THE DEVELOPMENT OF AZEOTROPIC AMMONIA REFRIGERANT BLENDS FOR INDUSTRIAL PROCESS APPLICATIONS

N. COX[a], V. MAZUR[b], D. COLBOURNE[c]

[a] Earthcare Products Limited, 405 Mill Studio, Crane Mead
Ware, Herts. SG12 9PY, UK
Facsimile: +44 845 2802334
njc@earthcareproducts.co.uk

[b] Department of Thermodynamics, Academy of Refrigeration
1/3 Dvoryanskaya Street, 65082 Odessa, Ukraine

[c] Re-phridge, PO Box 4745, Stratford-upon-Avon
Warwickshire CV37 1FE

ABSTRACT

It would be desirable to design an azeotropic ammonia mixture with higher pressure to avoid the disadvantages of pure ammonia. The objective is to determine the appropriate proportions for a mixture that would allow this blend to be employed for food blast freezing applications in the temperature range from - 55°C to + 50°C.

Ammonia has a high NBP and low specific heat. Low evaporating temperatures lead to sub-atmospheric operation allowing leakage of air into the system, and high compressor discharge temperatures. The selected blend overcomes these drawbacks by significantly reducing the NBP and allowing lower discharge temperatures. It will displace liquid nitrogen and carbon dioxide cryogenic freezers as well as carbon dioxide / ammonia cascade and two stage ammonia systems. The following findings were made relative to R717:

COP similar
Volumetric refrigerating effect (VRE) higher
Discharge temperature significantly lower, improving reliability
Improved heat transfer
Higher evaporating temperatures
Degradation of COP and refrigerating capacity with increasing temperature lift reduced

Patents have been filed and published and global licensees are now being sought.

1. INTRODUCTION

Food freezing is a huge industry with significant growth prospects, since frozen food results in much less wastage than chilled food. The UK frozen food market is worth over £7.5 billion per year, constituting the world's third biggest market for frozen food after the USA and Germany.

The effective freezing of food requires the lowest possible temperatures to allow rapid cooling and freezing, potentially improving quality, reducing weight loss, residence time and factory footprint for the process. For example, in the field of meat chilling evaporative weight loss from the meat is worth between 20 and 50 times the cost of the energy consumed. The best possible blast freezer would be of an open air cycle type, operating at, say -75°C, without the need for an internal evaporator heat exchanger. Unfortunately these designs are still at the concept stage and in the meantime the food processing industry makes extensive use of cryogenic freezers using liquid nitrogen or carbon dioxide sprayed directly onto the food. The safety requirements include the need to monitor the processing room atmosphere and a floor scavenging ventilation extraction system linked to the cryogen injection controls. Additional room air make-up systems are almost always required. Cryogenic freezing applications include high value, yield sensitive products and difficult to handle products including: steam cooked diced chicken; pizza; marinated chicken; instant quick freeze (IQF) shrimp; and cooked pasta.

However, the carbon footprint of cryogenic freezers is considerably higher than for ammonia based vapour compression freezers. It would therefore be advantageous if the refrigeration industry could satisfy the applications listed above using ammonia based natural working fluids. Unfortunately, ammonia possesses certain characteristics that are less than ideal for blast freezing applications. 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 other 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.

The adoption of carbon dioxide / ammonia cascade systems does not resolve all of the above issues. So work has been carried out to identify possible mixtures of ammonia with other refrigerants. The mixture should offer a lower NBP, lower discharge temperatures and be miscible with conventional oils. In addition, as blended zeotropic refrigerants cause differential frosting in blast freezers, an azeotropic solution is required. To estimate possible azeotropic phase behaviour in ammonia blends we considered more than sixty refrigerants, adopting a new approach employing artificial neural networks (Artemenko and Mazur, 2007) and global phase data to identify azeotropic and near azeotropic states; concluding that almost all ammonia – refrigerant blends have azeotropic states (Artemenko *et al.*, 2008). However, when we removed candidates with an ODP, GWP > 150 and NBP > -33°C, we were left with only four components to mix with ammonia (Table 1).

Clearly, any substantial reduction in NBP can only be achieved with the ammonia and ethane pair so we focused on this combination. An evaluation of the performance of the R717/R170 blend is difficult because it exhibits very complex phase behaviour, having two critical curves, two and three-phase equilibria, and azeotropic lines**.** Figure 1 illustrates the relationship between saturation pressure and composition for the R-170/R-717 mixture, showing a typical isotherm (line of constant temperature) including both azeotropic and Van Der Waals metastable states in the low-temperature region. The upper line indicates the pressure of the saturated liquid (i.e. the bubble-point) at the temperature, *T*, and the lower line indicates the pressure of the saturated vapour (i.e. the dew-point). The dashed lines correspond to the three-phase (liquid-liquid-vapour) equilibrium. The continuation

Table 1: Characteristics of suitable refrigerants

Refrigerant	**R-717**	**R-1270**	**R-290**	**R-161**	**R-170**
Chemical name	**ammonia**	propene	propane	ethyl fluoride	ethane
Chemical formula	$\mathbf{NH_3}$	$CH_3CH{=}CH_2$	$CH_3CH_2CH_3$	CH_3CH_2F	CH_3CH_3
Molar mass	**17.03**	42.08	44.1	48.06	30.1
NBP (°C)	**-33.3**	-47.7	-42.1	-37.6	-88.6
Critical temp (°C)	**132.3**	92.4	96.6	102.1	32.2
ATEL (ppm)	**25**	1000	1000	~1000	1000
LFL (% vol)	**14.8**	2.7	2.7	3.8	3.2
Safety class	**B2**	A3	A3	A2	A3
ODP	**0**	0	0	0	0
GWP (100)	**0**	3	3	12	3

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.

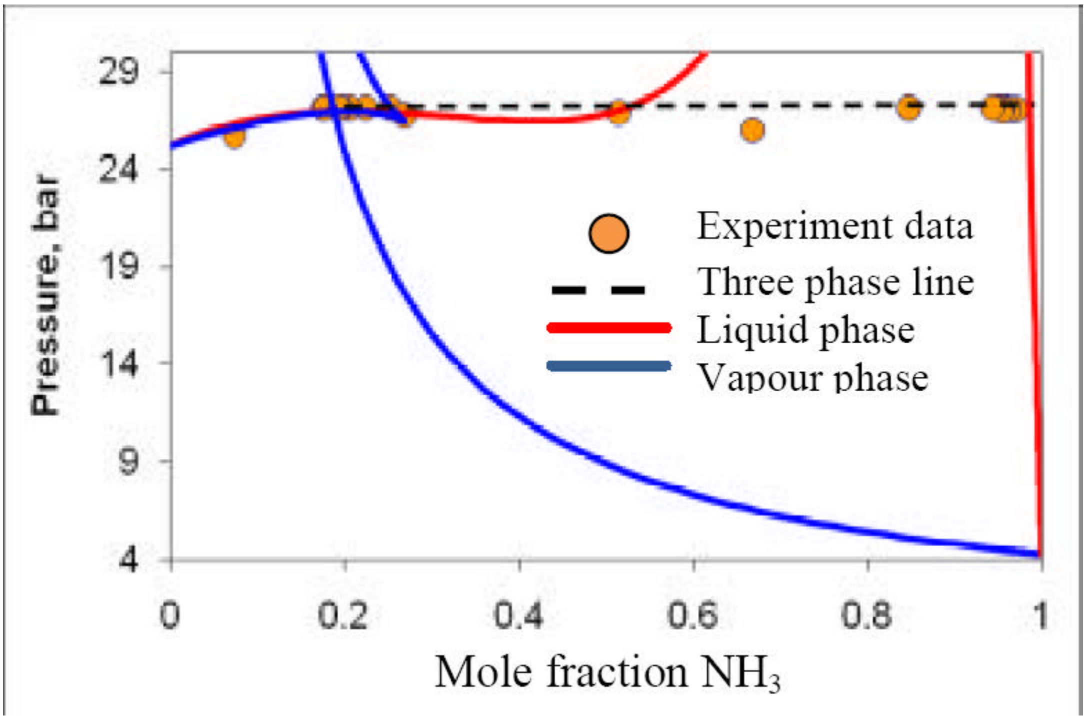

Figure 1: Pressure – composition diagram of heteroazeotropic R-170/R-717 blend at 0°C

The R-717/R-170 mixture forms positive azeotropes up to the critical region. With an 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 the components. However, for the R-717/R-170 blend the two lines converge at other compositions 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 (+44.9°C) (Brunner, 1988). 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.

2. 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. The property data has been used to analyse the performance with a cycle model, which provides quantitative indication of the performance over the range of compositions.

From Figure 2, it can be seen that a maximum of 35% ammonia can be used if we are to achieve a normal boiling point no higher than -55C, the lowest temperature that can be achieved using a CO_2 / NH_3 cascade.

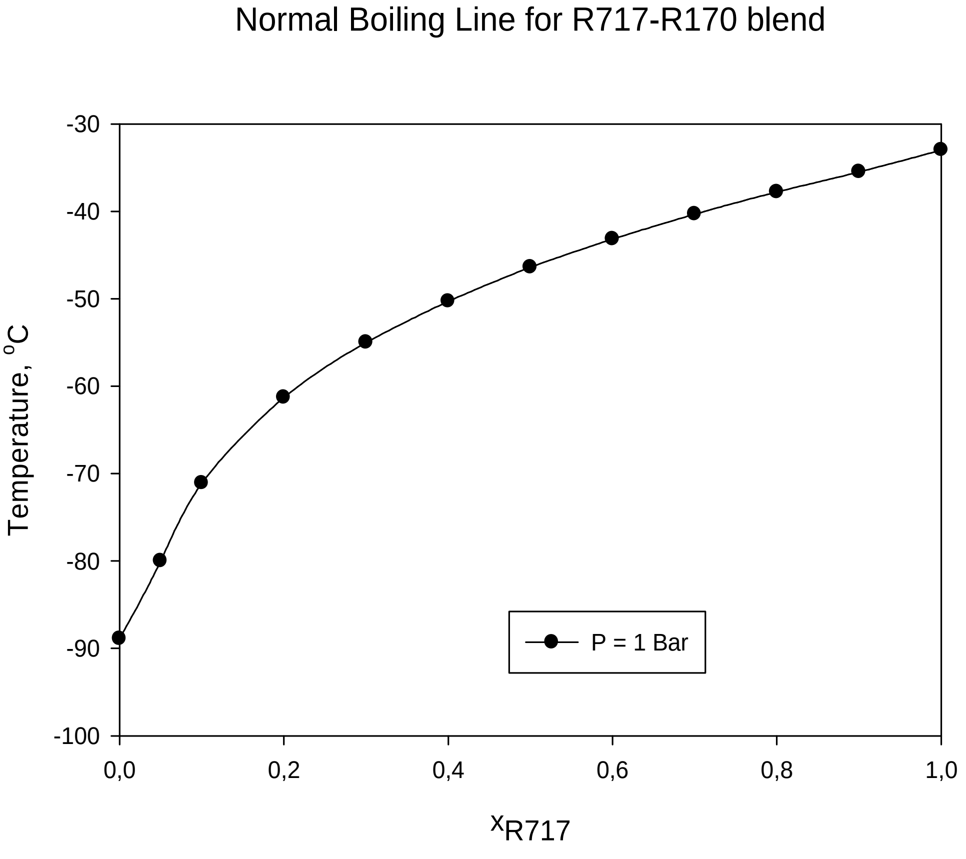

Figure 2: Normal Boiling Line for R-170/R-717 blend

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.

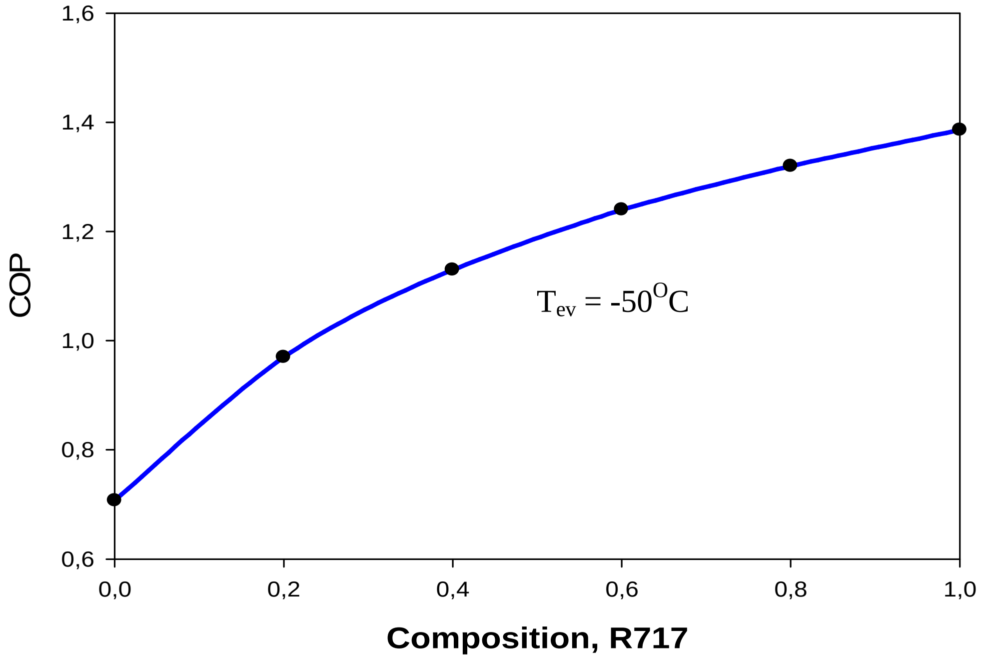

Figure 3: The relationship between R-170/R-717 composition and COP

In addition to efficiency, and the NBP of the mixture, the practical limitations of discharge pressure must also be considered.

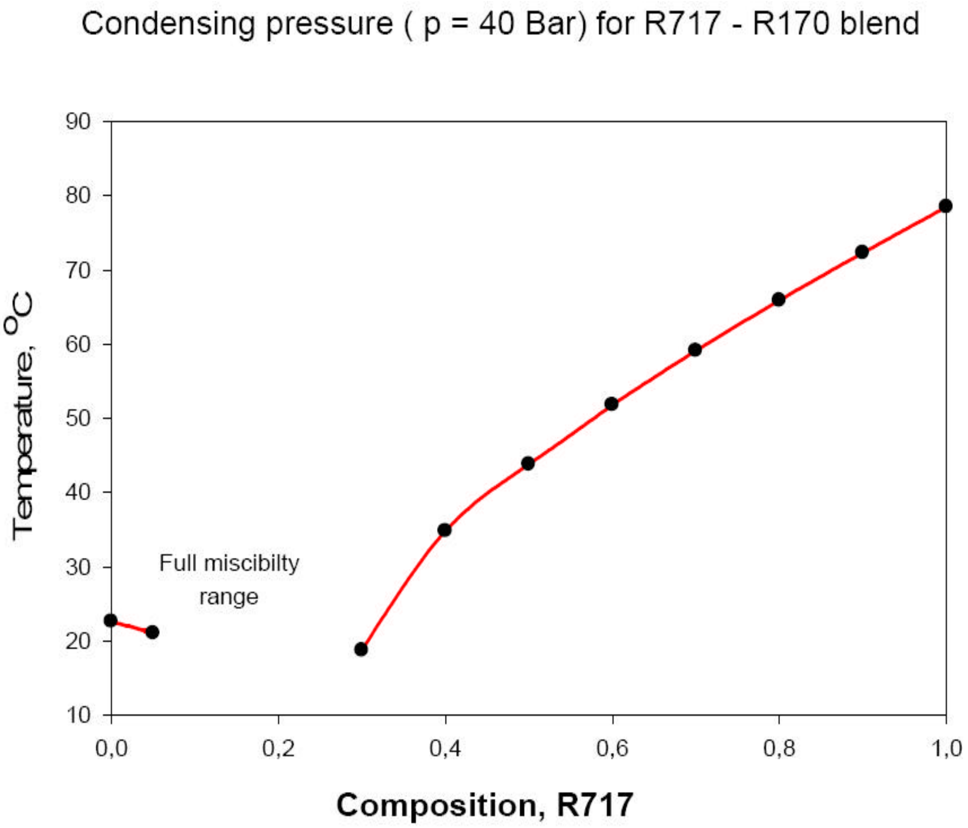

Figure 4: Relationship between R-170/R-717 composition on condensing pressure at 27^0?

From Figure 4, it can be seen that any ammonia concentration above 35% will allow us to condense below 40 bar in a 27^0? evaporative condenser.

The volumetric refrigerating effect (VRE) exhibits a synergetic behaviour and gives higher VRE values than pure components, necessitating a smaller compressor displacement than would be required for either of the single components for a given refrigerating capacity as shown in Figure 5 below.

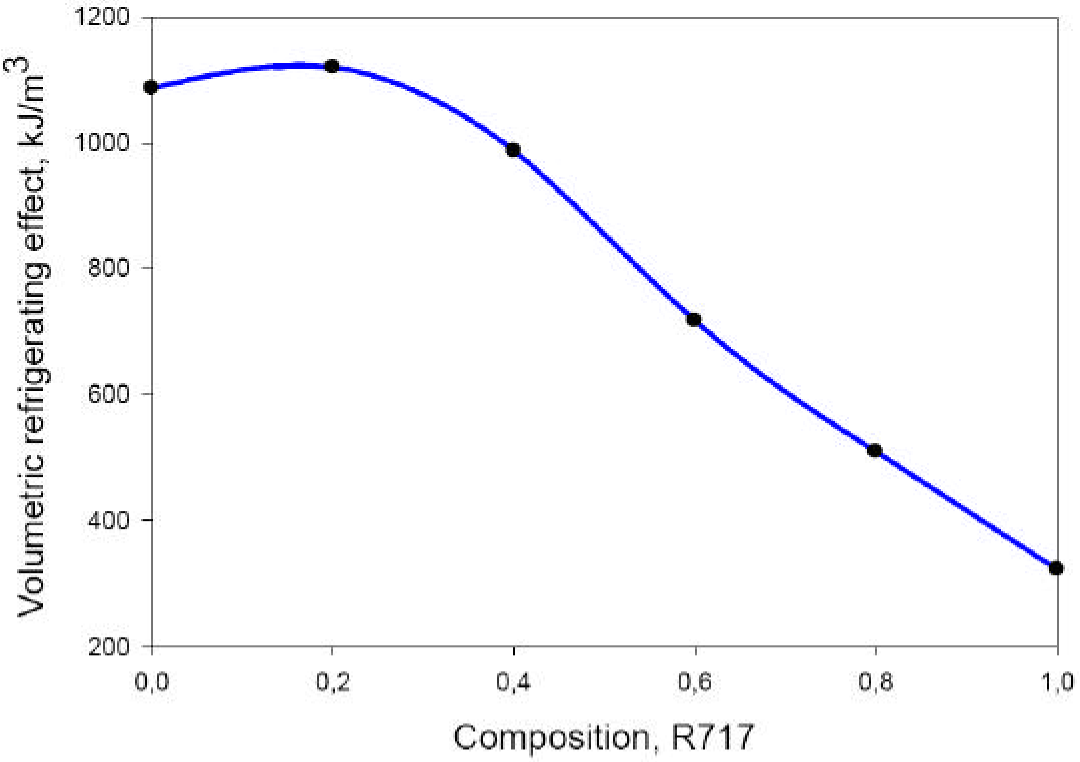

Figure 5: Relationship between R-170/R-717composition and volumetric refrigerating effect (VRE)

From a system performance perspective the composition may be within the range of 20% R-170/80% R-717, up to 80% R-170/20% R-717. It is 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 (2007), 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, a “B” classification results from any significant proportion of R-717. 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 “3” results from any significant proportion of R-170. Therefore, the mixture achieves a “B3” classification.

The chosen composition is 65% R-170/35% R-717; this achieves a sufficiently high critical temperature and low normal boiling point. This azeotropic blend is optimised for blast freezer applications.

An illustration of the cycle performance for the chosen composition is given in Table 2. 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 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. An illustration of the cycle performance for the chosen composition is shown in Table 2 below.

Table 2: An illustration of the cycle performance for the chosen composition

Refrigerants	Q_0, kW	T_{out}, ^oC	P_0,kPa	P_k, kPa	P_k/P_0	COP	V_S,m^3/h	V_D, m^3/h
R717/R170(35/65)	10	140	63	1320	20.9	0.899	72	91
R717	10	230	29.2	1086	37.2	1.235	124	155
?T_{SH} = 5 K					*?*T_{SC} = 2 K			
Isentropic efficiency 0.7					*Compressor heat loss factor 10%*			

3. CONCLUSIONS

The limited property data available for the R717/R170 mixture was used to analyze the performance with a property-based cycle model, which provides a quantitative indication of performance relative to other refrigerants. The following general findings were made: the COP is similar over the range of azeotropic compositions, albeit slightly lower than that of pure R717; the temperature of the refrigerant discharged from the compressor is significantly lower than R717, which favours system reliability; an improved heat transfer, particularly in the evaporator, was observed, resulting in higher evaporating temperatures, which equates to an incremental improvement in cycle efficiency; and the rate of degradation in system efficiency and refrigerating capacity as the heat rejection (or heat sink) temperature rises for the mixture is less than the rate of degradation of the pure components. 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.

A summary of the basic characteristics of the chosen blend are listed in Table 3.

Table 3: Characteristics of R-717/R-170 blend

Molar mass	NBP (^oC)	Upper critical end point temperature (^oC)	LFL (%vol)	Safety class	ODP	GWP(100)
25.5	- 52.5	41.9	4.0 – 4.2	B3	0	~2

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.

This refrigerant has particular utility for industrial process, food and blast freezing applications and may displace liquid nitrogen and carbon dioxide cryogenic freezers as well as carbon dioxide / ammonia cascade and two stage ammonia systems.

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NOMENCLATURE

p	pressure
R	universal gas constant (kJ $kmol^{-1}K^{-1}$)
x_i	mole fraction of component *i*
y_i	vapour composition of component *i*
COP	coefficient of performance
LFL	lower flammability limit
P_0	evaporating pressure,kPa
P_k	condensing pressure, kPa
P_k/P_0	pressure ratio
Q_v	volumetric capacity
Q_0	cooling capacity

T_{out}	compressor outlet temperature
V	molar volume (m^3mole^{-1})
V_S	volume flow in compressor suction inlet
V_D	compressor displacement rate
VRE	volumetric refrigerating effect

Subscripts

SH	superheating
SC	subcooling

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