THE DEVELOPMENT OF AN AMMONIA ETHANE AZEOTROPIC REFRIGERANT FOR LOW TEMPERATURE APPLICATIONS

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ABSTRACT

The use of ammonia as a refrigerant offers significant benefits over many conventional refrigerants, although it also possesses some less favourable characteristics, such as those associated with relatively high normal boiling point, high discharge temperature and oil miscibility. Therefore it would be desirable to develop an ammonia mixture that overcome these disadvantages of pure ammonia. An ongoing development project has identified one such mixture comprising ammonia (R-717) and ethane (R-170), which under certain compositions forms an azeotrope. The objective of this part of the project was to determine the appropriate proportions of R-717 and R-170 that would produce the most favourable properties. Since the R-717 and R-170 mixture produces rather unusual behaviour, a major part of this study was to better understand the phase characteristics.

Because of the relatively high normal boiling point, high discharge temperatures and poor miscibility with oils, systems operating at low evaporating temperatures are more likely to suffer from related problems. This blend overcomes these drawbacks by significantly altering the refrigerant properties so that it can be more readily applied in low temperature applications such as blast freezing.

1. INTRODUCTION

For a variety of refrigerating applications ammonia (R-717) is the natural working fluid of choice. However, it possesses certain characteristics that are somewhat undesirable. In particular, the normal boiling point (NBP) of R-717 is -33°C, so lower temperatures result in sub-atmospheric pressures and the risk of ingress of air and moisture into the system, which is detrimental to performance and reliability. Furthermore, ammonia has a low specific heat which leads to much higher discharge temperatures than experienced with other conventional refrigerants; this is normally handled by costly oil inter-cooling or multi-stage compression. Lastly, R-717 is immiscible with standard compressor oils, which in most systems results in the necessity for oil draining and also inhibits heat transfer, particularly at lower evaporating temperatures.

In order to overcome such disadvantages, work has been carried out to identify possible mixtures of ammonia with other refrigerants. Specifically, the mixture should offer a lower NBP, lower discharge temperatures and be miscible with conventional oils. The output of this part of a larger project to develop alternative refrigerants identified the R-717 and ethane (R-170) pair as an advantageous blend. A further advantage of this mixture is its azeotropy, as temperature glide can be detrimental to system performance; particularly freezers where it can lead to uneven frost build up. As our research found this azeotropy to be of a nature, the objective of this project was to understand the behaviour of this mixture and to determine the optimum proportions for the blend, in particular low temperature applications, below -33°C.

2. EQUATION OF STATE AND PHASE BEHAVIOUR

Vapour-liquid (VLE) and vapour – liquid – liquid (VLLE) equilibria data are essential for a proper representation of the thermodynamic properties of mixtures and subsequent estimation of refrigerating system efficiency. The quantitative picture of the phase behaviour in the R-717/R-170 blend based on the present pressure – temperature – concentration (P-T-x) measurements (Earthcare Products Ltd, 2007) and

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previous experimental study of critical curves (Brunner, 1988) is illustrated in Figure 1. The \( p \) (\( T \)) projections of (liquid + liquid) (ll), (liquid + gas) (lg), critical curves, and of (liquid + liquid + gas) (llg) three-phase curves for n-alkane + ammonia mixtures with alkane-carbon numbers \( i = 1 \) to 12, and \( i = 14, 16, 18, 19, 20, \) and 36 were measured earlier (Brunner, 1988; Khazanova et al., 1972). The critical curves for the R-717/R-170 mixture form an uninterrupted lg-critical curve and an llg three-phase curve that terminates in a (liquid + liquid) upper critical end point (ll-UCEP). The ll-critical curves start from this ll-UCEP and rapidly approach high pressures with increase in temperature.

At pressures close to atmospheric binary fluid mixtures exhibit various kinds of phase diagrams such as those shown in Figure 2 where temperature \( T \) is plotted against mole fraction \( x \) at constant pressure. The Figures in the left side illustrates a possible liquid – liquid equilibrium terminating in an upper critical end point (UCEP) intrudes. In the right side the three – fluid – phase consequences of the intersection of two 2 phase regions are shown. Positive azeotropy can lead either to three fluid phases (3F) in which the sequence of phases from left to right is liquid, liquid, and vapour; or to heteroazeotropy: namely, the occurrence of three fluid phases in which sequence is liquid, vapour, and liquid, the three fluid phases then coexisting at a lower temperature than the boiling temperature of either pure component.

Figure 1. Vapour pressure and critical curves (Brunner, 1988) in R717 – R170 mixture

Figure 2. Boiling temperature – concentration diagrams at constant pressure
The R-717/R-170 mixture forms positive azeotropes up to the critical region. The uninterrupted critical curve for ethane + ammonia mixture (Figure 1) passes through a temperature minimum and a pressure maximum (Brunner, 1988). From available experimental data the II-A – type of the Scott and van Konynenburg of phase behaviour classification for binary mixture was established.

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. A reliability of thermodynamic model allows forecasting of azeotropic behaviour for the R-170/R-717 system. Here the Peng – Robinson equation of state (Peng, Robinson, 1976) as model for thermodynamic and phase behaviour description of ammonia – ethane system is considered (equation 1).

\[
p = \frac{RT}{V - b} - \frac{a A(T)}{v^2 + 2bV - b^2}
\]

where \( A \) is from equation (2), and the EoS parameters \( a \) and \( b \) of the 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 (equations 3 and 4).

\[
A = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \frac{T}{Tc})]^2
\]

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

\[
a_{ij} = \sqrt{a_{ii}(T)a_{jj}(T)}; \quad b_{ij} = \frac{b_{ii}(T) + b_{jj}(T)}{2}
\]

Parameters of pure components are determined by the local mapping principle which provides very accurate description of saturation curves (Artemenko, Mazur, 2007).

Theoretical model developed here describes phase behaviour for ammonia mixtures quite well in all temperature region of interest. Some discrepancies between description phase equilibria data at high temperature are explained by the different methods restoring the interaction parameters from critical curve and phase equilibria data. Phase equilibria calculations based on existing information about pressure – temperature compositions measurements \((p - T - x)\) data allowed us to obtain the phase diagrams presented below in Figures 3 to 6. In the upper part of Figures 3 – 6 the adjusted parameters equation of state are given in the sequence \(k_{ij}, l_{ij}\). Figure 3 illustrates a typical isotherm including both azeotropic and the van der Waals metastable states in the low-temperature region for the R-717/R-170 blend.

### 3. RESULTS OF BEHAVIOUR PREDICTIONS

The model described above has been used to help understand the behaviour of the R-717/R-170 mixture. With any ideal binary mixture, the bubble and dew-point lines are separate for the entire range of compositions, and only converge when the composition reaches 100% or 0% of one or the other components. However, for the R-171/R-170 blend the two lines converge at compositions other than 100% and 0% to form an azeotropic region. A positive azeotrope exhibits a rise in the pressure/composition curve at low temperatures. At these compositions, the mixture behaves as if it were a pure, single component fluid. As temperature increases, the azeotropic vapour composition moves from the zone of the liquid – liquid miscibility gap in the direction of higher mole fractions of ammonia. At the high temperature limit, the homogeneous positive azeotropy disappears. The three-phase line terminates in the liquid-liquid upper critical end point (UCEP), which lies approximately 10 K above the critical temperature for pure ethane (about +44.9°C). At low temperatures in the liquid-liquid-vapour three-phase range, the liquid phase is richer.
in ammonia. The R-170/R-717 blend also forms heterogeneous positive azeotropes (where the two components are not homogeneously mixed) up to the liquid-liquid UCEP where the occurrence of three fluid phases is observed as a liquid, vapour, and liquid sequence (which is contrary to conventional three-phase equilibria with liquid-liquid-vapour sequence). The +50°C isotherm (Figures 5, 6) is terminated at intermediate compositions; these points represent the critical state, thus indicating the maxima for operation of a particular mixture.

Initial parameters for equation of state of pure components were chosen as follows:

\[ a = \frac{0.45724R^2T_C^2}{p_C}, \quad b = \frac{0.07780RT_C}{p_C} \]

R717 (NH₃): \( T_C = 405.65 \text{ K}, \ P_C = 11.3 \text{ MPa}, \ \beta = 0.2526 \)

R170 (C₂H₆): \( T_C = 305.39, \ P_C = 4.87 \text{ MPa}, \ \beta = 0.0995 \)

\[ k_{12} = 0.223743; \ l_{12} = 0.010208 \]

Figure 3: Pressure – composition diagram of heteroazeotropic R-170/R-717 blend at 0°C

Figure 3 illustrates the relationship between saturation pressure and composition for the R-170/R-717 mixture. The set of curves characterises the isotherm (line of constant temperature) as indicated for \( T = 0°C \). Figures 4, 5 and 6 show the phase equilibrium diagrams to cover the temperature range -55°C to +50°C, which represents the approximate limits of the anticipated operating conditions for low temperature refrigerating equipment. For each set of curves, the upper line indicates the pressure of the saturated liquid (also known as the bubble-point) at the temperature, \( T \), and the lower line indicates the pressure of the saturated vapour (also known as the dew-point). The dashed lines correspond to the three-phase (liquid-liquid-vapour) equilibrium. The continuation of dew and bubble point curves above three-phase lines (isotherms at 0°C) reproduces the metastable states, that is, where the equilibrium conditions of the mixture may be sustained even if the external conditions, such as pressure or temperature, are changed.
Figure 4: The R-717/R-170 mixture isotherm at low temperatures ($T = -55^\circ C$)

Figure 5: Comparison experimental data and model calculations at temperature $+50^\circ C$
(The model parameters were restored from critical line data)
4. SELECTION OF COMPOSITION

The choice of preferred composition requires a balance of a number of different factors. These include system performance, operating pressures, critical points and safety classification.

In order to assess the performance of the R-717/R-170 mixtures, a minimum of the thermodynamic properties are required. The main thermodynamic properties (the total enthalpy and entropy) evaluation of the R-717/R-170 blend requires additional calculations of VLLE in comparison with conventional procedure VLE calculation. The thermodynamic relationships for total enthalpy and entropy are as follows (equation 5 and 6).

\[
H(p,T,x) = \beta H_v + [aH_l + (1-a)H_{li}](1-\beta)
\]

\[
S(p,T,x) = \beta S_v + [aS_l + (1-a)S_{li}](1-\beta)
\]

(5) (6)

Where vapour \((a)\) and liquid \((\beta)\) quality factors are linked via mass balance equation for binary mixture (equation 7).

\[
z_i = \beta y_i + [a x_{i,l} + (1-a)x_{i,li}](1-\beta), \quad i = 1,2
\]

(7)

So far, the property data for this mixture has been used to analyse the performance with a cycle model, which provides quantitative indication of the performance over the range of compositions. Based on a condensing temperature of 27°C, an R-170 rich mixture tends to have a lower efficiency due to its low UCEP, as would be expected. Conversely, increasing the R-717 component tends to lead to a better COP, although this levels out once the composition increases the UCEP well above the condensing temperature. Considering these efficiency trends, the NBP of the mixture and limitation of discharge pressure, from a system performance perspective the composition may be within the range of 40% R-170/60% R-717, up to 70% R-170/30% R-717. It is also noted that there is sufficient R-170 within this composition range to adequately transport conventional low viscosity mineral oils, even at low evaporating temperatures.
Refrigerant safety classification is also an important consideration, since this dictates its applicability. According to ISO 817, the toxicity class of R-170 is “A”, whilst that of R-717 is “B”. Depending upon the composition of the mixture, either an “A” or “B” classification may result. Using the criteria set out within ISO 817, an “A” classification may be achieved by ensuring a molar composition of least 21% of R-170. In terms of flammability, R-170 has a “3” classification, whereas R-717 has a classification of “2”. Again, the ISO 817 criteria suggest that a flammability classification of “2” may be achieved with a molar composition of at least 27% of R-717. Therefore, in order for the mixture to achieve the more desirable “A2” classification, the molar composition should be between 21% R-170/79% R-717 and 73% R-170/27% R-717.

It was observed that both the most desirable performance and safety classification coincide with similar compositions. Thus, the chosen composition is 45% R-170/55% R-717; this achieves a sufficiently high critical temperature and an “A2” safety classification. This azeotropic blend is optimised for below -33°C applications.

An illustration of the cycle performance for the chosen composition is given in Table 1. Here the cycle performance is calculated using an evaporating and condensing temperature of -55°C and +27°C, respectively, and a cooling capacity \( Q_0 = 10 \text{ kW} \) for a single stage cycle. It is seen that the discharge temperature is significantly lower than pure R-717, as is the compression ratio. The theoretical COP shows a slight decline, although for a given system it is likely to exceed this due to the improved heat transfer because of better oil miscibility. The discharge pressure is 5403 kPa, and importantly, it is seen that the swept volume is 77 m³/h.

<table>
<thead>
<tr>
<th>Refrigerants</th>
<th>( Q_0, \text{kW} )</th>
<th>( T_{out}, ^\circ\text{C} )</th>
<th>( P_o, \text{kPa} )</th>
<th>( P_s, \text{kPa} )</th>
<th>( P_s/P_o )</th>
<th>COP</th>
<th>( V_s, \text{m}^3/\text{h} )</th>
<th>( V_D, \text{m}^3/\text{h} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R717/R170(55/45)</td>
<td>10</td>
<td>146</td>
<td>580</td>
<td>5403</td>
<td>9.3</td>
<td>0.988</td>
<td>77</td>
<td>96</td>
</tr>
<tr>
<td>R717</td>
<td>10</td>
<td>230</td>
<td>29.2</td>
<td>1086</td>
<td>37.2</td>
<td>1.235</td>
<td>124</td>
<td>155</td>
</tr>
</tbody>
</table>

\( V_s \) is volume flow in compressor suction inlet  
\( V_D \) is compressor displacement rate

### 6. CONCLUDING REMARKS

This project has achieved the objective of developing a natural refrigerant blend based on R-717, overcoming a number of the disadvantages associated with the pure refrigerant. In particular, it overcomes those issues related to low NBP, high discharge temperature and poor miscibility with oils. This blend is considered to offer utility as a refrigerant for applications with an evaporating temperature below -33°C including industrial process, food and blast freezing applications. This blend offers advantages over the use of R-744 (carbon dioxide) as the high triple point of R-744 prevents operation below -56.4°C. By offering positive pressure at evaporating temperatures down to -89°C, it can operate effectively at temperatures previously only attainable with liquid nitrogen cryogenic freezers.

A summary of the basic characteristics of the chosen blend are listed in Table 2.

<table>
<thead>
<tr>
<th>Molar mass</th>
<th>NBP (°C)</th>
<th>Upper critical end point temperature (°C)</th>
<th>LFL (% vol)</th>
<th>Safety class</th>
<th>ODP</th>
<th>GWP(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.9</td>
<td>-89.0</td>
<td>41.9</td>
<td>4.0 – 4.2</td>
<td>A2</td>
<td>0</td>
<td>~2</td>
</tr>
</tbody>
</table>

For this chosen composition, the following generalisations can be made about its characteristics when used in low temperature refrigeration systems:

- The mixture exhibits complex phase behaviour, but it is azeotropic throughout the operating range, thus avoiding complications associated with temperature glide.
- The NBP is significantly lower than pure R-717 and most other conventional refrigerants, thus avoiding problems associated with air and moisture ingress.
- Its COP is superior to pure R-717, particularly over greater temperature lifts.
Volumetric refrigerating effect (VRE) exhibits a synergetic behaviour and gives considerably higher values of VRE than the pure components, thus requiring a compressor with smaller swept volume.

Discharge temperature is dramatically lower than R-717, which favours system reliability, and also permits the use of single-stage compression with large temperature lifts.

It has good miscibility with mineral oils, thereby negating problems associated with highly hygroscopic PAG oils and avoids the necessity to use the new high-cost hydro-treated lubricants.

NOMENCLATURE

- a: equation of state parameter (long range attraction)  
- z_i: feed composition
- V: molar volume (m^3 mole^{-1})
- a_{ii}: long range attraction between i – i components
- H: enthalpy
- S: entropy
- A: equation of state parameter
- COP: coefficient of performance
- b: equation of state parameter (excluded volume)
- Q_v: volumetric capacity
- Q_0: cooling capacity
- b_{ii}: excluded volume for component i
- P_i/P_0: pressure ratio
- a_{ij}: long range attraction between i – j components
- T_{out}: compressor outlet T
- b_{ij}: equation of state parameter b for an i – j interaction
- k_{12}: binary interaction parameter for long range attraction
- a: liquid quality factor
- l_{12}: binary interaction parameter for excluded volume
- ?: acentric factor
- B: vapour quality factor
- p: pressure
- R: universal gas constant
- l: liquid phase
- (kJ kmol^{-1} K^{-1}): (kJ kmol^{-1} K^{-1})
- v: vapour phase
- \chi_i: mole fraction of component i
- \lambda: liquid composition \lambda
- \nu: component \nu

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