ходные процессы с учетом неодновременности размыкания-замыкания контактов выключателей, при отключениях фаз и работе ОАПВ и разрядников, восстанавливающиеся напряжения на контактах выключателей и др.

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Досліджено фазову поведінку та теплофізичні властивості сумішей типу R1234yf - HFE, як заміни R134a. Погрішність прогнозу за допомогою нейронних мереж холодильного коефіцієнту та відношення тиску не перевищує 3%.

Ключові слова: рівняння стану; азеотропний стан; нейронні мережі; критерій сталого розвитку; розпливчата логіка

Исследовано фазовое поведение и теплофизические свойства смесей типа R1234yf - HFE, как замены R134a. Погрешность прогноза с помощью нейронных сетей холодильного коэффициента и отношение давлений не превышает 3%

Ключевые слова: уравнение состояния; азеотропное состояния; нейронные сети; критерий устойчивого развития; нечеткая логика

The phase behavior and thermophysical properties of R1234yf – HFE systems as alternative to R134a are investigated. Accuracy of COP and pressure ratio predicted by neural networks does not exceed 3%

Keywords: equation of state; azeotrope; neural networks; sustainable development criteria; fuzzy logic

УДК 538.953:54.139

SUSTAINABLE REFRIGERANT SELECTION IN BINARY BLENDS OF THE R1234YF – HYDROFLUOROETHERS

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1. Introduction

The sustainable refrigerant selection is one of the most important stages in the design of refrigeration systems. The compromise among such properties as contribution to greenhouse effect, flammability, toxicity, thermodynamic behaviour, performance specifications, and the others define a sustainable decision. It is obvious; a pure substance that

combines all desirable properties and has no undesirable properties does not exist. The most promising roadmap to seek a harmonious decision is based on the improvement of "backbone" substance performances via the "breeding" components that amend its objectionable properties. The entire set of design indices includes: economic (LCC life cycle cost), thermodynamic (specific refrigerating effect, volumetric capacity, specific adiabatic work, condenser/evaporator pressure ratio, coefficient of performance, adiabatic power), and environmental (flammability, toxicity, and GWP) criteria. The attainment of the sustainable decision corresponds to a compromise among different criteria. The accuracy of prognosis for experimentally observable thermodynamic and design characteristics narrows the area of search in the space of competitive economic, environmental and technological criteria. The general approach to sustainable design of the refrigerants based on fuzzy thermoeconomic optimization was developed as a trade off solution of multicriteria problem [5]. The aim of present work is to apply a fuzzy set methodology providing sustainability among thermodynamic, economic, and environmental goals for the IV generation of refrigerants. The class of refrigerants under consideration scrutinizes most prospective working "backbone" fluid R1234yf [9] as R134a replacement for MAC applications in combination with hydrofluoroethers (HFE) as possible "breeding" components. The HFE additives enable to decrease high compressor discharge temperatures and to increase vaporization heat.

This paper is organized as follows. In Section 2 the Peng – Robinson one-fluid model of equation of state is applied to predict an azeotrope appearance in terms of critical parameters of mixture components and interaction parameters k12 and l12. It is shown that R1234yf – HFE blends form azeotrope practically for all systems under consideration. In Section 5 the cycle performances (COP, pressure ratio) for restricted number of refrigerants are considered as training set for ANN to reproduce missing data for all HFE refrigerants. Section 6 considers new approach to sustainable refrigerant selection based on a fuzzy set methodology providing a trade off solution among thermodynamic, economic, and environmental goals. The Bellman – Zadeh model as the intersection of membership functions (fuzzy criteria mappings) is applied to sustainable selection of refrigerants.

Nomenclature

a	equation of state parameter (long range attraction)	v	volume
a_{ii}	long range attraction between	X	control variable vector
b	i – i components equation of state parameter (excluded volume)	x_i	mole fraction of component i
b_{ii}	excluded volume for component	Z_i	dimensionless parameters of model.
COP	i	*Greek symbols*	
k_{12}	coefficient of performance	ω	acentric factor
K_i	binary interaction parameter	μ	relationship function
l_{12}	binary	ρ	density
M	local criterion	Ψ	flammability index
n_i	interaction parameter for		
p	excluded	*Subscripts*	
PR	molar mass	c	critical
T	number of atomic species (i)	k	condenser
	pressure	ev	evaporator
	pressure ratio	i	component i
	temperature, K	mod	model

2. Azeotropic states in the R1234yf – hydrofluoroether blends

The one-fluid modified Peng – Robinson model of equation of state (PR78) was used to simulate thermodynamic and phase behaviour of the R1234yf – HFE blends [8].

$$p = \frac{RT}{v - b_i} - \frac{a(T)}{v(v+b) + b_i(v-b)}, \quad (1)$$

$$b_{ii} = 0.07779607 \frac{RT_{c,ii}}{p_{c,ii}}, \quad (2)$$

$$a_{ii} = 0.45723553 \frac{(RT_{c,ii})^2}{p_{c,ii}} [1 + m_i(1 - \sqrt{\frac{T}{T_{c,ii}}})]^2, \quad (3)$$

$$m_i = 0.37464 + 1.5422\omega_i - 0.26992\omega_i^2, \quad \text{if } \omega_i \le 0.491;$$

$$m_i = 0.37964 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3, \quad \text{if } \omega_i > 0.491 \quad (4)$$

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j a_{ij}, \; b = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_{ij}, \; a_{ij} = (1 - k_{ij})\sqrt{a_i a_j},$$

$$b_{ij} = (1 - l_{ij}) \frac{b_{ii} + b_{jj}}{2} \quad (5)$$

where R is the universal gas constant, and the EoS parameters a and b of a mixture depend on the mole fractions xi and xj of the components i and j and the corresponding parameters aij and bij for different pairs of interacting molecules.

Critical properties of R1234yf, i.e., critical temperature T_c, critical density ρ_c, and critical pressure p_c, were taken from [10] measurements: molar mass M = 144.042 g/mol, T_c = 367.85 ± 0.01 K, p_c = 3382 ± 3 kPa, ρ_c = 478 ± 3 kg/m^3, and acentric factor ω = 0.280, respectively. Critical properties of HFEs were taken from [1]. Allocation of HFE critical points in vicinity of R134a and R1234yf vapour pressure curves is shown in Fig. 1.

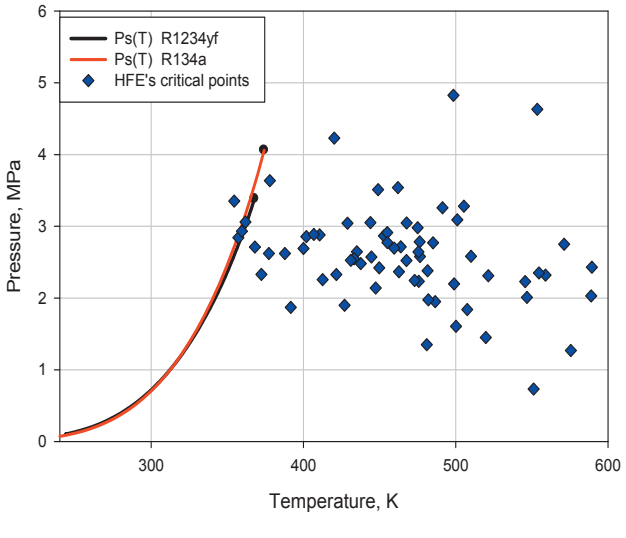

Fig. 1. Critical points of HFEs and vapour pressure curves of R1234yf and R134a

Critical properties of HFE components with critical temperatures below 500 K and their flammability indices correlated to atomic species by simple ratio of fluoride (n_F) and and hydrogen (n_H) atoms $\Psi = n_F/(n_F+n_H)$ are given in Table 1. The normal boiling points (acentric factor) for HFEs were restored from Murata et al. data [7].

Table 1

Critical parameters and flammability indices for hydrofluoroethers

HFEs	M, g mol^{-1}	T_c, K	p_c, MPa	ρ_c, g cm^{-3}	Z_C	$\Psi = n_F/(n_F+n_H)$
C_2HF_5O	136.021	354.49	3.35	0.579	0.267	0.83
$C_2H_2F_4O$	118.030	420.25	4.23	0.529	0.270	0.67
$C_2H_3F_3O$	100.040	498.50	4.82	0.485	0.240	0.50
C_3F_6O	166.022	361.90	3.06	0.610	0.277	1.00
C_3F_6O	166.022	357.20	2.84	0.540	0.307	1.00
C_3F_6O	166.022	359.60	2.93	0.570	0.285	1.00
$C_3F_8O_2$	220.018	372.40	2.33	0.610	0.271	1.00
C_3HF_7O	186.028	377.26	2.62	0.580	0.268	0.88
C_3HF_7O	186.028	387.80	2.62	0.550	0.275	0.88
$C_3H_2F_6O$	168.038	428.90	3.04	0.553	0.269	0.75
$C_3H_3F_5O$	150.047	462.03	3.54	0.553	0.259	0.63
$C_3H_3F_5O$	150.047	406.82	2.89	0.500	0.256	0.63
$C_3H_5F_3O$	114.066	449.05	3.51	0.412	0.260	0.38
C_4F_8O	216.029	400.00	2.69	0.680	0.257	1.00
$C_4F_{10}O$	254.026	391.70	1.87	0.630	0.232	1.00
$C_4HF_7O_2$	214.038	452.88	2.87	0.597	0.273	0.88
$C_4HF_7O_2$	214.038	435.06	2.65	0.569	0.275	0.88
C_4HF_9O	236.036	412.63	2.26	0.499	0.311	0.90
$C_4H_2F_8O$	218.045	421.60	2.33	0.533	0.272	0.80
$C_4H_2F_8O$	218.045	444.63	2.57	0.581	0.261	0.80
$C_4H_2F_8O_2$	234.045	449.81	2.41	0.571	0.265	0.80
$C_4H_3F_5O$	162.058	455.03	2.91	0.486	0.258	0.63
$C_4H_3F_7O$	200.055	455.10	2.77	0.576	0.255	0.70
$C_4H_3F_7O$	200.055	437.60	2.48	0.530	0.257	0.70
$C_4H_3F_7O$	200.055	433.21	2.55	0.542	0.261	0.70
$C_4H_3F_7O$	200.055	463.89	2.71	0.541	0.260	0.70
C4H4F6O	182.064	459.60	2.70	0.481	0.267	0.60
$C_4H_4F_6O$	182.064	476.31	2.78	0.500	0.256	0.60
$C_4H_5F_5O$	164.074	431.13	2.53	0.448	0.258	0.50
$C_5F_{10}O$	266.037	427.00	1.90	0.600	0.237	1.00
$C_5H_2F_6O_2$	208.059	485.10	2.77	0.720	0.198	0.75
$C_5H_2F_{10}O$	268.053	447.40	2.14	0.582	0.265	0.83
$C_5H_3F_7O$	212.066	476.55	2.58	0.538	0.256	0.70
$C_5H_3F_7O$	212.066	467.64	2.52	0.518	0.266	0.70
$C_5H_3F_9O$	250.062	475.74	2.23	0.563	0.251	0.75
$C_5H_3F_9O$	250.062	462.72	2.37	0.558	0.276	0.75
$C_5H_3F_9O$	250.062	473.01	2.24	0.550	0.259	0.75
$C_5H_5F_5O$	176.085	475.54	2.64	0.494	0.238	0.50
$C_5H_5F_7O$	214.081	481.54	2.38	0.497	0.256	0.58
$C_6H_3F_9O$	262.073	498.97	2.20	0.520	0.267	0.75
$C_6H_3F_{11}O$	300.070	486.48	1.95	0.567	0.255	0.79
$C_6H_5F_9O$	264.089	482.02	1.98	0.518	0.251	0.64

3. Azeotropy boundaries for R1234yf – HFE

Some criteria for azeotropy in binary fluids can be obtained analytically in the frameworks of global phase diagrams. The corresponding boundary state is called a degenerated critical azeotropic point and represents the limit of the critical azeotropy at $x_i \to 0$ or at $x_i \to 1$. As a result of solving the system of thermodynamic equations for a degenerated critical azeotrope:

$$\left(\frac{\partial p}{\partial v}\right)_{T,x} = \left(\frac{\partial^2 p}{\partial v^2}\right)_{T,x} = \left(\frac{\partial p}{\partial x}\right)_{T,v} = 0\,, \qquad (6)$$

one can obtain the following relationship for dimensionless interaction parameters [2]:

$$Z_2 = \mp Z_1 - 0.7(1 \pm Z_1)\left(\frac{1-Z_4}{1\pm Z_3} - 1\right), \qquad (7)$$

where the upper signs + or - correspond to $x_2 = 0$ and the lower signs - to $x_2 = 1$, respectively.

The set of dimensionless parameters for the Peng – Robinson model is defined as follows:

$$\begin{aligned} Z_1 &= (a_{22} - a_{11})/(a_{22} + a_{11})\,,\\ Z_2 &= (a_{22} - 2a_{12} + a_{11})/(a_{22} + a_{11})\,,\\ Z_3 &= (b_{22} - b_{11})/(b_{22} + b_{11})\,,\\ Z_4 &= (b_{22} - 2b_{12} + b_{11})/(b_{22} + b_{11})\,. \end{aligned} \qquad (8)$$

According to Eq. (7) the boundary between azeotropic and non-azeotropic states in Z_1 - Z_2 plane at fixed values of Z_3 and Z_4 is a straight line. A membership of binary mixture to azeotropic state is defined for given interaction parameter k_{12} as follows. Critical parameters (p_c, T_c) and the acentric factor (ω) or the normal boiling temperature (T_B) of the individual components are selected and the Z_1, Z_3 values are calculated via relationships (8). Value k_{12} generated from ANN model [2] for natural and synthetic refrigerants and critical parameters of pure components at $l_{12} = 0$ define the dimensionless co-ordinates Z_2 and Z_4 from (8). Azeotropy boundaries (7) are calculated and position of the characteristic point within the one of quadrants generated by the straight lines Z_2 (Z_1) intersection is established (Fig. 2).

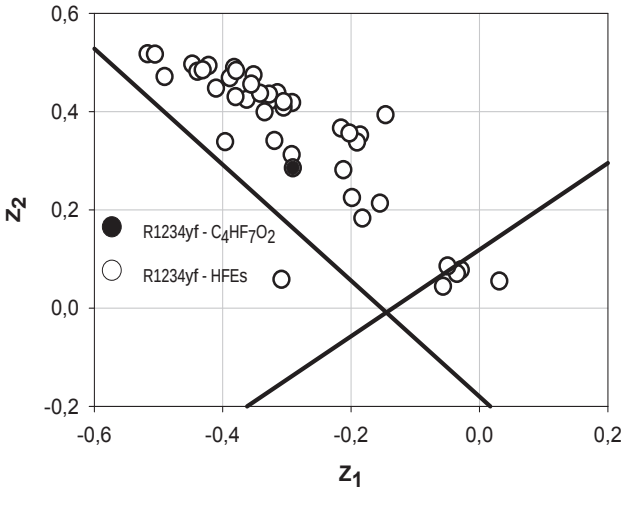

Fig. 2. Distribution of azeotrope pairs in the R1234yf — HFEs mixtures

To visualize the appearance of azeotrope for system R1234yf – $C_4HF_7O_2$ (T_c = 452.88 K, p_c = 2.866 MPa, ω = 0.390) boundaries were shown by solid lines in Figure 2. The characteristic point allocations both for the R1234yf – $C_4HF_7O_2$ and R1234yf – HFE blends are presented in Figure 2. If a characteristic point is located in the northern or southern quadrants (Fig. 2) then azeotropy phenomena should appear in the binary refrigerant mixture. It is apparent the overwhelming majority of the R1234yf – HFE gives evidence of azeotropy.

4. Phase equilibria in the R1234yf – HFE blends

Set of parameters for given equation of state model univocally defines a global phase diagram and, accordingly, evolution of phase behaviour for binary mixture in wide range of temperatures and pressures which include all possible phenomena (zeotropic and azeotropic states, liquid – vapour and liquid – liquid – vapour equilibria, and etc.). Some refrigerant mixtures can exhibit all varieties of the phase equilibria phenomena, including transitions from zeotropic to azeotropic state and vice versa with change of state parameters. This opportunity follows from the type of phase behaviour which is defined by the equation of state parameters.

Experimental phase equilibria data for R1234yf – HFE blends are not available in current literature and only theoretical estimations give an opportunity to make decision regarding new refrigerant blends. Phase equilibria calculations were realized in MATLAB software on the base of Michelsen, Mollerup algorithms [6]. The results for some R1234yf – HFE blends are presented in Figs. 3 – 6.

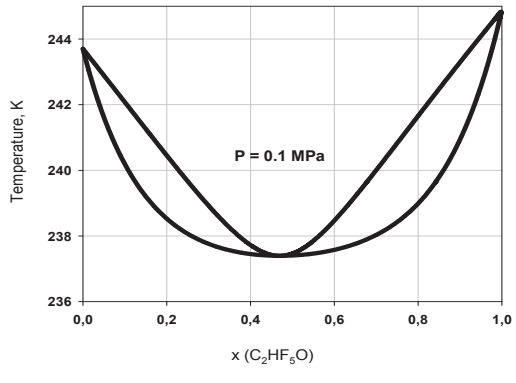

Fig. 3. T – x diagram for the R1234yf – C_2HF_5O

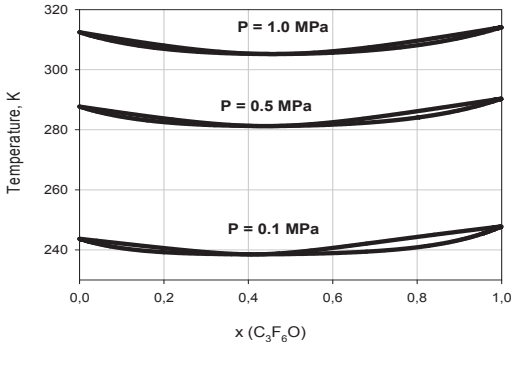

Fig. 4. T — x diagram R1234yf – C_3F_6O blend at 0.1 MPa blend at different pressures

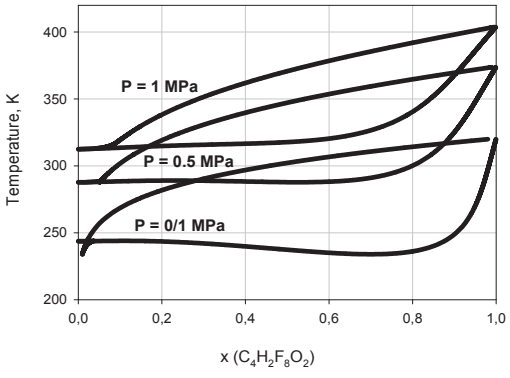

Fig. 5. T – x diagram for the R1234yf – $C_4H_2F_8O_2$

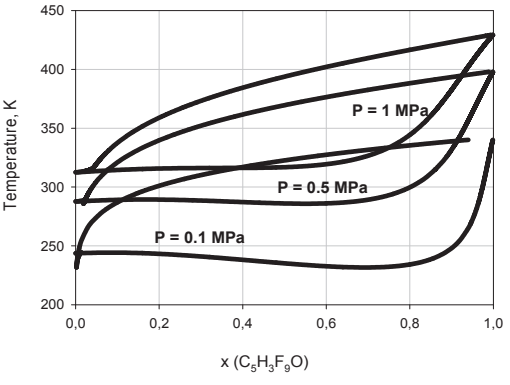

Fig. 6. T — x diagram R1234yf – $C_5H_3F_9O$ blend at different pressures blend at different pressures

The R1234yf – C2HF5O blend clearly exhibits a positive azeotrope (Fig. 3). Azeotropic and near azeotropic behaviour practically within all concentration range is observed for the R1234yf – C_3F_6O mixture (Fig. 4). An increase of carbon atoms (C_3 – C_5) leads to heteroazeotrope appearance at low R1234yf concentrations (Figs. 5 and 6). Main advantage of the R1234yf – HFE blends is a boiling temperature decreasing in comparison with pure components. For example, the R1234yf – C_2HF_5O mixture has a normal boiling temperature 6K below the low-boiling component. It compensates the lower energy efficiency R1234yf in comparison with R134a.

5. Performances of vapour compression cycle

To develop a blend with better properties than those of R1234yf we need preliminary to estimate properties of breeding components. Sustainable selection suggests a compromise among set of alternatives. It requires the assessment of different efficiency criteria. To evaluate the cycle performance data the ANN approach capable of learning to recognize complex input – output relationships is applied.

At first step the training set was used to calculate the main cycle characteristics. The cycle was chosen to simulate typical MAC operating conditions, and is specified by system cooling capacity of 5.8 kW, a constant evaporation temperature of 273 K, a constant condensation temperature of 323K, an evaporator superheat of 5 K, a condenser subcooling of 5 K, and a compressor isentropic efficiency of 70 %. Vapour compression cycle includes isentropic compression,

isobaric cooling + condensation + subcooling, throttling, and isobaric cooling + evaporation + superheating.

A multitude of R1243yf – HFE combinations puts obstacles in thermodynamic property calculations for little-studied refrigerants. To avoid this problem the cycle performance is restored from relationships "EoS parameters – cycle performance" based on artificial neural networks (ANN). The ANN correlations for COP and pressure ratio (output) as function of critical temperature, critical pressure and acentric factor – ω (input) are built on the known refrigerant database. The training set included 15 components (R134a, R123, R1270, R717, R600a, R290, R245fa, R245ca, R236fa, R227ea, R142b, R125, R113, R22, R32) where REFPROP 8.0 [4] was used to determine the thermodynamic properties of refrigerants. The ANN architecture for prediction of pressure ratio included the 2 layers with 6 and 1 neurons, correspondingly. The ANN for COP prognosis considered 3 layers with 2, 6, and 1neurons, correspondingly. The back propagation algorithm was applied for training procedure. The MATLAB Neural Network Toolbox is used in this application. The accuracy of ANN prediction for the cycle performances does not exceed 4% relative to the training set values. Figures 7 and 8 present the simulation results of COP and pressure ratio (PR) versus the critical temperatures of the individual HFEs. The ANN COP of the R1234yf cycle is 3.75 and that of the R134a cycle is 3.95, that is, the R134a COP is 5 % higher than the R1234yf cycle. The ANN model agrees with Zilio et al. [11] results within uncertainty of calculations.

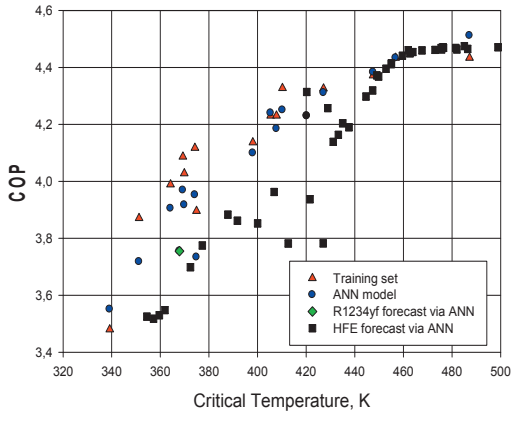

Fig. 7. COP – critical temperature relationships

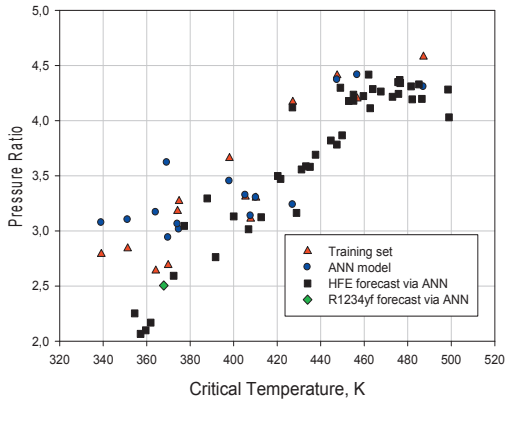

Fig. 8. PR – critical temperature relationships

6. Sustainable refrigerant selection

Design objectives usually contradict with each other, so that is difficult to provide sustainable solution, which simultaneously satisfies both of them. Meaningful analysis of this ill-structured situation should include uncertainty conception. For the multicriteria problems the local criteria usually have a different physical meaning, and consequently, incomparable dimensions. It complicates the solution of a multicriteria problem and makes it necessary to introduce the procedure of normalizing criteria or making these criteria dimensionless. There is no unique method for the criteria normalizing and a choice of method depends on statement of problem having subjective nature. In the present study, a next sequence of decision-making steps is applied [5]:

– Determination of the Pareto optimum (or compromise, or trade off) set X_P as the formal solution of multicriteria problem to minimize uncertainty sources;

– Fuzzification of goals as well as constraints to represent an ill-structured situation;

– Informal selection of convolution scheme to transform a vector criterion into scalar combination of vector components.

To illustrate our approach we consider only two local criteria: COP and pressure ratio that can be represented by membership functions. Mole fraction of HFE additive is chosen as X variable. The results of refrigerant blend composition selection for system R1234yf – C_4HF_7O are shown in Fig. 9 where concurrent criteria reflect the opposite tendencies for COP and PR. The membership functions $\mu_{COP}(X)$ and $\mu_{PR}(X)$ are varied from maximum (minimum) value (COP_{HFE} = 3.75; PR_{HFE} = 2.5) at mole fraction x_{HFE} = 1 to mini-mum (maximum) value for pure R1234yf ($COP_{R1234yf}$ = 4.35; $PR_{R1234yf}$ = 4.2). Sustainable decision corresponds x_{HFE} = 0.61 (Fig. 9).

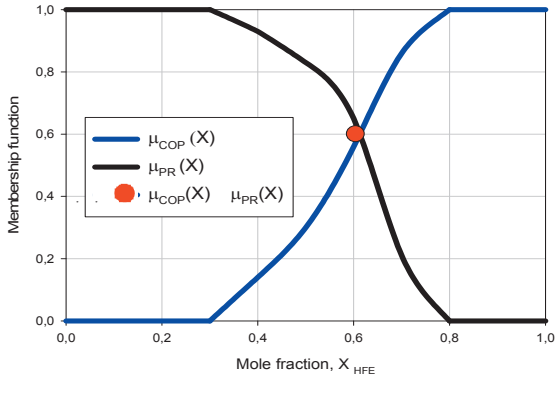

Figure 9. Sustainable decision as intersection membership function

7. Conclusions

A majority of R1234yf – HFE exhibits azeotropes and have no temperature glide in the heat exchangers similar pure refrigerants. A multitude of R1243yf – HFE combinations puts obstacles in thermodynamic property calculations for little-studied refrigerants. To avoid this problem the cycle performance is obtained from quantitative relationships "critical parameters – cycle performance" based on artificial neural networks (ANN). The ANN training set is chosen

to calculate the main cycle characteristics for well-studied refrigerants via REFPROP program. The sustainable performances of the R1234yf – HFE blends appear quite perspective. The disadvantage of R1234yf (low COP) is overcome through addition of HFE with high COP.

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