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# Transcritical R744 (CO<sub>2</sub>) heat pumps Technician's Manual

CENTRE TECHNIQUE DES INDUSTRIES AÉRAULIQUES ET THERMIQUES

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# **<u>1. NATURAL REFRIGERANTS</u>**

### 1.1.Refrigeration and heat pumping

Refrigeration and heat pumping effects can be produced via various processes. In this document, we will focus on the use of the vapor compression cycle, which has been the workhorse of the refrigeration industry for well over a century. Figure 1 shows the components of such a cycle in an air-to-air application.



Figure 1 : Components of a refrigeration/heat pumping cycle

This thermodynamic cycle consists in the compression of a vapor (the refrigerant, also called "working fluid"), followed by its liquefaction at a high pressure, during which the working fluid rejects heat to a medium, often air or water. This produces a *heating effect*, which is exploited in *heat pumps*.

Following liquefaction, the pressure is lowered through an expansion device. The resulting vapor-liquid mixture is then evaporated at low pressure while taking up heat from a medium and hence producing a *cooling effect*, which is used for *refrigeration*. The vapor is then compressed to complete the cycle.

In the so-called "traditional" cycle which may use HFCs of HCFCs, the liquefaction process occurs below the critical temperature<sup>1</sup> of the refrigerant – hence the name of "*sub-critical*" cycle. This requires that the refrigerant critical temperature be above the temperature of the medium where heat is rejected. Condensing refrigerant vapor then yields a *condensing* 

<sup>&</sup>lt;sup>1</sup> The temperature above which liquid cannot exist



*pressure* that is *below* the refrigerant critical pressure. In this cycle, condensing pressure and temperature are linked by a unique relationship that depends on the nature of the refrigerant. In a "*transcritical*" cycle, the liquefaction process (or gas cooling) occurs *above* the critical pressure, while evaporation occurs at a pressure *below* the critical pressure. With a few exceptions, all cycles use working fluids below their critical pressure.

# 1.2.A brief history of refrigerants

Briefly stated, the history of refrigerants can be divided into three periods :

- A first era which started roughly around 1830 and lasted up to about 1930, where any available substance that produced refrigeration was used. This era was qualified as the "whatever worked" period, since the main selection criterion for a refrigerant was its ability to be used in practical systems, regardless of its toxicity, flammability and compatibility with the environment.

Although most of them were toxic and/or flammable, solvents and volatile fluids were then used. With the development of comfort air conditioning and refrigeration to a very large scale and to the public at large, new and safer refrigerants became necessary.

- A second era, dating from 1931 to about 1994, marked by the development and promotion of the CFCs (Chloro-Fluro-Carbon refrugerants) and HCFCs (Hydoro-Chloro-Fluoro-Carbon refrigerant) as aerosol propellants, blowing agents and refrigerants. These refrigerants where named the "miracle substances" because they met all the criteria required to be used at the time: stability, safety, efficiency, etc. However, these substances (mostly chlorinated compounds) proved to be too stable and their long-term effects were totally ignored until their accumulation in the stratosphere resulted in the partial destruction of the ozone layer.



The ozone hole in the Southern Hemisphere (Nasa, 2006)

In order to restore the ozone layer, a scheduled worldwide phase-out of the CFCs and HCFCs was agreed upon by the Montreal Protocol and its subsequent amendments. As an example, HCFC refrigerant R 22 can no longer be used in new equipment in Europe since 2004.













- A third era, dating from 1994<sup>2</sup>, during which HFCs (Hydro-Fluoro-Carbon refrigerants) have been massively introduced in the AC&R industry. Because of their nil contribution to ozone depletion, these substances were promoted as the new "miracle" solution to the global environmental problems.



Kyoto 1999 : HFCs are put in a "basket" of GHG substances

However, the HFCs have been listed amongst the substances contributing to global warming (Greenhouse Gases – GHG) in the Kyoto Protocol in 1999, and the widespread use of these refrigerants is not expected to last.

This brief look at history shows that as refrigerants evolved, no global approach has been adopted to simultaneously address the various issues, mainly due to the lack of knowledge (the effect of chlorine in the ozone layer was only discovered in 1975), but also because scientific evidence of the effects of refrigerants was not acknowledged.

So far, mainly synthetic, man-made substances, have been used as refrigerants, and their environmental effects could only be identified on the long term.

Table 1 summarizes the properties and environmental impacts of some refrigerants. This Table shows that no progress has been made in terms of global warming potential when switching from HCFCs to the HFC family. With climate change becoming a major concern worldwide, the use of HFCs will be regulated.

It is noteworthy that for automotive air conditioning applications, the EC has already scheduled a progressive phase-out of R134a as of year 2011, while limiting the GWP value of refrigerants to be used in new car models to a value of 150. In September 2007, the German automakers association (VDK) selected carbon dioxide as its preferred R134a alternative for automobile air conditioning.

### 1.3. Natural refrigerants applications

Some European countries, such as Denmark, have already locally enforced rules to limit the use of HFCs. This trend is spreading to other European countries. With increasing environmental awareness, it is therefore expected that many refrigeration applications presently using HFCs will require other refrigerants.



<sup>&</sup>lt;sup>2</sup> This date marks the introduction of refrigerant R134a in automobile air conditioning







Fluid	Boiling point (°C)	Critical temperature (°C)	Critical pressure (bar)	ODP <sup>1</sup>	GWP (100 yrs)	Oil	Flam.
R12	-29	100.9	40.6	0.9	8100	mineral	no
R22	-40.8	96.2	49.8	0.055	1500	mineral	no
			Pure HFC	's		·	
R23	-82.1	25.6	48.2	0	12000	ester	no
R32	-51.6	78.4	58.3	0	650	ester	yes
R125	-48.5	68.0	36.3	0	2500	ester	no
R143a	-47.6	73.1	37.6	0	4300	ester	yes
R134a	-26.5	101.1	40.7	0	1200	ester	no
R152a	-25.0	113.5	45.2	0	140	ester	yes
		]	HFC mixtu	res			
R407C <sup>3</sup>	-44.0	86.8	46.0	0	1600	ester	no
R410A <sup>2</sup>	-50.5	72.5	49.6	0	1900	ester	no
R404A <sup>2</sup>	-46.4	72.1	37.4	0	3300	ester	no
			·				
		Nat	ural refrige	erants			
R290	-42.1	96.8	42.5	0	< 20	mineral	yes
(propane)							
R600a	-11.7	135.0	36.5	0	< 20	mineral	yes
(isobutane)	FCC @	21.0	72.0	0	1	DAC	
$(\mathbf{R744})$	-36.6 @ 5 2 hars	31.0	/3.8	0	1	PAG	no
R717	-33.3	132.2	113.5	0	0	mineral	Ves
(ammonia)	20.0	102.2	110.0			minorul	J 60

<b>TADIE I</b> . EITVITOINTEILLAI INIDACIS AND DIODELLIES OF SOME TEILISETAIL	Table 1	l :	Environm	ental impa	cts and pro	operties of	f some	refrigerants
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1: reference R11 2: azeotrope or quasi-azeotrope 3: average of dew and bubble point temperatures

However, as of year 2007, there is virtually no ideal alternative to the current HFC refrigerants and, provided all the technological challenges are dealt with (in terms of safety, equipment mechanical resistance to working pressures, flammability, etc), natural refrigerants seem to be the most viable options, particularly in heat pumping equipment. The applications of some natural fluids are discussed below, while a specific section will be devoted to carbon dioxide.





### 1.3.1. Isobutane (R600a)

Isobutane is a hydrocarbon, and hence is flammable. With thermodynamic properties that are very similar to those of R134a, isobutane was used in Germany as early as 1992 to replace R12. It is nowadays used in the great majority of domestic refrigerators. These appliances require small refrigerant charges (typically 70 to 150 g) and are hermetic. Hence, no accident has been reported so far in these household applications. Isobutane presents other advantages, such as its compatibility with mineral oil and better energy efficiency than that of R134a. As a by-product of the oil industry, isobutane is cheaper than R134a. The use of isobutane requires minimal design changes, such as the relocation of potential ignition sources outside of the refrigerated compartment. Isobutane is used worldwide, except in the USA, where legal liability fears over the long-term inhibit manufacturers to market hydrocarbon systems.

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### **1.3.2.** Propane (R290)

With a boiling point of -42°C, propane is an excellent alternative to R22 as it requires similar working pressures. An added advantage is that except for added safety measures because if its flammability, virtually no design change is required in systems when switching from R22 to propane. The combination of its good thermodynamic and thermophysical properties yields systems that are at least as energy efficient as those working with R22. The use of propane is increasing in countries where regulations allow it.

When used on the high temperature side of a cascade refrigeration system, propane provides cooling to condense a lower temperature fluid. Hence, propane can be combined with carbon dioxide in cascade systems that are used in large food processing or refrigeration plants with both high energy efficiency and minimum environmental impact. Propane can also be used for heat pump applications, particularly in systems using secondary fluids (water or glycols) to absorb and reject heat. In this case, a compact sealed unit can be designed, thus reducing both flammability risks and refrigerant charge.

### **1.3.3.** Ammonia (R717)

Ammonia has been continuously used throughout modern refrigeration history, i.e. more than 130 years, despite its numerous drawbacks. It is toxic and flammable in concentrations between 15.5 and 28% in air. It is not compatible with copper, thus requiring other materials of construction.

With its small molecular weight and high latent heat, ammonia systems require much smaller refrigerant flow rates than those using HFCs. Its thermodynamic and thermophysical properties also yield very efficient refrigeration systems. Because of its acute toxicity,





stringent regulations apply for ammonia systems, which require close monitoring and highly skilled engineers and technicians. Ammonia is often used in large stores and in process refrigeration. With the development of small-charge equipment, ammonia may be used in smaller capacity units.

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# 2. CARBON DIOXIDE

Carbon dioxide ( $CO_2$ ) is not a new refrigerant. Rather, it was "rediscovered" in the early 90's at the Norwegian University of Science and Technology (NTNU). The use of carbon dioxide as a refrigerant lasted for well over a century. Its application has been progressively discontinued, until it was abandoned in the mid-50s, with the widespread use of the CFC refrigerants, which were more efficient, more stable and safer. This section will summarize its physical properties and examine its particularities when applied as a refrigerant.  $CO_2$  refrigerant will be referred to as "R744" in the following.

### 2.1.Properties

R744 is a versatile material, being used in many processes and applications - each of which takes advantage of one or more these characteristics: reactivity, inertness and coldness (mostly when used in direct-contact refrigeration). Common uses include consumption as a raw material for production of various chemicals; a working material in fire extinguishing systems; carbonation of soft drinks; freezing of food products, chilling of meats prior to grinding; refrigeration and maintenance of ideal atmospheric conditions during transportation of food products to market, etc.

R744 is present in the atmosphere at concentration<sup>3</sup> levels of about 380 ppm. Exhaled air contains about 4% carbon dioxide. At normal conditions, it is gaseous. R744 is odorless at low concentrations and slightly toxic with a slightly pungent, acid taste.

It is widely available as it occurs naturally and it is a by-product of fossil fuel combustion and other industrial processes. It combines with water in air to form carbonic acid which corrodes metals, limestone and marble.

R744 will not burn or support combustion. Air with a carbon dioxide content of more than 10% will extinguish an open flame. Breathing air that contains more than 10% R744 can be *life-threatening*. *This corresponds to spreading uniformly about 24 kg of R744 in a workshop that is 4 m wide, 10 m long and 3 m in height.* 

<sup>&</sup>lt;sup>3</sup> one ppm is equivalent to one cubic centimeter per cubic meter



Gaseous R744 is 1.5 times heavier as air. Therefore, when released to the air it will concentrate at low elevations.

R744 will form "dry ice" at -78.4°C. One kg of dry ice has the cooling capacity of 2 kg of ordinary ice. Gaseous or liquid carbon dioxide, stored under pressure, will form dry ice through an auto-refrigeration process if rapidly depressurized.

Figures 2 and 3 show the thermodynamic properties of R744. Compared to other fluids traditionally used as refrigerants, its critical point at 31°C is very low and its critical pressure at about 74 bars is high. These differences have, as shall be discussed, important consequences on heat pumping cycles using R744.



Figure 2 : Pressure-Temperature phase diagram of R744 (Danfoss)





Figure 3 : Comparison of evaporating pressures

Note that below a pressure of 5.2 bar, solid and gaseous R744 phases may co-exist at low temperature. This behavior is totally different from that observed with traditional refrigerants, and will have important consequences on the operation, servicing and maintenance of a system working with R744. Figure 3 compares the evaporating operating pressures of R744 to those encountered with R410A and R404A. It can be observed that R744 systems will require to operate a much higher pressures than conventional systems.





Figure 4 : R744 Mollier Diagram







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### 2.2.1. Characteristics of subcritical cycles

One of the most important criteria for a refrigerant is its critical point – i.e. the point at which vapor can no longer be distinguished from liquid. This point is indicated by values of temperature and pressure which are the critical parameters and which are characteristics of the refrigerant.

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Figure 5 : A subcritical cycle using R22

Traditional refrigerants have been chosen or designed so that they can be condensed with an available cooling medium, often water or air. This requires that their critical temperature be well above the temperature of the cooling medium, i.e. typically in the range 80-110°C.

Refrigerant R22, for example, will yield a thermodynamic cycle that could be illustrated by Figure 5.

The R22 critical temperature is 96.2°C. This means that with water or air available at 40°C, R22 may condense at, say 55°C. Because there exists a unique relationship between pressure

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and saturation temperature for a condensing pure substance, its pressure will be 21.8 bars (abs).

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Note that, for a given installation, this condensing pressure will in practice depend mainly upon the following parameters :

- The water (or air) flow rate and available temperature;
- The charge of refrigerant into the system and the condenser size.

In this installation, the refrigerant flow rate is controlled by the expansion device (e.g. capillary tube, thermostatic expansion valve, electronic expansion valve). This device controls the amount of superheat at the suction of the compressor and ensures that no liquid droplets are carried out from the evaporator.

Put shortly, heat pumps using "traditional" fluids such as HFCs and HCFCs operate with :

- condensing pressures that depend only on cooling medium conditions and on the refrigerant charge. The condensing pressure is much lower than the refrigerant critical pressure. So far, R410A is the refrigerant that required the highest operating pressure its upper limit being roughly 40 bars.
- Refrigerant flow rates that are controlled via an expansion device in order to avoid carryover of liquid droplets to the compressor suction. The expansion device set point is a value of superheat at compressor suction.

### 2.2.2. Heat pumping with R744 : the transcritical cycle

As mentioned previously, the critical temperature of R744 is around 31°C. If ambient air is used to cool on the high pressure side and is available at 35°C for example, it will not be possible to condense the refrigerant. Rather, the refrigerant discharged from the compressor will be cooled as a "supercritical" fluid because this process occurs at a pressure higher than the critical pressure (74 bars). Such a cycle is illustrated in a Mollier Diagram in Figure 6. In this illustrative cycle, R744 evaporates at 30 bars and is then compressed to 120 bars. Upon compression, it reaches a temperature of 120°C. It is then cooled in a "gas cooler", expanded and is evaporated to complete the cycle.

The main features of the transcritical cycle are then as follows:

• The cycle operates at much high pressures than the traditional cycle – typically between 30 bars (evaporator side) and 130 bars (gas cooler side);

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- The high pressure is no longer fixed by the cooling fluid temperature or flow rate; therefore, there is a need to control this parameter;
- The high pressure refrigerant is not "condensed" it is cooled as a supercritical fluid;
- In most cases, the refrigerant flow rate is not fixed based on the value of superheat at compressor suction.
- The more refrigerant charge there is in the high pressure side, the higher the pressure will be.



Figure 6 : A transcritical cycle using R744

### 2.3. Optimum pressure with the transcritical cycle

It was seen that for the subcritical cycle, the condenser pressure was fixed by the condensing temperature, which in turn is a function of the condenser size and the cooling fluid flow rate and temperature.

For the transcritical cycle, the gas cooler pressure is not a function of the R744 temperature, because there is no unique relationship between temperature and pressure above the critical point. This means that the system can operate at different values of high pressure, which can be set by the control scheme.



In such a system, the pressure is therefore fixed by a control device so that the cycle operates under optimum conditions, yielding the best energy efficiency.

Energy efficiency is defined as the amount of useful energy divided by the amount of input energy. Hence, in heating mode, the energy efficiency, or Coefficient of Performance is defined as :

 $COP = \frac{HeatingDuty(kW)}{Electric Power(kW)}$ 





Figure 7a : Duty vs. Electric power

Figure 7b : Performance vs. Discharge pressure

Figure 7a shows a cycle operated at a given value of high pressure. At this value, the system requires a heat input q at the evaporator and a work input w to the compressor. The delivered heat duty at the gas cooler is therefore q+w.

Under these conditions, the R744 refrigerant at exit of the gas cooler reaches a temperature T. If the cycle is operated at a different values of high pressures and a constant value of temperature T, both q and w will vary, and so will the value of COP.

Figure 7b shows the variation of COP when the high pressure is allowed to vary. It can observed that there exists a value of pressure (called "optimal pressure") for which the COP is highest.

Thus, the most efficient heat pumps will use control schemes that enable high pressure control during operation. However, some systems also use simpler methods such as expansion through a capillary tube, or some simple control scheme that enables operation at fixed high pressure. As a rule of thumb, the optimal pressure is approximately given by the following equation :

$$P_{opt} = 2.6T_{exit} + 8$$



where  $P_{opt}$  is expressed in bars and  $T_{exit}$  is the R744 temperature in °C at exit of the gas cooler. Thus, a gas cooler exit temperature of 45°C requires a high pressure of about 125 bars. This equation is valid for temperatures between about 38 and 53°C.

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### 2.4. Transcritical cycle vs. Traditional cycle

Table 2 summarizes the main design differences between the subcritical (traditional) cycle and the R744 transcritical cycle.

As mentioned in the previous sections, the main differences lie in the pressure levels (both during operation and at standstill) and the methods implemented to ensure the control of high pressure and refrigerant flow rate.

Cycle parameters	Subcritical	Transcritical CO2
High pressure cooling – heat rejection device	Condenser – Vapor condenses at constant temperature	Gas cooler – CO2 undergoes large temperature change
Discharge pressure	HFCs : from 10 to 40 bars	from 90 to 130 bars
Suction pressure	HFCs : from 2 to 9 bars	from 25 to 50 bars
Refrigerant discharge temperature	Usually less than 95°C	Up to 140℃
Expansion device controls	By superheat set point or fixed flow expansion device	Usually used to control high pressure of CO2
High pressure controls (excluding safety shut-down controls)	Not controlled - Pressure is set by condensation temperature – usually 40 bars max	Required - Up to 130 bars
Refrigerant state @ standstill	Partly liquid and partly vapor	Gas (supercritical) above 31℃ ambient; vapor –liquid mixture below 31℃. Can become solid upon cooling below P<6 bars !
System pressure @ standstill (T ambient >31℃)	Refrigerant vapor pressure at ambient air temperature	At least 74 bars – can be higher, depending on charge and temperature.

**Table 2** : Main differences between transcritical R744 cycle and subcritical cycle

# 3. R744 HEAT PUMPS TECHNOLOGY

In Section 2, the basics of the transcritical cycle were examined. In this section, some R744 applications (both for cooling and/or heating) will be surveyed, with a focus on the

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technology of the components. Only applications which are marketed or are at a noteworthy stage of development as of year 2007 will be included herein. Industrial applications, air conditioning and mobile air conditioning systems will not be covered.

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Marketed applications cover :

- Tap water heating;
- Space heating;
- Chilled water for air conditioning;
- Commercial refrigeration (positive and negative temperature levels).

While the water heating applications have been marketed only in Japan, some commercial refrigeration and air conditioning applications have been commercialized in Europe. During 2007, a few Japanese heat pumps have been installed in Europe (mainly in Sweden) for tap water heating and residential heating.

### 3.1. The Ecocute system for tap water and heating

EcoCute is a brand name that applies to a system which is made by 6 Japanese manufacturers (Denso, Sanyo, Matsushita Electric Industrial, Daikin, Hitachi Appliances, Mitsubishi Electric and Sanden) and marketed under about 14 names. The brand name is derived from the Japanese word "kyuto" which means "hot water". The development of the Ecocute was motivated by the need to produce hot water at a cheaper cost, while operating at reduced electricity tariffs. Sanyo is one of the main manufacturers, releasing an Ecocute unit that produces hot water and heating water. Figure 8 shows the heat pump and associated water tank.



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(www.sanyoaircon.com)

It is noteworthy the heat pump looks just like any other traditional air outdoor unit or minichiller on the market. This outdoor unit has neither an integrated water tank, nor a water pump. In addition to the electrical connections, only the water connections are required. The water distribution system inside the house remains the same as with other heating systems.

Figure 9 shows the flow diagram of such a unit. The water circulates inside the tank and is heated by the heat pump unit, as required. Water is withdrawn from the tank to feed the radiators or space heating system and then returns to the tank. The tap water from the main



water supply is fed to a coil inside the tank. It is then heated and routed to the different taps (kitchen, shower, etc.). Supplemental electrical heaters inside the tank allow for an increase in water temperature if the heat pump does not provide sufficient heating.



Figure 9 : Flow diagram of the Sanyo Ecocute (www.sanyoaircon.com)

Table 3 shows the claimed performance of this product, depending on the water tank model electrical input (3-phase and single-phase).

Note that this unit is claimed to work down to outdoors temperatures of -15°C without loss in heating duty. Various Ecocute models from other manufacturers are shown in Figure 10. A Hitachi model shown in Figure 10 is made up of two units connected in series. This heat pump does not have a large tank. It produces instant hot water, and is not intended for space heating. It is designed to be installed outdoors, thus saving indoors space.



Figure 10 : Various Ecocute models (www.heatpumpcentre.org)







Hea	at pump Unit		SHP-C45DEN				
	Tank unit		SHP-TH22DDN	SHP-TH22DHN			
Performance							
*1 Heating capacity / i	nput	kW	4.5 / 1.20				
C.O.P. (Outdoor temp	o. 20℃)	W/W	3.7	75			
*2 Heating capacity / i	nput	kW	4.5 /	1.45			
C.O.P. (Outdoor temp	o. 7℃)	W/W	3.1	10			
*3 Heating capacity / i	nput	kW	4.5 /	2.48			
C.O.P. (Outdoor temp	o15℃)	W/W	1.8	81			
Electrical Rating							
Power supply	Heat pump unit	V	220-23	30-240			
	Tank unit	V	400 / 3+N	230 / 3+N			
Maximum current		A	20	30			
Tank unit							
Tank capacity			22	23			
Maximum working pre	essure	kg/cm <sup>2</sup>	2.	5			
Auxiliary electric heate	er capacity	kW	9.0	7.05			
Dimensions Net	H/W/D	mm	1547 x 5	97 x 609			
	Shipment H/W/D	mm	1736 x 7	00 x 737			
Weight	Net/Shipping	kg	170.0 /	′ 180.0			
Heat pump unit							
Refrigerant (amount)		(kg)	CO2 (	(0.86)			
Pressure sound level		dB-A	45.0				
Compressor			DC Rotary two stage compression				
Dimensions	Net H/W/D	mm	690 x 840 x 290				
	Shipment H/W/D	mm	765 x 943 x 433				
Weight	Net/Shipping	kg	65.0 /	72.0			

### Table 3 : Sanyo Ecocute Performance (<u>www.sanyoaircon.com</u>)

Figure 11 (Hitachi catalogues) shows the installation configuration for this model. Note that Hitachi also sells "classical" Ecocute models with a separate water tank.



Figure 11: A Hitachi Ecocute model





To avoid water freezing between the tank and the heat pump, the water temperature in the pipe connections is controlled via an outdoor temperature sensor. This sensor will activate heat pump operation if needed. In order to avoid water pipe freezing in very cold climate

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areas, a manufacturers has marketed an Ecocute version with a water-to-R744 heat exchanger (the gas cooler) located just below the water tank. This tank is then installed indoors, while the heat pump is installed outdoors. Since only hot R744 circulates in the pipes between the heat pump and the water tank, there is no risk of water freezing.

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In Europe, a 5 kW heat pump with features similar to that of the Ecocute unit is marketed by *Stiebel Eltron*. Annex 1 shows a brochure relevant to the "Compact series 5 kW" from this manufacturer and from **CTC**, a Sweden-based manufacturer which proposes similar heat pumps.

Annex 1 also shows excerpts of Instruction Manuals from Ecocute manufacturers. Residential Ecocute units yield heating duties of the order of 4.5 kW. Japanese manufacturers claim to have produced a million Ecocute units up to year 2007 (cumulated).

Some larger capacity R744 heat pumps are under development, targeting the commercial market. The simplest models use two small domestic Ecocute units in series for water and space heating (see example in Figure 11). Some Japanese manufacturers also market larger units aiming industrial and large residential applications (hotels, hospitals, cafeterias etc).

Figure 12 shows an Itomic system installed on a building roof. It uses a large water capacity (6 times 500 l). Figure 13 shows the water and R744 circuits.



Figure 12 : Large Ecocute systems from Itomic (<u>www.itomic.co.jp</u>)









Figure 13 : Flow diagram of Ecocute from Itomic (<u>www.itomic.co.jp</u>)

# 3.2. Green and Cool Chiller Systems

**Green and Cool** are Swedish manufactured refrigeration and air conditioning units using R744, for high, medium and low temperatures applications.



Figure 14 : Atlantic chiller front view

Figure 15 : Side view 1



These chillers can be operated either under sub-critical or transcritical conditions. Figures 12 to 15 show pictures of an "Atlantic" chiller.

Figures 12 and 13 show the control panel, the compressor rack (3 black units) and the R744 high pressure tanks (in green).



Figure 16 : Atlantic chiller back view

Figure 17 : Side view 2

Annex 2 shows the Green and Cool "Atlantic" product range with a performance table. The Atlantic product range is normally equipped with air-cooled gas cooler (not shown in Figures 12 to 15), and can handle duties up to 200 kW, depending on the evaporating temperature.

Green and Cool sources finned coils (gas coolers) from other manufacturers.

The Green and Cool Atlantic is a liquid chiller unit that is available as an air conditioning unit (HT), a chiller unit (MT) and a freezer unit (LT) with a partially indirect system.

On the cold side the HT uses water for air conditioning, the MT uses 37% Propylene glycol solution for chilling applications and the LT uses R744 as the heat transfer medium for freeze units.

### 3.3. Vending machines and bottle coolers

Transcritical R744 cycles are also used for small commercial refrigeration systems. The Coca Cola Company (TCCC) has pledged to reduce to the lowest possible its uses of synthetic refrigerants. As of year 2007, they operate 6000 transcritical vending machines with duties ranging from 300 W to a few kW.





Figures 18 and 19 show the cassette type refrigeration system working with R744. Figure 20 shows the product range potentially covered by transcritical cycles.



Figure 18 : R744 cycle components



Figure 19 : R744 Cooling cassette



Figure 20 : Coca-Coal vending machines range of products







# 4. COMPONENTS FOR R744 HEAT PUMPS

Components for R744 systems have to withstand much higher pressures than their HFC and HCFC counterparts. Pressure differentials are higher by one order of magnitude. Other issues are introduced by the particularity of R744, e.g. high discharge temperatures, compatibility with lubricating oils, potential degradation of seals after decompression, etc. These issues hinder the fast development of a "component chain".

In Japan, the mostly available components for transcritical cycles are those used in the Ecocute systems, viz. air coils (evaporators), compressors, electronic expansion valves (EEVs) and water-to-R744 heat exchangers ("gas coolers"). In Europe, few manufacturers have an offer for R744 components, except Danfoss, which mainly markets compressors, and valves.

In this section, we will examine the marketed items (or to-be-marketed as claimed by component manufacturers), and describe their respective technologies.

### 4.1. Compressors

**Bock** markets semi-hermetic, electrical driven compressors for transcritical R744 cycles aiming at industrial and commercial refrigeration or air-conditioning applications.

The two-cylinder fixed-displacement compressors have an integrated gas cooled electric motor 4- pole version (1,500 rpm), with swept volumes ranging from 90 to 190 cc (which yields displacement volumes from  $7.70 \text{ m}^3/\text{h}$  to  $20 \text{ m}^3/\text{h}$ ).

The HGX2 and HAX2 compressor series can handle variable rotational speed, with a maximal 1800 rpm. They are equipped with HP and LP safety valves and use synthetic oil. Their overall weight is about 160 kg.



Figure 21 : Bock Series HGX2



Figure 22 : Bock Series RKX26/31





The RKX26/31 semihermetic compressor takes advantage of a new design with 6 radial pistons. This enable a slimmer version than the HGX2 series. The motor is gas cooled in 2 or 4- pole version (3000/1500 rpm – maximum speed of 3600 rpm). With a swept volume of 31 cc, it enables a displacement volume of 2.60 m<sup>3</sup>/hr to 6.70 m<sup>3</sup>/h. This compressor can be mounted both in horizontal and vertical positions. It uses Bock C120E (Synthetic Oil), has an integrated oil separator and HP/LP safety valves.

**Danfoss** offers small displacement volume compressors (see Figure 23), with capacity ranging from about 500 W to 2 kW. Figure 24 shows the claimed performance for the product range. The size is about the same as those used in domestic refrigerators, i.e. from 1 to 3 cc displacement volume. These compressors are used in some of the Coca Cola vending machines refrigeration cassettes.



Figure 23 : Danfoss R744 compressor (www.danfoss.com)

Refrigerant	ge	Freqency	Com								į	Capac	ity [W	1						,	con	Power	tion	co	)P [W/	W]
	Volta		Freqe	pressor	pressor	Code no									Ev	apora	ting te	mper	ature ['	°C]						
-				8	-45	-40	-35	-30	-25	-23.3	-20	-15	-10	-6.7	-5	0	5	7.2	10	15	-35	-10	5	-35	-10	5
	>		TN1406	106B0001								335	405	455	483	574	680	733				288	291		1,41	2,34
	20-240	50Hz	TN1410	106B0002								573	692	779	827	981	1162	1253				428	432		1,62	2,69
CO <sub>2</sub>	2	5	TN1416	10680003								1006	1214	1366	1450	1721	2039	2198			1	706	715		1,72	2,85
	SV	Hz	TN1410	106B0004								712	860	967	1027	1219	1444	1556				538	545		1,6	2,65
115	ш	60	TN1416	106B0005								1187	1433	1612	1711	2031	2406	2594				851	863		1,68	2,79

 Test conditions
 90 ba

 Discharge pressure
 90 ba

 Gas cooler outlet temp.
 20°C

 Suction gas temperature
 32°C

Figure 24 : Danfoss compressors characteristics





The Brazilian manufacturer **Embraco** makes reciprocating compressors (see Figure 25) with displacement volumes that are within the same range as the Danfoss series (1 to 3 cc). Figure 26 shows the claimed (refrigeration) performance for these compressors. For heat pumps, the Embraco range of compressors enable a maximum heating duty of about 2.7 kW at 50 Hz.

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Figure 25 : Embraco R744 compressor

An	olication	Compressor	Voltage / Frequency	Displa	cem enf	Cooling Capacity*	Estimated
				<b>cc</b>	cu in	W	Samples Release
	LBP	EK2140CD	220-240V 50Hz 1~	1.75	0.11	482	41" Quarter/2007
	LBP	EK2178CD	220-240V 50Hz 1~	3.00	0.18	878	1º Quarter/2008
1	м/нвр	EK6160CD	220-240V 50Hz 1~	1.00	0.06	630	4 <sup>1</sup> " Quarter/2007
분	M/HBP	EK6210CD	220-240V 50Hz 1~	1.75	0.11	1149	1 <sup>er</sup> Quarter/2007
8 1	м/нвр	EK6217CD	220-240V 50Hz 1~	3.00	0.18	2008	3 <sup>40</sup> Quarter/2007
1	м/нвр	EK6160CD	100V 50-60Hz 1~	1.00	0.06	600	2 <sup>46</sup> Quarter/2007
	м/нвр	EK6210CD	100V 50-60Hz 1~	1.75	0.11	1100	4 <sup>™</sup> Quarter/2007
1	м/нвр	EK6217CD	100V 50-60Hz 1~	3.00	0.18	1980	4 <sup>th</sup> Quarter/2007
4	M/HBP	EK6210CD	115V 60Hz 1~	1.75	0.11	1 423	1" Quarter/2008
8	M/HBP	EK6217CD	115V 60Hz 1~	3.00	0.18	2482	2** Quarter/2008

\*Estimated Data

# **Test Conditions**

	Evaporating Temperature °C (°F)	Discharge Pressure bar	Return Gas Temperature °C (°F)	Ambient Temperature °C (°F)	Approach Temperature °C (°F)
LBP	-23.3 (-10)	85.0	32.2 (90)	32.2 (90)	32.2 (90)
м/нвр	7.2 (45)	85.0	35.0 (95)	35.0 (95)	35.0 (95)

Figure 26 : Embraco R744 compressor product line

The Italian manufacturer **Dorin** markets a range of compressors for transcritical operation. With displacement volumes from 3.5 to 12.6  $m^3$ /hr, Dorin covers the largest range of duties available on the market.





The TCS Dorin product line features single stage compressors that operate under transcritical conditions and are suitable for :

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- Refrigerated transport
- Commercial refrigeration
- Hot water production and heating
- Chiller and HVAC systems

The TCS are also proposed in tandem arrangement (T-TCS line).



**Figure 27 : Dorin compressor** 

RLA: con

locked rotor our

Figure 28 shows the main features of the TCS Dorin compressors. Figure 29 shows a drawing of a sample compressor with dimensions.

transcritical single stage													
model	rpm	swept volume [m3/h]	suction NPT	discharge NPT	weight [kg]	oil charge [kg]							
TCS340/4-D	1450	3,5	1/2	1/2	123	1,8							
TCS350/4-D	1450	4,3	3/4	1/2	126	1,8							
TCS362/4-D	1450	5,4	3/4	1/2	130	1,8							
TCS340-D	2900	7,0	3/4	1/2	133	1,8							
TCS351-D	2900	8,8	3/4	1/2	136	1,8							
TCS362-D	2900	10,7	3/4	1/2	140	1,8							
TCS373-D	2900	12,6	3/4	1/2	140	1,8							

transcritical single stage											
model	FLA [A] 380V / 50hz	LRA [A] 380V / 50hz	nominal motor power [kW]								
TCS340/4-D	11,0	75,4	4,0								
TCS350/4-D	15,0	83,2	5,0								
TCS362/4-D	17,0	90,2	6,0								
TCS340-D	24,0	172,6	12,0								
TCS351-D	33,0	215,1	15,0								
TCS362-D	38,0	255,3	18,0								
TCS373-D	38,0	255,3	18,0								

Figure 29 : Dorin TCS product line









Figure 30 : Compressor dimensions

Standard compressors from Dorin are PED certified and equipped with:

- electric motors with thermistor protection
- oil pump and oil cooler : the oil temperature is controlled so as to remain within the 30 to 65°C range in order to reduce oil carry-over and R744 solubility.
- low and high pressure relief valve with relieving set point of respectively 100 bar (Pss) and 163 bar (PS)
- crankcase heater
- special lubricant for R744 transcritical application.

In Japan, all Ecocute manufacturers use their own, proprietary transcritical compressor, but only **Sanyo** has a complete product line that is marketed independently of their Ecocute model. These rotary, double-stage compressors are used in some of the Coca Cola vending machines. The compressor shell is at the intermediate pressure, as shown by Figure 31.









Figure 31 : Sanyo double-stage rotary compressor

As of Jan.15 <sup>th</sup> , 20	004										
	S	Single Sp	eed Mode	el	Variable Speed Model						
Rated Power	300W	400W	500W	650W	500W INV.	600W INV.	900W INV.	1100W INV.	2200W INV.		
Model	C-C30	C-C40	C-C50	C-C60	C-CV53	C-CV63	C-CV93	C-CV113	C-CV223		
Comp. HP	1/3HP	1/2HP	2/3HP	3/4HP	1/3-1HP	1/3-1HP	1-1.5HP	1-2HP	3-5HP		
Comp. Speed	50Hz 60Hz	50Hz 60Hz	50Hz 60Hz	50Hz 60Hz	Variable	Variable	Variable	Variable	Variable		
R&D Status	+	+	+		+	+	+	+	+		
Compressor		<b>J</b>	<b>J</b>		\$	\$	Ĵ	1			
Application											
Heat Pump							• • •	• • •	•••		
V. Machine	• • •	• • •	•••		•••	•••					
GDM	•••	•••	•••	•••	•••	••					
Showcase		• • •	•••	•••	• • •	•••	•••	• • •	•••		

### SANYO CO2 Compressor series • • •

+• •Mass Production Base ----• •Under Development

Figure 32 : Sanyo compressor product line

**Daikin** uses an inverter swing-type compressor with a high pressure shell. Figures 33 and 34 show details of the Daikin compressor construction.









Figure 33 : Daikin compressor



Figure 34 : View of Daikin swing compressor

### 4.2. Evaporators

Heat pump evaporator technologies use either finned coils, plate-and-tube (air source), or plate heat exchangers and shell-and-tube (for liquids).



Figure 35 : Daikin air-to-refrigerant evaporator with fan on Ecocute chassis





Refrigerant-to-liquid plate heat exchangers are not available for pressures higher than about 40 bars, except for very costly, customized, industrial applications. Plate heat exchangers are therefore not used in transcritical cycle because of the pressure constraints (as of 2007).

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The Ecocute units use finned-tube air-to-refrigerant evaporators that use copper tubes and aluminum fins. Basically, these evaporators are not different from heat exchangers using HFC refrigerants. However, they are equipped with thicker tubes and specific circuitry that takes into account the special R744 properties. Figure 35 shows such an evaporator from Daikin. The "all-aluminum" evaporators are used for mobile air conditioning, but their use is

### 4.3. Gas coolers

envisaged in stationary equipment for cost considerations.

The gas cooler is the R744-to-water heat exchanger that heats up water in a heat pump. Most gas cooler designs use a double wall separation between R744 and water. In the event of a leak, R744 will thus never mix with water. Some sample gas coolers are shown in Figures 36 to 39. Plate heat exchangers are not used, due to pressure limitations on their design (as of 2007).

The **Sanyo** gas cooler uses superimposed wounded coils, with alternate circulation of water and R744. Water flows through flattened tubes, while R744 flows through flat tubes with several ports.

**Stiebel Eltron** (Figure 37) use a layout that is similar to that used by Denso (Figure 38). In these designs, R744 flow through small diameter copper tubing that is welded to copper plates though which water flows. The **Denso** design uses extra fins/baffles between the water plates to increase surface area and turbulence.

The **Daikin** design uses regular water tubing around which is soldered to small helically wounded copper tubing (see Figure 39).











Figure 37 : Stiebel Eltron gas cooler



Figure 38 : Denso gas cooler



Figure 39 : Daikin gas cooler





### 4.4. Expansion devices and controls

Transcritical heat pumps require high pressure control to minimize power consumption, as covered in Section 2.3. This optimal pressure is a function of evaporating pressure (or temperature) and R744 gas cooler outlet temperature. Figure 40 shows the location of a motorized control expansion valve, a solenoid valve (for defrost) and of a pressure sensor in a typical Ecocute unit for hot water supply.

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Figure 40 : Control valves and pressure sensor in an Ecocute unit



Figure 41 : Control valves and sensor from Saginomiya

The Ecocute units use electronic valves from **Saginomiya**, as shown in Figure 41. Electronic expansion valves that use information from operating parameters (water or R744 outlet





temperature from the gas cooler, evaporating temperature or air outdoors temperature) provide the best control system. These controls are implemented in the Ecocute unit and the Stiebel Eltron heat pump.

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If transcritical operation at fixed pressure is possible, Danfoss proposes two pressure regulators:

- A manual pressure regulator the pressure can be set manually on the valve (MBR);
- An automatic back pressure regulator, which uses the gas cooler outlet temperature to control high pressure (BPR)



Figure 42 : Danfoss MBR regulator for transcritical R744 systems

These two valves are shown in Figures 442 and 43.







# Thermal Back Pressure Regulator

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### Function:



Figure 43 : Danfoss TBR regulator for transcritical R744 systems

For large transcritical refrigeration duties, Danfoss markets an expansion valve for pressure control (see Figure 44).



Figure 44 : Danfoss pressure control/expansion valve for larger duty transcritical systems







# 5. SAFETY GUIDELINES WHEN USING R744 IN HEAT PUMPS

Section 2.1 provided some basic physical and thermodynamic data of R744 that were used as background information to understand the transcritical cycle operation. This Section will provide more information and safety guidelines regarding the practical use of this refrigerant.

Annex 3 contains a Safety Data Sheet from a main R744 producer which should consulted for safety precautions for this refrigerant.

Transcritical heat pumps are not fundamentally different from subcritical heat pumps. *Hence all usual, basic safety precautions taken for the operation of conventional heat pumps equally apply to R744 heat pumps*. Some additional rules will be introduced by the transcritical cycle distinct features, which are the higher operating pressures and temperatures, the specific control schemes and the use of R744 as a refrigerant.

### 5.1.R744 effects on health

Gaseous R744 is colorless and odorless at low concentrations. It is not flammable. It is stable under normal conditions but can become dangerous if inhaled at concentrations roughly around 2%. Due to the fact that it is odorless, it is not selfalarming in case of leaks from systems.

Table 4 summarizes the effects and symptoms related to R744 inhalation depending on its concentration in the air.



Conc. in air	Effects and Symptoms
2%	50% increase in breathing rate
3%	10 Minutes short term exposure limit; 100% increase in breathing rate
	300% increase in breathing rate, headache and sweating may begin after about an hour
5%	(Com.: this will tolerated by most persons, but it is physical burdening)
8%	Short time exposure limit
	Headache after 10 or 15 minutes. Dizziness, buzzing in the ears, blood pressure increase,
8-10%	high pulse rate, excitation, and nausea.
	After a few minutes, cramps similar to epileptic fits, loss of consciousness, and shock (i.e.;
10-18%	a sharp drop in blood pressure) The victims recover very quickly in fresh air.
18-20%	Symptoms similar those of a stroke

Table 4 : Effects of R744 on hum	han health
----------------------------------	------------

Note that with a relative density of 1.53, R744 is heavier than air; thus, it tends to concentrate near the ground level when spilled.





Air-source heat pumps are always installed outdoors – that is where they pick up heat. Since connecting pipework between the heat pump and the hydraulic system contains only water, and because of the double-wall separating water and R744 in the water heater, there is no possibility of leakage of R744 in the water circuit.

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A water-source heat pump can be installed indoors. Installation should be carried out correctly to avoid accumulation of R744 in specific locations should a leak occur:

- Ventilation must be provided. Avoid working with R744 where it can be collect in low or confined areas.
- Do not remain near the heat pump in the event of a large carbon dioxide release. Before returning to the premises, make sure that the R744-concentration is low enough. The R744 concentration can be analyzed with specific sensors.
- R744 containers must stand upright when gas is being withdrawn. Cold R744 can form a very thick mist with moist air.
- Persons who succumb to R744 poisoning must be taken into the open air quickly. Artificial respiration should be administered if the victims stop breathing

### 5.2.R744 in heat pumps

### 5.2.1. Pressure at standstill

Because of their high value of critical temperature, the pressure at standstill (i.e. when the system is shut-down) for conventional refrigerants is a function of ambient temperature (assuming the system temperature has reached that value). Even under severe ambient temperatures, most HFC/HCFC refrigerants systems exhibit pressures lower than 40 bars at standstill.

For R744, the standstill pressure evolves as follows :

- For ambient temperatures under 31°C, the pressure is equal to that above the vapor phase, i.e. the standstill pressure is equal to the saturation pressure of R744. At a temperature of 31°C, this pressure reaches about 75 bars.
- For ambient temperatures above 31°C, all the R744 contained in the system is under "supercritical" conditions. Thus, the standstill pressure is above 75 bars, but depends on the ambient temperature, the mass of R744 charged into the system and the internal volume of the system.





### **5.2.2.** Operating temperatures and pressures

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For ambient temperatures of about 7°C, typical pressures for air source heat pumps under operation are as follows :

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- Low pressure side : pressures between 25 and 50 bars and evaporating temperature between -12°C and 20°C. Under lower ambient temperatures, these values may be lower.
- **High pressure side** : pressures between 90 and 130 bars, temperatures between 90 and 130°C.

Refrigerant piping on the high pressure side will be therefore very hot and will cause burning. Direct contact must be avoided when the unit is operating or has just been shut down.

### 5.2.3. Material compatibility

The information contained in Table 5 has been compiled from Air Liquide (sources : International Standards: Compatibility of cylinder and valve materials with gas content; Part 1: ISO 11114-1 (Jul 1998), Part 2: ISO 11114-2 (Mar 2001)), and must be used with extreme caution.

No raw data such as this can cover all conditions of concentration, temperature, humidity, impurities and aeration. It is therefore recommended that this table be used to choose possible materials and then more extensive investigation and testing is carried out under the specific conditions of use. The collected data mainly concern high pressure applications at ambient temperature and the safety aspect of material compatibility rather than the quality aspect.







1 abic 5 . K/44 com	
Material	Compatibility
IV	letals
Aluminium	Satisfactory
Brass	Satisfactory
Copper	Satisfactory
	Satisfactory but risk of corrosion in
Ferritic Steels (e.g. Carbon steels)	presence of CO and/or moisture, Cold
	brittleness.
Stainless Steel	Satisfactory
PI	astics
Polytetrafluoroethylene (PTFE)	Satisfactory
Polychlorotrifluoroethylene (PCTFE)	Satisfactory
Vinylidene polyfluoride(PVDF) (KYNAR™)	Satisfactory
Polyamide(PA) (NYLON™)	Satisfactory
Polypropylene(PP)	Satisfactory
Elas	stomers
Buthyl (isobutene - isoprene) rubber (IIR)	Non recommended, significant swelling.
	Non recommended, significant swelling and
Nitrile rubber (NBR)	significant loss of mass by extraction or
	chemical reaction.
	Non recommended, significant swelling and
Chloroprene (CR)	significant loss of mass by extraction or
	chemical reaction.
	Non recommended, significant swelling and
Chlorofluorocarbons (FKM) (VITON™)	significant loss of mass by extraction or
	chemical reaction.
Silicon (Q)	Acceptable but strong rate of permeation.
	Acceptable but important swelling and
Ethylene-Propylene (EPDM)	significant loss of mass by extraction or
	chemical reaction.
Luk	pricants
Hydrocarbon based lubricant	Satisfactory
Fluorocarbon based lubricant	Satisfactory

### Table 5 : R744 compatibility with materials

### 5.2.4. Water and R744

Figure 45 (from Danfoss technical literature) shows what the combination of water and R744 leads to.







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Figure 45 : R744 expansion processes (www.danfoss.com)

In a first step, R744 and water combine to yield carbonic acid, with a mild effect. However, this acid further combines with R744 to give a hydronium ion, which has the effect of an activated acid and reacts with construction materials such as steel.

The acid attack shown in Figure 46 is a form of R744 corrosion that occurs in flowing environments, and occurs where a protective iron carbonate coating is worn away in areas.



Figure 46 : Pipe corrosion in flowing environment (<u>octane.nmt.edu/waterquality/corrosion/CO2.htm</u>)







With very high concentration of water in R744 systems, the R744 gas hydrate can be formed. The R744 gas hydrate (see Figure 47) looks like ice, but exists also at higher temperatures than 0°C. The CO2 gas hydrate can create problem, e.g. plugging filters and pipes. CO<sub>2</sub> gas hydrate - CO<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>



Figure 47 : R744 gas hydrates (www.danfoss.com)

Water can also enter the system via the lubricant oil. With synthetic mineral oil such as Poly-Alpha-Olefin lubricant oil, oxygen (generated by corrosion for example) reacts and yields water and a strong organic acid. This acid in turn reacts on construction materials.



Figure 48 : Effect of oxygen on mineral oil (<u>www.danfoss.com</u>)

With ester oil, free water combines to form an alcohol and a relatively weak acid (see Figure 48). However, when these reaction products are carried around in the refrigeration system, high temperatures will be encountered, with an amplification of the acidic effects.



Figure 49 : Effect of water on ester oil (<u>www.danfoss.com</u>)





Water can enter the system mainly because of the following reasons :

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- Incomplete water removal during installation / commissioning;
- Water-contaminated lubricant charged into the system;
- Water-contaminated CO2 charged into the system.

### It is therefore very important to avoid water contamination through good service practices :

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- Thoroughly vacuum systems (same procedure and duration as HCFC/HFC refrigerants;
- Avoid letting oil cans open always put the cap back to avoid water contamination of oil;
- Avoid letting the circuit open to the air during servicing when not required always remove caps or bolts just before welding/tightening;
- Change filter/dryer cartridge upon servicing.

# 6. SERVICING AND MAINTENANCE ASPECTS

This Section attempts to explain the fundamentals of R744 behavior and its consequences on the Servicing and Maintenance aspects of R744 heat pumps.

R744 heat pumps must be treated as "hot water heaters". In particular, the refrigerant circuit is tuned in the factory and should therefore not be tampered with, except by fully authorized personnel. Note that Annex 1 contains information material from an Ecocute manufacturer. Consult this Annex for further advice on how to handle such heat pumps.

### 6.1.1. Evacuating R744 : the expansion process

Upon expansion, refrigerants tend to cool. R744 possesses a high triple point around  $-56^{\circ}$ C and 5.2 bars. Therefore, care must be taken to avoid sudden pressure release that would bring it to solid state, or any expansion process which could lead to such a state. Figure 50 illustrates the R744 expansion processes from different pressure levels:

- Expanding vapor from point C (35 bars) to the triple point pressure will result first in the partial vaporization of R744, and will then lead to gaseous state.
- Expanding vapor from point B (50 bars) will lead to a 5% of the refrigerant in solid state ("dry ice") at the triple point pressure.
- Expanding liquid from any pressure (e.g. point A at 20 bars) will lead to a substantial amount of R744 dry ice in the equipment. This also occurs when the expansion process starts from other higher pressures, e.g. higher saturation temperatures.





Figure 50 : R744 expansion processes

# As a rule of thumb, the expansion of liquid R744 from any pressure level, and the expansion of gaseous R744 from a pressure higher than 35 bars will lead to the formation of dry ice if the final pressure is lower than about 5.2 bars. This specific behavior should be borne in mind, for example when discharging R744 from systems.

As of year 2007, there is no obligation to recover R744 from refrigeration/heat pump systems. Hence, R744 can be discharged to the atmosphere.

In the event of a R744 release from the heat pump via a safety valve or when discharging R744 from a system, care must be taken not to deteriorate equipment by dry ice. In particular, when evacuating R744, avoid pipe lengths that could be plugged by dry ice formation due to pressure expansion.

### 6.1.2. Recharging R744 heat pumps

When servicing heat pumps, refrigerant recharging for *conventional* refrigerants (HFCs and HCFCs) is carried out using the value of nominal charge and the following information:

- the values of high pressure and subcooling after the condenser and/or superheat at compressor suction;
- the refrigerant state before expansion (view through a liquid line sight glass, when available).





### Transcritical **R744** heat pumps are fundamentally different because:

• there is no distinction between liquid and vapor phase before expansion;

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• there is no value of "subcooling" after the gas cooling process – because subcooling does not exist as such;

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• the relationship between high pressure and refrigerant charge in the system is more complex than for conventional refrigerants.

Transcritical R744 domestic systems are normally factory-charged. The refrigerant charge has numerous effects, particularly on the value of the compressor discharge pressure. Inappropriate refrigerant charge could thus lead to improper heat pump operation and/or equipment damage. This explains why most residential heat pumps are only serviced in the manufacturer workshop or at an authorized service station.

# Thus, any attempt to recharge R744 heat pumps should not be made, unless it is authorized by the manufacturer. Recharging a R744 system can only by carried out if full and explicit instructions are provided by the heat pump manufacturer.

Annex 1, which shows excerpts from an Ecocute Service Manual issues important warnings against attempts to recharge the unit.

Systems using R744 must be thoroughly evacuated like conventional refrigeration systems. Before any servicing, make sure that all the following is available to carry out refrigerant recharging :

- Instructions from the manufacturer, including required information, e.g. the total amount of refrigerant for recharge.
- Components required, e.g. filter/driers for R744 and suitable for the required design operating pressures should be used.
- Appropriate recharging station if specified by manufacturer.

Recharging R744 systems like conventional systems is not readily possible. With HFC refrigerants and other systems it is common practice to recharge liquid via the liquid line upon completion of the evacuation i.e. when the plant is still under vacuum. This is not possible with an R744 system because dry ice would form internally at the charging point when the system pressure is less than around 6 bar, because of expansion (see Section 6.1.1).

Before charging liquid R744 into the system on the high pressure side, it is therefore necessary to increase the system pressure to a level of about 6 bar using gaseous R744.





Once this value is reached, recharging may proceed with liquid R744. The correct system charge must be known from the Service Manual. *Do not attempt to charge an R744 system when the amount of refrigerant charge is unknown*. This may lead to system overcharge and to high pressure increase.

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### 6.1.3. R744 containers and recharge system

Refrigerant R744 is available in pressurized cylinders with contents ranging from about 3 to 35 kg. R744 is produced by chemical companies such as Linde Gas, Air Liquide and Praxair. Cylinders are made of steel or aluminum, with a service pressure between 125 and 200 bars.

Linde Gas available cylinders are listed in Table 6. The first column indicates the cylinder reference and the second column the R744 net content. The equivalent volume in gaseous form at 1 atm and ambient conditions is shown in the third column.

Assuming a workshop with a width of 4 m, a length of 10 m and a height of 3 m, the last column shows the air R744 concentration in the air (in percent), should the entire cylinder spill into the room.

Cylinder	R744 (kg)	m3 @ 1 atm/20℃	% in air in 120 m3 workshop
Mini	3.7	1.88	1.6
B20	15	7.64	6.4
B30	22	11.20	9.3
B33	25	12.73	10.6
B40	30	15.27	12.7
B47	34.5	17.56	14.6

Table 6 : Linde Gas R744 pressurized cylinders

Table 6 shows that cylinder B30 reaches the lethal limit of 9%. However, the calculation shown in Table 6 assumes a uniform spread throughout the workshop. Since R744 is heavier than air (relative density of 1.52), it will stagnate in lower parts. Thus, even spills from cylinders B20 and B30 can be dangerous. Spills from the "mini" cylinder can cause health problems (see Table 4). *It is therefore recommended to store R744 cylinders in ventilated areas.* 

If R744 is charged directly from the cylinder into the system (with compressor being shutdown), the following will happen :



- the cylinder pressure will progressively decrease. After a small number of recharges, the cylinder pressure decreases. It will not be sufficient to charge refrigerant when the system pressure reaches the R744 vapor pressure; the cylinder will not be fully exploited and part of refrigerant will be left in the cylinder and wasted.
- the efficiency of charging operation depends on the pressure in the cylinder, and thus on the ambient temperature.

In a workshop, it is recommended to use a charging station that is suitable for R744 refrigerant. This station (see Figure 51 and 52) will enable fine charge tuning and full cylinder exploitation.



Figure 51 : Charging station for R744 refrigerant



Figure 52 : R744 charging system (www.agramkow.dk)







# ANNEX 1 : INFORMATION ON MARKETED DOMESTIC HEAT PUMPS

### STIEBEL ELTRON HEAT PUMP

# Compact series 5 kW

Powerful technology for your home.

The WPL 5 N sets new benchmarks for environmental responsibility and efficiency. Thanks to the variable speed compressor, only as much energy as is currently required is actually consumed. Using carbon dioxide as a natural refrigerant is a pioneering step for heat pump technology. The small footprint and extremely quiet operation makes this system of heat pump and cylinder universally suitable. The heat pump is suitable for wall mounting, and it is connected electrically and hydraulically to the cylinder module. The module consists of an enamelled 200 litre DHW cylinder and the integral heat pump manager. All essential circulation pumps for heating and DHW, as well as the booster heater for a mono-energetic heating operation, are already integrated as standard.



### The most important features

Ideally suited to new build
Optimised for the combined heating of the heating water and DHW
Maximum flow temperature 70 °C
Compact heat pump section for installation on an external wall
200 I DHW cylinder
Natural refrigerant CO2
Integral energy-saving, electronically regulated circulation pump







### STIEBEL ELTRON HEAT PUMP

	e.,
	0
Туре	
Туре	WPL 5 N
Part no.	221143
Height	650 mm
Width	820 mm
Depth	300 mm
Output at A2/W35	5 kW
Available from October 2007	
Specification	
Weight	62 kg
Heat pump connection	1/2"
Power consumption for A2/W35	2 kW
Starting current	<30 A
Output at A2/W35	5 kW
Coefficient of performance for A2/W35	3
Sound power level	43 dB
Rated capacity	200 l
Height cylinder module	1.878 mm
Width cylinder module	600 mm
Depth cylinder module	650 mm
Height of unit when tilted	1.900 mm
Connection on the heating system side	22 mm plug-in connector
Preliminary specification	







### CTC AIR-TO-WATER HEAT PUMPS



### Air-to-water R744 heat pumps from CTC (<u>http://www.ctc-heating.com</u>)

Measurements, WxHxD	1547 x 597 x 619 mm	690 x 840 x 290 mm
Wainht	· · · · · · · · · · · · · · · · · · ·	
weight	180 kg	65 kg
Power supply	400V 3N~	220-230-240V 1~
Maximum current supply	20A	
Electrical heating capacity	9 kW	
Output limit	1.5 kW / step	
Water volume	223 litre	
Max operating pressure	2.5 bar / 100°C	
DHW type/volume	Coil / 5.7 litre	
Max operating pressure DHW coil	9 bar	
Load pump included	Yes	
Internal pressure guard	Yes	
Heating capacity / input at 20 / 50°C*		4.5 / 1.2 kW
Heating capacity / input at 7 / 50°C*		4.5 / 1.45 kW
Heating capacity / input at -15 / 50°C*		4.5 / 2.48 kW
Pressure sound level		45 dB **
Refrigerant / amount		CO2 / 0.86 kg
Compressor		DC Rotary two stage
Design pressure high/low		14 / 8 MPa







### EXCERPTS FROM SANYO ECOCUTE SERVICE MANUAL

### 2. Outline drawings

SHP-C45DEN









### EXCERPTS FROM SANYO ECOCUTE SERVICE MANUAL





### **EXCERPTS FROM SANYO ECOCUTE SERVICE MANUAL**

# **Handling instructions**

The extract from Users Manual (SHP-TH22DDN/DHN-SW)

### **△** CAUTION

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Prohibited.	Do not touch the fins of the heat pump unit and do not poke your hands or any bar-shaped objects into the air intake and outlet. • You may injure yourself.	Disassembly prohibited!	Do not attempt to disassemble and repair the unit yourself: leave these jobs to a qualified repair technician. • There is a risk of combustion and you may injure yourself as a result of an abnormal operation.
Inspect this!	<ul> <li>When snow has piled up, remove it from and around the unit.</li> <li>Snow allowed to pile up on and around the heat pump unit and tank unit may cause malfunctioning and/or failures.</li> </ul>	Prohibited.	Do not sit on the unit or apply force to the pipes. • An accident may occur or you may burn yourself as a result.

### SHP-C45DEN Outdoor temperature versus operating current characteristics



- The current level drops when the capacity limiting device is activated by the inverter.
- · When measuring the operating current, use a clamp-on meter to measure it at the black or white power line of the 4P terminal board of the heat pump unit.
- The unit is operating properly if the operating current is within the shaded area.





### EXCERPTS FROM SANYO ECOCUTE SERVICE MANUAL

Sustainable Heat and Energy Research for Heat Pump Applications

### Troubleshooting procedures

### 1. H05 (Trouble in high pressure switch)

This trouble is confirmed after repeated 8 retries when the refrigerant pressure has exceeded the pressure setting.

### [Checkpoints]

- (1) Is the circulation pump locked?
- (2) Is any air trapped in the connecting pipes between the heat pump unit and tank unit?

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- (3) Has water been poured into the tank unit?
- (4) Have you forgotten to open the tank unit's shut-off valves?

### [Remedial action]

- Unlock the circulation pump by referring to the trial run section in the heat pump unit's installation instructions.
- (2) Turn off the power and disconnect the pipes. Thoroughly purge the air from the pipes, and then re-connect the pipes.
- (3) Pour water into the tank unit.
- (4) Refer to page 11 in the tank unit's Technical Manual, and open the three valves.

### 2. H23 (Boil-up trouble)

The boil-up temperature is at variance from the target value.

### [Checkpoints]

When the boil-up temperature is too high (this kind of trouble occurs when it is not possible to provide the circulation flow required for boil-up)

- (1) Is the water failing to circulate between the tank unit and heat pump unit?
- (2) Is a pipe whose diameter does not satisfy the rating (which is smaller than the rating) being used?

When the boil-up temperature is too low (this kind of trouble occurs when the circulation flow is too high or heat quantity is insufficient)

- (3) Is a pipe whose diameter does not satisfy the rating (which is larger than the rating) being used?
- (4) Have the pipes been insulated properly?

### [Remedial action]

- (1) Turn off the power, and replace the circulation pump.
- (2)(3)Use pipes with the rated diameter and length in accordance with the installation instructions.
- (4) Insulate the pipes and areas where the units are connected.

### 3. H27 (Incorrect water circuit piping connection)

The pipes between the heat pump unit and tank unit are crossed and connected in reverse.

### [Checkpoint]

Is the circulation pump side of the tank unit connected to the water side (B) of the heat pump unit?

### [Remedial action]

Turn off the power, close the shut-off valves of the tank unit, and change over the connecting pipes.





### EXCERPTS FROM SANYO ECOCUTE SERVICE MANUAL

Sustainable Heat and Energy Research for Heat Pump Applications

### Before replacing the heat pump unit

Be absolutely sure to check the following points before diagnosing the trouble as originating in the refrigerant circuit.

- (1) Do the outdoor temperature and current levels stand in their proper relationship? (See page 25) (If the levels are within the reference values, there is no trouble in the closed circuits.)
- (2) Is power supplied to the heat pump unit? (230V between black and white)

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- (3) Is there any trouble with the thermistors? (Check the error history.) See pages 26 28.
- (4) Is the fan running?
- (5) Are the electrical wires between the tank unit and heat pump unit plugged into the terminal board securely?

Prohibited.	Do not install the heat pump unit indoors. • The oxygen in the air may become deficient if the refrigerant should leak.	Prohibited.	Do not damage or rework the power cord, and do not use a damaged or bundled cord.		
Do this!	<ul> <li>Be absolutely sure to ground the unit.</li> <li>Otherwise, you may receive an electric shock if the unit should fail or power should leak.</li> </ul>	Danger of	Do not touch the heat pump pipes. • You may burn yourself.		
Prohibited.	Do not install the unit near a source of gas or objects which may ignite or catch fire. • There is a risk of combustion or a fire.	burning!	Do not touch the fins of the heat pump unit and do not poke your hands or		
Prohibited.	Do not charge the refrigerant in the heat pump unit. • The unit is not constructed to be amenable to refrigerant charging.	Prohibited.	<ul> <li>any bar-shaped objects into the air intake and outlet.</li> <li>You may injure yourself.</li> </ul>		
Disassembly prohibited!	Do not attempt to disassemble and repair the unit yourself: leave these jobs to a qualified repair technician. • There is a risk of combustion and you may injure yourself as a result of an abnormal operation.	Do this!	<ul> <li>Be absolutely sure to have a qualified contractor do the water supply and electrical work.</li> <li>Otherwise, accidents or malfunctioning may result.</li> </ul>		







# **ANNEX 2 : CHILLERS**

### **GREEN AND COOL PRODUCTS**





MISTICALITY	Direct expansion on the evaporator/gas cooler/condenser side		40-200 kW	
BREEZE HT	Direct expansion on the evaporator side with liquid cooled gas cooler/con	denser	40-200 kW	
ATLANTIC HT	Liquid chilled unit for air cooled gas cooler/condenser		40-200 kW	
PACIFIC	Liquid chiller unit for air cooled gas cooler/condenser		40-200kW	
Chiller Unit	(medium temp)			
Model	Type of Unit		Output	
MISTRAL MT	Direct expansion on the evaporator/gas cooler/condenser side		30-120kW	
BREEZE MT	Direct expansion on the evaporator side with liquid cooled gas cooler/con	denser	30-120kW	
ATLANTIC MT	Liquid chilled unit for air cooled gas cooler/condenser		30-104 kW	
BOTHNIA	Liquid chiller unit with liquid cooled gas cooler/condenser		30-96kW	
	billoci oxpanolori on inclorapor alon gao coordin condonoci orac	expansion on the evaporator gas cooler/condenser side		
Model	Type of Unit		Output	
MISTINALLI		xpansion on the evaporator side with liquid cooled gas cooler/condenser		
BREEZE LT	Direct expansion on the evaporator side with liquid cooled gas cooler/con	denser	15-60kW	
BREEZE LT ATLANTIC LT	Direct expansion on the evaporator side with liquid cooled gas cooler/con Liquid chilled unit for air cooled gas cooler/condenser	denser	15-60kW 15-60kW	
ARCTIC	Direct expansion on the evaporator side with liquid cooled gas cooler/con Liquid chilled unit for air cooled gas cooler/condenser Liquid chiller unit for pump circulation freezer with liquid cooled gas cooler/co	denser ondenser	15-60kW 15-60kW 15-60kW	
BREEZE LT ATLANTIC LT ARCTIC BALTIC	Direct expansion on the evaporator side with liquid cooled gas cooler/con Liquid chilled unit for air cooled gas cooler/condenser Liquid chiller unit for pump circulation freezer with liquid cooled gas cooler/co For cascade systems. Direct expansion on evaporator side. Secondary flui condensorside is connected to the evaporator side on glycol chiller MT.	denser ondenser d on	15-60kW 15-60kW 15-60kW 15-60kW	
BREEZE LT ATLANTIC LT ARCTIC BALTIC Chiller unit/ Model	Direct expansion on the evaporator side with liquid cooled gas cooler/con Liquid chilled unit for air cooled gas cooler/condenser Liquid chiller unit for pump circulation freezer with liquid cooled gas cooler/co For cascade systems. Direct expansion on evaporator side. Secondary flui condensorside is connected to the evaporator side on glycol chiller MT. Freezer unit Type of Unit	denser ondenser d on Output, Chilk	15-60kW 15-60kW 15-60kW 15-60kW ar Output, Freezer	
BREEZE LT ATLANTIC LT ARCTIC BALTIC Chiller unit/ Model CRYSTAL CH	Direct expansion on the evaporator side with liquid cooled gas cooler/con Liquid chilled unit for air cooled gas cooler/condenser Liquid chiller unit for pump circulation freezer with liquid cooled gas cooler/co For cascade systems. Direct expansion on evaporator side. Secondary flui condensorside is connected to the evaporator side on glycol chiller MT. Freezer unit Type of Unit Liquid chilled unit with a combined freezer unit for direct expansion.	denser ondenser d on Output, Chille 60-90kW	15-60kW 15-60kW 15-60kW 15-60kW ar Output, Freezer 10-30kW	







### **GREEN AND COOL PRODUCTS**



# ATLANTIC

ATLANTIC is a liquid chiller unit for air cooled gas Options cooler/condenser.

ATLANTIC is available as an air conditioning unit (HT), a chiller unit (MT) and a freezer unit (LT) with a partially indirect system. ATLANTIC has an air cooled gas cooler on the hot side and on the cold side the HT has: water, MT: Propylene glycol 37% and the LTs use R744 as the Secondary fluid. ATLANTIC is designed for the refrigerant carbon dioxide

(R744) for the lowest possible environmental impact.

- Superheat exchanger (model HE)
- Noise reduction
- Antivibration mounts
- Flexible sleeves on the evaporator side and the
- condenser side
- Flexible sleeves on the Heat exchanger
- Extra liquid reciver(62 liter)
- Compressor oil

High temperature (HT)	140 HT	280HT	3120HT	4150HT	4200H
Chiller units		Air Conditio	nina unit - Partly	indirect system	IL COTTO OVOXID
Refrigerant			R744		
Refrigeration output (kW)	44	88	132	176	200
Compressor (augntity)	1	2	3	4	4
Secondary fluid	2.		Water		
Temp of Secondary fluid (C°) In/Out	+12 /+7	+12 /+7	+12 /+7	+12 /+7	+12 /+7
Evaporation temperature (°C)	+2	+2	+2	+2	+2
Medium temperature (MT)	130 MT	260 M	NT	390MT	4120MT
Chiller units		Chiller	unit - Partly indir	ect system	
Refrigerant	R744				
Refrigeration output (kW)	26	52		78	104
Compressor (quantity)	1	2		3	4
Secondary fluid	Propylene glycol 37%				
Temp of Secondary fluid (C°) In/Out	-4/-8	-4/-8		-4/-8	-4/-8
Evaporation temperature (°C)	-12	-12		-12	-12
Low temperature (LT)	11517	230	T	345IT	460IT
Chiller units	Freezer unit - Partly indirect system				
Refrigerant		R744			
Refrigeration output (kW)	15	30		45	60
Compressor (quantity)	1	2		3	4
Secondary fluid			R744		
Temp of Secondary fluid (C°)	-30	-30		-30	-30
Evaporation temperature (°C)	-35	-35		-35	-35
Discharge temperature from gas cooler: +30°C	Refri outp as ai	geration outputs sh uts are preliminary mbient temperatury	own in the table and should be a and water tem	are based on desig letermined in actual perature will influence	n temperatures. Some operational conditions te the output values.







	SAFETY DATA SHEET	Page : 2 / 4 Revised edition no : Date : 15/7/2005 Supersedes : 0/0/0		
C	arbon dioxide	AL018A		
5 FIRE-FIGHTING MEASURES	(continued)			
Special protective equipment for fighters	or fire : In confined space use self-contained breathing ap	paratus.		
6 ACCIDENTAL RELEASE MEA	SURES			
Personal precautions	: Evacuate area. Wear self-contained breathing apparatus when er proved to be safe. Ensure adequate air ventilation.	tering area unless atmosph		
	Prevent from entering sewers, basements and wo accumulation can be dangerous.	: Try to stop release. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous.		
Clean up methods	: Ventilate area.			
7 HANDLING AND STORAGE				
Storage Handling	<ul> <li>Keep container below 50°C in a well ventilated pla</li> <li>Suck back of water into the container must be pre Do not allow backfeed into the container.</li> <li>Use only properly specified equipment which is su pressure and temperature. Contact your gas supp Refer to supplier's container handling instructions.</li> </ul>	ce. vented. itable for this product, its sι lier if in doubt.		
B EXPOSURE CONTROLS / PEF				
Personal protection Occupational Exposure Limits	: Ensure adequate ventilation. : Carbon dioxide : TLV© -TWA [ppm] : 5000 Carbon dioxide : TLV© -STEL [ppm] : 30000 Carbon dioxide : OEL (UK)-LTEL [ppm] : 5000 Carbon dioxide : OEL (UK)-STEL [ppm] : 15000 Carbon dioxide : MAK - Germany [ppm] : 5000	: Ensure adequate ventilation. : Carbon dioxide : TLV© -TWA [ppm] : 5000 Carbon dioxide : TLV© -STEL [ppm] : 30000 Carbon dioxide : OEL (UK)-LTEL [ppm] : 5000 Carbon dioxide : OEL (UK)-STEL [ppm] : 15000 Carbon dioxide : MAK - Germany [ppm] : 5000		
	ROPERTIES			
9 PHYSICAL AND CHEMICAL P	· Liquefied gen			
9 PHYSICAL AND CHEMICAL P Physical state at 20 °C	. Liquelled gas.			
PHYSICAL AND CHEMICAL P Physical state at 20 °C Colour	: Colourless.			
PHYSICAL AND CHEMICAL P Physical state at 20 °C Colour Odo(u)r	: Colourless. : No odour warning properties.			
<ul> <li>PHYSICAL AND CHEMICAL P</li> <li>Physical state at 20 °C</li> <li>Colour</li> <li>Odo(u)r</li> <li>Molecular weight</li> <li>Molecular point 701</li> </ul>	: Colourless. : No odour warning properties. : 44			
<ul> <li>PHYSICAL AND CHEMICAL P</li> <li>Physical state at 20 °C</li> <li>Colour</li> <li>Odo(u)r</li> <li>Molecular weight</li> <li>Melting point [°C]</li> <li>Boiling point [°C]</li> </ul>	: Colourless. : No odour warning properties. : 44 : -56.6 : 76.5 (c)			
<ul> <li>PHYSICAL AND CHEMICAL P</li> <li>Physical state at 20 °C</li> <li>Colour</li> <li>Odo(u)r</li> <li>Molecular weight</li> <li>Melting point [°C]</li> <li>Boiling point [°C]</li> <li>Critical temperature [°C]</li> </ul>	: Colourless. : No odour warning properties. : 44 : -56.6 : -78.5 (s) : 30			
<ul> <li>PHYSICAL AND CHEMICAL P</li> <li>Physical state at 20 °C</li> <li>Colour</li> <li>Odo(u)r</li> <li>Molecular weight</li> <li>Melting point [°C]</li> <li>Boiling point [°C]</li> <li>Critical temperature [°C]</li> <li>Vapour pressure 20°C</li> </ul>	: Colourless. : No odour warning properties. : 44 : -56.6 : -78.5 (s) : 30 : 57.3 bar			
<ul> <li>PHYSICAL AND CHEMICAL P</li> <li>Physical state at 20 °C</li> <li>Colour</li> <li>Odo(u)r</li> <li>Molecular weight</li> <li>Melting point [°C]</li> <li>Boiling point [°C]</li> <li>Critical temperature [°C]</li> <li>Vapour pressure, 20°C</li> <li>Relative density. gas (air=1)</li> </ul>	: Colourless. : No odour warning properties. : 44 : -56.6 : -78.5 (s) : 30 : 57.3 bar : 1.52			
<ul> <li>PHYSICAL AND CHEMICAL P</li> <li>Physical state at 20 °C</li> <li>Colour</li> <li>Odo(u)r</li> <li>Molecular weight</li> <li>Melting point [°C]</li> <li>Boiling point [°C]</li> <li>Critical temperature [°C]</li> <li>Vapour pressure, 20°C</li> <li>Relative density, gas (air=1)</li> <li>Relative density, liquid (water=</li> </ul>	: Colourless. : No odour warning properties. : 44 : -56.6 : -78.5 (s) : 30 : 57.3 bar : 1.52 1) : 0.82			
<ul> <li>PHYSICAL AND CHEMICAL P</li> <li>Physical state at 20 °C</li> <li>Colour</li> <li>Odo(u)r</li> <li>Molecular weight</li> <li>Melting point [°C]</li> <li>Boiling point [°C]</li> <li>Critical temperature [°C]</li> <li>Vapour pressure, 20°C</li> <li>Relative density, gas (air=1)</li> <li>Relative density, liquid (water=</li> <li>Solubility in water [mg/l]</li> </ul>	: Colourles gas. : Colourless. : No odour warning properties. : 44 : -56.6 : -78.5 (s) : 30 : 57.3 bar : 1.52 1) : 0.82 : 2000			
<ul> <li>PHYSICAL AND CHEMICAL P</li> <li>Physical state at 20 °C</li> <li>Colour</li> <li>Odo(u)r</li> <li>Molecular weight</li> <li>Melting point [°C]</li> <li>Boiling point [°C]</li> <li>Critical temperature [°C]</li> <li>Vapour pressure, 20°C</li> <li>Relative density, gas (air=1)</li> <li>Relative density, liquid (water=</li> <li>Solubility in water [mg/l]</li> <li>Flammability range [vol% in air]</li> </ul>	: Colourless. : Colourless. : No odour warning properties. : 44 : -56.6 : -78.5 (s) : 30 : 57.3 bar : 1.52 1) : 0.82 : 2000 : Non flammable.			







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### 5 FIRE-FIGHTING MEASURES (continued)

Special protective equipment for fire : In confined space use self-contained breathing apparatus. fighters

6 ACCIDENTAL RELEASE MEASURES		
Personal precautions	: Evacuate area. Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. Ensure adequate air ventilation.	
Environmental precautions	<ul> <li>Try to stop release. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous.</li> </ul>	
Clean up methods	: Ventilate area.	
7 HANDLING AND STORAGE		
Storage Handling	<ul> <li>Keep container below 50°C in a well ventilated place.</li> <li>Suck back of water into the container must be prevented. Do not allow backfeed into the container. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Contact your gas supplier if in doubt.</li> </ul>	
	Refer to supplier's container handling instructions.	

### 8 EXPOSURE CONTROLS / PERSONAL PROTECTION

Personal protection	: Ensure adequate ventilation.
Occupational Exposure Limits	: Carbon dioxide : TLV© -TWA [ppm] : 5000
	Carbon dioxide : TLV© -STEL [ppm] : 30000
	Carbon dioxide : OEL (UK)-LTEL [ppm] : 5000
	Carbon dioxide : OEL (UK)-STEL [ppm] : 15000
	Carbon dioxide : MAK - Germany [ppm] : 5000

### 9 PHYSICAL AND CHEMICAL PROPERTIES

Physical state at 20 °C	: Liquefied gas.
Colour	: Colourless.
Odo(u)r	: No odour warning properties.
Molecular weight	: 44
Melting point [°C]	: -56.6
Boiling point [°C]	: -78.5 (s)
Critical temperature [°C]	: 30
Vapour pressure, 20°C	: 57.3 bar
Relative density, gas (air=1)	: 1.52
Relative density, liquid (water=1)	: 0.82
Solubility in water [mg/l]	: 2000
Flammability range [vol% in air]	: Non flammable.
Other data	: Gas/vapour heavier than air. May accumulate in confined spaces, particularly at or below ground level.

#### AIR LIQUIDE SA France







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	Carbon dioxide			
10 STABILITY AND REACTIV	VITY			
Stability and reactivity	: Stable under normal conditions.			
11 TOXICOLOGICAL INFOR	MATION			
Toxicity information	: In high concentrations cause rapid circulatory insu headache, nausea and vomiting, which may lead t	fficiency. Symptoms are o unconsciousness.		
12 ECOLOGICAL INFORMA	TION			
Ecological effects informati Global warming factor [CO2	<ul> <li>on : When discharged in large quantities may contribut</li> <li>2=1] : 1</li> </ul>	e to the greenhouse effect.		
13 DISPOSAL CONSIDERAT	IONS			
General	: Do not discharge into any place where its accumul To atmosphere in a well ventilated place. Discharge to atmosphere in large quantities should Contact supplier if guidance is required.	: Do not discharge into any place where its accumulation could be dangerous. To atmosphere in a well ventilated place. Discharge to atmosphere in large quantities should be avoided. Contact supplier if guidance is required.		
14 TRANSPORT INFORMAT	ION			
UN No.	: 1013			
H.I. nr	: 20			
ADR/RID				
- Proper shipping name	: CARBON DIOXIDE			
- ADR Class	: 2			
- ADR/RID Classification co	de : Z A			
- Labelling ADR	Laber 2.2 . Non irammable, non toxic gas.     Avoid transport on vehicles where the load space i	s not separated from the driver's		
	compartment. Ensure vehicle driver is aware of the potential haze to do in the event of an accident or an emergency. Before transporting product containers	<ul> <li>Avoid transport on venicles where the load space is not separated from the driver's compartment.</li> <li>Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency.</li> <li>Before transporting product containers :</li> </ul>		
	<ul> <li>Ensure that containers are firmly secured.</li> </ul>			
	<ul> <li>Ensure cylinder valve is closed and not leaking.</li> <li>Ensure valve outlet can put or plug (where provid</li> </ul>	led) is correctly fitted		
	<ul> <li>Ensure valve outlet cap nut of plug (where provided)</li> <li>Ensure valve protection device (where provided)</li> </ul>	is correctly fitted.		
	<ul> <li>Ensure there is adequate ventilation.</li> <li>Compliance with applicable regulations.</li> </ul>			
	approase regulatere.			
15 REGULATORY INFORMA	TION			
EC Classification	: Not classified as dangerous preparation/substance Not included in Annex I.	: Not classified as dangerous preparation/substance. Not included in Annex I.		
EC Labelling	: No EC labelling required.			
- Symbol(s)	: None.			
- R Phrase(s)	: None.	: None.		
<ul> <li>S Phrase(s)</li> </ul>	: None.			
AIR LIQUIDE SA				

France







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		Revised edition no : 1
		Date : 15/7/2005
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Carbon dioxide		AL018A

### **16 OTHER INFORMATION**

Asphyxiant in high concentrations.

Keep container in a well-ventilated place.

Do not breathe the gas.

Contact with liquid may cause cold burns/frostbite. Ensure all national/local regulations are observed.

The hazard of asphyxiation is often overlooked and must be stressed during operator training.

This Safety Data Sheet has been established in accordance with the applicable European Directives and applies to all countries that have translated the Directives in their national laws.

Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.

Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted.

Recommended uses and restrictions : This SDS is for information purposes only and is subject to change without notice. [ Prior to purchase of products, please contact your local AIR LIQUIDE office for a complete SDS (with Manufacturer's name and emergency phone number).]

End of document

AIR LIQUIDE SA France







# **SELECTED REFERENCES**

Further documents and information can be found from the following Internet web sites :

www.sherhpa.com

www.r744.com

www.danfoss.com

www.itomic.co.jp

www.sanyoaircon.com

www.heatpumpcentre.org

www.agramkow.dk

www.greenandcool.se

http://www.ctc-heating.com