is out of the scope of composition modeling.

Based on the above analysis, the mathematical model to calculate the circulation composition for a zeotropic refrigerant system has been developed:

$$z_i = \frac{M_{chg\_i} - \sum M_{hx\_i} - \sum M_{oil\_i} - \sum M_{vs\_i}}{M_{chg} - \sum M_{hx} - \sum M_{oil} - \sum M_{vs}} \quad (1)$$

where z_i represents the circulation composition for the component i for a multi-component refrigerant system. In the denominator, M_{chg} represents the total amount of refrigerant charge in the whole system, M_{hx} is the total amount of refrigerant in the heat exchanger two phase region, M_{oil} is the total amount of refrigerant dissolved in the lubricant oil, M_{vs} accounts for the refrigerant holdup in the liquid receivers or accumulators. Similar items appear in the numerator, except that every item is suffixed with the subscripts of $\_i$, which denote the component i in the corresponding mechanism.

For heat exchanger refrigerant holdup calculation, the work in this paper has been concentrated on the cases with refrigerant flow being arranged inside tubes. For the cases of shell & tube condensers and flooded evaporators, some modifications may be necessary before using the models presented in this paper.

To calculate the refrigerant holdup in the two phase region in a condenser or evaporator, an element model is developed (as shown in Fig. 1). The whole two phase region can be divided into n elements. Each element will consist of a fraction of space occupied by vapor, and the rest of the space occupied by the liquid.
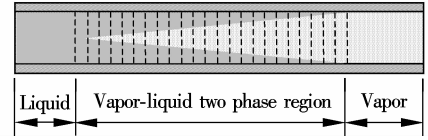

Fig. 1 Schematic diagram of element model for a heat exchanger vapor-liquid two phase region

If the two phase region has been divided into a sufficient number of elements, the variation in thermodynamic properties across the element length can be neglected. Hence calculation in each element can be divided into two parts — homogenous vapor area and homogenous liquid area.

As an approximation equilibrium flow was assumed in each element between the vapor and liquid, therefore the local vapor and liquid densities (ρ_v and ρ_l) and compositions (x_i and y_i) can be calculated from an equation of state. To calculate the two phase region refrigerant holdup, it is necessary to use the void fraction parameter $\alpha^{[6]}$, which stands for the fraction of the vapor flow area to the whole refrigerant flow section area in an element.

$$\alpha = K_H\beta$$

$$\beta = \frac{X_q/\rho_v}{X_q/\rho_v + (1 - X_q)/\rho_l}$$

$$K_H = 0.726648 - 3.481988 \times 10^{-4}Z_K - \frac{0.845427}{Z_K} + 0.0601106Z_K^{\frac{1}{3}}$$

While the parameter Z_K is a function of Reynolds number Re, Froude number Fr, and the liquid volume fraction L_F,

$$Z_K = \frac{Re^{\frac{1}{6}}Fr^{\frac{1}{8}}}{L_F^{\frac{1}{4}}}$$

$$Re = \frac{DG}{\mu_l + \alpha(\mu_v - \mu_l)}$$

$$Fr = \frac{1}{gG}\left(\frac{GX_q}{\beta\rho_v}\right)^2$$

$$L_F = 1 - \beta$$

where D is the hydraulic diameter, G is the refrigerant mass velocity, g is the acceleration due to gravity, μ_v and μ_l are the viscosities for refrigerant vapor and liquid, respectively.

Referring to Eq. (1), the effect of a heat exchange on the circulation composition Z_i can be evaluated from the total amount of refrigerant holdup $\sum M_{hx}$ and the total amount of component i $\sum M_{hx\_i}$ in the two phase region. The total amount of refrigerant holdup in the two phase region can be calculated from the liquid phase mass M_l plus the vapor phase mass

M_v:

$$\sum M_{hx} = M_1 + M_v$$

Considering the refrigerant flow section area A and the element length L, the liquid phase refrigerant mass can be calculated from

$$M_1 = \sum_{k=1}^{n} AL(1 - \alpha_k)\rho_1$$

Similarly the vapor refrigerant mass can be calculated from

$$M_v = \sum_{k=1}^{n} AL\alpha_k\rho_v$$

The term M_{hx_i}, representing the total amount of component i dissipated in the heat exchanger two phase region, can be evaluated from

$$\sum M_{hx\_i} = M_{1\_i} + M_{v\_i}$$

where M_{1_i} is the total amount of component i in liquid refrigerant in the two phase region, which can be calculated as

$$M_{1\_i} = \sum_{k=1}^{n} AL(1 - \alpha_k)\rho_1 x_k$$

While the total amount of component i in vapor refrigerant in the two phase region can similarly be calculated as

$$M_{v\_i} = \sum_{k=1}^{n} AL\alpha_k\rho_v y_k$$

The other items in Eq. (1) can be calculated similarly with some modifications. To calculate the amount of refrigerant component $\left(\sum M_{oil}\right.$ and $\left.\sum M_{oil\_i}\right)$ dissolved in the crankcase oil, experimental values of the solubility coefficients are required[7]. To calculate the refrigerant holdup in the refrigerant vessels $\left(\sum M_{vs}\right.$ and $\left.\sum M_{vs\_i}\right)$ one must know refrigerant volume, as well as the temperature and pressure.

It was found that the contribution of oil differential solubility to the composition shift was very small. The major contribution to the composition shift effect was caused by vapor liquid two phase **holdups in the heat exchangers and vessels.**

2 Simulation and Results

To assess the validity for the developed refrigerant flow mechanisms and the mathematical models presented above, simulation was made for a vapor compression type refrigeration system.

For this work we concentrated the investigation of composition shift on the two phase refrigerant holdup in heat exchangers. Therefore the system simulated was considered to have no liquid receiver and no suction accumulator. Both condenser and evaporator were considered to have refrigerant flow inside the tube.

Three zeotropic refrigerants were considered as alternative working fluids:
- R407C ($m(R32)$: $m(R125)$: $m(R134a) = 0.23$: 0.25: 0.52)
- R404A ($m(R125)$: $m(R143a)$: $m(R134a) = 0.44$: 0.52 : 0.04)
- R32/R134a ($m(R32)$: $m(R134a) = 0.30$: 0.70)

To simplify the simulation some assumptions were made: co-current flow of vapor and liquid in both condenser and evaporator; steady state running conditions; pressure drops in heat exchangers having negligible effect on the refrigerant thermodynamic performance. The simulated system was a 4 kW air conditioner unit, with a water cooled coaxial condenser and a fine & tube evaporator. The condenser had a refrigerant flow section $A = 155$ mm^2, channel length $L = 4.15$ m, and 40 ℃ water inlet. The evaporator had 5 passes of parallel refrigerant flow, each with a refrigerant flow section of $A = 34.2$ mm^2, tube length $L = 3.15$ m, and 30 ℃ air inlet. Regarding the heat transfer amount in the two phase region, 84% was accounted for in the condenser, while 97% was accounted for in the evaporator.

Tab.2 shows the simulation results for each zeotropic refrigerant. For zeotrope R407C the predicted circulation compositions were 25.11%, 26.55% and 48.34% for the components R32, R125 and R134a, respectively, with a maximum magnitude of predicted circulation composition shift of about 3.2%. This prediction generally agrees with the composition shift 3% in steady state measured in a residential heat pump[5]. For the binary R32/R134a the predicted composition shift was about 3.4%, which is very close to a measured composition shift of 4.1% in air conditioners. For the near azeotrope R404A the calculated composition shifts were 0.13%, 0.07% and −0.20% for the components R125, R143a and R134a, respectively. The simulated R404A composi-

Tab.2 Simulation results for circulation mass composition　%

Blend	Composition	R32	R125	R143a	R134a
	Original z_{orig}	23.00	25.00		52.00
R407C	Circulation z_{circ}	25.11	26.55		48.34
	$z_{shift} = z_{circ} - z_{orig}$	+2.11	+1.55		−3.66
	Original z_{orig}	30.00			70.00
R32/R134a	Circulation z_{circ}	33.39			66.61
	$z_{shift} = z_{circ} - z_{orig}$	+3.39			−3.39
	Original z_{orig}		44.00	52.00	4.00
R404A	Circulation z_{circ}		44.13	52.07	3.80
	$z_{shift} = z_{circ} - z_{orig}$		+0.13	+0.07	−0.20

tion shift is very close to a measured composition shift of 0.9% in a freezer-refrigerator. The deviations between the simulation and the measurements of references may be caused by the refrigerant holdup vessels existing in the referenced applications.

The composition shift magnitude can be related to the temperature glide. R407C and R32/R134a each have a high glide temperature over 7 K, corresponding to their high composition shift values over 3%. While R404A has a small temperature glide of 0.7 K, corresponding to its low composition shift value of less than 1%.

3 Conclusion

A study has been made to analyze the composition shift of zeotropic refrigerants used in air conditioning and refrigeration systems. Based on thermodynamic analysis, it is concluded that the composition shift behavior originates from the composition difference between vapor phase and liquid phase.

Four mechanisms are considered as the contributing forces to the composition shift, namely, differential holdup in the heat exchanger two phase region, differential solubility from the lubricant oil, differential holdup of refrigerant in receivers and accumulators. With those mechanisms being taken into consideration, comprehensive models have been developed to predict the circulation composition.

Simulations were carried out to calculate the composition shift effect in a refrigerant circulation system with three zeotropic refrigerants: R407C, the binary mixture R32/R134a and R404A. The calculated maximum composition shifts for R407C, the binary mixture R32/R134a and R404A were about 3.7%, 3.4% and 0.2%, respectively, which agreed with experimental data. It was found that the composition shift magnitude in general was related to the temperature glide.

The models proposed in this work were based on the assumption of refrigerant flow inside tubes. For other cases of refrigerant flow some modifications **may be required before using those models.**

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计算非共沸制冷剂循环浓度的有效方法

陈九法

(东南大学动力工程系, 南京 210096)

摘要: 研究了现代空调和制冷系统中非共沸制冷剂发生的组分迁移问题. 研究发现, 组分迁移现象的 4 种引发机理都与混合工质的分馏有关. 本文模拟了工质在换热器中的分馏滞流. 将换热器分解成若干微元, 选用恰当的空泡数学模型, 计算各组分在换热器中的滞留量. 系统的循环浓度根据换热器中制冷剂的分馏滞留程度来计算. 通过模拟研究, 证明了模型的可靠性. 该研究结果可以应用于提高非共沸制冷剂在制冷设备应用中的可靠性和效率.

关键词: 非共沸制冷剂; 组分迁移; 循环浓度

中图分类号: TB61