

IS CO₂ THE NATURAL ALTERNATIVE TO R410A OR ARE THERE OTHER OPTIONS?

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ABSTRACT

Our initial desktop study suggested that there is no direct natural substitute for R410A. R170, ethane and R744, carbon dioxide, both have good potential but their higher pressure and lower critical temperature limit their suitability in R410A applications. We therefore investigated azeotropic and near azeotropic (i.e. glide of 6K or less) mixtures with similar pressure characteristics to R410A. We found 68 theoretical permutations, although some, such as ammonia / carbon dioxide and ammonia / hydrogen sulphide are not chemically compatible. Our aim was to match the temperature / pressure characteristics of R410A, whilst achieving a higher critical temperature to improve the likely energy efficiency. We clearly needed computer modelling to predict viable options. The industry standard is NIST REFPROP, although this does not accurately predict azeotropic behaviour.

We conclude that CO₂ is not a direct natural substitute for R410A and that a single component direct substitute with a global warming potential (GWP) of less than 150 does not exist. However, by using neural networks to predict binary azeotropes we have been able to identify nine potentially azeotropic or near azeotropic substitutes for R410A, all formed from natural refrigerants or synthetic chemicals with a global warming potential (GWP) less than 150. These are currently undergoing practical testing.

1. INTRODUCTION

For a long time now, refrigeration engineers have been working towards more environmentally friendly refrigerants. First CFCs were replaced with HCFCs, and then HCFCs were replaced with HFCs. Now HFCs are being replaced by natural refrigerants. This process seemed fairly straight forward until the advent of the higher pressure HFC, R410A. The path beyond R410A is not yet clear, but a superficially attractive option exists in the form of pure unblended HFC32, an option which has been advocated at least since 1996 (Dellino,1996). Following the “keep it simple” philosophy, why use a blend when a single component refrigerant can do the same job better? HFC32 demonstrates superior performance over HFC R410A using all criteria other than flammability and is classified as an A2 group refrigerant under EN378, so the same restrictions as with ammonia apply.

So is HFC32 the miracle refrigerant that we have been waiting for? If only life were that simple! Unfortunately, there are significant environmental problems associated with HFC32, most notably a

GWP of 670, which exceeds the EU F gas regulation threshold of 150 by a considerable margin. This project investigates whether CO₂ is the natural alternative to R410A or if other options exist.

The objective is threefold:

- to apply a new viewpoint employing neural networks and global phase diagram approaches for the prediction of possible azeotrope formation between components in a mixture that does not require vapour-/liquid equilibrium (VLE) calculations;
- to estimate an evaporating (condensing) pressure of an azeotropic mixture for a given evaporating (condensing) temperature;
- to establish correlations between crucial performances of refrigeration cycles and evaporating (condensing) pressures for final selection of the targeted mixture.

2. SELECTION OF ALTERNATIVES

There is huge commercial potential for a natural R410A substitute so we carried out an extensive desktop study which suggested that there is no single component direct natural substitute for R410A. R170, ethane and R744, carbon dioxide, both have good potential, but their higher pressure and lower critical temperature limit their suitability as R410A substitutes, particularly in air conditioning applications. Firstly, we examined the semi synthetic blend of R32/ R600a (90/10) as recommended in published literature (Calm and Domanskii, 2004). This blend has a slightly higher pressure than R-410A. It offers higher efficiency, and a reduced GWP of 603, better than R410A with a GWP of 2060, but still well above the EU target of 150. It is flammable (though not as flammable as pure hydrocarbons). It appears to be compatible with mineral oil in addition to synthetic lubricants.

Then, we examined hydrocarbon blends. The two graphs (Fig. 1) show evaporating pressure (at -6°C and -30°C) against volumetric refrigerating capacity (+35°C condensing). The data points are for R410A, an R290/R170 mix and R1270/R170 mix. The data-points for the HCs are for a composition ranging from 0.70/0.30 to 0.90/0.10 for each mix.

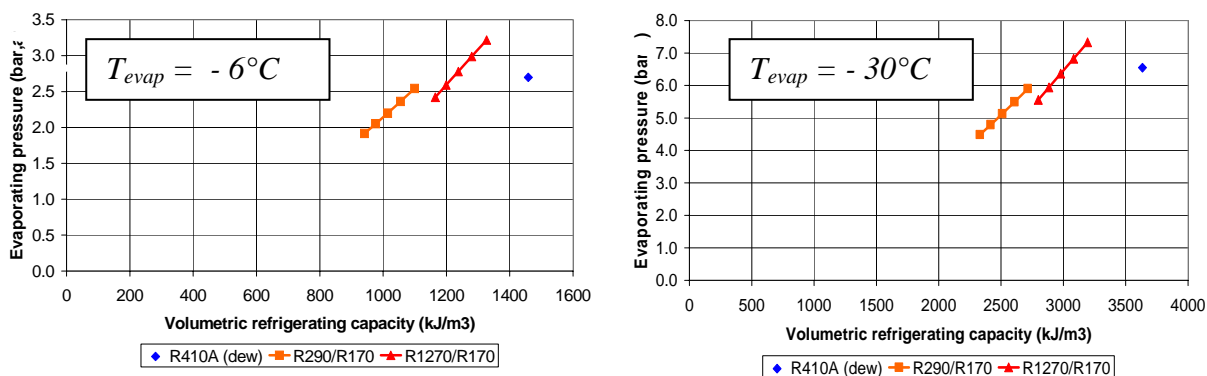


Figure 1. Evaporating pressure against volumetric refrigerating capacity

We note that whilst R1270/R170 can achieve the desired pressure, the volumetric refrigerating capacity is much lower. In other words, if the blend is selected for the same evaporating pressure, the cooling capacity will be about 15% less than R410A. We also note the temperature glide of up to 15K, which could be detrimental. We will need to consider the thermodynamics of the system, how to control the expansion valve etc before we make any meaningful tests, otherwise we risk liquid overfeed from the evaporator, and achieving steady state operation is likely to be difficult.

We therefore concluded that we needed to find an azeotropic or near azeotropic (i.e. glide of 6K or less) mixture with similar pressure characteristics to R410A. Azeotropes occur when there are departures from ideal behaviour in mixtures. For components with similar vapour pressures (boiling points) it takes only a small departure from ideality to cause an azeotrope. For larger differences in boiling point, a larger departure is necessary. We considered two sets of pure components:

Firstly, we considered binary mixtures of natural refrigerants (Table 1) using one higher pressure component and one lower pressure component. With 4 high pressure options and 17 low pressure ones, we have 68 theoretical permutations, although some, such as ammonia / carbon dioxide and ammonia / hydrogen sulphide are not chemically compatible. Our aim was to match the temperature / pressure characteristics of R410A, whilst achieving a higher critical temperature to improve the likely energy efficiency. Secondly, we considered synthetic chemicals with a global warming potential (GWP) less than 150.

Since azeotropic forecasts from experimental data are expensive and time-consuming, the availability of theoretical predictions for azeotropic behaviour not only reduces costs, but also saves time by narrowing the experimental search field. So, we clearly needed computer modelling to predict viable options. The industry standard is NIST REFPROP, although this does not accurately predict azeotropic behaviour. To avoid lengthy calculations or experimental testing for every permutation of working fluid it is desirable to establish correlations between targeted values of refrigeration cycles and thermodynamic parameters of refrigerants. The saturation properties are preferable for these correlations due to the rigorous thermodynamic relationships between pressure and temperature on the saturation line. The following reverse cycle specifications are chosen:

evaporator and condenser temperatures, $T_{ev}^0 = -10^{\circ}C$, $T_{cond}^0 = 35^{\circ}C$;

refrigerating capacity $q_0^0 = 0.5kW$,and

condenser/ evaporator pressure ratio $P_r < 10$.

The main processes in the single-stage vapour compression cycle include isentropic compression, isobaric cooling + condensation + subcooling, throttling, and isobaric cooling + evaporation + superheating. Thermodynamic properties of working fluids and appropriate design specifications are simulated by COOLPACK. Databases for critical parameters of concurrent refrigerants were chosen from published data (Calm, Hourahan, 2001). The training set for calculation of cycle performance characteristics included the refrigerants R12, R22, R290, R404A, R407C, R410A, R502, R507a, R600a, R717, R134a. The correlation V_s (volumetric flow) versus evaporation pressure is given in Fig. 2.

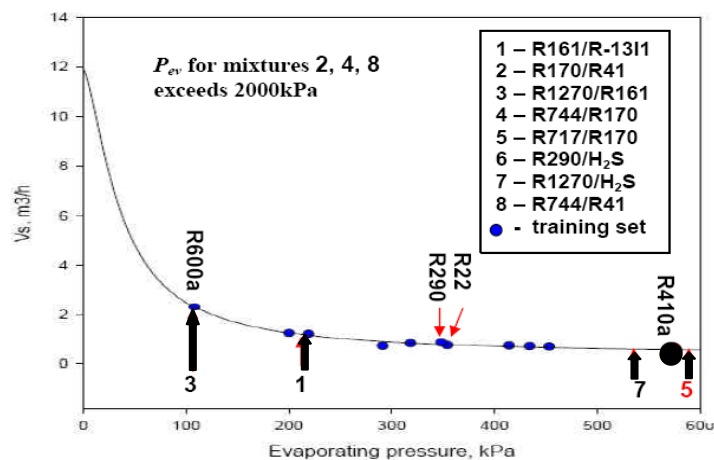


Figure 2. Volumetric flow – evaporating pressure relationship

Table 1. Possible natural component of R410A substitutes

Number	Name	T _c , °C	P _c , bar	P _{evap} - 30°C, bar	P _{cond} + 20°C, bar	Food safe
R410A	Blend of 50% 32, 50% 125	72.0	47.7	2.75	14.48	Yes
High Pressure Components						
R744	Carbon dioxide	31.0	73.8	14.28	57.35	Yes
C₂H₂	Ethyne / acetylene	35.5	61.37	10.96	41.77	
R1150	Ethene / ethylene	9.51	50.6	19.67	Supercritical	
R170	Ethane	32.2	48.72	10.56	37.91	Yes
H₂S	Hydrogen Sulphide	100.0	89.4	5.28	17.9	Toxic
Low Pressure Components						
R2250	Propadiene / allene	120.7	52.5	1.25	6.8	
C₃H₄	Propyne	129.2	56.3	0.74	5.1	Unstable
R1270	Propene / propylene	91.9	45.9	2.12	10.2	Yes
R290	Propane	96.6	42.5	1.70	8.5	Yes
RC270	Cyclopropane	125.1	55.8	1.14	6.4	Yes
E170	Dimethylether	126.9	52.7	0.81	5.1	Yes
R717	Ammonia	132.5	110.0	1.19	8.6	No
R764	Sulphur dioxide	157.5	78.8	0.35	3.3	Toxic
R3350	n-butatriene	181.2	49.6	0.19	1.7	
R2380a	Iso- butadiene1,2	176	48.7	0.16	1.4	
R2380	n-butadiene1,3	152	43.2	0.33	2.4	
R1390a	Isobutene	144.7	40.0	0.37	2.6	
R1390	Trans-butene	155	40.8	0.26	2.0	
R600a	Isobutane	134.7	36.3	0.47	1.2	Yes
R630	Methylamine	156.9	76.1	0.31	2.9	Toxic
H₂CO	Formaldehyde	134.8	65.9	0.61	4.5	Toxic
Synthetic Components						
R 41	Fluoromethane	44.1	59.0	0.81	4.94	
R 152a	1,1 Difluoroethane	123.3	45.2	0.78	5.04	A2
R 161	Fluoroethane	102.2	47.0	1.72	9.50	
R 131I	trifluoroiodomethane	67.1	39.6	0.30	2.05	A1
R E254cb2	1 hydro 1,1,2,2 tetrafluoroether	-	-	0.48	2.98	
R E7200	1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane	-	-	0.009	0.13	

2.1. Azeotropic behaviour modelling

To simulate the azeotropic behaviour of different refrigerant mixtures, models based on the equation of state (EoS) presentation for thermodynamic properties are preferable. We consider here the cubic type models of the EoS:

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

where R is the universal gas constant, and the EoS parameters a and b of mixture depend on the mole fractions x_i and x_j of the components i and j and on the corresponding parameters a_{ij} and b_{ij} for different pairs of interacting molecules:

$$a = \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j a_{ij} (1 - k_{ij}), \quad b = \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j b_{ij}. \quad (2)$$

The set of dimensionless parameters for the model (1) is defined as follows:

$$\begin{aligned} Z_1 &= (a_{22} - a_{11}) / (a_{22} + a_{11}), & Z_2 &= (a_{22} - 2a_{12} + a_{11}) / (a_{22} + a_{11}), \\ Z_3 &= (b_{22} - b_{11}) / (b_{22} + b_{11}), & Z_4 &= (b_{22} - 2b_{12} + b_{11}) / (b_{22} + b_{11}), \end{aligned} \quad (3)$$

The boundary separating azeotropic and non-azeotropic states in a global phase diagram is called degenerated critical azeotropic point and represents the limit of the critical azeotropy at $x_i \rightarrow 0$ or at $x_i \rightarrow 1$. As a result of solving the system of thermodynamic equations for a degenerated critical azeotrope:

$$\left(\frac{\partial p}{\partial V} \right)_{T,x} = \left(\frac{\partial^2 p}{\partial V^2} \right)_{T,x} = \left(\frac{\partial p}{\partial x} \right)_{T,V} = 0 \quad (4)$$

one can obtain the following relationship of dimensionless parameters Z_i (Artemenko, et al, 2004):

$$Z_2 = \mp Z_1 - (1 \pm Z_1) \left(\frac{1 - Z_4}{1 \pm Z_3} - 1 \right) \Lambda \quad (5)$$

where the upper signs + or - correspond to $x_2 = 0$ and the lower signs + or - to $x_2 = 1$, respectively. The value of constant Λ depends on the chosen EoS type. Here, the Peng-Robinson EoS (Peng, Robinson, 1976) is chosen for reasons of simplicity and prevalence. In that case:

$$\Lambda = \frac{\Xi^{pr}}{\Theta_{ab}(\Theta_b - 1)^2} + \frac{2(\Theta_b - 1)}{\Xi^{pr}}, \quad (6)$$

where $\Xi^{pr} = \Theta_b^2 + 2\Theta_b - 1$, $\Theta_{ab} = \frac{\Omega_a}{\Omega_b}$, $\Theta_b = \frac{z_c}{\Omega_b}$.

According to Eq. (5) 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. For the Peng-Robinson equation of state $\Omega_a = 0.45724$, $\Omega_b = 0.07780$ and $z_c = 0.307$, value of Λ evaluated as 0.7027.

Knowledge of interaction parameters k_{12} , l_{12} allows estimating a possible azeotrope appearance in refrigerant blends from Eqs. (3) and (5) using information about critical parameters and acentric factors of each component only. Reliability of azeotropy recognition in binary refrigerant blends depends on the values k_{12} , l_{12} , which define a membership of mixtures to the azeotropic state. But for the overwhelming majority of mixtures considered here these parameters are unknown. To restore missing k_{12} , l_{12} data we have built artificial neural networks.

2.2. Neural network forecast of azeotropic behaviour

It is assumed implicitly that our forecast model includes a set of submodels such as equation of state, combination and mixing rules, thermodynamic relationships, neural networks construction, phase equilibrium data, etc. The final result, i.e. the azeotrope forecast is based only on critical parameters of components and their acentric factors. The algorithmic chain is as follows: critical parameters and acentric factors for pure components are given, binary interaction parameters are estimated from neural network, and azeotropy criterion is calculated to classify an azeotropy membership. Reliability of azeotropy recognition in binary refrigerant blends using neural networks

depends on choice of output value, which classifies a membership of mixtures to the azeotropic state.

To explore the existing databases for binary interaction parameters we have confined only the interaction parameter k_{ij} for the one-fluid Peng – Robinson EoS. The training set contains the selected data from k_{ij} - database (Laugier, et al, 1994; Artemenko, et al, 2004) and restored k_{12} data set for systems: R32-R143a, R32-R116, R32-R125, R32-R290, R23-R116, R116-R744, R125-R717, and (R218, R134a, R152a, R32) + R290, (R218, R134a, R152a, R32, RC318) + R600a, (R600, R600a, R290, R218, R152a, RC318, R170) + R717, (R290, R600a, R600) + R744. The class of component pairs under consideration is presented by the potential refrigerants for the R410A replacements presented in Tables 2, 3.

Table 2. Possible azeotropy states and interaction parameters in refrigerant blends with a GWP of less than 150

Components	R-41	R-152a	R-161	R – 131I	R-E 254cb2	R-E7200
R - 41		<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>
R -152a	0.0205		<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>
R -161	0.0134	- 0.025		<i>N</i>	<i>N</i>	<i>N</i>
R – 131I	0.0191	- 0.005	0.013		<i>N</i>	<i>N</i>
R - E254cb2	0.0144	- 0.001	0.011	0.054		<i>N</i>
R - E7200	0.0920	-0.005	0.053	0.003	0.0659	

The binary interaction parameter database for the Peng-Robinson EoS of the refrigerants includes more than 100 binary systems. As an input vector \mathbf{P} , values of critical temperature, critical pressure, and acentric factor for each of components were used. Training efficiency function was defined as a root mean square error (RMSE). Training was performed using standard algorithms from Neural Network Toolbox for a MATLAB (MATLAB is a trademark of The MathWorks, Inc.). The best approximation result was demonstrated by two – layer backpropagation network with 8 neuron in hidden layer ($RMSE = 2.14e-7$). A detailed description of the Neural Network will be given alio loco (Artemenko, Mazur, 2006). Here we present final results of interest for our goals (Tables 2, 3).

Table 3. Possible azeotropy states and k_{12} parameters in binary natural refrigerant mixtures

Components	R744		C ₂ H ₂		R1150		R170		H ₂ S	
R2250	<i>N</i>	0.115	<i>N</i>	0.110	<i>N</i>	0.031	<i>N</i>	0.017	<i>N</i>	0.065
C ₃ H ₄	<i>N</i>	0.073	<i>N</i>	0.105	<i>N</i>	0.047	<i>N</i>	0.054	<i>N</i>	0.078
R1270	<i>N</i>	0.120	<i>N</i>	0.103	<i>N</i>	0.027	<i>N</i>	0.018	A	0.049
R290	<i>N</i>	0.128	<i>N</i>	0.082	<i>N</i>	0.051	<i>N</i>	0.006	A	0.081
RC270	<i>N</i>	0.011	<i>N</i>	0.099	<i>N</i>	0.034	<i>N</i>	0.017	<i>N</i>	0.044
RE170	<i>N</i>	0.098	<i>N</i>	0.109	<i>N</i>	0.063	<i>N</i>	0.156	<i>N</i>	0.063
R717	<i>N</i>	0.115	<i>N</i>	0.118	<i>N</i>	0.159	A	0.156	<i>N</i>	0.126
R764	<i>N</i>	0.009	<i>N</i>	0.115	<i>N</i>	0.094	<i>N</i>	0.105	<i>N</i>	0.162
R3350	<i>N</i>	0.094	<i>N</i>	0.081	<i>N</i>	0.014	<i>N</i>	0.004	<i>N</i>	0.071
R2380a	<i>N</i>	0.105	<i>N</i>	0.067	<i>N</i>	0.028	<i>N</i>	0.005	<i>N</i>	0.063
R2380	<i>N</i>	0.123	<i>N</i>	0.063	<i>N</i>	0.018	<i>N</i>	0.012	<i>N</i>	0.065
R1390a	<i>N</i>	0.137	<i>N</i>	0.047	<i>N</i>	0.007	<i>N</i>	0.027	<i>N</i>	0.047
R1390	<i>N</i>	0.135	<i>N</i>	0.044	<i>N</i>	0.017	<i>N</i>	0.030	<i>N</i>	0.033
R600a	<i>N</i>	0.093	<i>N</i>	0.084	<i>N</i>	0.027	<i>N</i>	0.079	<i>N</i>	0.020
R630	<i>N</i>	0.001	<i>N</i>	0.093	<i>N</i>	0.072	<i>N</i>	0.030	<i>N</i>	0.088
H ₂ CO	<i>N</i>	0.073	<i>N</i>	0.009	<i>N</i>	0.106	<i>N</i>	0.087	<i>N</i>	0.114

3. VERIFICATION OF R410A ALTERNATIVES

We have been able to identify five potentially azeotropic and four near azeotropic substitutes for R410A, all formed from natural refrigerants or synthetic chemicals with a global warming potential (GWP) less than 150. Our research suggests that:

Carbon dioxide/ethane has a recognized azeotropic blend, R744/R170 concentration 0.35-0.36/0.65-0.64 mole/mole (Rowlinson, Swinton, 1982). It has a lower triple point and hence a higher operating pressure than CO₂ and might be a useful industrial refrigerant for low temperature blast freezers, but it is probably unsuitable as an R410A substitute in variable refrigerant flow multi-split (VRF) systems, unless the critical temperature for the blend is unusually higher than for the two components. An alternative view of the CO₂/hydrocarbon azeotrope concept is contained in research work done by N. Flacke at the University of Essen under the supervision of Prof Fritz Steimle. Flacke's thesis, suggests that the azeotrope is at 77% CO₂, and that the mixture is flammable. Rowlinson & Swinton's mole fraction of 35.5% CO₂ implies a mass fraction of 42.5% CO₂, sufficiently different from Flacke's 77% to suggest that CO₂ / ethane may be poly-azeotropic?

Although an R717/ethane azeotrope has been described (Brunner, 1988), strangely for such a detailed paper, it does not give the proportions of the ammonia / ethane azeotrope that it describes, suggesting that perhaps ammonia / ethane is poly-azeotropic? This blend should have a significantly higher vapour pressure than either ammonia itself or the more common ammonia / DME azeotrope, R723. This would prevent sub atmospheric situations in freezer applications, should improve energy efficiency and cooling capacity for a given swept volume, and improve oil miscibility, although flammability would be higher.

Hydrogen Sulphide / Propane - has a recognized azeotropic blend (Jou, Carroll, and Mather, 1995). In addition, we believe that we have identified a propylene / hydrogen sulphide azeotrope: However odour, corrosion, and possible chemical reactions need further investigation before using in existing compressors.

4. CONCLUSIONS

R410A has a bubble / dew point of 221.55K, whereas the figures for our near azeotropes are:

R161, ethyl fluoride and CF ₃ I, methyl iodide	$T_{bubble} = 241.75$	$T_{dew} = 244.27$
R1270, propene / R161, ethyl fluoride	$T_{bubble} = 228.84$	$T_{dew} = 230.37$
R744, Carbon Dioxide / R41, methyl fluoride	$T_{bubble} = 188.63$	$T_{dew} = 190.40$

Moreover, from the table below, it can be seen that of our five azeotropes two appear to be suitable as direct substitutes for R410A.

Table 4. Summary of azeotropes

Mixtures	Azeotropy membership	P_{dew} , kPa T = - 10°C	P_{bubble} , kPa T = - 10°C
R410A	A	544.7	550.5
1 R170, ethane / R41, methyl fluoride	A	1912	1912
2 R744, Carbon Dioxide / R170, ethane	A	2888	3003
3 R717, ammonia / R170, ethane	A	593.4	?
4 Hydrogen Sulphide / R290, Propane	A	537.2	658.4
5 Hydrogen Sulphide / R1270, Propene	A	648.8	736.1

? More detailed analysis is required

We would therefore conclude that a near azeotropic blend of R1270, propene / R161, ethyl fluoride, an azeotropic blends of Hydrogen Sulphide / R290, Propane and R717, ammonia / R170, ethane all have potential as substitutes for R410A. Of these we would hope to achieve a safety classification in accordance with ASHRAE 34 of A2 for the R1270 / R161 near azeotrope, but B3 for hydrogen sulphide / propane and ammonia / ethane.

NOMENCLATURE

A	azeotropic state	R	universal gas constant (kJ kmol ⁻¹ K ⁻¹)
a	equation of state parameter (long range attraction)	T	temperature, K
a_{ii}	long range attraction between $i - i$ components	x_i	mole fraction of component i
b	equation of state parameter (excluded volume)	V	molar volume (m ³ mole ⁻¹)
b_{ii}	excluded volume for component i	Z_i	dimensionless parameters of model. Equation (3)
a_{ij}	long range attraction between $i - j$ components	<i>Greek letters</i>	
b_{ij}	equation of state parameter b for an $i - j$ interaction	Λ	constant. Equation (5,6)
k_{12}	binary interaction parameter for long range attraction	ω	acentric factor
l_{12}	binary interaction parameter for excluded volume	Ω	constant. Equation (6)
NA	near azeotropic state	Ξ	constant. Equation (6)
N	zeotropic state	<i>Subscripts</i>	
HA	heteroazeotropic	c	critical
p	pressure (MPa)	$cond$	condenser
		exp	experimental
		i	component i
		mod	model

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