TRANSCRITICAL CO_2 HEAT PUMPING SYSTEMS

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ABSTRACT

The paper outlines key developments of transcritical CO_2 systems, mainly focusing on projects where SINTEF and Shecco have been or are involved. CO_2 as refrigerant in heat pumping systems has gained interest due to its environmental and safety advantages. The paper reviews applications where transcritical CO_2 systems have been introduced in the market and applications where developments are ongoing. These include heat pump water heaters, heat pumps for space heating, and mobile air conditioning and heat pump systems. Both technology and market information is presented. Where applicable, comparison to alternative system technology will be made.

Initially, a brief summary of environmental issues and an introduction to the particulars of CO_2 as a refrigerant is given, before the status and trends within selected areas of the technology are discussed. It is shown that CO_2 is a viable alternative refrigerant for all these application areas.

Keywords*: Carbon dioxide, CO_2, heat pumps, natural refrigerants, refrigeration.*

1 INTRODUCTION

Although CO_2 (R-744) was widely used as refrigerant in the early 20th century, its use disappeared from around 1940 with the advent of the fluorocarbon refrigerants. Triggered by the proposed ban of CFCs in the Montreal Protocol 1987, Professor Gustav Lorentzen at NTNU/SINTEF in the late 1980s proposed to reconsider the use of CO_2. Increasing focus on environmental issues of fluorocarbon chemicals created a strong interest in systems using natural refrigerants in general, and CO_2 in particular due to its non-flammability and non-toxicity (Lorentzen and Pettersen 1992). This was later reinforced by the inclusion of the HFCs in the Kyoto Protocol 1997.

New concepts of high-side pressure control in what came to be called a “transcritical” cycle were devised in early patent applications by Gustav Lorentzen and his co-workers. The industrial group Norsk Hydro acquired all commercial rights to this technology in 1990, and a joint R&D program at SINTEF/NTNU in the early 1990s demonstrated the feasibility and competitiveness of the technology. Norsk Hydro offers licenses and technology development under the trademark Shecco™ (www.shecco.com).

CO_2 systems have proven to be viable alternatives in several applications. The first full scale commercial use of transcritical CO_2 systems was in Japan 2001 with the launch of the EcoCute heat pump water heaters. Until now some 60-70 prototype cars have been equipped with CO_2 based A/C, including fuel cell hybrid vehicles. Commercial refrigeration systems for full supermarket systems have been introduced, and very soon light commercial refrigeration units will be launched. The Coca Cola Company in June 2004 announced that CO_2 based refrigeration is their current choice for future sales and marketing equipment (TCCC 2004).

This paper concentrates on heat pumping systems featuring transcritical operation. There has been an extensive development during the last 10 years in using CO_2 as a volatile heat transfer fluid for indirect systems or in a low temperature stage of cascade systems, especially within industrial and commercial applications, but such applications are not discussed in this paper.

2 EMISSIONS AND REGULATORY ISSUES OF REFRIGERANT USE

Since the discovery in 1974 that CFCs devoured the ozone layer, the fluorocarbon refrigerants have been under increasing scrutiny and periodical attack, first due to their ozone depletion, later also from their strong greenhouse effect.

The Montreal Protocol 1987 was one of the first comprehensive international agreements with a fixed timetable for global phase-out of a group of chemicals. The immediate refrigerant alternatives were the less harmful HCFCs, but they are also gradually being phased out. The EU has banned HCFC refrigerants in new equipment from 2001, leaving HFCs as the only fluorocarbon option.

The biggest source of fluorocarbon emissions in the late 80s was leakages from automotive air-conditioning (MAC).This triggered an early response from the car industry to phase out their use of CFCs. The industry in 1990-91 agreed to adopt HFC-134a as their common non-ODP refrigerant, and since 1995-96 all new car ACs in the OECD area are filled with this refrigerant. However, by 1995 global warming and curbs to greenhouse gas emissions had risen to the top of the agenda. The fluorocarbons (F-gases) are among six greenhouse gases listed in the 1997 Kyoto Protocol to be monitored with the purpose of reducing GHG emissions.

A study made for the German environmental agency (Schwarz 2000) shows that a full replacement of HFC-134a by CO_2 in mobile AC systems from 2007 would cut the greenhouse gas emissions of Germany by 1 million tonnes CO_2-equivalents in 2010 and completely eliminate the emissions by 2021, Fig. 1. A comprehensive study using statistical data from German automobile workshops showed that the average annual emission rates relative to the system charge from HFC-134a in mobile AC systems was 10.2% (Schwartz 2002).

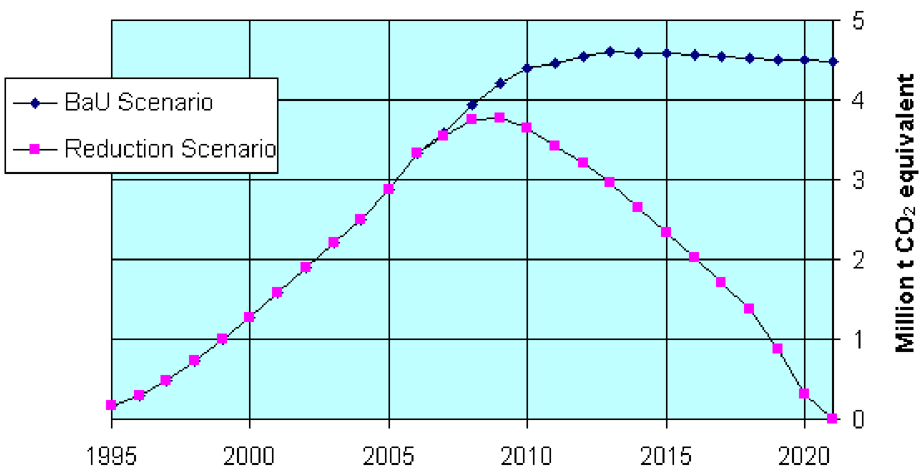

Fig. 1. Refrigerant emissions (in million tonnes CO_2-equivalents) from mobile AC systems in Germany, using a Business-as-Usual scenario (BaU) and a reduction scenario with phase-in of CO_2-based AC systems from 2007. From Schwartz (2000).

Commercial refrigeration systems for shops, supermarkets, larger kitchens etc. also have large refrigerant emissions. Palandre et al. (2004) reported that commercial refrigeration on average has annual leakage rates around 30% of the system charge. A recent study of a chain of 220 supermarkets in Norway showed a leakage rate of 14% (not including stand-alone equipment) (Veiby 2003). The Norwegian supermarket chain has a great focus on the issue, so the percentage is probably in the lower end of the sector leakage rates. Leakage reduction has also been encouraged in Norway through the introduction of very high CO_2 (greenhouse gas) taxes on F-gases.

After extensive stakeholder consultations the European Commission in August 2003 proposed legislation to reduce emissions of fluorinated greenhouse gases (the so-called F-gases: HFCs, PFCs,

SF_6) (EC 2003). Annual emissions from leakages in the automotive sector is expected to increase from 1.4 mill t in 1995 to 20 mill t CO_2-equivalents in 2010 without any measures, with a similar volume of refrigerants leaking from the stationary refrigeration sectors in 2010. Together the two sectors will represent over 40% of projected EU F-gas emissions in 2010.

The legislation includes a complete ban on HFC-134a in MAC from 2013 after a phase out period starting 2009. The legislation is still in progress, but is likely to conclude with a ban on refrigerants with a GWP above 150 in new vehicle types (platforms) from 2011, allowing flammable HFC-152a as well as hydrocarbons as alternatives, in addition to CO_2. Due to the wide variety of non-automotive refrigeration and heat pump applications and technologies, the legislation does not propose phase-out of HFCs in these sectors, but instead focuses on strict monitoring, training and recovery.

The US is not proposing any new legislation to reduce F-gas emissions from any sector of refrigeration, while in Japan there is a voluntary agreement with the car industry to reduce emissions. The California Air Resources Board has proposed legislation to reduce total GHG emissions from cars, including both drive train and air conditioning system. This encourages use of CO_2 in MAC to earn credits in the system. The US and Japan for several years have had regulations for training and recovery activities in the sector, which have been mostly absent in Europe. The European and Japanese car industry has accepted the gradual phase out of HFC-134a, while the US industry has not finally decided on its course of action.

3 CARBON DIOXIDE AS A WORKING FLUID

Compared to conventional refrigerants, the most remarkable property of CO_2 is the low critical temperature of 31.1^{o}C. Vapour compression systems with CO_2 operating at normal ambient temperatures thus work close to and even above the critical pressure of 73.8 bar. This leads to three distinct features of CO_2 systems:

- **Heat is rejected at supercritical pressure** in many situations. The system will then use a *transcritical* cycle that operates partly below and partly above the critical pressure. High-side pressure in a transcritical system is determined by refrigerant charge and not by saturation pressure. The system design thus has to consider the need for controlling high-side pressure to ensure sufficient COP and capacity. An example of the measured effect of varying high-side pressure (compressor discharge) on heating capacity and COP in a heat pump water heater system is shown in Fig. 2.
- **The pressure level in the system will be quite high** (around 30-100 bar) but the thermodynamic properties of CO_2 allow significant reduction of inner diameters of tubes. Components therefore have to be redesigned to fit the properties of CO_2. Due to smaller volumes of piping and components, the stored explosion energy in a CO_2 system is not much different from a conventional system (Pettersen 1999). A benefit of high pressure is the 80-90% smaller compressor displacement needed for a given capacity. Compressor pressure ratios are low, thus giving favourable conditions for high compressor efficiency.
- **Large refrigerant temperature glide during heat rejection**. At supercritical or near-critical pressure, all or most of the heat transfer from the refrigerant takes place by cooling the compressed gas. The heat rejecting heat exchanger is then called *gascooler* instead of condenser. Gliding temperature can be useful in heat pumps for heating water or air. With proper heat exchanger design the refrigerant can be cooled to a few degrees above the entering coolant (air, water) temperature, and this contributes to high COP of the system.

Several interesting end-user features also result from the near critical operation:

- **High temperature yield**. Water up to 90^{o}C can easily be produced, allowing for direct use in food and beverage industry, hotels, restaurants and hospitals requiring sterilisation etc.
- **Low temperature source.** The system may maintain a relatively high efficiency at very low heat absorption temperatures, i.e. at –25^{o}C or lower.

- **High volumetric capacity**. The thermodynamic properties resulting in high volumetric capacity allow much faster cooling (pull down) and heating than conventional HFC systems. This is of particular interest in cars to reach comfortable temperature more quickly, or fast defogging or defrosting of windows.
- **Downsizing**. The good thermodynamic properties allow reduction of pipe diameters, and also of total heat exchanger size. The latter is useful in applications where space is at a premium (cars, aircraft).

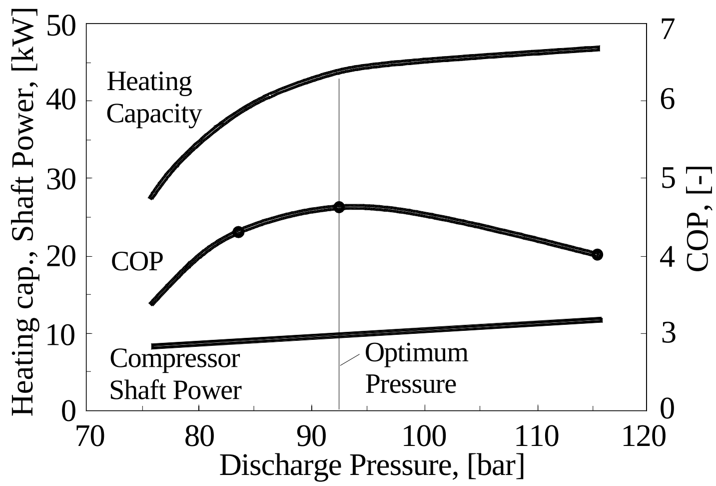

Fig. 2. Variation of heating capacity, heating-COP and compressor shaft power with the discharge pressure for a CO_2 heat pump water heater.

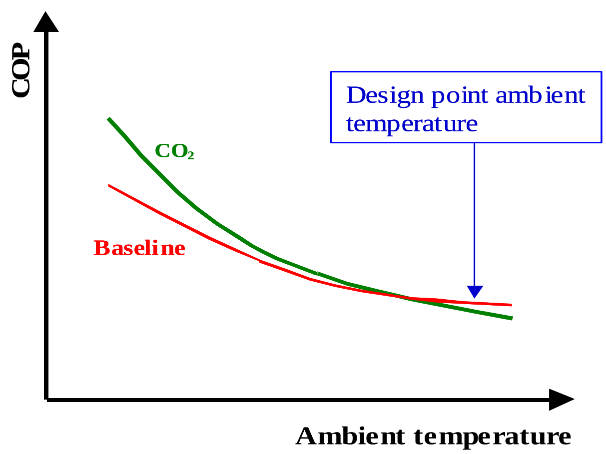

Fig. 3. Principal COP behaviour of CO_2 system and conventional (baseline) system at varying ambient temperature.

Experience from testing and modelling of CO_2 refrigeration and air conditioning systems shows that cooling COP is more sensitive to ambient temperature variation than conventional refrigerants. This typically leads to the situation shown in Fig. 3, where the CO_2 system is superior at moderate and low ambient temperature, but slightly inferior at very high temperature. The crossover for some applications lies around 35°C (95F). However, the capacity of the CO_2 system to deliver cooling at very high ambient is not inferior. In this situation, it is misleading to base the comparison on extreme, high ambient temperature design-point conditions. For the user, the total annual energy consumption to achieve the desired cooling is more relevant. This means using mean/average conditions, or an analysis based on actual seasonal variations.

4 EFFICIENT HEAT PUMP WATER HEATERS

The first regular commercial application of CO_2 systems is heat pump water heaters, where the thermodynamic properties are very favourable. Fig. 4 shows, in a temperature-entropy diagram, how the temperature characteristics of the transcritical cycle matches the temperature profiles of the heat source and heat sink, giving small heat transfer losses and high efficiency.

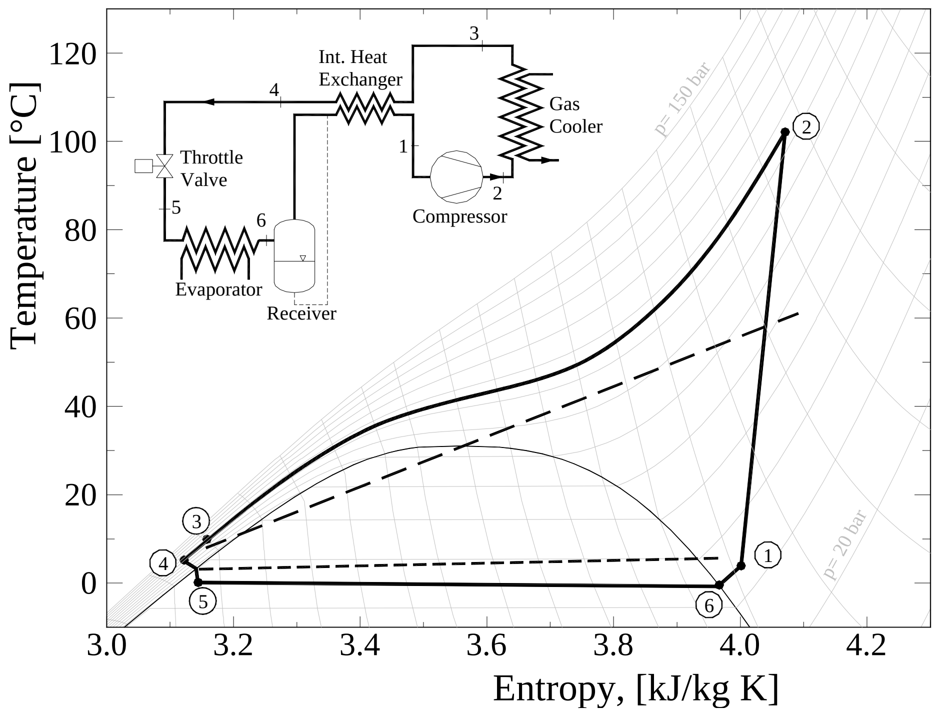

Fig. 4. T-s-diagram showing the transcritical CO_2 cycle used for water heating.

Fig. 5. 50-kW prototype heat pump water heater in SINTEF/NTNU laboratory

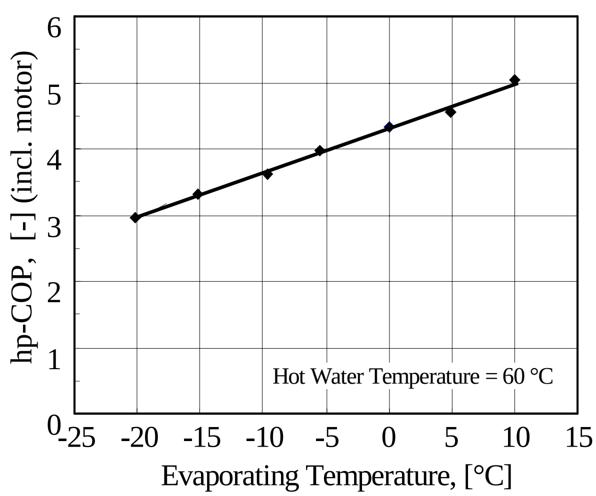

Fig. 6. Measured heating COP of laboratory prototype system, at water inlet temp 10^{o}C

Studies on CO_2 heat pump water heaters were initiated at SINTEF/NTNU from the late eighties, and a full-scale laboratory prototype system of 50 kW heating capacity was completed in 1996, Fig. 5. Results from extensive measurements on this early prototype showed that a COP above 4 was achievable for a hot water temperature of 60^{o}C, Fig. 6 (Nekså, et al. 1998). Increasing the required hot water temperature from 60°C to 80°C reduces the heating COP from 4.3 to 3.6 at an evaporating temperature of 0°C. The high process efficiency is partly due to good adaptation of the process to the application, but also due to efficient compression and the good heat transfer characteristics for CO_2. Thus one of the big advantages of this technology is the ability to supply water at high temperature with good COP. Important application areas for commercial-size systems are in hotels, apartment houses, hospitals and food industries.

A 25 kW pilot plant was installed in a food-processing factory in Larvik, Norway in 1999, using waste heat from an industrial NH_3 refrigerating system as a heat source. Performance exceeded the initial expectations with a COP around 5.5 during is first two years of operation (Zakeri et al. 2000).

In 2001, Denso Corporation, together with the major Japanese utilities, incl. Tokyo Electric (TEPCO) and Kansei Electric (KEPCO), launched a small CO_2 hot water heat pump for family homes based on the Shecco™ technology. Later Sanyo and Daikin have entered the market with the same technology. The first generation units had 4-5 kW heating capacity, storage tanks of 300-400 litre capacity, and were intended only for hot tap water. Second generation units were launched late 2003, with heating capacity up to 8 kW, and include additional outlets for floor heating, hot water to fan dryer, and a bath tub warm water circulation circuit. Together the three primary manufacturers in 2004 sold over 100 000 units through a dozen brands.

Marketed under the common trade name of *Eco Cute* (Japanese pronunciation has the meaning environmental "supply of hot water"), the Japanese government has subsidised the launch with some 20% of the consumer installation price. The Japanese government has publicly targeted an accumulated volume of over 5 mill units by 2010 to enable a reduction in domestic sector GHG emissions of 3%.

The success of the Eco Cute in Japan is due to three factors. Japanese families use more hot water than anyone else, some 37% of home energy consumption, and mostly for a hot tub bath. Secondly the utilities have offered special low night power tariffs, saving the families some 80% of the energy cost for hot water. And finally the government supported the initiative through subsidies because of the contribution to reduced GHG emissions in Japan.

Interestingly the Eco Cute units are all air-source units, avoiding the considerable cost of ground heat loops. In particular, the manufacturers offer special models adapted to cold northern Japan with ambient temperatures below –20C. The solutions include both appropriately designed evaporators as well as optimised reverse flow circuitry (Mukaiyama 2003).

Both Denso and Sanyo in 2004 presented their Eco Cute units at HVACR fairs in Europe to sample market interest.

Since 2003 Carrier/UTRC is actively developing commercial HPWH units of 60kW heating capacity for the US market with financial support from the Department of Energy (In Hot Water 2004, UTC 2003). The company also runs a parallel product development programme for the European market. Several prototypes have been placed with big users of hot water for field-testing and verification.

Concepts combining tap water heating with cooling purposes is also a very interesting option, especially for hot climates zones. Adriansyah (2001, 2003) investigated this option in detail with very interesting results. However, in northern climate zones the combination of hot tap water at 60°C with central water heating systems is important for market success. In a space heating circuit the return water temperature is relatively high, some 30°C in a floor circuit or some 40°C in traditional radiators. The standard transcritical CO_2 system is not so efficient lifting this back to 60°C or 70°C. Alternative solutions are presently being researched at SINTEF in cooperation with Shecco Technology (see also Stene 2004).

5 MOBILE AIR CONDITIONING

Lorentzen and Pettersen (1992) published the first experimental data on CO_2 in a mobile air conditioning laboratory prototype system in 1992, demonstrating COP data that were competitive to baseline CFC-12 system performance. Based on these positive test results, the automobile industry initiated several development projects and further studies on CO_2 systems. The European RACE project from 1994 to 1997 included development and testing of car-installed prototype systems, with results confirming the potential for CO_2-based car air conditioning (Gentner 1998). Members in the RACE project included car manufacturers (BMW, Daimler-Benz, Rover, Volvo, Volkswagen), system suppliers (Behr, Valeo), and a compressor manufacturer (Danfoss).

Since the late 1990s, the German Motor Vehicle Industry Association (VDA) has coordinated development and testing of CO_2 systems, and several car manufacturers have had test vehicles on the road since the late nineties. Mager et al. (2002) presented studies by BMW, Audi and DaimlerChrysler showing consistent results by the three companies:

- higher performance in cool-down mode for R-744 (CO_2) than for R-134a
- lower compartment temperature and faster temperature pull-down with R-744
- reduced fuel consumption for R-744 system

A presentation given in 2003 by a group of 17 members from car manufactures and companies involved in manufacturing of MAC systems worldwide, considered CO_2 systems the most promising alternative, and estimated that the remaining technical issues can be solved within 2 to 3 years (Mager et al. 2003).

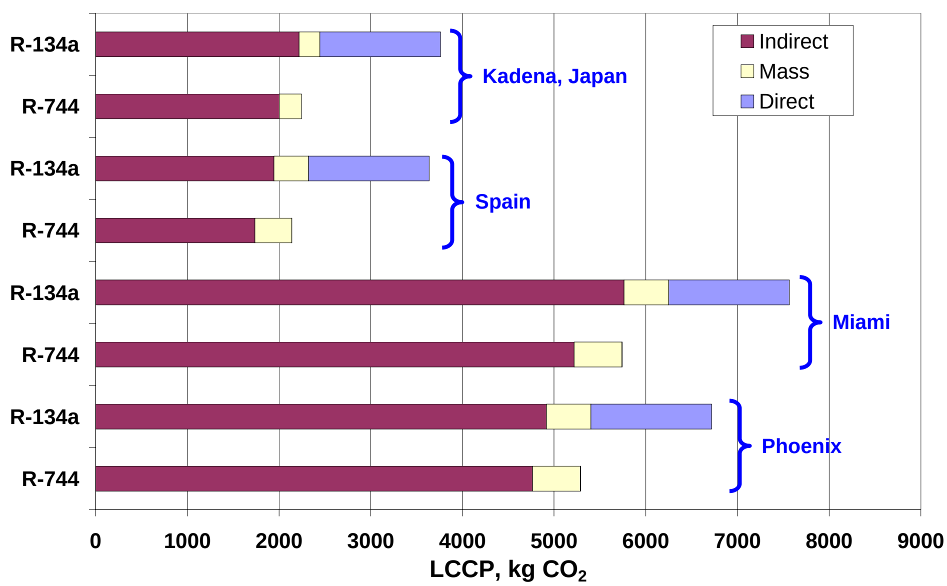

Fig. 7. LCCP comparison between enhanced R-134a and enhanced CO_2 (R-744) systems for warm climates (R-134a leakage: 80 g/year). Contribution due to fuel consumption for running the ac-system (indirect), fuel consumption due to the ac-system mass (mass) and direct contribution due to leakage (direct) are shown. From Pettersen and Nekså. (2003).

Based on data from the SAE Alternative Refrigerant Program (Hrnjak 2003), a Life Cycle Climate Performance (LCCP) study was conducted by Pettersen and Nekså (2003) and Hafner et al (2004). It showed 20-40% reduced LCCP values for the CO_2 (R-744) system compared to the enhanced R-134a system (Fig. 7). In particular, it was shown that the fuel consumption to run the air conditioning system would be significantly less for the CO_2 system, and was equally good even in the very hot climate of Arizona.

Summarizing the SAE Alternate Refrigerant Cooperative Research Program 2002-2004, Wertenbach (2004) reported that the energy consumption of Enhanced R-134a and R-744-2002 where 23% and 31% lower than Baseline R-134a (European annualised driving cycle, NEDC).

City bus air conditioning systems with CO_2 have also been developed, and the results from two years (1800 hours) of road testing are very positive (Köhler 1999). For applications in public transport CO_2 is probably the only alternative to HFC-134a due to the flammability of HFC-152a and hydrocarbons in the large volumes required in a bus (10-15 kg). Such charge size of flammable refrigerants would require extensive measures influencing cost, system weight and energy efficiency due to safety.

The automotive industry has been worried that the high pressure CO_2 systems would lead to increased weight. However, the high volumetric efficiency provides for smaller internal volumes enabling downsizing of components. Parsch (2002) showed a compressor where the potential for a compact design with CO_2 has been exploited, Fig. 8. In a recent paper, Wolf (2005) presented a CO_2 fixed displacement compressor weighing 700 g less than a similar capacity HFC-134a compressor. Adding the potential downsizing of the heat exchangers due to the high capacity of CO_2, the total weight and thus future production cost will be on par with state of the art HFC-134a systems.

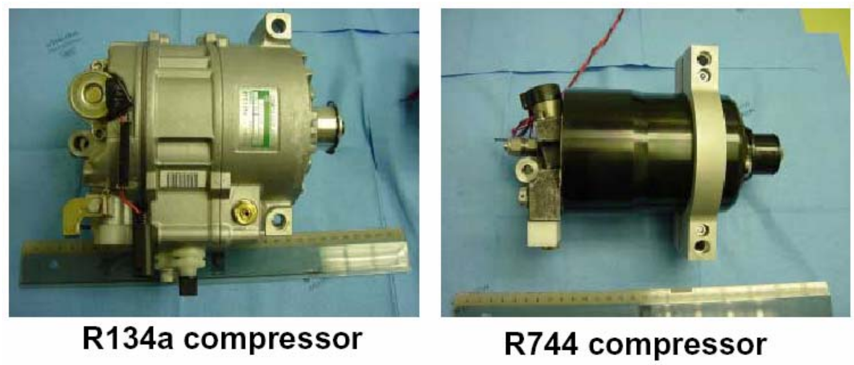

Fig. 8. Mobile AC compressors with variable displacement. State-of-the-art HFC-134a design (left) and a design for CO_2 by LuK-Sanden (right). From Parsch (2002).

6 HEAT PUMPS IN AUTOMOBILES

Modern diesel or hybrid engine cars have insufficient waste heat for heating the passenger compartment in winter, and they are mostly equipped with fuel burning supplementary heating. The long heating-up period and slow defroster action from the engine heat is unacceptable both in terms of safety and comfort. An attractive alternative is to operate the air conditioning system as a heat pump. Carbon dioxide systems have special benefits in heat pump mode even at ambient temperatures below -20C An added advantage of CO_2 heat pumps is the almost instant high capacity in heating mode, enabling very fast defrosting on a cold morning, and generally much faster heating of the passenger compartment compared to standard heating.

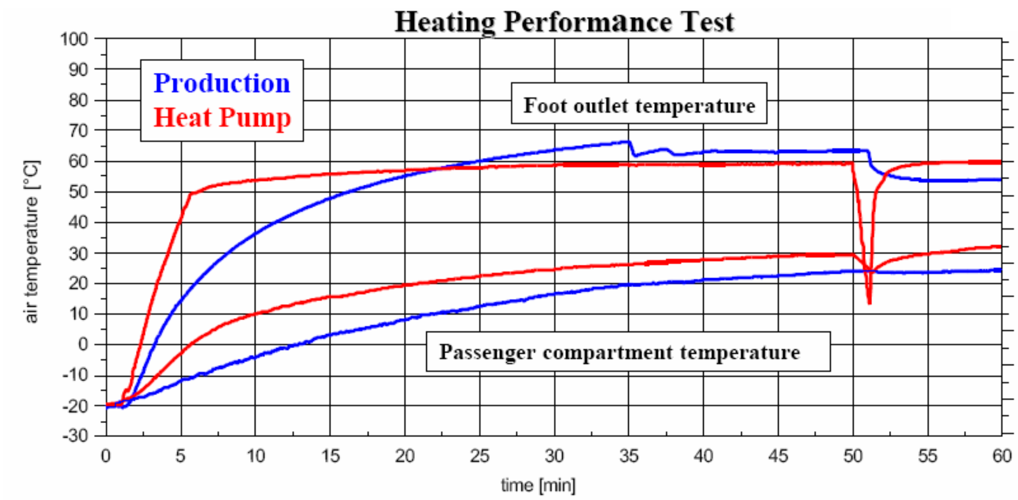

Fig. 9. Measured air temperatures in during start-up of an Audi A4 test vehicle (”Production”) and same car with CO_2 heat pump (“Heat pump”). From Hammer and Wertenbach (2000).

Hammer and Wertenbach (2000) showed test data for an Audi A4 car with 1.6-litre gasoline engine, comparing a standard heater and a CO_2 heat pump system based on engine coolant as heat source. Figure 9 shows measured air temperatures at foot outlet nozzles and passenger compartment temperatures using standard heater core (“Production”), and a CO_2 heat pump system (“Heat Pump”).

The CO_2 heat pump demonstrates almost 50% reduction in the heating-up time from –20 to +20^{o}C. Since the heat pump used engine coolant as heat source, the possible risk of extended heating-up time for the engine was of some concern. Measurements showed that owing to the added load on the engine by the heat pump compressor, the heating-up time was in fact slightly reduced even when heat was absorbed from the coolant circuit.

Hafner et al. (1998) proposed an advanced circuit for reversible cooling and heating, but work is also progressing on simplified system concepts for internal-combustion engine cars and electric/hybrid vehicles.

Systems using air as heat source will be simpler and less costly, and there is quite some interest in clarifying the practical possibilities and limits of reversible air-to-air systems. Frost build up may in many situations be slow enough to allow heat pump operation until the heating system can take over, and solutions may be developed that control and delay frost build up.

7 HEAT PUMPS FOR SPACE HEATING

Until now, most of the interest in CO_2 heat pumps has been for tap water heating. As shown above, the Japanese HPHW market is in the process of being extended to water based central heating. The other extension is hot air supply.

Nekså (2002) investigated several options within a system design as shown in Fig. 10. To achieve a lowest possible return temperature from the heating system, radiator and air heating are connected in series. Tap water is pre-heated in parallel with the space heating and heat exchange against hot discharge gas is used to achieve the required hot water temperature.

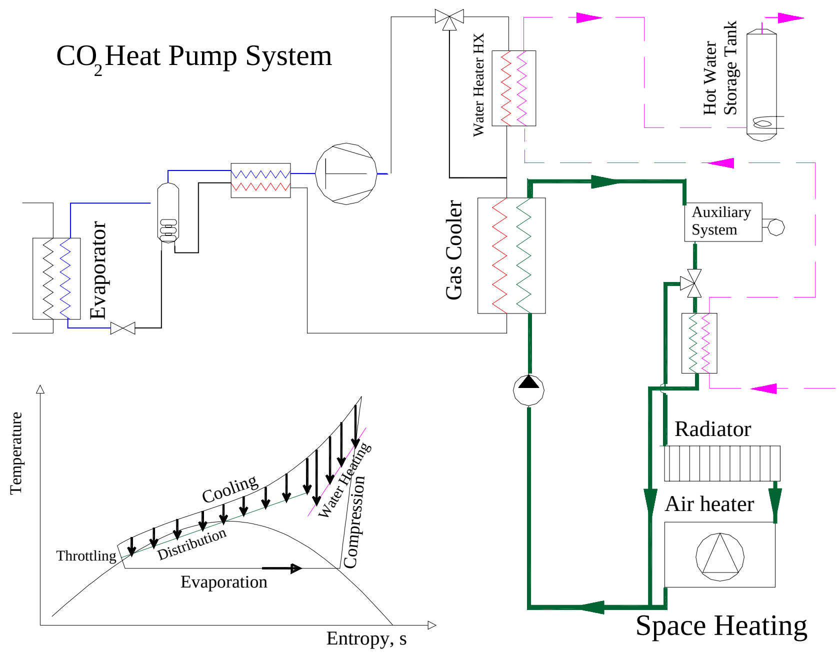

Fig. 10. System design for a combined space and water heating system. The process is also illustrated in the T-s diagram.

A comparison with a system using HFC-134a as working fluid showed favourable seasonal performance for the CO_2 system when more than 30% of the heating demand for space heating was from the air heating system, and the rest from the radiator system. In large commercial buildings in Norway more than 50% of heating demand is air heating and this percentage is increasing due to better insulation and increased air quality requirements. This indicates that CO_2 is a promising candidate for this application. The system may easily be implemented as an air conditioning system in the summer.

Residential heat pumps without air conditioning are quite common in northern Europe, and in certain other areas in the world. Stene (2004) studied both experimentally and theoretically a residential brine to water CO_2 heat pump for combined space heating and hot water heating. He found that the seasonal performance factor of integrated CO_2 brine to water heat pump system was competitive to state of the art systems if the tap water heating demand constituted minimum 25% of the total annual heating demand and if the return temperature for the space heating system was sufficiently low (30°C). It was crucial to avoid heat transfer from hot to cold water in the storage tank.

Rieberer and Halozan (1998) made detailed theoretical studies of controlled ventilation air heating systems with an integrated CO_2 heat pump with very promising results. The overall system seasonal performance factor for a Graz, Austria climate was calculated to be in the range 6.15 to 6.5. This corresponds to a seasonal performance factor of the heat pump of above 4 (author's remark).

Ground source heat is important as heat source for heat pumps in Europe. The brine systems frequently used may cause problems regarding polluting ground water if leakages occur. Both Univ. of Graz (Halozan et al. 2003) and FKW in Hanover have developed earth probe systems with CO_2. The probes are filled with CO_2 and collecting heat from the ground by evaporation and rejecting heat in a cold head as heat source for a heat pump. The principle can be compared to that of a heat pipe. Very promising results have been reported, and the product is already commercialised.

Several studies have investigated air-to-air reversible heat pumps with CO_2 as refrigerant. This has been well summarised in Kim et al. (2004). In general it was found that the CO_2 heat pumps compete with the HFC systems in heat pump mode, while air conditioning mode at high ambient temperatures lacked in efficiency. Even though the annual performance for the CO_2 systems in cold climates may be superior, these systems have not yet found their way to the market. SINTEF is doing development work on an Asian/European type of mini-split system, using a state of the art R-410A system as baseline. So far, the CO_2 system performs better than the baseline system in heating mode, while lacking somewhat in efficiency in cooling mode. Heat exchangers better adapted to reversed cycle operation are expected to improve the system performance.

8 CONCLUSION

The revival of CO_2 as a refrigerant started in Europe more than 15 years ago, and there has been a strong development of new technology worldwide using this refrigerant in several application areas since then. Developments which initially were driven primarily by environmental concerns have often resulted in disclosing additional advantages by using CO_2, such as higher COP, higher cooling and heating capacity, better comfort, and added possibilities of heat recovery.

Cost- and energy efficient systems have been developed and commercialised for some applications and more seem to come in the near future. The most important applications are heat pump water heaters, heat pumps for space heating and air conditioning, mobile air conditioning and heat pumps, and commercial refrigeration systems.

With increasing focus on climate gas emission reductions, strict regulations on the use of HFC chemicals may be expected, possibly followed by phase-out targets and dates as announced by some European countries. These trends will clearly drive the interest in the direction of natural refrigerants in general and CO_2 in particular.

9 REFERENCES

Adriansyah W. 2001. "*Combined Air-conditioning and Tap Water Heating Plant, Using CO_2 as Refrigerant for Indonesian Climate Condition*", Dr.ing (PhD) thesis no. 2001:54, Norwegian University of Science and Technology, Trondheim, Norway.

Adriansyah W. 2003. Development of combined air conditioning and tap water heating CO_2 test rig in Indonesia - Preliminary results. *International Conference on Fluid and Thermal Energy Conversion*, FTEC 2003, Bali, Indonesia.

EC 2003. Proposal for a European Parliament and Council Regulation on certain fluorinated gases. *COM (2003) 492 Final, 2003/0189 (COD).* Brussels, Belgium.

Gentner H. 1998. "Passenger car air conditioning using carbon dioxide as refrigerant". *Proc. Natural Working Fluids'98, IIR-Gustav Lorentzen Conference on Natural Working Fluids*. Oslo, Norway.

Hafner A., J. Pettersen, G. Skaugen, P. Nekså 1998. "An Automobile HVAC System with CO_2 as the Refrigerant". *IIR – Gustav Lorentzen Conference on Natural Working Fluids*. Oslo, Norway.

Hafner A., P. Nekså and J. Pettersen 2004. "Life Cycle Climate Performance (LCCP) of Mobile Air-Conditioning Systems with HFC-134a, HFC-152a and R-744", *Mobile Air Conditioning Summit 2004*, Earth Technologies Forum. Washington D.C.

Halozan, H., R. Rieberer et al. 2003. "Direct expansion ground coupled heat pumps". *Proceedings of the 21st IIR Int. Congress of Refrigeration*. Washington, D.C.

Hammer H., and J. Wertenbach 2000. "Carbon dioxide (R-744) as supplementary heating device". *SAE Automotive Alternate Refrigerants Systems Symposium 2000.* Scottsdale, Arizona.

Hrnjak P. 2003. "Design and performance of improved R744 system based on 2002 technology". *SAE Automotive Alternate Refrigerant Systems Symposium 2003*. Scottsdale AZ, USA.

In Hot Water 2004. "United Technologies Research Center Developing Commercial HPWH using CO2 Refrigerant." *In Hot Water (Newsletter)*, Vol.2, Issue 4 (March 2004), pp.3-4

Kim M.H., J. Pettersen and C. Bullard 2004. "Fundamental process and system design issues in CO_2 vapor compressin systems". *Progress in Energy and Combustion Science*, Vol 30, pp. 119-174.

Köhler J. 1999. "Update – Second year of CO_2 air conditioning operation on German city bus". *SAE Automotive Alternate Refrigerants Symposium 1999.* Scottsdale, Arizona.

Lorentzen G., and J. Pettersen 1992. "New Possibilities for Non-CFC Refrigeration". *International Symposium on Refrigeration, Energy and Environment.* Proceedings, pp. 147-163. Trondheim, Norway.

Mager R., H. Hammer, J. Wertenbach 2002. "Comparative Study on AC and HP-systems using the Refrigerants R-134a and R-744".- *VDA Alternate Refrigerant Wintermeeting 2002.* Saalfelden, Austria.

Mager R. et al. 2003. "New Technology: CO_2 (R-744) as an Alternative Refrigerant", *MAC Summit 2003*, EU Commission, Brussels, Belgium.

Mukaiyama H. 2003. "Development and performance evaluation of CO2 heat pump water heaters for cold climates". *IEA Heat Pump Centre Newsletter*, Vol. 21, No. 4, pp.9-12.

Nekså P., H. Rekstad, G.R.Zakeri and P.A.Schiefloe 1998. "CO_2-Heat Pump Water Heater: Characteristics, System Design and Experimental Results", *Int. Journal of Refrigeration*, Vol. **21**: 172-179.

Nekså P. 2002. "CO_2 Heat Pumps". *Int. Journal of Refrigeration*, Vol. 25, pp. 421-427.

Palandre L., D. Clodic, and L. Kuijpers 2004. "HCFCs and HFCs emissions from the refrigerating systems for the period 2004-2015". *Earth Technologies Forum 2004, Washington D.C.*

Parsch W. 2002. "Status of Compressor Development for R-744 Systems", *VDA Alternate Refrigerant Wintermeeting*, Saalfelden, Austria.

Pettersen, J. 1999. "Comparison of explosion energies in residential air-conditioning systems based on HCFC-22 and CO_2", *20^{th} International Congress of Refrigeration (IIR)*, Sydney, Australia.

Pettersen J. and P. Nekså 2003. "Consequences of the Newest Improvements in R-744 Systems". *SAE Automotive Alternate Refrigerant Systems Symposium*, Scottsdale AZ, July, USA.

Rieberer R. and H. Halozan 1998. "CO_2 heat pumps in controlled ventilation systems".. *3^{rd} IIR-Gustav Lorentzen conference on Natural Working Fluids*. Proceedings, pp. 212-222. Oslo, Norway.

Schwartz W. 2000. "Forecasting R-134a emissions from car air conditioning systems until 2020 in Germany". *DKV Deutsche Kaelte-Klima-Tagung*, Bremen, Germany. November 2000. http://www.oekorecherche.de/english/ac-2000.html

Schwartz W. 2002. "R-134a Emissions from Passenger Car Air Conditioning Systems". *VDA Alternate Refrigerant Wintermeeting 2002.* Saalfelden, Austria.

Stene J. 2004. *Residential brine to water CO_2 heat pump for combined space heating and hot water heating.* Dr.ing (PhD) thesis, Norwegian University of Science and Technology, Trondheim, Norway.

TCCC 2004. The Coca Cola Company, Alternative Refrigeration. www.refrigerantsnaturally.com/speeches/The%20Coca-Cola%20Company%20speech.pdf

UTC 2003: http://www.utc.com/investors/2003-09-24_techday/heat_pump.pdf

Veiby O.J. 2003. Internal records/documentation in the ICA supermarket chain in Norway, Oslo, Norway.

Wertenbach J. 2004. "Energy Analysis of Refrigerant Cycles." *VDA Alternate Refrigerant Wintermeeting 2004*. Saalfelden, Austria.

Wolf F. 2005. "R744 refrigerant technology – Development of innovative components." *Technologies of New A/C Refrigerants*. Japan SAE Symposium No. 02-05, January 24-25, 2005. Tokyo, Japan.

Zakeri G.R., P. Nekså, H. Rekstad, K. Lang-Ree and T. Olsen 2000. *Results and experiences with the first commercial pilot plant CO_2 heat pump water heater*, 4th IIR-Gustav Lorentzen Conference on Natural Working Fluids, Purdue, USA.