CENTER for ENVIRONMENTAL ENERGY ENGINEERING

Theoretical Study on Binary Isentropic Refrigerant Mixtures

Paper 2387

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16th International Refrigeration And Air Conditioning
Conference at Purdue, July 11-14, 2016, Purdue, Indiana

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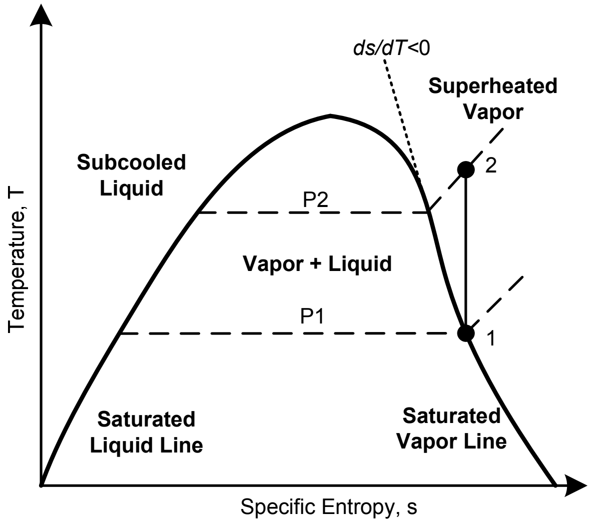
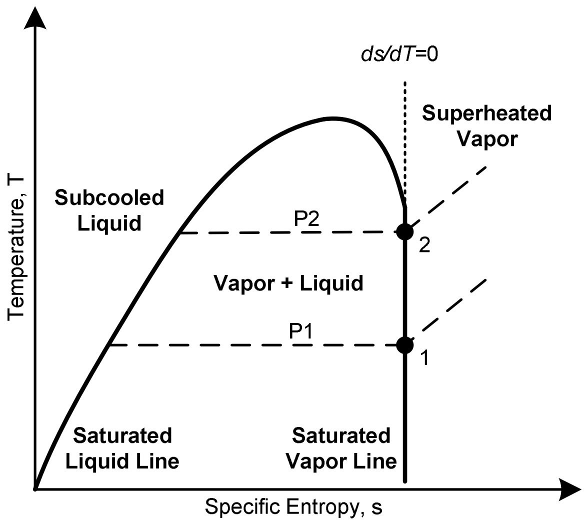
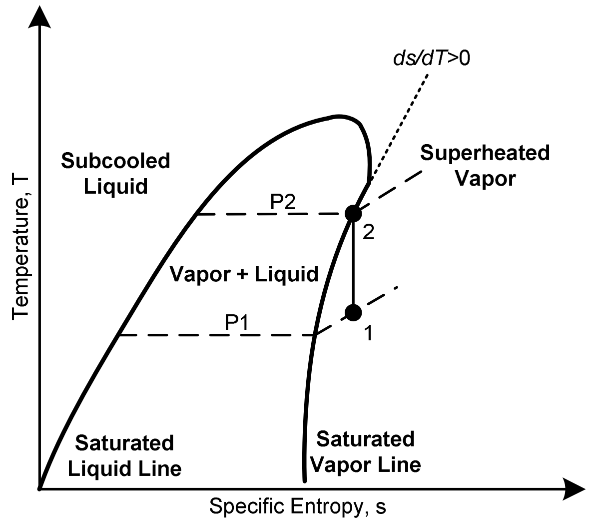
Working Fluids Types in VCC



Dry Fluids



Isentropic Fluids



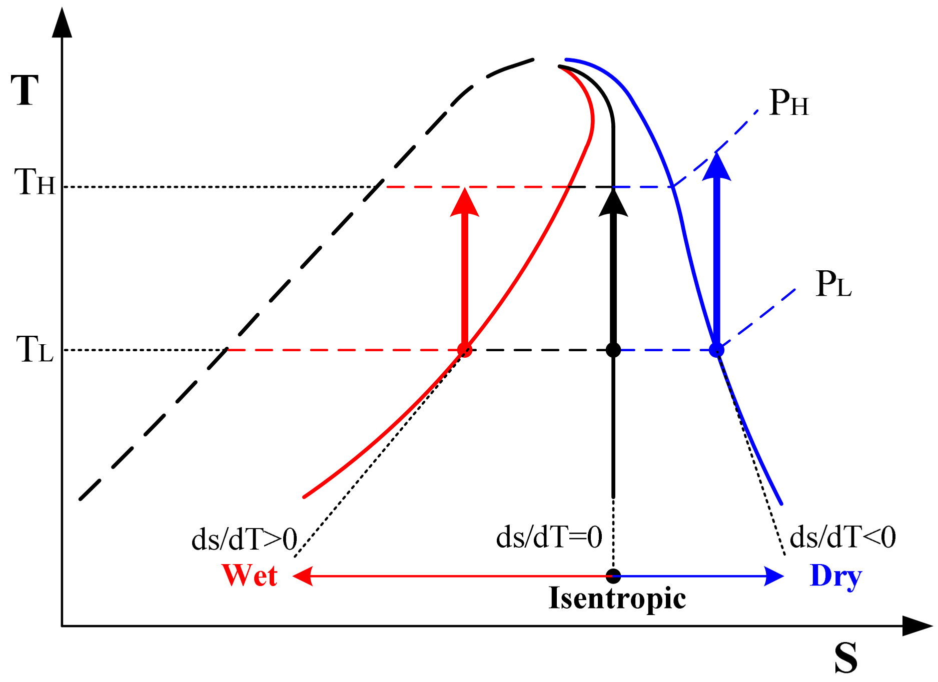
Wet Fluids

For Isentropic compression process:

- Wet fluids: saturated vapor → two-phase
- Dry fluids: saturated vapor → superheated vapor
- Isentropic fluids: saturated vapor → saturated vapor

Superheat Parameter ζ

- Relation between SHD and ζ



$$SHD \approx \int_{T_{evap}}^{T_{cond}} (\zeta - 1) dT \qquad (1)$$

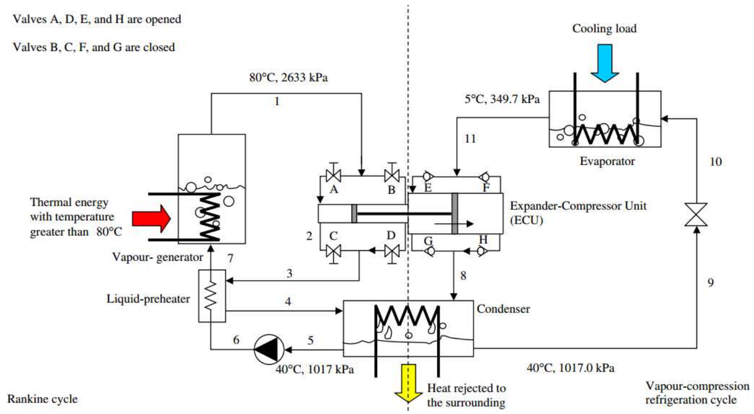
$$\zeta \equiv \beta \Delta H_{lv} V / C_P \Delta V \qquad (2)$$

β: coefficient of thermal expansion (1/K)

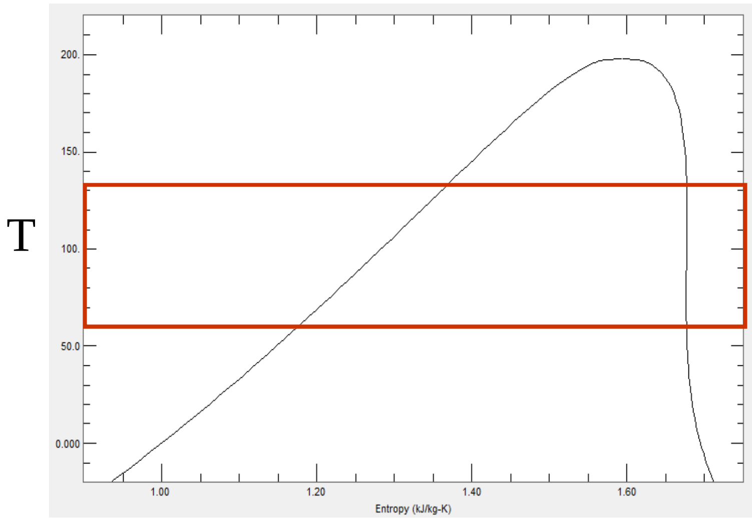
Classification based on ζ:

- **ζ>1: dry refrigerants**
- **ζ<1: wet refrigerants**
- **ζ=1: isentropic refrigerants**

Isentropic Refrigerant



Combined ORC-VCC system



T-s diagram for R11

Ideal working fluids, due to:

- Lower risk of liquid slugging
- Lower SHD, effective utilization of HX
- Lower compression work in theory

Restrictions

- Limited availability (e.g: R11 and R123)
- ODP restriction
- ζ varies as temperature changes

Make Isentropic mixtures

ζ of Binary Mixtures

- When T_r=const and $T<T_{crit}$, ζ could be simplified as:

ε: Intermolecular interactions

σ^3 : Molecule dimensions

$$\zeta \propto P_r \begin{cases} \zeta \approx \dfrac{\Delta H_{lv}}{C_P} \propto \dfrac{\varepsilon}{f\left(\sigma^3\right)} & \begin{cases} \Delta H_{lv} \propto \varepsilon \\ C_P \approx H^{kin} = \dfrac{3}{2} n K_T T \end{cases} \\ P_r \propto \dfrac{\varepsilon}{\sigma^3} & \end{cases}$$

Law of Equipartition

Principle of Corresponding States

- Assume R1, R2 and their mixture RM

$$P_{crit,R1} > P_{crit,RM} > P_{crit,R2} \Longrightarrow \zeta_{R1} > \zeta_{RM} > \zeta_{R2}$$

- If $\zeta_{R2} > 1$, then $\zeta_{RM} > 1$
- If $\zeta_{R1} < 1$, then $\zeta_{RM} < 1$
- If $\zeta_{RM} = 1$, then $\zeta_{R1} > 1 > \zeta_{R2}$

Isentropic mixture should be made by mixing wet and dry fluids

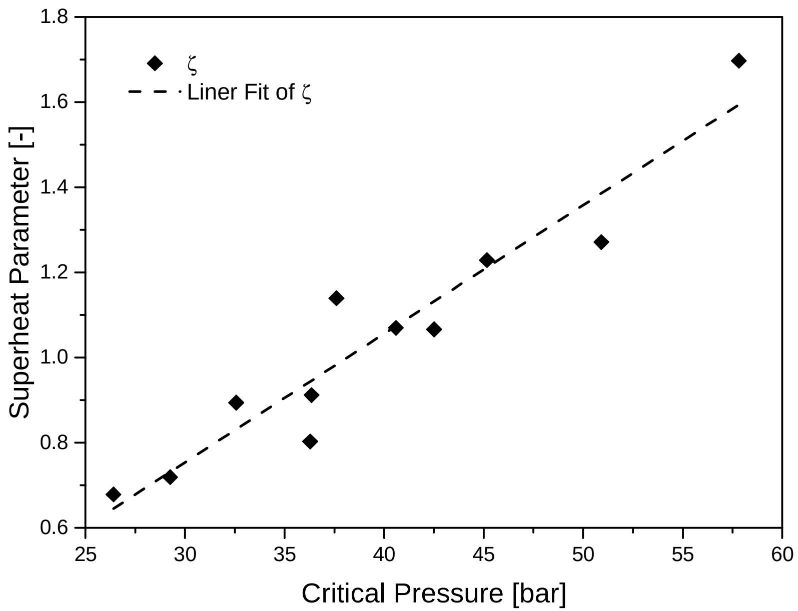
Selection of Component Refrigerants

Specified Working Conditions

HTF at Condenser		HTF at Evaporator	
Inlet T (ºC)	Outlet T (ºC)	Inlet T (ºC)	Outlet T (ºC)
45	55	-8	-13

Initial selection criteria:

- $T_{nb,\,max}$ = -8 ºC
- $T_{crit,\,min}$ = 70 ºC
- ODP = 0



Properties of Candidate Refrigerants

Fluid	M (g/mol)	P_{crit} (bar)	T_{crit} (ºC)	T_{nb} (ºC)	ζ (-)
R218	188.02	26.4	71.87	-36.79	0.6782
R227ea	170.03	29.25	101.75	-16.34	0.7187
R600a	58.12	36.29	134.66	-11.75	0.8027
R1234yf	114.04	32.57	94.70	-29.45	0.8937
R1234ze	114.04	36.36	109.37	-18.95	0.9115
R134a	102.03	40.59	101.06	-26.07	1.0694
R290	44.10	42.51	96.74	-42.11	1.0659
R143a	84.04	37.61	72.71	-47.24	1.1393
R152a	66.05	45.17	113.26	-24.02	1.2286
R161	48.06	50.91	102.15	-37.55	1.2709
R32	52.02	57.82	78.11	-51.65	1.6971

wet

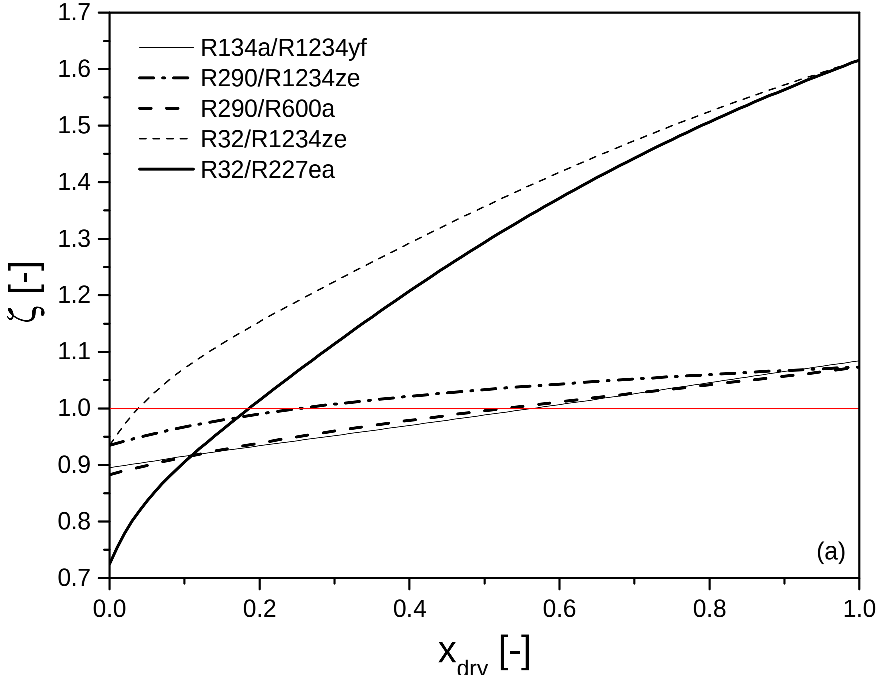
dry

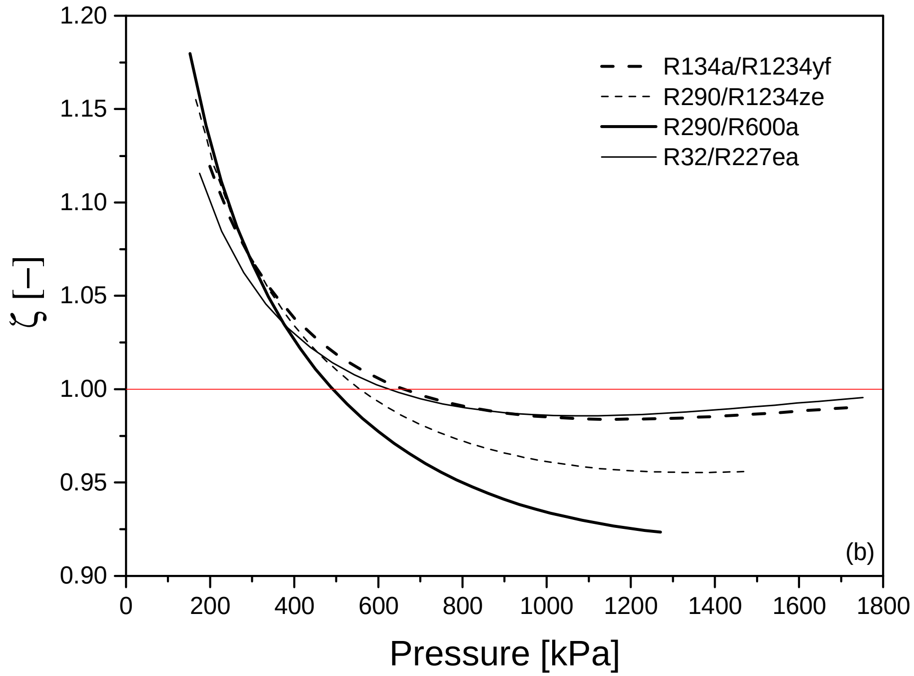
Potential Binary Isentropic Mixtures

Mixture	x_{dry}(%)	ΔT_{gl}(K)	Mixture	x_{dry}(%)	ΔT_{gl}(K)	Mixture	x_{dry} (%)	ΔT_{gl}(K)
R32/R218	46.74	0.4	R290/R218	68.18	0	R134a/R218	74.54	4.8
R32/R1234yf	7.46	7.8	R290/R1234yf	42.01	0.8	R134a/R1234yf	56.39	0.1
R32/R1234ze	3.82	6.3	R290/R1234ze	25.38	3.3	R134a/R1234ze	43.10	0.8
R32/R227ea	18.60	12.6	R290/R227ea	62.78	0.3	R134a/R227ea	74.14	0.3
R32/R600a	2.82	19.2	R290/R600a	52.63	7.4	R134a/R600a	75.47	0.8
R143a/R218	67.86	0.2	R161/R218	36.11	6.5	R152a/R218	46.12	1.9
R143a/R1234yf	41.73	2.9	R161/R1234yf	16.08	1	R152a/R1234yf	23.87	0
R143a/R1234ze	24.81	6.4	R161/R1234ze	9.01	2.3	R152a/R1234ze	15.11	0.5
R143a/R227ea	63.45	4.4	R161/R227ea	29.54	3.3	R152a/R227ea	40.51	0.5
R143a/R600a	60.04	15.4	R161/R600a	20.80	10.6	R152a/R600a	35.93	6.7

- 30 binary isentropic mixtures are obtained.
- Temperature glide is calculated based on condensing pressure.
- 5 typical mixtures include HC/HC, HC/HFC, and HFC/HFC.

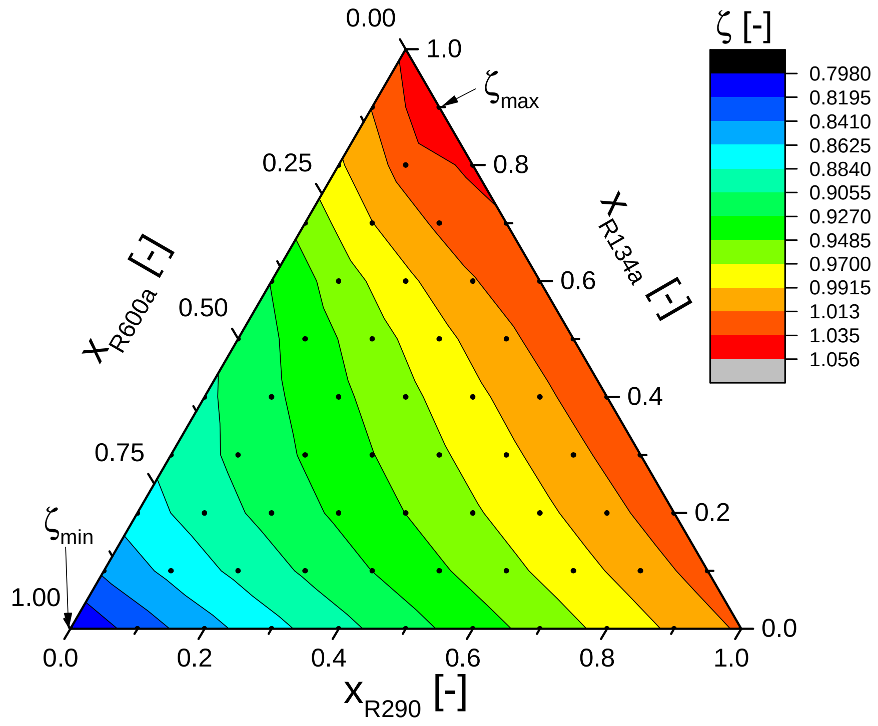
Influence of Composition and Pressure on ζ



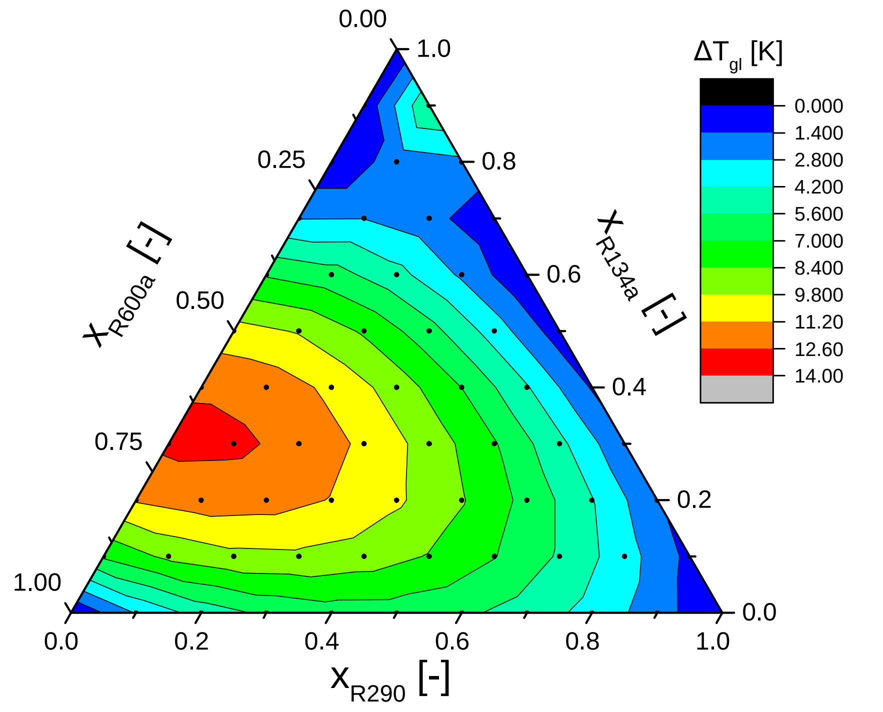


- ζ increases from <1 to >1 with x_{dry}.
- ζ decreases from >1 to <1 with pressure.
- How to reduce the influence of pressure for R290/R600a?

Method I: Adding a Third Component



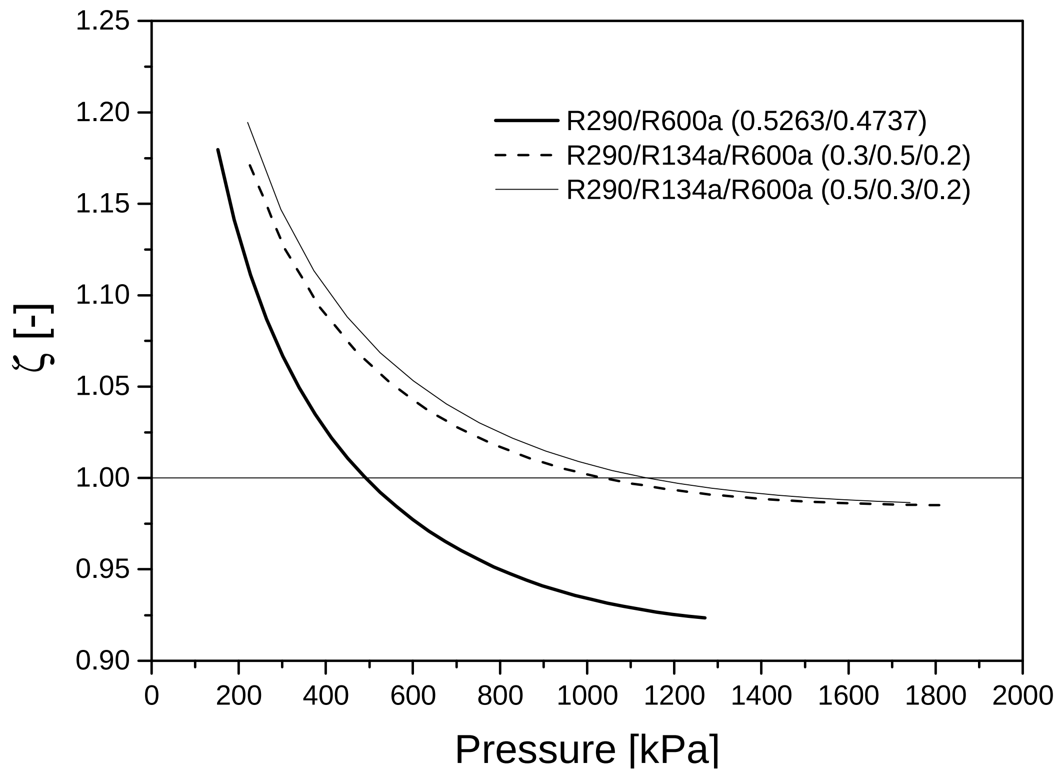
ζ-x relation in colored ternary map



ΔT_{gl}-x relation in colored ternary map

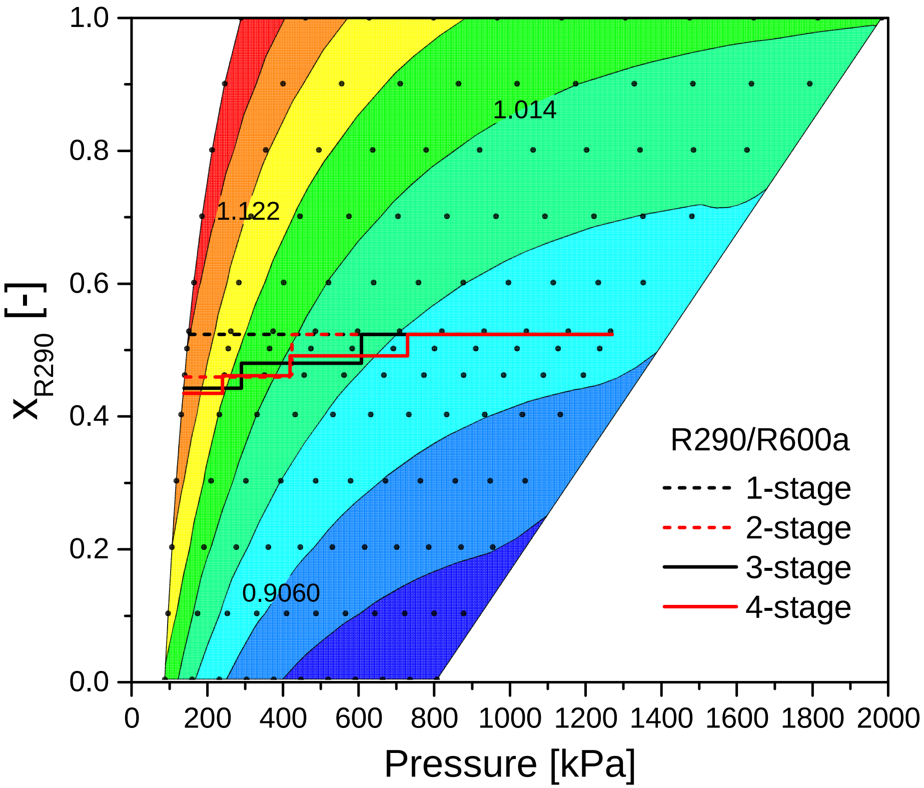
- T_{crit}: R290<R134a<R600a, P_{crit}: R290>R134a>R600a
- Banding distribution of ζ: x_{R600a}≈0.2, ζ=1
- Round distribution of ΔT_{gl}: 0.1<x_{R134a}<0.6, ΔT_{gl} > 5 ºC

Method I: Adding a Third Component



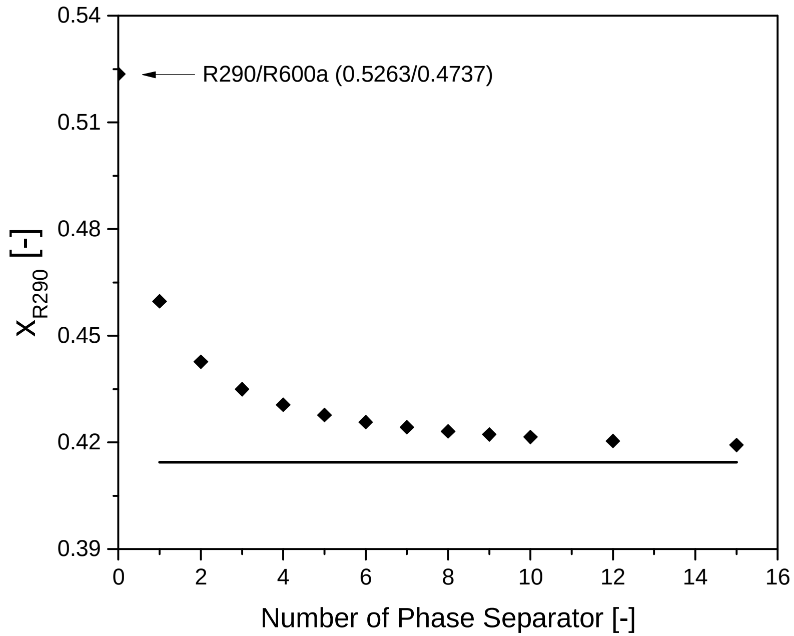
Adding third component could not reduce ζ within low pressure range.

Method II: Controlling Circulation Composition



Counter map of ζ versus composition and pressure

- ζ decreases as P_{evap}→P_{cond}
- Multistage compression with refrigerant injection



Thermodynamic Model and Fluids

Model Assumptions:

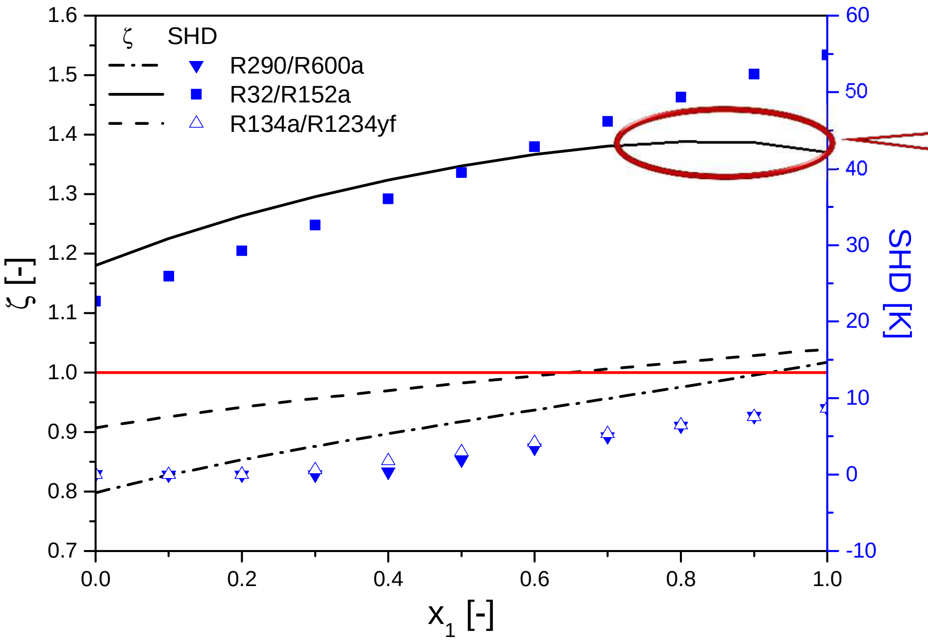
- Counter-flow type heat exchangers
- Constant overall heat transfer coefficient, U
- Constant total heat transfer conductance per unit heating capacity, as follows:

$$0.36 \leftarrow \frac{UA_{total}}{Q_c} = \frac{Q_e}{Q_c}\frac{1}{\Delta T_{lm,e}} + \frac{1}{\Delta T_{lm,c}}$$

Fluids:

Fluid Type	Zeotropic	Azeotropic
Isentropic	R290/R600a	R134a/R1234yf
Dry	R32/R152a	

Superheat Degree and ζ



R32 has much lower critical T (78.11 ºC).

- ζ is calculated based on saturated T under condensing P
- Mixture composition: mass fraction of the first component fluid (x_1)

- Generally, SHD increases with ζ.
- Dry mixture shows much higher SHD (max=55 ºC) than isentropic mixtures.

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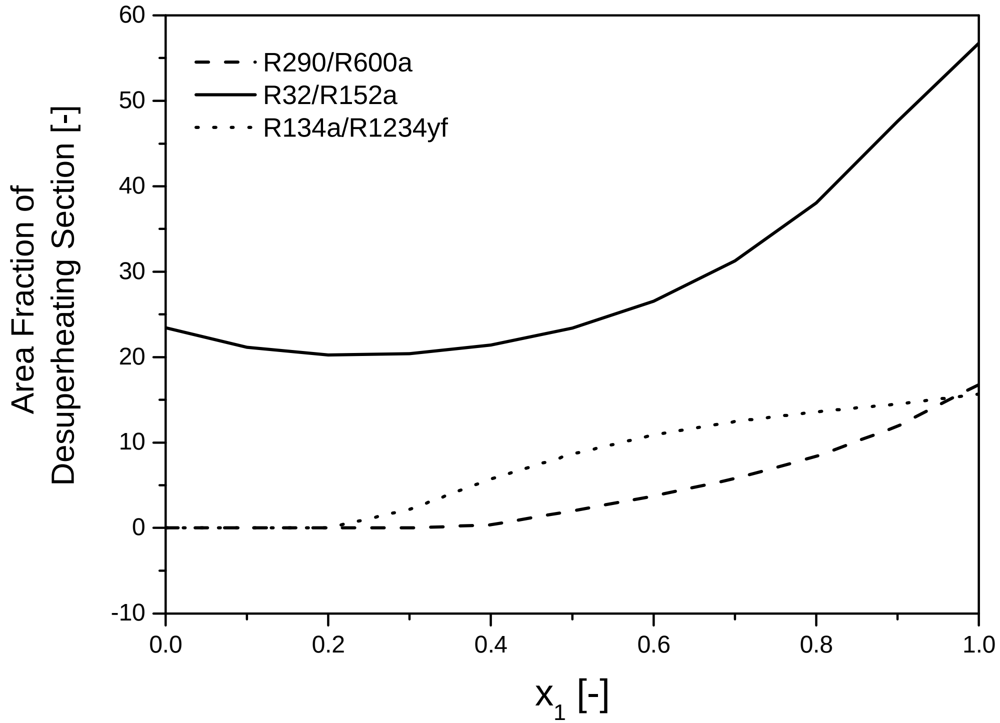
Heat Transfer Area for Desuperheating



The fraction of condenser area for desuperheating could be estimated by:

$$\frac{A_{desup}}{A_{cond}} = f_{desup}\left(\frac{\Delta T_{lm,c}}{\Delta T_{lm,desup}}\right)\times 100$$

- For dry mixture R32/R152a, maximum fraction of A_{desup} is 55%.

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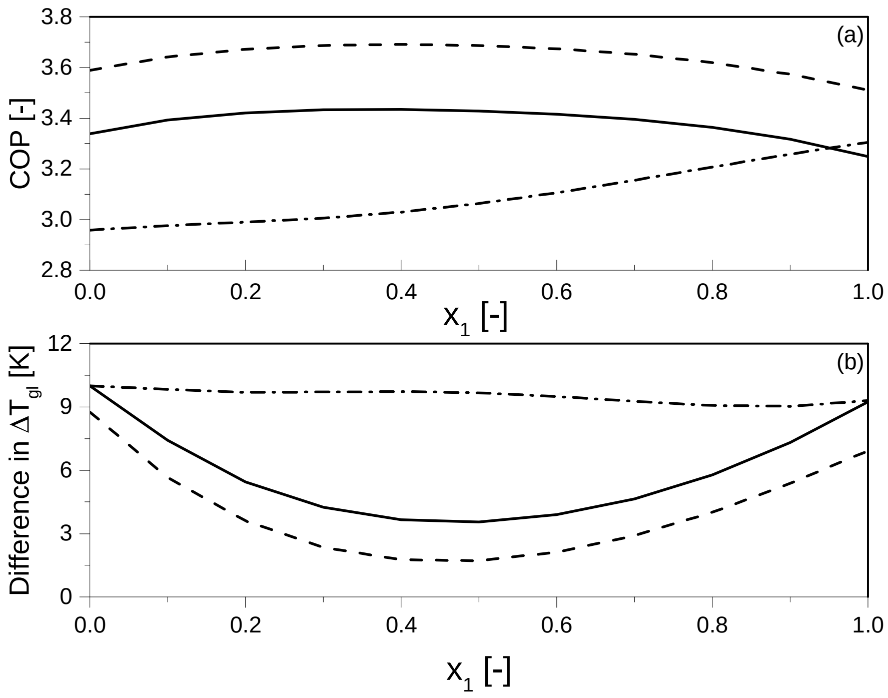
Heating COP

- Maximum COP: R32/R152a>R290/R600a>R134a/R1234yf



Solid line: R290/R600a; Dash line: R32/R152a;
Dash dot line: R134a/R1234yf

- **R32/R152a: maximum COP=3.69 (x_1=0.4), minimum ΔT_{gl}=1.7 K (x_1=0.5)**
- **R290/R600a: maximum COP=3.43 (x_1=0.4), minimum ΔT_{gl}=3.6 K (x_1=0.5)**
- **The ever-increasing SHD hinders the better match of temperature glides.**

Conclusions

- **Introduce the concept of isentropic mixtures.**
- **Mixing dry and wet fluids could lead to binary isentropic mixtures.**
- **By using isentropic mixtures, SHD as well as condenser area for desuperheating could be reduced.**

Acknowledgement

This work was sponsored by the National Nature Science Foundation of China (51476110). The support of the Center for Environmental Energy Engineering (CEEE) at the University of Maryland and the China Scholarship Council (CSC) are gratefully acknowledged.

Thank You!