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Carbon Dioxide as the Working Fluid in Heating and/or Cooling Systems

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SUMMARY

The last article reviewing the position of carbon dioxide as a refrigeration/air-conditioning/heat-pump fluid appeared in the *Bulletin of the IIR* in 1999.[1] In it, a vast research activity was reported (124 papers) but combined, at that time, with a small level of market place application. The research activity, then as now, has been provoked by fear engendered by the Montreal and Kyoto Protocols that the synthetic HFC refrigerants may be made difficult or impossible to obtain by legislation. Even in the US, where use of HFC refrigerants is less restricted than in certain European countries, carbon dioxide research has been vigorous and of high quality though small in volume for a large economy. However, in the last four years the increase in the practical use of carbon dioxide has been small, relative to the size of the heating/cooling market worldwide.

Four years ago only one application of carbon dioxide had achieved market acceptance: carbon dioxide as a volatile secondary fluid used mainly for supermarket application. Since then, three more have been added: carbon dioxide/ammonia cascade systems for industrial applications, small-scale water heating and vehicle air conditioning in Toyota's fuel-cell hybrid vehicle.

It is well-known that the large volume automobile manufacturers are actively working on carbon dioxide air-conditioning systems for their vehicles — a very large market which to date is served principally by synthetic fluids. An academic modelling study conducted in the US[2] reported that for automobile air conditioning R134a had a significantly higher COP.

I. THE REVIVAL OF CARBON DIOXIDE

As Kruse et al[1] pointed out in the last IIR review article on carbon dioxide, carbon dioxide was one of the earliest refrigerants to be used in the period of modern industrial history. It and other early refrigerants were replaced by the more convenient and efficient (synthesized) chlorofluorocarbons (CFCs) beginning in 1930. When it was discovered that the CFCs were capable of causing severe damage to the ozone layer, a protective shield vital to life on Earth, they were replaced (during the 1990s) by the hydrofluorocarbons (HFCs), also synthesized substances but zero in ozone depletion potential. Unfortunately, they are not zero in global warming potential when released into the atmosphere. Concern for global warming grew during the 1990s and found expression in the Kyoto Protocol of 1997, an international statement of intent to mitigate emissions of a 'basket of gases' among which were the HFCs.

Three countries named dates for the introduction of legislation banning the HFCs: Austria, Denmark and Luxembourg. The European Union is preparing a Directive on fluorinated gases.

The net result has been the creation of doubt about the long-term availability of HFCs. No successful profitable business, if it is to remain successful and profitable, can afford to be caught unprepared by legislation, which bans or severely restricts its use of a key substance. Hence the desire to use substances which are zero in ozone depletion potential and also zero in direct global warming potential.

Sustainable development in the refrigeration and air-conditioning fields implies the weighing up of options and now lays emphasis on the 'natural' substances available, namely: ammonia, the hydrocarbons, air, water and carbon dioxide. Given the toxic and/or flammable nature of ammonia and the hydrocarbons, the poor efficiency of air and limited range of applications of water, many research workers around the world have pinned their hopes on carbon dioxide, a benign fluid if simple precautions are taken.

II. COMPETITIVENESS, ATTRACTIVENESS AND THE ART OF THE POSSIBLE

A reduction in man-made global warming caused by refrigeration systems is the stated objective of those proposing the use of carbon dioxide (and/or other natural refrigerants). Hence it is reasonable to assume that critical assessments of competing systems are available from them based on the total of all contributions to global warming from conception through construction and a lifetime of operation to eventual decommissioning. The well-known concept of 'total equivalent warming impact' (TEWI) accounts for part of the grand total, the part deriving from two plant effects, namely refrigerant escape (the direct effect) and the escape of greenhouse gases which results from the plant energy consumption (the indirect effect).

Given that an average around 0.65 kg of carbon dioxide is released into the atmosphere for every kWh of energy consumed by a refrigeration plant, whether generated locally in an internal combustion engine or remotely in a power station, it is obvious that plant efficiency can influence greatly the total man-made global warming effect.

It is interesting to speculate on the consequences of a sudden complete ban[3] on HFC refrigerants at this stage in the development of carbon dioxide systems. It is quite clear that man-made global warming would, at least for a number of years, become worse due to the poorer efficiency (and higher TEWI rating) of carbon dioxide as a refrigerant for many applications. Indeed for some applications it is possible that carbon dioxide may never match HFCs in TEWI score. Also, when the higher costs of running less efficient plant began to be felt, pressure would grow for further change, either back to HFCs or for a relaxation of the restrictions on the (flammable) HCs given that the HCs are comparable in efficiency with HFCs for almost all applications for which HFCs are currently used.

III. DEVELOPMENTS PROMOTING THE USE OF CARBON DIOXIDE AS A REFRIGERANT

Co-operating groups

An important development occurred when the *International Energy Agency's* Heat Pump Programme introduced Annex 27, "Selected issues on CO_2 as a working fluid in compression systems" in March 1999. Five countries are participating: Japan, UK, Sweden, USA and Norway, with the objective of improving CO_2 technology by focusing on selected issues as a means for shortening the time to market.

Also worthy of note is the foundation of a new public research organization in Japan, the *National Institute of Advanced Industrial Science and Technology (AIST).* It began operations on April 1, 2001. 'The "f-centre" at AIST will study and propose new alternative technologies to fluorinated greenhouse gases. Based on a global standard, a scientific evaluation of the greenhouse effects and physical properties of fluorinated compounds will be conducted to select the best candidates. To realise this target, new fluorine chemistry as well as computational chemistry will be used, leading to preferable molecular structures and reasonable synthetic routes.[4] This challenges the wisdom accepted elsewhere that natural fluids are more promising than new synthetic substances. However, it seems reasonable to assume that systems making use of natural fluids such as carbon dioxide will also receive attention.

The *Carbon dioxide interest group* (known as *c-dig*) which began in Bern in July 2000 with a membership barely into double figures, in less than three years has grown to a membership of nearly 100. Meetings have been held in London, Berlin, Hannover, Aarhus, Apeldoorn and Beauvais. Its objective is to promote the use of carbon dioxide as a refrigerant in industrial systems through the exchange of information etc. Although the group has academic members, their numbers are few. Very significantly, most of the members are from the (European) market sector, as users, designers, manufacturers or contractors, none of whom is willing to take the risk of relying solely on synthetic refrigerants. Many of course believe that long-term environmental benefits are to be derived from shifting to carbon dioxide and other natural fluids. The meetings are held in private and the proceedings are not published.

Conferences on natural working fluids

Kruse[1] summarized the work on carbon dioxide carried out during the 1990s, work that was initiated by the Montreal Protocol of 1987 and accelerated by the Kyoto Protocol of 1997. Lorentzen in Trondheim, Norway made the first patent application[5] of the post–Montreal period concerning the use of carbon dioxide. Not only were a substantial number of papers produced during the 1990s and on into the 21st century but conferences, workshops and meetings dedicated to natural fluids in which carbon dioxide featured prominently came into being: of particular importance are the IIR conferences in Hannover in 1994, in Aarhus in 1996, in Oslo in 1998, in Lafayette, Indiana (Purdue) in 2000 and in Guangzhou in November 2002. In 1998 the decision was made to name conferences in this series after Gustav Lorentzen, a pioneer in the use of carbon dioxide as a refrigerant. Due to the timing of the decision, only the proceedings of 2000 and 2002 bear his name in the title. The 2002 proceedings were not available to the writer of this paper at the time of writing.

Published work

A healthy publication rate of papers has continued since 1999. Encouragingly, the number of the experimental studies has increased, normally a good indicator of seriousness of commitment. The focus on the most promising applications is now sharper. The vast majority of the recent papers on CO_2 known to this writer are to be found in the IIR Gustav Lorentzen Conferences[6], the IIR Congress of 1999[7], the Purdue conferences of 2000 and 2002[8], the proceedings of the Institute of Refrigeration, London[9] and the *International Journal of Refrigeration.*[10]

Clearly, the areas chosen for research effort reflect the opinions of publishing authors and/or their management as to which are most promising. It is useful to examine the range of work reported by Kruse[1] and to look at the changes since then:

1. large heat pumps
2. CO_2 cascaded with other refrigerants
3. CO_2 with solvents such as acetone in absorption – compression systems
4. CO_2 as a component in blends e.g. CO_2/R152a, CO_2/R134a, CO_2/HC
5. CO_2 as a secondary fluid in a supermarket
6. commercial refrigeration
7. transcritical heat pumps, high glides
8. automotive air conditioning
9. railway air conditioning
10. cooling and hot water production combined
11. controls to maximize COP
12. district heating
13. air heating
14. domestic water heating
15. domestic comfort heat pump
16. cooling of reefer containers
17. heat pump for the food processing industries
18. compressor development
19. heat exchangers (evaporators and gas coolers)
20. lubricants and CO_2/lubricant behaviour

There is evidence in the papers published since 1998 of continuing interest in almost all 20 areas, though interest in 3 and 4 seems to have weakened. The bulk of the effort is now being made in two areas believed to be close to market application: water heating and mobile air conditioning. An impression of the growth of interest in carbon dioxide as a refrigerant/heat-pump fluid may be derived from the total number of papers on carbon dioxide submitted to the Gustav Lorentzen conferences.

1994	6 papers
1996	10 papers
1998	21 papers
2000	39 papers
2002	37 papers

With regard to compressors, hermetic[11], semi-hermetic[12], vane[13] and scrolls[14] all received attention, which is encouraging given that the earlier progress of carbon dioxide systems was inhibited by a lack of suitable compressors. The experimental testing of different compressor types was reported by industrial workers[15,16] and academics.[17,18] Industrial contributors were most prominent in reporting experimental work[19-22] in lubrication. Heat transfer research is more popular in universities and in government laboratories[23-28] than in industry[29] if judgement is made on the basis of the presentations at the largest conference, the 4th IIR-Gustav Lorentzen Conference (at Purdue in 2000).

Heat pumps for high temperature heating have received detailed attention,[30] as has a drying application[31] which includes details of an experimental plant. Nekså[32] gives consideration to six applications for carbon dioxide as a heat pump fluid.

IV. CARBON DIOXIDE AS A REFRIGERANT IN THE MARKETPLACE

Carbon dioxide will become viable as a refrigerant when it is chosen on a significant scale by users under normal market conditions. At present only four applications are known to this writer to fall into this category, namely:

1. Carbon dioxide in cascade with ammonia in industrial plant [33-37]
2. Carbon dioxide as a volatile secondary refrigerant [38-41]
3. Small scale service water heating in Japan
4. Air conditioning in Toyota's fuel cell hybrid vehicle (FCHV).[42]

Four years ago number 1 was still in development but has become accepted technology since then. Number 2 became established during the 1990s. Toyota's FCHV was introduced to the market in December 2002 and three Japanese companies, Denso, Sanyo and Daikin are now marketing residential carbon dioxide heat pump water heaters in the capacity range four to six kW. Denso are producing more than 3000 per month.[43]

CONCLUSIONS

Despite vigorous research, the use of carbon dioxide in the market is still relatively small. Two influences predominate: i) the technical difficulties of developing efficient, acceptable carbon dioxide systems and ii) legislation, current and anticipated, restricting the availability of the refrigerants with which carbon dioxide has to compete (synthetics [HFCs] and natural refrigerants which suffer from toxicity [ammonia] or flammability [ammonia and the hydrocarbons]). Past experience suggests that a reasonably high level of confidence that the difficulties of i) will be overcome, is justified. However, a much lower level of confidence in our ability to predict future legislation is appropriate.[44]

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