2008

New High Pressure Low-GWP Azeotropic and Near-Azeotropic Refrigerant Blends

Nicholas Cox
Earthcare Products Ltd.

Victor Mazur
Odessa Academy of Refrigeration

Daniel Colbourne
Re-phridge

NEW HIGH PRESSURE LOW- GWP AZEOTROPIC AND NEAR-AZEOTROPIC REFRIGERANT BLENDS

N. COX (a) *, V. MAZUR (b), D. COLBOURNE(c)

(a) Earthcare Products Limited, 405 Mill Studio, Crane Mead, Ware, Herts. SG12 9PY, UK
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, UK

ABSTRACT

This paper describes the latest findings of a project to identify azeotropic and near azeotropic mixtures with a normal boiling point of between -40°C and -80°C. The aim was to match the saturated pressure-temperature characteristics and refrigerating capacity of existing refrigerants within this range (such as R410A and R744), whilst achieving higher critical temperatures and – where relevant – lower triple point temperatures. Thus, the intended outcome is an extended range of applicability and an improvement in energy efficiency. Of a large number of potential combinations, three azeotropic and near azeotropic mixtures have been selected, all formed from natural refrigerants or synthetic chemicals with a global warming potential (GWP) of less than 150. These mixtures were subject to a variety of analyses, including thermodynamic, performance and safety assessments. Patents have been filed and published and global licensees are now being sought.

1. INTRODUCTION

The amount of refrigerant in use around the world is 475 Ktonnes. Global refrigerant leakage is 132 Ktonnes per annum, i.e. a Global annual leak rate of 27.8%. There is growing pressure to limit the use of HFC refrigerants due to their global warming effect, which are more than 2000 times more powerful than that of carbon dioxide. Control of refrigerant matters because 13% of man-made global warming comes from halocarbons. The EU has agreed a directive and a regulation dealing with fluorinated gases. The directive will phase-out HFC-134a in vehicle air conditioning systems from 2011. The effectiveness of the regulation will be assessed in 2011, additional applications for F-gas restrictions will be identified, and the most likely outcome will be the rapid phase out of refrigerants with a GWP above 150 in new refrigeration, air conditioning and heat pump applications.

There are distinct advantages of fluids that possess low normal boiling point (NBP) – or high saturation pressure – such as more compact systems, possibilities for achieving higher system efficiency, and advantages associated with operating above atmospheric pressure. However, the currently available refrigerants, such as R-410A, R-32, R-744 and R-170 suffer from negative characteristics such as high GWP and/or low critical temperature. There is no single-component refrigerant with low-GWP and high critical temperature using these fluids, and most mixtures that may achieve these criteria are zeotropes with high temperature glide. It was therefore concluded that azeotropes or near-azeotropes (less than 2 K glide) with thermodynamic characteristics similar to R-410A and R-744 would be commercially attractive. A development project was subsequently undertaken with the objective of identifying such blends.

The use of an azeotropic refrigerant has specific benefits over zeotropic mixtures, particularly since the dissimilar compositions in liquid and vapour phase result in a number of effects that may ultimately contribute negatively to cycle efficiency and changes in system operating parameters:

- Fractionation, or partial separation, of components that manifest as a variation of composition of the circulating refrigerant.
- Fractionation results in disproportionate amounts of the refrigerant components being released from the system in the event of a leak.
- Temperature glide in the evaporator and condenser reduces the heat exchanger performance.
- Heat transfer of the component undergoing phase change is inhibited by the other refrigerant components thereby further reducing heat exchanger performance.
- System design and selection of components is a more complex, and consequently optimisation becomes less precise.

In addition to the above points, there are greater practical problems associated with using zeotropes, such as interpretation of system performance by service and maintenance technicians, and augmenting the uneven frosting of some evaporators.

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. A novel approach for the prediction of azeotrope formation between components in a mixture that does not require vapour-liquid equilibrium calculations has been developed (Artemenko and Mazur, 2007; Artemenko, Khmel'njuk and Mazur, 2004), and adopted for the current work. The method employs neural networks and the development of global-phase diagrams to correlate azeotropic data for binary mixtures based only on critical properties of the individual components in the mixture.

2. GENERAL METHODOLOGY

The development of the new refrigerant mixtures was carried out using a staged approach for analysing the various physical, chemical, environmental and thermodynamic characteristics of the fluids. The development process followed an iterative procedure starting from prioritisation of acceptance criteria through to identification of mixtures that achieved a compromise between the acceptance criteria and system performance.

Initially, a set of criteria believed to represent the "ideal" refrigerant was included: zero ODP, negligible GWP, favourable thermodynamic and transport properties, sound chemical and material compatibility, high critical temperature, low triple point, good solubility with oils, low cost, low temperature glide, low toxicity, and non-flammable. A number of substances of primary interest were identified: R-1270 (propene), R-161 (ethyl fluoride), R-170 (ethane), R41 (methyl fluoride), R-717 (ammonia), R-744 (carbon dioxide). The basic characteristic data for these fluids is listed in Table 1.

Table 1: Characteristics of selected refrigerants

Refrigerant	R-1270	R-161	R-170	R-41	R-717	R-744
Chemical name	propene	ethyl fluoride	ethane	methyl fluoride	ammonia	carbon dioxide
Chemical formula	CH3CH=CH2	CH3CH2F	CH3CH3	CH3F	NH3	CO2
Molar Mass	42.08	48.06	30.1	34.03	17.03	44.01
NBP (°C)	-47.7	-37.6	-88.6	-78.3	-33.3	-78.4
Critical temp (°C)	92.4	102.1	32.2	44.1	132.3	31.1
ATEL (ppm)	1000	~1000	1000	~1000	25	5000
LFL (% vol)	2.7	3.8	3.2	7.1	14.8	none
Safety class	A3	(A2)	A3	(A2)	B2	A1
ODP	0	0	0	0	0	0
GWP (100)	~3	12	~3	97	<1	1

Following the selection of these substances, the next stage involved identifying suitable mixtures and then evaluating their thermophysical, chemical and environmental aspects. The possible refrigerant pairs, where the potential azeotropic or near azeotropic behaviour appeared, are given in Table 2, and the preferred mixtures are highlighted.

Table 2: Azeotropy membership of low GWP refrigerant blends

Refrigerant	R-744	R-717	R-41	R-170	R-161	R-1270
R-1270	Zeotrope	Azeotrope	Zeotrope	Zeotrope	**Azeotrope**†	
R-161	Zeotrope	Azeotrope	Azeotrope	Zeotrope		
R-170	Azeotrope	**Azeotrope**†	Azeotrope			
R-41	**Near azeotrope**†	Zeotrope				
R-717	Reaction ††					
R-744						

† pairs selected for this work
††Ammonia and carbon dioxide react to form ammonium carbamate, a white solid material, which is detrimental to a refrigeration system

Upon determination of preferred mixtures, it is necessary to ensure that their performance within the intended refrigeration systems is achieved. This is carried out initially by system performance simulations, and latterly by experimental evaluation. In addition to checking that the minimum performance is met, simulation and experimental exercises are additionally used to precisely optimise the composition to obtain the highest efficiency across the range of likely equipment.

3. IDENTIFICATION OF BLENDS

Three mixtures have arisen from this work:

- **R-1270/R-161** hereafter referred to as ECP410A
- **R-170/R-717** hereafter referred to as ECP717
- **R-744/R-41** hereafter referred to as ECP744

Thermodynamic modelling and experimental studies forecast azeotropic behaviour for R-170/R-717 and R-1270/R-161 but near azeotropic behaviour for R-744/R-41. Two types of concurrent cubic equation of state (EOS) – the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) – were considered and EOS selection was carried out. Results of detailed phase behaviour evaluation for blends under consideration are given in Figs 1 – 3. Each of these has distinct characteristics and is therefore suited to certain types of application. They also possess significant advantages over currently used refrigerants for these applications.

3.1. ECP410A – Blend for domestic and commercial air conditioning and heat pumps

Advantageous properties. The first blend is a mixture of R-1270 and R-161, which under typical operating conditions was found to exhibit azeotropy around molar compositions of 10% to 50% of R-161 (Figure 1). Across this range, the saturated pressure-temperature characteristics and volumetric refrigerating capacity are close to that of R-410A. The critical temperature is significantly higher (almost 20 K), indicating improved performance, particularly at higher ambient temperatures. Given these aspects, the blend is considered to be broadly applicable to systems used for domestic and commercial air conditioning, and heat pumping. Furthermore, the lower operating pressures enable a larger range of standard refrigeration components and fittings to be used, compared to R-410A. This is particularly advantageous for heat pump systems or equipment operating in higher ambient temperatures.

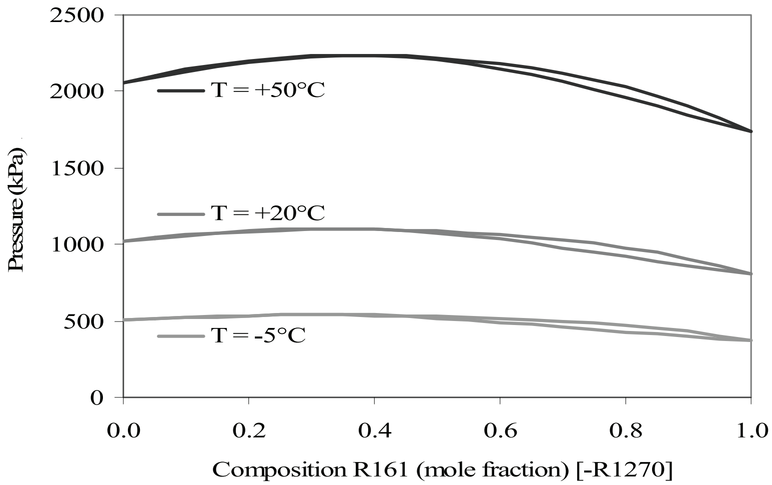

Figure 1: Evolution of isotherms for R-161/R-1270 mixture (T = -5°C, T = +20°C, T = +50°C)

Performance evaluation. This was carried out in order to determine the preferred composition from an operational perspective, and to compare its efficiency and capacity against R-410A. The preferred mixture will have as high a refrigerating capacity as possible, and as close to an azeotropic composition as possible. An initial theoretical analysis showed this to correspond to a range of the 20% R-161/80% R-1270 and 50%R-161/50%R-1270, although a negligible temperature glide was observed consistently over this range of compositions. System performance evaluations with a detailed system simulation model suggested that the performance of the mixture was similar throughout this range of compositions. The simulations suggested that both the cooling and heating capacity would be around 15% lower than R-410A, whilst cooling and heating COP would be around 5 – 10% higher than R-410A. An initial set of measurements of two different systems conducted around European rating conditions revealed the following, when compared to R-410A:

- Evaporating capacity was a little greater than the theoretical results, being about 85% of R-410A, and condensing capacity being a little less.
- Cooling COP was between 6 – 10% higher than R-410A, whilst heating COP was at least 15% higher.
- Evaporating temperature was up to 4 K higher than R-410A, condensing temperature is about 1 K lower for the mixture and discharge temperature around 2 – 4 K lower than R-410A.

There is a marginal benefit for capacity at the 50%/50% mixture. Alternatively, the azeotropic concentration is around 30% R-161, suggesting that this may be the preferred composition.

Safety evaluation. According to the criteria within ISO 817 the toxicity class of both fluids, is “A”, thus any composition of R-1270 and R-161 is also likely to achieve an “A” classification. In terms of flammability, R-1270 has “3” classification, whereas the lower flammability limit (LFL) data for R-161 places it in classification “2”. Therefore, in order for the mixture to achieve the more desirable “A2” classification, the molar composition of R-1270 should be less than 18% – 46%, depending upon the LFL.

Chosen composition. It was concluded that more favourable thermodynamic properties take precedence over safety classification, and therefore a mixture with a higher proportion of R-1270 should be chosen. Thus the commercial product contains 75% R-1270, 25% R-161; this maximizes the benefits of the natural component (R-1270) whilst accepting an “A3” safety classification.

3.2. ECP717 – Blend for industrial process, food and blast freezing applications

Advantageous properties. The second blend is a mixture of R-170 and R-717, which under typical operating conditions was found to exhibit azeotropy around molar compositions of 40% to 70% R-170 (Figure 2). This mixture possesses some advantages over the refrigerants normally used in industrial type applications. In the case of pure ammonia, which has a relatively high NBP and low specific heat, low evaporating temperatures lead to subatmospheric operation which allows for the leakage of air into the system, and high compressor discharge temperatures. A mixture of R-170 and R-717 overcomes these drawbacks by significantly reducing the NBP and also allowing much lower discharge temperatures. Consequently single-stage compression may be used instead of two-stage, which requires an additional compressor. In comparison to the use of R-744, the problem of high triple point is also overcome. Lastly, there are ongoing problems with refrigeration oils given the poor miscibility with R-717, which the introduction of R-170 overcomes. Given these aspects, the blend is considered to be broadly applicable in systems used for industrial process, food and blast freezing applications.

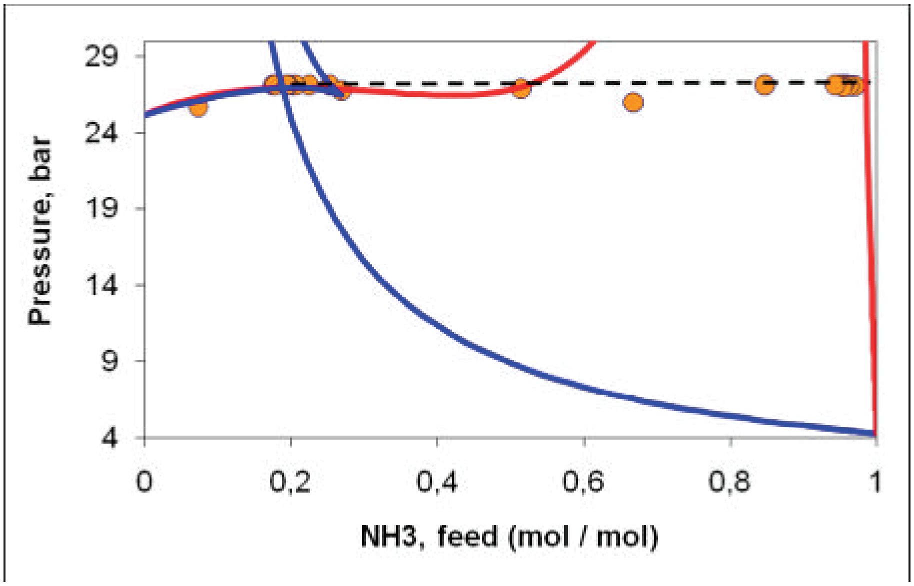

Figure 2: Pressure –composition diagram of heteroazeotropic R-170/R-717 blend at 0°C

Fig. 2 illustrates the relationship between saturation pressure and composition for the R-170/R-717 mixture. The set of curves characterizes the isotherm (line of constant temperature) as indicated for T = 0°C. The temperature range -55°C to + 50°C represents the approximate limits of the anticipated operating conditions for blast freezing 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 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.

The bubble and dew-point lines for most blends 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 this blend the azeotropic region is where the two lines converge at compositions other than 100% and 0%. 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 +44.9ºC). 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 is terminated at intermediate compositions; these points represent the critical state, thus indicating the maxima for operation of a particular mixture.

Performance evaluation. 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 relative to other refrigerants. The following general findings were made:

- COP is similar over the range of azeotropic compositions, although this is lower than that of pure R-717 at smaller temperature lifts, but is comparatively better at greater temperature lifts.
- Volumetric refrigerating effect (VRE) exhibits a synergetic behaviour and gives considerably higher values of VRE than the pure components.
- Discharge temperature is significantly lower than R-717, which favours system reliability.
- Improved heat transfer, particularly in the evaporator, resulting in higher evaporating temperatures.
- The degradation in COP and refrigerating capacity with increasing temperature lifts in a single stage cycle is reduced relative to pure ammonia.

Safety evaluation. 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% and 73% of R-170.

Chosen composition. It was concluded that both the most desirable performance and safety classification coincide with similar compositions. Thus, commercial product contains 45% R-170 and 55% R-717; this achieves a sufficiently high critical temperature and should attain an "A2" safety classification. The azeotropic blend is optimised for below -33℃ applications. It has particular utility for industrial process, food and blast freezing applications and will displace liquid nitrogen as well as two stage ammonia systems.

3.3. ECP744 – Blend for commercial point-of-sale refrigeration and vehicle air conditioning equipment

Advantageous properties. The third blend is a mixture of R-744 and R-41, which under typical operating conditions was found to exhibit near-azeotropy over the entire range of compositions (Fig 3). The addition of R-41 to R-744 has additional advantages in terms of property changes, specifically, raising the critical temperature and lowering the triple point. For pure R-744 these introduce hindrances in its application which result in super-critical operation at high ambient temperatures and solid formations when it undergoes rapid reduction of pressure towards atmospheric. Whereas R-744 is being introduced into commercial refrigeration and point-of-sale applications, the characteristics of this mixture could help overcome several of the existing problems.

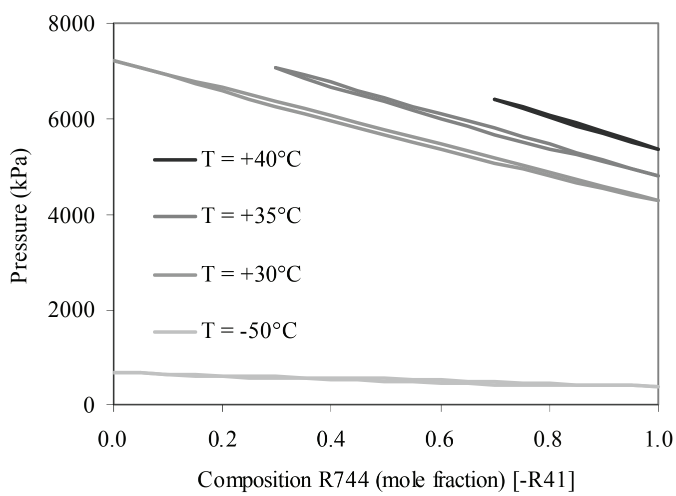

Figure 3: Evolution of isotherms for R-744/R-41 mixture (temperature range T = -50°C to +40°C)

Performance evaluation. The choice of composition was also considered with respect to system performance, and for this a detailed system simulation model was employed. In terms of evaluating different compositions, it was found that, the refrigerating capacity and pressure was significantly greater than that of R-410A, and less that pure R744, as would be expected. Both evaporating and condensing capacity increase notably as R-744 composition increases, as well as a notable reduction in both heating and cooling COPs. However, evaporating and condensing temperatures show little variation across the range of compositions, whereas discharge temperature rises slightly with higher proportions of R-744. The maximum temperature glide occurs around 40% R-744 although it is relatively small (around 1.5 K) over the expected operating pressure range.

Other factors that affect the choice of composition should be based according to availability of components that can handle the relatively high pressure of this mixture. Further considerations include maintaining as high a critical temperature as possible and minimising temperature glide. System performance evaluations were also carried out for a 50% R-744/50% R-41 mixture, in comparison with a simulated transcritical R744 cycle (assuming a gas cooler pressure of 100 bar and an outlet temperature of 45°C). Under these conditions, the cooling COP was found to be about 6% higher than pure R-744. This was attributed to the higher critical temperature of the mixture, which reduces linearly as the molar composition of R744 is increased. These characteristics suggest that the chosen composition favours a higher proportion of R-41, from the point of view of performance. An additional consideration is the potential reduction in pressure rating of the system. For the compositions evaluated, there is a trade-off between refrigerating capacity and efficiency, since there is an almost linear reduction in COP and increase in capacity with a higher composition of R-744.

Safety evaluation. According to ISO 817 the toxicity class of both fluids is “A”, thus any composition of R-744 and R-41 is also likely to achieve an “A” classification. In terms of flammability, R-744 is non-flammable, thus it has “1” classification, whereas the mild flammability of R-41 places it in classification “2”. Thus, increasing the composition of R-744 gradually reduces the flammability of the mixture until a flame cannot be sustained. Thus, by increasing the proportion of R-744 to ensure flammability classification of “1” requires a molar composition of around 50% to 70% R-744. Therefore, in order for the mixture to achieve the more desirable “A1” classification, the molar composition of R-744 should be at least 50%.

Chosen composition. It was concluded that both the most desirable performance and safety classification coincide with similar compositions. Thus, the commercial product contains 50% R-744 and 50% R-41; this maximises the critical temperature whilst attaining an “A1” safety classification.

The higher critical temperature, lower triple point and more efficient refrigeration cycle are all significant benefits, but the commercial benefit arises from a reduced high-side pressure (compared to R-744), allowing a larger number of standard refrigeration components to be used, and the use of silver soldered joints. Since a major problem for R-744 refrigeration systems is the high-side pressure, realistically all joints should be TIG welded stainless steel, but most refrigeration technicians rarely have the necessary skills and specialist welding services are not commercially viable. Consequently, most R-744 installations (in the UK) have used compression fittings or silver soldered joints, which, as a result leak at more than 25% per annum. Thus, the lower operating pressure of ECP744 would help to overcome this hindrance.

4. CONCLUSIONS

Using a combination of novel property modelling, safety analyses and comprehensive system simulation, a number of previously unidentified azeotropic and near-azeotropic blends have been identified for use in certain applications where existing refrigerant options are subject to a variety of hindrances. A summary of the characteristics of these new blends is provided in Table 3.

Table 3: Characteristics of new blends

Name	**ECP410A**	**ECP717**	**ECP744**
Composition (molar)	75% R1270, 25% R161	45% R170, 55% R717	50% R744, 50% R41
Molar Mass	43.6	22.9	39.0
NBP (°C)	-49.2	-89.0	-84.5
Critical temp (°C)	94.9	41.9	37.9
Freezing temp (°C)	-160	-97	-121
ATEL (ppm)	No data	550 – 570	No data
LFL (% vol)	2.7 – 2.9	4.0 – 4.2	No data
Likely safety class	A3	A2	A1
ODP	0	0	0
GWP (100)	~7	~2	~46

These new blends offer notable advantages over existing refrigerants, in particular:

- Zero ODP and low GWP, below 150, and mainly “naturally” occurring
- Improved thermodynamic properties (such as critical temperature and minimal temperature glide) over similar existing refrigerants
- Good solubility with oils
- Low toxicity, and reduced flammability
- Known and understood chemical and material compatibility

REFERENCES

1. Cox, N, Working Towards More Environmentally Friendly Refrigerant Blends, 12th European Conference, United Nations UNEP, Centro Studi Galileo, Associazione Tecnici del Freddo, Milan (2007)Cox, N, Mazur, V,
2. Is CO2 The Natural Alternative To R410A Or Are There Other Options? 7th IIR Gustav Lorentzen Conference on Natural Working Fluids, Trondheim (2006)
3. Report Of The Refrigeration, Air Conditioning And Heat Pumps Technical Options Committee UNEP (2006)
4. Artemenko S., Mazur V., Azeotropy in the natural and synthetic refrigerant mixtures, Int. J. Refrigeration (2007), v.30, pp. 831 – 839 doi:10.1016/j.ijrefrig.2006.11.010
5. Artemenko S., Khmel’njuk M., Mazur V. Azeotropy in the natural and synthetic refrigerant mixtures. 6th IIR Gustav Lorentzen Conference on Natural Working Fluids, Glasgow (2004)
6. Air-Conditioning and Refrigeration Technology Institute (ARTI), Refrigerant Database, Calm, JM, July 2001, Arlington, USA.
7. Lemmon, EW, Huber, ML, McLinden, MO. NIST Reference Fluid Thermodynamic and Transport Properties – REFPROP. Version 8.0. National Institute of Standards and Technology, Boulder, USA. 2007.
8. UNEP. 2006 Report of the Refrigeration, Air Conditioning and Heat Pumps Committee. United Nations Environment Programme, Ozone Secretariat, Nairobi, Kenya, 2007.
9. ISO 817: 2007, Refrigerants – Designation and Safety Classification. BSI, London. 2007.
10. Climate Change 2007:The Fourth Assessment Report of the IPCC

ACKNOWLEDGEMENT

The authors would like to acknowledge the Odessa State Academy of Refrigeration in the Ukraine, Earthcare Products Ltd and the E-Synergy Sustainable Technology Fund for the resources to complete this work.