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**OAK RIDGE
NATIONAL
LABORATORY**

MARTIN MARIETTA

Proceedings of the 1993 Non-Fluorocarbon Insulation, Refrigeration and Air-Conditioning Technology Workshop

**Wiesbaden, Germany
September 27-29, 1993**



**MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY**

PROCEEDINGS OF THE 1993 NON-FLUOROCARBON INSULATION,
REFRIGERATION AND AIR CONDITIONING TECHNOLOGY
WORKSHOP

Wiesbaden, Germany
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Prepared by the
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INTRODUCTION

Chlorofluorocarbons (CFCs) will be phased out of virtually all applications in refrigeration and air conditioning in industrialized countries before 1996 under the terms of the Montreal Protocol and its subsequent revisions. Some individual countries have agreed to an even more rapid phaseout of CFCs and of HCFCs (hydrochlorofluorocarbons), which are also controlled under the Montreal Protocol with a virtual phaseout by the year 2030. In some countries, actions are being considered to regulate HFCs (hydrofluorocarbons) as greenhouse gases (Zurer 1993, Clinton 1993). Many fundamentally different technologies could serve as alternatives to vapor compression refrigeration or plastic foam insulation using CFCs, HCFCs or HFCs. These include vacuum insulations, Stirling cycle refrigeration, gas-fired absorption chillers, thermoelectric cooling, magnetic refrigeration, and acoustic compression, among others. Conventional compression equipment using ammonia or hydrocarbons is another viable alternative. It is extremely important that policies regulating the uses of HCFCs and HFCs be developed with an accurate understanding of what technologies could be developed to replace conventional systems.

Questions need to be answered concerning when end-use equipment based on these technologies could be available; what segments and fractions of the market would be affected; and perhaps most important, how system installed costs, the equipment efficiencies, energy use, and, ultimately, indirect CO₂ emissions compare with equipment designed to use HCFCs or HFCs. Incorrect decisions could be made in formulating policies without knowledge of these issues. There may be prolonged periods when essential products are not available because fluorocarbons were forced out of use before viable alternative technologies could be developed. There could also be substantial increases in worldwide energy use and CO₂ emissions because decisions were made on incomplete or theoretical predictions of system energy efficiencies.

The Alternative Fluorocarbon Environmental Acceptability Study (AFEAS), a consortium of fluorocarbon manufacturers, and the U.S. Department of Energy (DOE) are collaborating on a project to evaluate the energy use and global warming impacts of CFC alternatives. The goal of this work is to identify technologies that could replace the use of CFCs in refrigeration, heating, and air-conditioning equipment and insulation; to evaluate the direct impacts of chemical emissions on global warming; and to compile accurate estimates of energy use and indirect CO₂ emissions resulting from substitute technologies. The first phase of this work focused on alternatives that could be commercialized before the year 2000, and the results and conclusions are presented in the 1991 report, *Energy and Global Warming Impacts of CFC Alternative Technologies*. The time frame under consideration limited this phase of the study primarily to HCFC and HFC replacements for CFCs.

The second phase of the project is examining not-in-kind and next-generation technologies that could be developed to replace CFCs, HCFCs, and HFCs over a longer period. As part of this effort, Oak Ridge National Laboratory held a workshop in Breckenridge, Colorado, on June 23-25, 1993. A second workshop was held in Wiesbaden, Germany on September 27-29, 1993. Information from the Wiesbaden workshop is contained in these proceedings; proceedings from the Breckenridge workshop are published separately. The preliminary agendas for both workshops covered a broad range of

alternative technologies, and at least one speaker was invited to make a brief presentation on each technology. Some of the invited speakers were unable to participate, and in a few cases other experts could not be identified. As a result, some alternative technologies were not represented at either workshop.

Each speaker was asked to prepare a five- to seven-page paper addressing six key issues concerning the technology he/she is developing. These issues are listed in the sidebar. All the experts also spoke for 20 to 25 minutes at the workshop and answered questions from the other participants concerning their presentations and areas of expertise. The primary goal of the presentations and discussions was to identify the developmental state of the technology and to obtain comparable data on system efficiencies. The papers submitted by each speaker at Wiesbaden are reproduced in Appendix F; note that the material in Appendix F has not been edited or reviewed, and its technical accuracy is not endorsed by AFEAS, ORNL, or DOE.

The technical sessions at the Wiesbaden workshop were moderated by a panel of experts representing academia, quasi-governmental organizations, manufacturers, and environmental interest groups. The moderators were as follows:

- Dr. Lambert Kuijpers of the United Nations Environment Program (UNEP),
- Dr. Alan Fine of the University of Kentucky in the United States,
- Dr. Horst Kruse of the University of Hannover in Germany,
- Dr. Leonard Swatkowski of the Association of Home Appliance Manufacturers (AHAM) in the United States, and
- Mr. Corin Millais of Greenpeace UK in the United Kingdom.

At the conclusion of the workshop, this panel worked together to reach a consensus and to write a summary of the technical merit and market potential of the technologies presented at the workshop. The panel summary is presented in the following paragraphs. Mr. Corin Millais submitted his own comments to the drafts of the summary which were circulated; as far as possible, his viewpoints were considered in the panel summary.

However, ORNL chose to include Mr. Millais' contribution to this summary in Appendix C. Aside from minor editorial changes, Mr. Millais' contribution is included as he submitted it. Some of the statements that he makes, such as 60% improvements in energy efficiency through the use of hydrocarbons in a refrigerator, need to be placed in context with regard to the baseline for comparison and cost premiums to achieve equal or improved efficiencies, and should not be used without careful consideration (such large changes are not due solely to using one refrigerant or process rather than the current CFC- or HCFC-based technology, but include significant design changes and component improvements). The principal value in Mr. Millais' dissenting view is the legitimate challenge that he presents to the established industry.

For example, there was no consideration of hydrocarbon blowing agents for polyurethane (PUR) insulation or as refrigerants for refrigerator/freezers in 1991 or 1992, yet major European manufacturers are producing such products in 1993 and 1994. Change can be fast and can take different directions from those the "experts" anticipate; Mr. Millais' insights and perspective are interesting and their addition to the workshop provides the perspective of some spokesmen for the environmental movement.

Outline for Written Materials

Written Submission (5-7 pages)

1. Technology Description:
Briefly describe the technology. (2 pages)
2. Application:
What is the intended application? (1/4 page)
3. Benefits:
What are the benefits of the technology and what is the energy efficiency? (1/4 page)
4. Technical Issues:
What are the technical issues and problems that need to be solved? (2 pages)
5. Economics:
What are the anticipated first costs of the system, how were these calculated, and how do they compare with existing systems that perform the same function? (1 page)
6. Technology Outlook:
What is the development status of the technology, and what is the timetable for commercialization? Provide a qualitative assessment of market penetration. (1 page)

Oral Presentation (20-25 minutes)

1. Current state of development.
2. Realistic efficiency goals.
3. Appropriate equipment applications.
4. Market and technical obstacles to further development.
5. Realistic time frame to get product on the market.
6. Qualitative assessment of market penetration.

Len Swatkowski drafted brief paragraphs of comments on each of the presentations at the workshop from his perspective as a representative of appliance manufacturers. These remarks contain specific comments regarding efficiencies, safety, and manufacturing and marketing considerations are included in Appendix D.

The summary prepared by the panel chaired by Dr. Kuijpers is contained in the following sections on insulation and vapor compression alternatives. Comments have been inserted by ORNL as necessary to include information from the discussions and question and answer periods at the workshop that is relevant to the statements prepared by the panel. These additions are clearly identified as editorial comments.

Fluorocarbon Blown Insulation

Based upon efficiency arguments, some panel members considered HCFC-141b an efficient and appropriate option to replace CFC-11. However, HCFC-141b is only a transitional alternative and faces eventual phaseout as an HCFC (January 1, 2003 in the U.S. and January 2030 by the international agreement made in Copenhagen, 1992), so it was agreed that a change to non-ozone-depleting substances is required. Options, such as fluorinated ethers, HFC-245 (isomers), HFC-365, and HFC-356 are seen as being potentially useful. However, some time is needed to bring these compounds to market (1996-1998), because of the need for toxicity testing. Cyclopentane would be a more realistic non-chlorine containing option for the short term, depending on local conditions and regulations.

Whereas U.S. manufacturers need to focus on federally mandated energy-efficiency standards and therefore state that they are unable to switch to hydrocarbons (mainly for efficiency and safety reasons), cyclopentane is an option which has already been accepted by the European polyurethane and appliance manufacturers. Favorable aging characteristics of cyclopentane blown foam are being emphasized; higher investments for the production (to cope with flammability), noted at the workshop to be eight to ten times higher than the capital costs for HCFC-141b, may be balanced with lower material costs for cyclopentane (editor's note: there is also insufficient toxicity data on cyclopentane for some governments to accept its use in consumer appliances. This issue needs to be addressed with acute and chronic inhalation tests of proposed hydrocarbon blowing agents and refrigerants).

Although HFC-134a was not considered as a blowing agent, mainly because of high conductivity values, the nongovernmental organization (NGO) panel member questioned the use of any HCFC or HFC blowing agent, stating that in his opinion other options are available to avoid their use. He also stated that he believes the barriers between HFCs and other options with less global warming potential (GWP) are not technical but are the result of differences between companies and market places. However, in considering the GWP of HFCs used in refrigerators, there was agreement that a time horizon for the GWP between 20 and 100 years would be more applicable than the 20-year horizon.

The nongovernmental organizations panel member emphasized that cyclopentane is already a feasible option at very short notice for all worldwide operations [editor's note: cyclopentane is an option only when higher energy use is acceptable, at present cyclopentane blown foam has a 6% higher thermal conductivity than 50% reduced CFC-11 blown foam and approximately 12% higher thermal conductivity than CFC-11 blown foams used in the U.S. HCFC-141b blown foam has thermal

efficiencies intermediate to 50% reduced and 100% CFC-11 foam. Improved thermal conductivities for cyclopentane foam may be possible with optimized formulations].

In conclusion, it is very difficult, according to the panel, to forecast what the long-term alternative to CFCs will be, globally speaking: cyclopentane or fluorocarbon blown foam. Lessons to be learned from the last 5 years are few. The unanticipated changeover to cyclopentane that is in progress in Europe is a striking example of the difficulty of making accurate predictions. Developments in the near future will be driven by the marketplace and by technical progress.

HCFCs were presented as the only short-term alternative blowing agent for extruded polystyrene insulation (XPS). The panel questioned the cost based considerations, implying that no non-ozone-depleting chemicals are available. It emphasized the importance of commercial efforts, namely which sophisticated selling philosophy (underscoring energy efficient construction) is available. Consumer acceptance of cost premiums for energy efficient construction would make it possible to switch to other alternatives at shortest notice.

Vacuum Insulation and Vacuum Panels

Vacuum insulation was seen as an option with commercial potential; however, many questions remain about vacuum reliability, the weight of the insulation, and about the cost once it is commercially applied. This concern holds true both for diatomaceous earth and aerogel-based vacuum insulation.

Use of this insulation method is already feasible in certain sectors, such as industrial cold storage rooms and pipelines, but it is not as feasible for consumer products such as domestic refrigerators. Further development is needed in that sector.

Powder-based insulating panels—which are more or less commercially available—are considered to have a fair chance of being applied on short notice. Although relatively expensive compared to polyurethane, they are considered to improve lifetime characteristics substantially, which implies a 10 to 15% energy consumption advantage when applied in concert with polyurethane foam to household refrigerators and freezers.

Although there will be a substantial cost increase for domestic refrigeration products using vacuum powder panels, other aspects (such as a high interior/exterior volume ratio, particularly advantageous in built-in refrigerators) are making this option technically attractive.

Stating that changes are due not only to pure technical performance related to costs, but also to efforts to commercialize that option, the panel saw a breakthrough for vacuum panels already occurring and saw growing markets in the short to mid-term time frame.

Summary

- Cyclopentane and (future) HFC blowing agents are options for polyurethane and polyisocyanurate foams. Cyclopentane has the advantage of being commercially applied at present in Europe, and of having potential for better insulation values than HFC blown foams in the 1993–1996 time frame (editor's note: HCFC-141b foams will be available for use in the U.S., Japan, and other major markets during the 1993–1996 transition time period). Other long-term options are difficult to forecast. It is likely that cyclopentane may be the only nonfluorocarbon option that may become

similar to CFC blowing agents in energy efficiency (and in particular to low CFC-water blown options, however, at present, the energy penalties could be as high as 10 to 15% relative to 100% CFC blown foam).

- Certain HFCs may be efficient; however, aside from global warming considerations, some HFCs (such as HFC-356 and HFC-365) that are attracting interest as blowing agents have the disadvantages of uncertain future costs (related to production levels and economies of scale) and unknown toxicity and need to undergo toxicity testing.
- XPS foam manufacturers are unlikely to switch from HCFCs to other chemicals unless the market accepts cost premiums for high efficiency products or unless regulatory incentives are provided.
- There will be increased marketing of vacuum powder panels for refrigerators in the 1993-1996 time frame. This development will result in a 10-15% decrease in energy use, at a certain increase in costs. Particularly in the beginning, the marketplace and commercial efforts will determine the potential.

Vapor Compression Substitutes

Hydrocarbons were seen as an alternative to fluorocarbons as refrigerants in small domestic systems for part of the global market. The presentations by German appliance manufacturers underscored the positive picture for this application; nevertheless, so far only a minor part of the German appliance production has been converted to the use of hydrocarbons. However, U.S. manufacturers perceive many liability problems, due to flammability, in automatic defrosting (frost-free) systems. This position was supported by the information given by German manufacturers on risk analyses in typical frost-free products.

There were important differences of opinion among the panel members:

- Some members underlined the "two worlds" of hydrocarbons, product liability and the consumers' attitude toward environmental issues when choosing products. They consider hydrocarbons a good option if their use can be made energy-efficient, but they certainly provide no clear efficiency superiority (editor's note: questions raised during the workshop and the ensuing discussions included concerns about technical problems in sustaining efficiencies in refrigerator/freezer combinations using very low charges of hydrocarbons and about technical/safety problems that must be overcome before hydrocarbons could be used in automatic defrost cabinets. These issues are raised in the papers in Appendix F).
- Several panel members also expressed the importance of using a mixture that is available now (propane/isobutane). The use of mixtures, either hydrocarbons or HFCs, would make it theoretically possible to improve energy efficiency because of the Lorenz cycle gliding temperatures. This conclusion was also supported by one U.S. panel member.
- Another panel member emphasized the problem of making mixtures suited for all types of appliances because of the differences in oil solubility of the hydrocarbons concerned; a solution, however likely, would require substantial development time. [editor's note: concerns were also raised that each size and model of appliance and ambient and internal operating conditions would require a different mixture.]

- On the other hand, the NGO panel member considered hydrocarbon technologies as cutting-edge technologies that can be adopted worldwide at short notice, as demonstrated by the German appliance manufacturers. He also underscored the large gains that he thought hydrocarbons would make possible in energy efficiency.

Alternatives to Vapor Compression

Absorption was seen as feasible for large systems in special industries. Its potential will be affected by specific energy-supply situations and utility rate structures. Although the technology is currently mature, it is considered to have only limited long-term market potential.

Zeolite systems are perceived as having very limited potential because of their weight, cost, and uncertainty over whether the cycle can be waste-heat driven. The principal future application was thought to be in trucks and buses.

The Stirling cycle also has limited potential; problems with lifetime and gas bearing technology still have to be solved. Although it will be possible to increase its efficiency, the Stirling cycle is not seen as superior to the vapor compression cycle (one stage with a high-efficiency compressor) for most applications.

The air-conditioning cycle using water has promising aspects, such as the pumping of liquid ice (flocice), but only a limited number of applications on the industrial market are likely because of the high investment required. It is difficult to estimate the future potential of this concept in the chiller market, mainly because of the many development difficulties and the huge investments involved in the compressor. Licensing agreements with the company that has developed applications could accelerate development.

Carbon dioxide systems for mobile air conditioners provide an interesting alternative for HFC-operated compression systems, although many questions arise concerning the development time and about the impacts of the very high operating pressures on safety, design, and reliability. Therefore, this option was not considered feasible before the end of the decade. Nevertheless, application of CO₂ systems could have a tremendous impact.

Thermoacoustic compression development will be hampered by a poor energy efficiency (5 to 6% of Carnot, where vapor compression cycles have typical efficiencies of 35 to 40% of Carnot for refrigerator/freezer conditions) and by many technical problems that can be expected in the development of the compression device. Although a commercial product is expected by the manufacturer by 1996, the panel considered a somewhat longer time frame likely. They expect development to be highly dependent on a commercial stimulus.

The air cycle has very limited potential beyond aircraft air conditioning, mainly because of efficiency problems. However, there is potential for certain applications in transport air conditioning and refrigeration (such as railway air conditioning and truck refrigeration).

Ammonia has excellent system efficiencies in refrigeration systems with direct heat transfer, and it has the most interesting potential of non-fluorocarbon and non-hydrocarbon alternatives, both in refrigeration and air conditioning. Institutional procedures to ensure user and community safety (e.g., building codes, permitting procedures) are obstacles to expanding the use of ammonia refrigeration;

these barriers are greatest in the U.S. and Japan and less of a problem in Europe and the developing countries. The feasibility for air-conditioning applications is shown by the fact that compressors are already commercially produced. In large industrial refrigeration applications, ammonia has been used for a long time (e.g., industrial food processing, breweries). When application can be extended to smaller capacity uses, for example, supermarkets using systems with indirect or secondary heat-transfer loops (perhaps using CO₂); it provides a good short-/medium-term alternative for CFCs, and HCFCs. [Editor's note: direct application of ammonia in low temperature refrigeration such as freezer display cases and in small unitary air-conditioning equipment is unlikely because of technical and cost considerations related to material compatibility and high discharge temperatures. Particularly small systems requiring secondary heat transfer loops will incur significant cost and efficiency penalties with increased CO₂ emissions and may compare unfavorably with HFC based systems.]

In a dissenting opinion, the nongovernmental organizations panel member stated that all technologies can come to the market quickly and that ammonia, hydrocarbons, and the air cycle can completely take over all the areas where HCFC-22 is currently being used.

Summary

- Hydrocarbons could be widely applied in domestic refrigeration; however, much depends on the local characteristics of the market (e.g. the U.S. market is especially sensitive to flammability and energy efficiency aspects). The theoretical possibility of realizing a highly efficient Lorenz cycle using hydrocarbon or HFC mixtures could provide extra impetus for their application.
- Apart from hydrocarbons and ammonia compression cycles (for industrial and commercial refrigeration and air conditioning), most of the options presented were considered suitable for specific applications; but they were not considered likely to gain wide markets because of the investments required, reliability problems, lack of efficiency, and utility rate structures.
- Generally speaking, hydrocarbon and ammonia compression systems and the air cycle are seen as the most relevant non-fluorocarbon candidates, although there are differences of opinion among panel members as to the time needed to bring technologies to market. These cycles are already being marketed in certain product ranges, while development is taking place for other products.
- Larger differences of opinion among the panel members can be identified in estimating how far these alternatives can go toward replacing the (existing or future) fluorocarbon technologies, where estimates of market penetration vary from 20 to 100%.

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Clinton, W. and Gore, A. 1993. The Climate Change Action Plan, October, p. 24.

Zurer, P. 1993. "*Looming Ban on Production of CFCs, Halons Spurs Switch to Substitutes*," Chemical and Engineering News, November 15, p. 14.

APPENDIX A: AGENDA

1993 Non-Fluorocarbon Insulation, Refrigeration and Air-Conditioning Technology Workshop

Monday, September 27

1:30-1:45 Welcoming Remarks and Introductions

1:45-3:15 HFC Blown Polyurethanes

- Wilhelm Lamberts, Bayer
- Ian Shankland, Allied Signal
- Stefan Adams, BASF

3:15-3:45 Break

3:45-4:45 CO₂ Blown Foam & Extruded
Polystyrenes

- Holger Beddies, Universität Stuttgart
- Godfrey Abbott, DOW

4:45-5:30 Plastic Foam Insulations: General
Discussion

Tuesday, September 28

8:30-8:45 Opening Remarks

8:45-10:15 Evacuated Panel Insulation I

- Jürg Nipkow, ARENA
- Lothar Schilf, Messer Schmidt
- J. Fricke, Universität Würzburg

10:15-10:30 Break

10:30-12:00 Evacuated Panel Insulation II

- Roland Reuter, Degussa AG
- Ralph McGrath, Owens Corning
- Bob McMarlin, Pittsburgh Corning

12:00-12:30 Summary Observations by Panel
Members and General Discussion

12:30-1:30 Lunch

1:30-1:45 Opening Remarks for Refrigeration &
Air Conditioning

1:45-3:15 Absorption, Adsorption, and Stirling
Cycle Refrigeration

- Georg Alefeld, Technische Universität München
- Jörn Schwarz, Zeo-Tech Zeolith-Technologie GmbH
- Per Lundqvist, Swedish Royal Institute of Technology

3:15-3:30 Break

3:30-5:30 Innovative Cooling Technologies

- Tashitsuga Hara, Nippon Institute of Technology
- Joachim Paul, Integral Technology GmbH
- Stig Sørensen, Danish Energy Analysis A/S
- Eberhard Laevemann, ZAE Bayern

Wednesday, September 29

8:30-8:45 Opening Remarks

8:45-10:15 "Natural" Refrigerants

- Jostein Pettersen, SINTEF (CO₂)
- Albrecht Meyer, FORON Hausgerate GmbH (R/F)
- Helmut Lotz, Bosch-Siemens

10:15-10:30 Break

10:30-11:30 "Natural" Refrigerants

- Ulrich Hesse (supermarket and air cycle)
- Dr. Mosemann, Kühlautomat (chillers)

11:30-12:45 Summary Observations from Panel
Members and General Discussion

12:45-1:00 Closing Remarks

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APPENDIX C: SUMMARY COMMENTS AND REMARKS

BY CORIN MILLAIS, GREENPEACE UK

1. INSULATION

1.1 Blown Foam Insulation

HCFC-141b: HCFC-141b cannot be considered an efficient option, based on efficiency data and on its ozone depletion impact and its rejection by major industries. It has also been rejected as a technical solution by most European industry. HCFC-141b also attacks plastics and the inner lining and plastics used in refrigerator/freezers.

HFC-245 isomers and HFC-356: These do not represent a realistic option because of the length of time to market, cost, toxicity testing, and the existence of more commercially available nonfluorocarbon options. The estimated time to market is 2000 or later.

Cyclopentane blown foam: Cyclopentane blown foam is more than "interesting." It is a technology proven successful throughout Europe, with excellent commercial possibilities in America and Asia. The applications are refrigeration and all other major rigid polyurethane foams (i.e., spray, cavity, sandwich, district heating, hot water, and slabstock). The cost of cyclopentane was quoted as less than one-seventh that of HCFC-141b.

HFC-134a: It is discounted as a blowing agent due to its expense and poor efficiency record, as well as rejection of this route by major industries.

In considering the global impact of HFCs in refrigeration, the short-term GWP time horizon (i.e., 20 to 100 years) is the most appropriate, given the lifetime of the HFC itself (15.6 years for HFC-134a) and the lifetime of refrigeration equipment—about 10 to 20 years.

The consensus view is that "lessons to be learned from the last 5 years are few," yet in relation to cyclopentane foam, it is apparent that HCFCs and HFCs were rejected by virtually all of European industry for a number of valid and compelling reasons; and the time frame to switch to what was previously considered a nonoption was very short—a matter of months.

Extruded polystyrene insulation: One XPS manufacturer failed to present an alternative to its use of HCFCs. However, it was agreed by all companies interviewed by the panel, including that particular company, that all XPS applications could be satisfied by other non-HCFC alternative insulation technologies that were presented at the workshop. As one example, foam glass is commercially available globally and can be used for all major commercial and industrial applications, especially in the construction industry.

In conclusion, cyclopentane blown foam represents the most commercially available and suitable technology. Fluorocarbon blown foams fail to satisfy most of the criteria and are thus rejected.

1.2 Vacuum Insulation and Vacuum Panels

Vacuum insulation and vacuum panel technologies are already proven, state of the art technologies; have vastly superior energy efficiencies; and represent an excellent option for all key commercial and industrial applications, for example, cold storage, pipelines, refrigeration, and building insulation. The

barriers to wider commercial acceptability are not of a technical nature, and it is already apparent that significant commercial breakthroughs will occur.

Powder-based insulating panels are commercially available and have an excellent chance of a significant market share in the short term. Many different companies have substantial investments and market ambitions for these technologies. The costs to domestic refrigeration manufacturers are not a barrier in the production process. Major reductions in energy costs over the lifetime of the products are an obvious advantage, as well as extended lifetime characteristics. Panels can be used in conjunction with cyclopentane blown foams.

1.3 Summary

- Cyclopentane blown foams are a mature, competitive, and widely available technology that is one of the best options for the global marketplace.
- HFC blown foams have already been rejected by most of industry; and because of global warming concerns, poor efficiency results, and toxicity problems, future commercial acceptability appears doubtful.
- XPS insulating foam makers should abandon HCFCs; in any case, the end uses of XPS can be replaced by other products in all construction applications.
- Vacuum insulation and powder panels are mature, available technologies that have superior energy advantages and have the capacity to take over the global market in the near term.
- The rapid deterioration of the ozone layer and increasing restrictions on HCFCs will act as powerful forces to accelerate a 100% switch to the major insulation alternatives of cyclopentane foam and vacuum/powder panels. HCFC and HFC foams are not necessary.

2. REFRIGERATION AND AIR CONDITIONING

2.1 Vapor Compression Substitutes

Hydrocarbons are an excellent alternative for domestic systems and already have been proved commercially by major European manufacturers. They could be used by the whole global market in the short term. The energy efficiency of appliances is already excellent compared with CFC and HFC models, and one company envisages major additional short-term energy gains of around 60% for some new models. The use of different mixtures of propane and isobutane would further increase efficiency gains. Flammability and product safety are not presented as a technical problem, and for the specific U.S. market, product liability does not actually present a technical or market barrier because of basic design modifications and construction changes. Hydrocarbon compressor development will be rapid in the short term and will substantially accelerate the swift changeover.

Hydrocarbon cooling technology could take over up to 100% of the European market in the near term. One company reported that the trend is toward a decline in use of HFCs for coolant in favor of hydrocarbons. Most manufacturers aim to switch all models over to hydrocarbon coolants, and one company has reported that it will switch to pure hydrocarbon coolant by mid-1994. Market demand will force additional technical developments at a rapid pace to further entrench the technology across all models. There are no technical barriers in conjunction with the oils. The conservatism of the manufacturers, in fact, belies the true nature of the rapid developments. The technology also has significant advantages for developing countries.

2.2 Alternatives to Vapor Compression

Absorption technology is commercially mature; it already has a large market share in Asia, China, and India, and rapid market penetration is likely for Europe and the U.S. Energy efficiency gains are also a major benefit. Significant investment is being made to increase market share. One of the market constraints noted is the sale of HCFC and HFC technology.

Zeolite systems could be used for transport applications, especially trucks, buses, etc.

The Stirling cycle has good market possibilities if commercial users adopt the technology.

Thermoacoustic technology represents another promising technology that is hampered only by lack of a commercial stimulus.

Flo-ice is a commercially available technology with the capacity to be used widely, especially given the nature of the licensing agreements that would enable rapid use by different companies in the industrial and commercial field.

Carbon dioxide car air conditioning has a number of economic, practical, and environmental advantages over CFC and HFC systems: low cost of fluid, lack of need for recovery and recycling, compatible weight and dimensions, well-known properties, and excellent availability. The use of HFC-134a in car air conditioning is subject to considerable skepticism from industry as a real solution, and HFC-134a adds a significant global warming burden to a car from direct emissions. Early commercialization of CO₂ air conditioning is expected; this technology has the capacity to take over 100% of the global market very rapidly.

Ammonia represents one of the most significant alternatives in the world for refrigeration and air conditioning, and it is undergoing a major industrial resurgence. It is a long-established technology with advantages such as proven reliability, excellent system efficiency, thermodynamic superiority, low cost and wider availability than HFCs or HCFCs, lower energy consumption, and environmental benefits (zero ozone-depletion potential and GWP). Globally, ammonia can be used in the major sectors: industrial, food processing and breweries, air conditioning, and commercial (supermarket) refrigeration. In this last sector, ammonia typically is used in conjunction with secondary cooling loops and provides an excellent alternative to HCFC/HFC systems.

2.3 Summary

- Hydrocarbons are already commercially used and could be widely applied in domestic refrigeration. They offer a number of significant advantages. Additional developments in efficiency, mixtures, and compressor technology will further entrench this technology as a global force.
- In general, ammonia, hydrocarbons, absorption, and air cycle technologies offer the best alternatives that can be used for all refrigeration and air conditioning applications. They have the capacity to take 100% of the existing and future fluorocarbon market.
- Other technologies are promising and only lack of market stimulus acts against rapid adoption.

Additional comments

It is apparent from the speakers at Wiesbaden that a wide range of nonfluorocarbon technologies can be used for all major refrigeration and insulation applications, eliminating the need for fluorocarbons. Other factors give additional proof that this is the case:

1. Continuing news of worsening ozone depletion (particularly this year's Antarctic ozone hole, projected losses in the northern hemisphere in 1994, and mounting revelations about impacts from UVB increases) over the coming months will increase pressure on the phaseout schedule for HCFCs. This will make HCFC technology increasingly more scarce and more expensive and will mitigate against any realistic commercial decisions based on use of these chemicals, as another changeover is inevitable.
2. The Wiesbaden meeting attracted only a small number of nonfluorocarbon technologies that have solid commercial availability; these represent only a small part of industry's nonfluorocarbon capabilities worldwide. For example, there was a notable absence of additional companies using hydrocarbon coolants (e.g. the company mentioned by the Bosch representative that will transform its total production to hydrocarbons by mid-1994) or ammonia refrigeration, including secondary cooling systems, either for the industrial or the commercial/retail sector.
3. Examples of uses in sectors other than refrigeration and air-conditioning (e.g. electronics and aerosols, in particular) demonstrate that the phaseout of ozone-depleting substances is in practice cheaper, easier, and much more rapid than industry perceives. This belies the claim that more cannot be done. The European Community regulation on HCFCs states that *"In general terms, both within the Community and globally, the experience of the last five years has shown that the phase-out of ozone-depleting substances is proceeding rapidly and at a much lower economic cost than expected. Contrary to expectations, the quality of goods and services has been maintained without price increases and in many cases it has been relatively inexpensive, and sometimes even profitable, to find alternatives to ozone depleting substances...itis clear that the benefits of regulatory action outweigh the costs even if quantification is not precise."*
4. There is a mistaken tendency to underestimate the true commercial possibilities of a technology that superficially seems to be a "distant" prospect. This tendency arises from perceptual barriers and innate conservatism, rather than technical barriers or experience; the rapid development of hydrocarbon domestic fridge technology (both coolants and foams) in recent months proves that a conservative philosophy is fallacious. Therefore, a mixture of the globally available and the near-market technologies can easily meet the need to replace ozone-depleting substances worldwide with nonfluorocarbon technology. The continued use of HCFCs acts as another barrier, and many companies report this problem; as was stated in the United Nations Environment Program Technology and Economic Assessment Panel, *"The development of technologies which do not use either controlled or transitional substances [HCFCs] can be inhibited because the prospect of technology using transitional substances discourages investment in technology that would only be profitable if transitional substances were not acceptable."*
5. It is hard to understand why the consensus summary continues to be so ambivalent and overcautious on the subject of hydrocarbon coolants in domestic refrigeration. The summary assessment is a startling anomaly compared with the nature of assessments made for other sectors; it leads one to believe that the consensus judgement on hydrocarbons is misconceived. The arguments presented at Wiesbaden on their own give sufficient grounds for optimism and approval. Furthermore, a wealth of practical experience and knowledge among companies, governments, policy makers, and others adds significant weight to favorable arguments. Much of this experience and knowledge is totally separate from Greenpeace. There is no reasonable justification to question hydrocarbon cooling technology, and to do so gives a highly misleading picture.

APPENDIX D:

SUMMARIES AND COMMENTS BY LEONARD SWATKOWSKI, ASSOCIATION OF HOME APPLIANCE MANUFACTURERS (AHAM)

1. INSULATING/INSULATION TECHNOLOGIES SUMMARY ONE

Speaker No. 1:

Wilhelm Lamberts, Bayer

TOPIC: "1,1,1,4,4,4Hexafluorobutane (HFC-356)"

HFC-356 has no short-term potential since three to four years of toxicology testing (including a multi-million dollar inhalation study) need to be completed before commercialization. Its thermal conductivity properties and boiling point which are similar to R-11 make it an attractive alternative. Potentially high price per pound and pressure from environmental concerns could stop any and all research on this chemical at any time in the near future.

Speaker No. 2

Ian Shankland, Allied Signal

TOPIC: "Three and Four Carbon HFCs"

The limited survivors screened from a three and four carbon HFC analysis by Allied Signal (i.e., HFC-245ca, HFC-245eb, HFC-245fa, and HFC-356) all have the same long and short term situations as stated in the previous section. The HFC-245 isomers are further behind in toxicity testing than HFC-356. If GWP issues force the high GWP, HFC chemicals out of the market, the HFC-245 chemicals may gain acceptance for future research. However, if HFCs are banned worldwide, these chemicals will be eliminated from any future concerns.

Speaker No. 3

Stefan Adams, BASF

TOPIC: "Cyclopentane Polyurethane Foams"

Germany, followed by other European countries, will continue to phase cyclopentane in as a replacement for CFC-11. Its application is a legal problem in Japan, a technical (energy) and liability (flammable) issue in the U.S. and may have other obstacles in Australia, Asia, and Africa. Since it has been successfully implemented in full production in Europe, these obstacles are being examined carefully to gauge cyclopentane's potential implementation. For the U.S., the energy efficiency aspects, liability during manufacture, and reliability over long-term usage (aging) are the most critical issues.

Speaker No. 4

Holger Beddies, University of Stuttgart

TOPIC: "Water/CO₂ Foam"

Water blown foams are being used in production today in Japan (Sharp) in concert with powder-filled vacuum panels (to maintain energy efficiency). Long-term application of water blown foams will be limited to "niche" applications such as pipe insulation. Thermal, aging, and structural stability characteristics will prevent this technology from becoming acceptable in household refrigerators and freezers.

Speaker No. 5

Godfrey Abbot, Dow

TOPIC: "HCFC-22/HCFC-142b Extruded Polystyrene Board Stock"

A quick and available replacement for CFC-type board stock was used in energy efficient construction, this technology was implemented very early in the worldwide effort to replace CFCs. Being quick to respond to environmental concerns, this industry finds itself forced to undergo another quick and expensive change to another chemical. Yesterday's environmental solutions have become today's environmental problems. This situation raises the simple question of timing and individual company's ODP reduction effort as well as the value of energy efficient technologies.

Speaker No. 6

Lothar Schilf, Messer Schmidt

TOPIC: "Vacuum Super Insulation (VSI)"

Vacuum super insulation incorporates diatomaceous earth which is in itself a very heavy material. It is expensive, difficult to handle, and difficult to transport (compared to polyurethane foam or polystyrene). Application to U.S. refrigerator/freezers is unlikely due to its high weight (which would add over 300 pounds (135 kg) to each refrigerator) and extremely critical process controls.

Speaker No. 7

Jurg Nipkow, ARENA (Swiss Research Organization)

TOPIC: "VSI in Household Refrigerators"

As stated in the presentation by Lothar Schilf (which was focused on pipe and warehouse insulation) this technology cannot realistically be applied to U.S. products where the additional weight of over 300 pounds (135 kg) per cabinet will prevent it from being commercialized.

Speaker No. 8

R. Caps/J. Fricke, University of Wurzburg

TOPIC: "Aerogel Powders"

This technology is very expensive compared to similarly efficient powder-filled panels. The energy cost used to produce solid aerogels is very high (estimates are in the 400-500 Watts/board foot (4300-5300 Watts/m²) range). The manufacturing process to produce aerogel panels is very expensive and difficult to maintain.

Speaker No. 9

Roland Reuter, Degussa AG

TOPIC: "Powder Insulated Panels"

This technology is relatively expensive compared to other energy saving options. The life characteristics of this technology are improving, however, maintaining thermal-dynamic performance upwards of 10-20 years. A realistic energy savings of 15-20% has been measured when this technology is applied to household refrigerators and freezers.

Speaker No. 10

Ralph McGrath, Owens Corning

TOPIC: "Fiberglass Vacuum Panels"

Another currently viable insulation assist technology, fiberglass vacuum panels, have been shown to perform from R-30 to R-35 (2.83 to 2.43 mK/mW) when applied to household refrigerator/freezers.

This compares to R-20 (1.39 mK/mW) for powder-filled panels. The cost/performance ratio for this technology is still high for the U.S. refrigerator/freezer industry, but may be an economical choice for 1998 National Appliance Energy Conservation Act (NAECA) compliant refrigerators and freezers.

Speaker No. 11
Bob McMarlin, Pittsburgh Corning
TOPIC: "Cellular Glass Insulation"

A current industrial/commercial product, cellular glass insulation is three to four times the cost and half the insulating value of polyurethane or polystyrene foam. Application to domestic refrigerator/freezers would not be feasible. However, application to industrial/commercial sectors, such as building exterior and roofing materials, could provide economical energy savings.

2. REFRIGERATION AND AIR CONDITIONING SUMMARY 2

Speaker No. 1
Georg Alefeld, Technische Universität München
TOPIC: "Absorption Refrigeration"

Absorption refrigeration technology is currently being used worldwide in household refrigeration and room air conditioning applications. This technology may only produce energy benefits when applied to furnaces in commercial and industrial settings. It may also have limited applications to large chiller units in specialized industries.

Speaker No. 2
Jorn Schwarz, Zeo-tech Zeolith-Technologie GmbH
TOPIC: "Zeolite Sorption Technology"

While this technology may not provide an energy benefit when applied in a traditional application, it could provide energy savings when used in a "hybrid" technology (such as operating on waste heat in a heat pump or car exhaust).

Speaker No. 3
Per Lundqvist, Swedish Royal Institute of Technology
TOPIC: "Stirling Cycle Refrigerators"

Stirling cycle refrigeration has not lived up to the energy efficiencies now realized by typical piston-type compressors. There are free-piston type Stirling cycle compressors that have come close to the energy efficiency of traditional compressor technologies. This is, however, an in-kind technology that could replace applications that are currently being held by halogenated refrigerants, be it at some degree of energy efficiency loss.

Speaker No. 4
Tashitsuga Hara, Nippon Institute of Technology
TOPIC: "Thermal Acoustic Refrigeration"

Thermal acoustic refrigeration is an in-kind technology that needs considerable development before its feasibility can be determined. Long-term estimates of efficiency exceeding vapor compression refrigeration are based on speaker, or sound generator, efficiency reaching 80-90%. Sound generator efficiencies today are approximately 40%.

Speaker No. 5

Joachim Paul, Integral Technology GmbH

TOPIC: "Water as a Refrigerant"

The use of water as a refrigerant in any sense is restricted to industrial/commercial chiller technology and not applicable to household refrigerators and freezers. This technology utilizes an ice-slurry or "pumpable ice." It claims the same energy efficiency as current chiller systems with a 50% cost penalty.

Speaker No. 6

Stig Sorensen, Danish Energy Analysis A/S

TOPIC: "Outdoor Air/Ground Water Cooling"

Outdoor air/ground water cooling is another industrial/commercial technology restricted to certain geographic locations. A ready supply of ground water is critical to this technology which can complement as well as supplement traditional chillers.

Speaker No. 7

Eberhard Laevemann, ZAE Bayern

TOPIC: "Regenerative Sorption Reactors"

This technology is an open sorption system using salt spray that can carry corrosive aerosols inside living areas. While it is an in-kind technology, it is also an expensive alternative for residential applications.

Speaker No. 8

Helmut Lotz, Bosch-Siemens Hausgerate GmbH

TOPIC: "Hydrocarbons in Domestic Refrigerators (and Foams)"

The replacement of CFCs with hydrocarbons in Germany has been driven by global warming potentials of halogenated chemicals and Blue Angel Certification. Technical obstacles remain energy efficiency and safety concerns in products with exposed heat exchangers. The implementation of hydrocarbons as refrigerants in household refrigerators and freezers in Germany is currently limited to those with evaporator coils imbedded in the foam insulation in walls.

Speaker No. 9

Albrecht Meyer, Foron Hausgerate GmbH

TOPIC: "Hydrocarbons in Domestic Refrigerators"

This presentation was indicative of the direction that Foron is going relative to implementation of hydrocarbon refrigerants. Focused on the application of a 50/50 mixture of hydrocarbon 290/600a (propane/isobutane), Mr. Meyer claimed energy efficiency improvements of over 10% using hydrocarbons compared to CFC-12. This claim was also made based on a single-size charge of approximately 24 grams \pm 2 grams for all the Foron products inclusive of refrigerators, freezers, and refrigerator/freezers of various volumes.

Speaker No. 10

Heinz Jurgensen, AEG Hausgerate GmbH

TOPIC: "Flammable Refrigerants in Household Appliances"

The application of hydrocarbons to German appliances has had a significant impact on energy efficiency. The assessment in this presentation was that refrigerator/freezer energy consumption

increases due to the implementation of hydrocarbons. Eventually, equivalent energy usage to HFC-134a may occur as hydrocarbon type compressors are developed.

Speaker No. 11

Jostein Pettersen, SINTEF, Norwegian Institute of Technology

TOPIC: "CO₂ as a Refrigerant"

A seemingly viable alternative for auto air conditioning, serious concerns revolve around very high pressures produced during operation which create lubrication and design problems.

Speaker No. 12

Ulrich Hesse, University of Hannover

TOPIC: "Air Cycle Refrigeration/Ammonia"

Air cycle cooling seems a viable option as applied to high speed trains, although cost impact and reliability are uncertain. Ammonia systems are more expensive, less safe, and less energy efficient than current vapor compression as applied to supermarkets. This technology does not have a household refrigerator/freezer application.

Speaker No. 13.

Dr. Mosemann, Kuhlautomat

TOPIC: "Ammonia Chillers"

As applied to supermarket refrigeration, ammonia cooling appears to be a viable alternative. However, slightly higher installation costs as well as safety issues (toxicity and flammability), will impede implementation on a large scale. Dr. Mosemann contradicted the last author by stating that ammonia is more energy efficient than currently used CFC chillers.

APPENDIX E: OBSERVATIONS

Steve Fischer
Oak Ridge National Laboratory
Oak Ridge, Tennessee, U.S.A.

Undoubtedly, it is unusual for representatives of the host organization of a meeting to insert their own comments into the meeting record. If they do so, as this is obviously the case, it is far better for those observations to be clearly identified and perhaps even tucked away at the end of a lengthy document.

Two issues were raised at the workshop which have not received much attention in the summary prepared by the panelists or in the comments by Corin Millais and Len Swatkowski in Appendices C and D. These are the toxicity of alternative foam blowing agents and refrigerants and the safety of appliances and refrigeration systems using flammable and/or toxic refrigerants. Strict requirements are placed on the chemicals used in industrial, commercial, and consumer products and processes by manufacturers and governments for the protection of employees and customers. In some instances the properties of the desired chemical are not known, in other cases, the desired compounds are known to be non-toxic, non-carcinogenic, non-mutagenic, but the exact nature and effects of the impurities in the chemicals are questionable or just not known. Typically manufactured fluorocarbons are 99+ % pure, yet extensive toxicity testing is done to identify the effects of the desired compound and also trace amounts of isomers (such as HCFC-123a in batches of HCFC-123) or impurities (HFC-133a in HFC-134a) that may appear. The same concerns for consumer and employee safety should motivate future toxicity testing of hydrocarbons and new fluorocarbons proposed as refrigerants and blowing agents.

The question of flammability and fire risk was broached by several speakers on household refrigerators and ammonia refrigeration systems for supermarkets or building air conditioning. Major European appliance manufacturers are using hydrocarbons safely on the assembly line and the companies are comfortable marketing isobutane refrigerators for certain product lines. This information was presented in Wiesbaden, but it was not intended by all of the speakers as an endorsement of the safe use of hydrocarbons in all size ranges, designs, or models of refrigerator/freezers. The paper by Helmut Lotz in Appendix F shows the results of a risk assessment performed by Bosch-Siemens on the use of isobutane (R-600a) in different models of refrigerators. This drawing is reproduced in Figure E.1. Clearly not all possible applications of isobutane pose the same fire-risk to the homeowner; very low risk is associated with small refrigerators with the evaporator embedded in foam insulation, greater risk is associated with exposed steel and aluminum evaporator coils, and high risks are posed by the possible ignition sources from automatic defrost systems. A refrigerant that has acceptable risks in one application or appliance may have unacceptable risks in another, though similar, application. Similar concerns were raised by other speakers at the workshop and have been raised by Underwriters Laboratory and appliance manufacturers in the U.S.

Every manufacturer has a social responsibility to provide a safe working environment for their employees and safe products for their customers. These obligations are particularly important when they are developing a new product to replace a home appliance that has been virtually risk-free for three generations.

Finally, there is an almost overpowering desire among those not responsible for developing or manufacturing equipment to discount or ignore the difficulties or problems associated with most of the alternative refrigeration and air-conditioning technologies. Just looking at a few:

Risk Assessment For HC R-600a In Different Refrigerator-Types

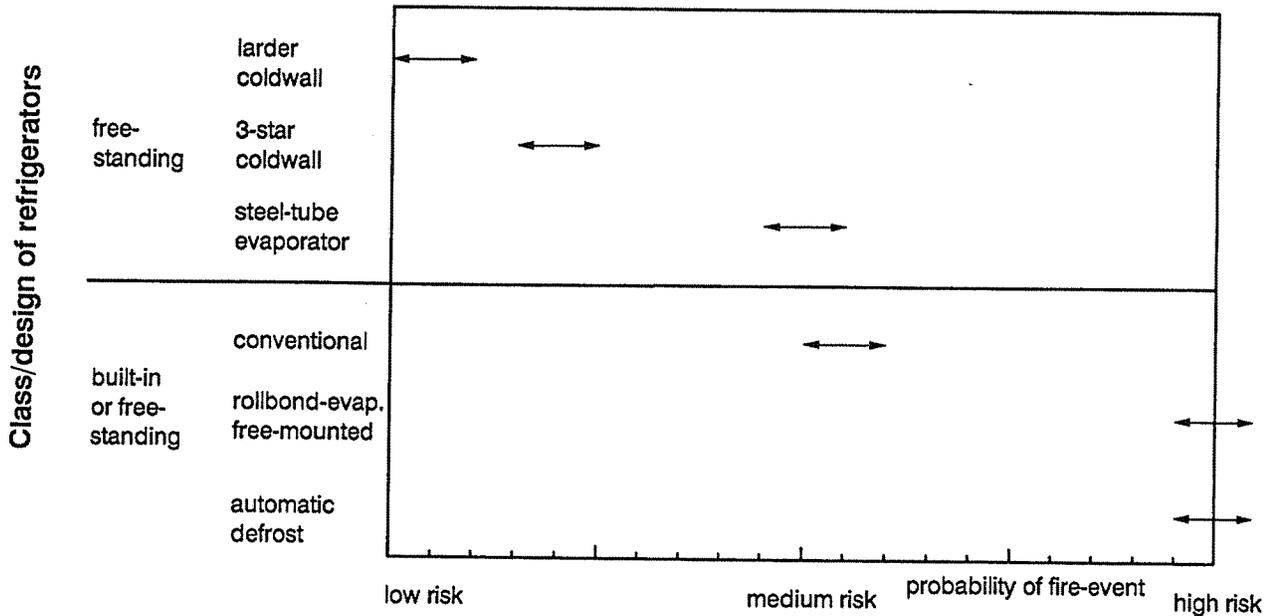


Fig. E.1. Risk assessment of R-600a in refrigerator/freezers.

- ammonia (NH₃) compression air conditioning and refrigeration; toxic, flammable, major material incompatibilities,
- CO₂ compression; extremely high pressures impact safety, reliability, durability, and costs,
- flo-ice; very large equipment limits applications and impacts costs,
- Stirling cycle; seals, heat transfer, and lifetime,
- evacuated panel insulation; lifetime, weight, and cost,
- absorption chillers; efficiency, first cost, and gas/electric price ratio,
- acoustic compression; low efficiency, and
- thermoelectric refrigeration; materials breakthrough needed to boost efficiency.

All of these technologies have been demonstrated to some degree in viable pieces of equipment. None, however, are in a position to displace fluorocarbon compression or foam insulation in broad application. Development time measured in years to tens of years are still needed to resolve problems, engineer around obstacles, and bring products to market. It is unlikely that there will be a free lunch in any instance; solving the problems associated any of these technologies is likely to

bear a cost either monetarily for more complicated equipment or in terms of lost efficiency. In the absence of regulatory mandates, only those developers who are successful in providing greater quality or performance at an acceptable price and risk will displace fluorocarbon technologies as they evolve to use chlorine-free compounds with short atmospheric lifetimes.

It is left as a policy decision to determine whether or to what degree global and national interests are served by imposing regulatory mandates restricting one technology to guide (or force) development of others. There is precedent even within the refrigeration industry for doing so. In the past such actions were used in the interest of communities to severely limit where and under what conditions ammonia could be used in refrigeration. Although national and private R&D programs may be called for in developing emerging alternative technologies, careful consideration must be paid to the monetary and energy costs in the current debate to regulate and restrict the uses of HCFCs in the short term to accelerate closing of the ozone hole and HFCs based on direct global warming potentials.

APPENDIX F: TECHNICAL PAPERS

1,1,1,4,4,4 Hexafluorobutane, a New Non-Ozone-Depleting Blowing Agent for Rigid PUR Foams

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ABSTRACT

HCFCs are widely accepted to be technically promising replacements for CFCs in rigid PUR foams, especially for appliance applications. Despite this, political pressure is rising to limit their use to a transition period. One of the reasons is their residual ozone depletion potential.

In the search for long term substitutes for both CFCs and HCFCs, we have identified and developed a new blowing agent and insulation gas: 1,1,1,4,4,4 hexafluorobutane (HFC-356).

Important properties of hexafluorobutane are:

- chlorine-free/non-ozone-depleting
- very short atmospheric lifetime/minor greenhouse activity
- non-flammable
- no explosion limits
- suitable boiling point
- low gas phase thermal conductivity
- compatibility with appliance inner liner plastics

These properties allow the use of established appliance construction and foaming technology. Nevertheless, reformulation of the PUR components was necessary to design the first PUR appliance system with hexafluorobutane. Extensive laboratory scale testing including foaming of cabinets has been conducted with good results. In comparison with 50% CFC-reduced systems, it fulfills the technical standards of the European appliance industry concerning

- cell size/cell structure
- flow properties/foam density
- thermal conductivity/energy consumption
- aging behaviour
- demould properties
- dimensional stability/compressive strength
- compatibility with SB and ABS inner liners

According to the regulations on chemical substances worldwide, hexafluorobutane is a new chemical substance which requires notification before commercialization. Ecological and toxicological testing of hexafluorobutane is in progress, but not yet completed. Results from acute and subacute inhalation toxicity testing are acceptable and encourage further development of this product.

INTRODUCTION

Based on the theory of Molina and Rowland [1] during the 1980's, scientific and public discussion about man-made ozone depletion and the antarctic ozone hole as a consequence of CFC production and emission had been rising. This discussion resulted in numerous members of the international community agreeing to the first international treaty on the protection of the environment, the Montreal Protocol, in September 1987. The Montreal Protocol regulates the production and consumption of CFCs (among other substances). Meanwhile, the reduction plan for CFCs has been significantly accelerated as committed to in the London amendment to the Montreal Treaty in June 1990:

| CFC Reduction (Based on 1986 Production) | Montreal | London |
|---|----------|--------|
| freeze on 1986 level | 1989 | 1989 |
| -20% | 1993 | 1993 |
| -50% | 1998 | 1995 |
| -85% | — | 1997 |
| -100% | — | 2000 |

Very soon it was clear that CFC-11 would disappear in many applications such as flexible slabstock of very low density or flexible moulded foams, where only the blowing effect is needed. In these cases CFC-11 can be replaced by CO₂ from the water/isocyanate reaction.

Unlike as in the above-mentioned applications, in rigid PUR insulation foam, CFC-11 or any other "insulation gas" is part of the product and contributes to its unique profile of properties. Nevertheless, raw material suppliers and the European appliance industry succeeded in 1988/89 in reducing the amount of CFC-11 used in PUR insulation systems by 50% without sacrificing more than an average of 5% of the insulation properties.

But what about the committed total phase out of CFCs by the end of this decade? It means that the world is going to discontinue the use of the best insulation gases for foamed insulations when the public discussions about reducing energy consumption and greenhouse effect caused by CO₂ emissions from fossil energy sources just start.

For the time being HCFCs are widely accepted as technically promising replacements for CFCs in insulation foams especially for appliance insulation. These have almost equal properties compared to CFC-11, but improved ecological data. Nevertheless today, political pressure grows to limit their use to a transition period, and to phase out HCFCs also sometime in the 21st century.

The question arises: transition to what kind of substitute?

OUR ROUTE TO 1,1,1,4,4,4 HEXAFLUOROBUTANE

Trying to answer this question we found that most of the potential third generation cell gases have serious disadvantages:

- CO₂:
 - poor insulation properties
 - very poor aging behaviour due to rapid gas exchange with air if not diffusion tight
- alkanes:
 - flammable and explosive in mixtures with air
- perfluoro-compounds:
 - persistent in the atmosphere and highly IR-active, therefore bearing significantly higher global warming potentials than CFCs and HCFCs
 - very expensive

Since none of the above available species is satisfactory, we decided to design our own substitute molecule. Our idea was to identify candidates in the class of hydrofluoroalkanes, HFCs (see also References [2-4]), according to a profile of properties as listed in Table 1.

- no chlorine for zero ozone depletion potential
- as much fluorine as necessary for
 - high molecular weight (low thermal conductivity)
 - being non-flammable and non-explosive

Table 1. 1,1,1,4,4,4 hexafluorobutane (HFC-356) CFC-alternates design criteria.

| |
|---|
| — no chlorine for zero ozone depletion potential |
| — as much fluorine as necessary for <ul style="list-style-type: none"> • high molecular weight (low thermal conductivity) • being non-flammable and non-explosive |
| — as little fluorine as possible for <ul style="list-style-type: none"> • minimum IR absorption • short atmospheric lifetime • both of the above properties leading to minimal global warming potential • reasonable polarity and compatibility with PUR components • being cost effective |
| — boiling point in the range of 20–40°C to <ul style="list-style-type: none"> • maintain usual foaming equipment and processability • avoid condensation effects in the foam cells at low insulation temperatures |
| — lowest possible toxicity and ecotoxicity |
| — viable production process for <ul style="list-style-type: none"> • high selectivity, yield and purity • being cost effective |
| no attack on inner liner plastics used today in appliance industry |

- as little fluorine as possible for
 - minimum IR absorption
 - short atmospheric lifetime
 - both of the above properties leading to minimal global warming potential
 - reasonable polarity and compatibility with PUR components
 - being cost effective
 - boiling point in the range of 20–40°C to
 - maintain usual foaming equipment and processability
 - avoid condensation effects in the foam cells at low insulation temperatures
 - lowest possible toxicity and ecotoxicity
 - viable production process for
 - high selectivity, yield and purity
 - being cost effective
- and, if possible
- eliminate attack on inner liner plastics used today in the appliance industry

Although we could not answer all the questions of this list of requirements beforehand for each candidate, one species seemed to be a compromise: 1,1,1,4,4,4 hexafluorobutane or R-356 as it is called in the nomenclature of refrigerants.

PROPERTIES OF 1,1,1,4,4,4 HEXAFLUOROBUTANE

In Table 2 important properties of 1,1,1,4,4,4 hexafluorobutane are listed in comparison to CFC-11.

The boiling point is very close to that of CFC-11 providing normal processability and acceptable condensation effects in the foam cells at low temperatures.

Hexafluorobutane is non-flammable and does not form any explosive mixtures with air.

Table 2. 1,1,1,4,4,4 hexafluorobutane (HFC-356) product properties.

| | HFC-356 | CFC-11 |
|--|--|---------------------|
| Formula | C ₄ H ₂ F ₆ | CFCl ₃ |
| Molecular Weight | 166 g/mol | 137.5 g/mol |
| Boiling Point | 24.6°C | 23.8°C |
| Flashpoint | | |
| Ignition Temperature | none below 600°C | none below 600°C |
| Explosion Limits | | |
| Gas Phase Thermal Conductivity, 20°C | 0.0095 W/Km | 0.008 W/Km |
| ODP | 0 | 1 |
| GWP | 0.015 0.03* | 1 |
| Atm. Lifetime | ~0.4 a* | 60 a |
| Compatibility with Appliance Inner Liner Plastics: | | |
| PS | ++ | - |
| SB | ++ | 0 |
| ABS | +- | + |
| Toxicity | not complete | TLV/MAK 1000 ppm |

*Est. by Prof. Dr. R. Zeller, Göttingen

The gas phase thermal conductivity of hexafluorobutane at room temperature is only about 1.5 mW/Km higher than that of CFC-11 measured with the same equipment.

The ecological data of hexafluorobutane is some of the best known today for halocarbons (Figure 1):

- ODP is zero by definition.
- GWP has been estimated by Prof. Dr. R. Zellner, Göttingen, FRG, to be 0.02 with a reliability range of -0.005 and +0.01 [5] mainly influenced by a short atmospheric lifetime of 154 days [5].

This is the same global warming potential as reported for HCFC-123.

There is less attack with hexafluorobutane on typical appliance inner liner plastics than with CFC-11 or, of course, HCFCs. Samples of PS, SB and ABS have been immersed for weeks in hexafluorobutane and showed no negative effects. The same kind of result can be obtained with a simple condensation test by cooling down a plastic sheet over saturated blowing agent vapours.

Toxicology testing of hexafluorobutane is in progress but not complete. Acute and subacute toxicity testing has been performed. The results show a low level of toxicity and encourage further development.

All things considered, these properties found for 1,1,1,4,4,4 hexafluorobutane fit our list of requirements very well, as shown in Table 1.

How does HFC-356 perform in PUR rigid foam systems?

PUR RIGID FOAM WITH 1,1,1,4,4,4 HEXAFLUOROBUTANE

The first trial to be done with any new blowing agent is of course to use it as drop-in product in established PUR systems. Table 3 shows the results of trials using HFC-356 in a commercial European-type 50% reduced CFC-11 product, *Baytherm VP PU 1632. For equimolar quantities, we should have used about 20 pbw of HFC-356 in the processing formula, but this was not successful due to reduced solubility of HFC-356 in PU 1632. Running with only 10 pbw of HFC-356 (3.9% at the mixhead), free rise and over-

Table 3. 1,1,1,4,4,4 hexafluorobutane (HFC-356) PUR foam based on commercial product *Baytherm VP PU 1632.

| Processing Formula: | | | |
|-------------------------------------|-------------------|-------|-------|
| * Baytherm VP PU 1632 A 0 | pbw | 100.0 | 100.0 |
| * Desmorapid 726 b | pbw | 1.5 | 1.5 |
| HFC-356 | pbw | | 10.0 |
| CFC-11 | pbw | 17.0 | |
| * Desmodur 44V20 | pbw | 148.0 | 148.0 |
| Blowing Agent in Mix | % | 6.4 | 3.9 |
| Handmix Results (1000 rpm, 7 s): | | | |
| Cream Time | s | 11 | 10 |
| Gel Time | s | 69 | 65 |
| Free Rise Density | kg/m ³ | 22.5 | 27.3 |
| Machine Results (High Pressure): | | | |
| Gel Time | s | 48 | 38 |
| Free Rise Density | kg/m ³ | 22.1 | 27.0 |
| Cell Size/Structure | | fine | fine |
| Minimum Fill Density (Brett Mould) | kg/m ³ | 30.7 | 35.5 |
| Overall Density | kg/m ³ | 32.7 | 37.2 |
| Core Density | kg/m ³ | 30.0 | 35.5 |
| Compressive Strength | MPa | 0.137 | 0.170 |
| Dimensional Stability (14 d, -30°C) | % | 0 | 0 |

all densities are considerably higher than with double the molarity of CFC-11. In any case, our goal was to learn something about thermal conductivity and aging behaviour.

Figure 2 shows thermal conductivities (Anacon, 24 °C) of both foams as a function of time during open aging at room temperature. The initial value of k for HFC-356 is about 10% higher than when using CFC-11, but after aging, both foams show the same level of thermal conductivity.

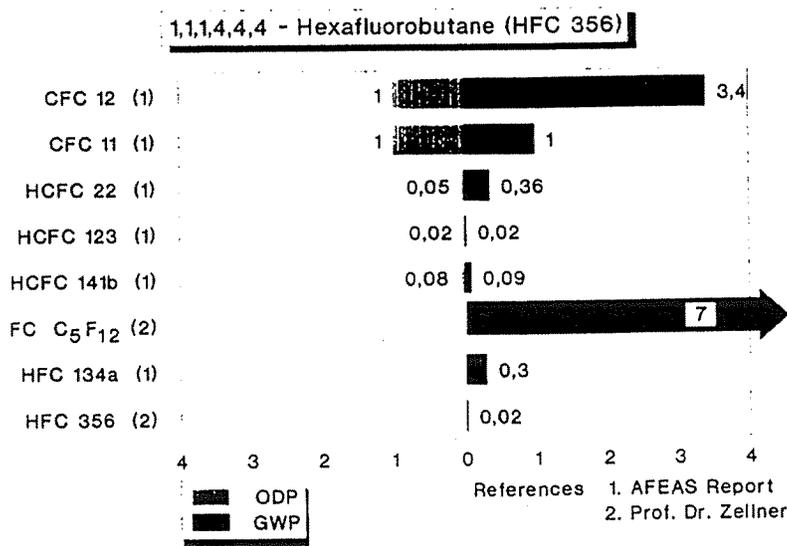


Figure 1. ODP (ozone depletion potential) and GWP (global warming potential) of CFCs, HCFCs, FCs and HFCs

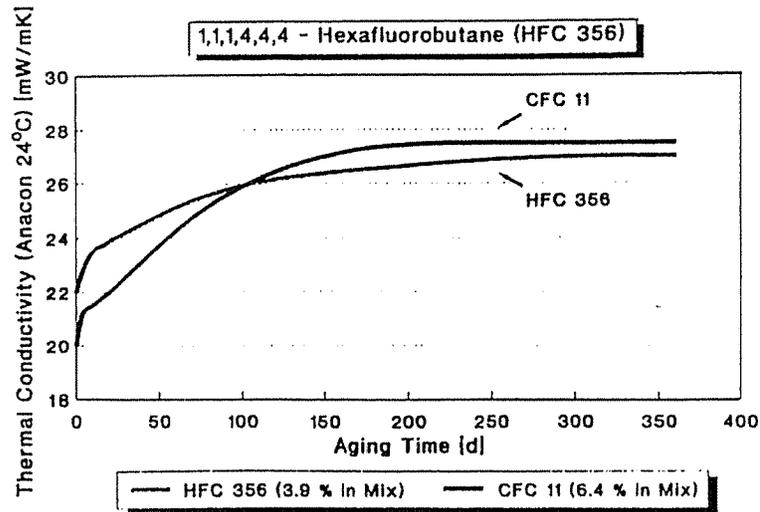


Figure 2. PU 1632: aging at RT, open to diffusion.

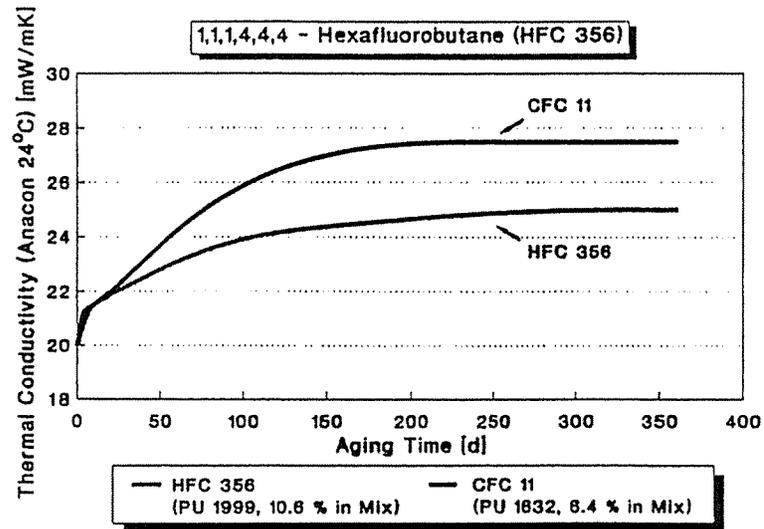


Figure 3. Aging at RT, open to diffusion.

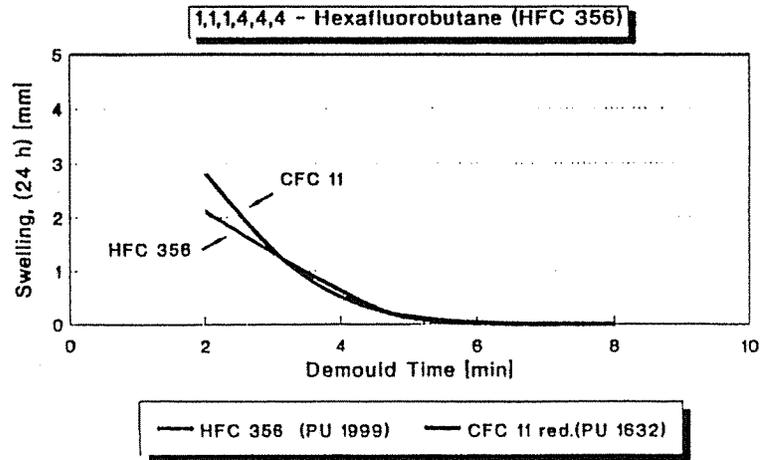


Figure 4. Demould time. Brett Mould (200 x 20 x 5 cm)

Table 4. 1,1,1,4,4,4 hexafluorobutane (HFC-356) PUR foam based on optimised product Baytherm VP PU 1999.

| Processing Formula: | | |
|-------------------------------------|-------------------|-------|
| Baytherm VP PU 1999 | pbw | 100.0 |
| Desmorapid 726 b | pbw | 2.9 |
| HFC-356 | pbw | 29.0 |
| Desmodur 44V20 | pbw | 142.0 |
| Blowing Agent in Mix | % | 10.6 |
| Handmix Results (1000 rpm. 4s): | | |
| Cream Time | s | 4 |
| Gel Time | s | 47 |
| Free Rise Density | kg/m ³ | 26.4 |
| Machine Results (HK 270): | | |
| Gel Time | s | 32 |
| Free Rise Density | kg/m ³ | 24.8 |
| Cell Size/Structure | | fine |
| Minimum Fill Density (Brett Mould) | kg/m ³ | 31.4 |
| Overall Density | kg/m ³ | 33.8 |
| Core Density | kg/m ³ | 32.2 |
| Compressive Strength | MPa | 0.142 |
| Dimensional Stability (14 d. -30°C) | % | 0 |
| Open Cells | % | 6 |

To optimise flow, densities and thermal conductivity, reformulation work on the polyol side of the PUR system had to be done. So we designed the first PUR appliance system specially for the use of hexafluorobutane, [®]Baytherm VP PU 1999.

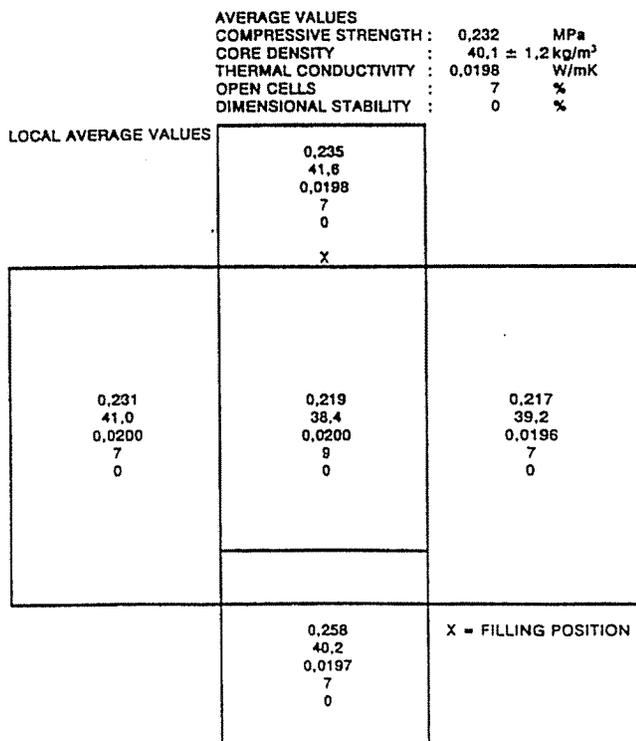


Figure 5. Baytherm VP PU 1999/HFC-356 cabinet results

In Table 4 equivalent results for PU 1999/HFC-356 are listed. These look quite typical for PUR appliance insulation systems, except for some fine tuning. Of course, we again monitored thermal conductivity and aging behaviour (Figure 3). Initial *k* is at the same level as for CFC-11-reduced PU 1632, but aging behaviour is significantly better.

Demould properties were checked in the Brett-Mould. Figure 4 shows the swelling of the panel as function of demould time for PU 1999/HFC-356 and PU 1632/CFC-11. Demould behaviour of both is very similar.

Figure 5 shows the distribution of the physical properties of the foam in a normal refrigerator cabinet.

All things considered, this hexafluorobutane system fulfills the technical standards of the European appliance industry compared to 50% CFC-11-reduced products.

CONCLUSIONS

HCFCs may be technically the most favourable replacements for CFC-11 as blowing agents and insulating cell gases in PUR rigid foams, especially for appliance applications during the next couple of decades. If HCFCs are going to be phased out sometime in the 21st century due to their residual ozone depletion potential, 1,1,1,4,4,4 hexafluorobutane could offer an option to:

- maintain the insulation properties of PUR rigid foams with even improved aging behaviour
- stay with well known foaming equipment and process parameters
- keep established appliance construction including today's inner liner plastic materials

But we should not forget: we still have a long way to go.

According to the regulations on chemical substances worldwide, hexafluorobutane is a new chemical substance which requires notification before commercialization.

Toxicology testing has to be continued to make sure that hexafluorobutane can serve as a safe substitute for CFC-11 in foam applications. In addition, research on side reactions in the masterbatch and the produced PUR foam has to be done.

Ecotoxicological studies on the degradation of hexafluorobutane in the atmosphere and in the ground, and positive results thereof, are necessary to find acceptance by ecological and political authorities.

Fluorine chemistry is expensive and so are the resulting products. That is why HFC-356 surely will not be a solution for the whole range of PUR rigid foam applications. For reasons of costs the use of HFC-356 more likely will be for applications in which the value of the foam insulation including blowing agent is low compared to the value of the final sales product.

To conclude, we think 1,1,1,4,4,4 hexafluorobutane is among other, similar products [2] a promising candidate for a third generation of blowing agents and deserves your kind attention.

ACKNOWLEDGEMENTS

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Last but not least, I wish to thank all those people at Bayer who supported the project giving their expert advice, particularly Dr. C.-D. Sommerfeld and Dr. H. Thomas.

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BIOGRAPHY

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Wilhelm M. Lamberts is responsible for the development of PUR appliance insulation systems in the Applications Development Department of Bayer AG, Polyurethane Division, in Leverkusen, FRG. He is a member of the Bayer World Appliance Technical Committee which meets regularly to exchange information on basic developments and technologies being created for this global market.

Dr. Lamberts received his Dr. rer. nat. degree in Inorganic Chemistry in 1985 from the Rheinisch-Westfälische Technische Hochschule in Aachen, FRG. He joined the Appliance Group of Bayer AG's Applications Development Department in 1986.

HFC 356, a Zero ODP Blowing Agent Candidate for North American Appliance Foam Formulations

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ABSTRACT

The household refrigeration industry in the U.S.A. is being challenged on two issues. These issues are depletion of the ozone layer by CFCs and federally mandated energy consumption standards for the products sold in the U.S. The global issue of ozone depletion affects all domestic appliance producers in North America. The energy consumption issue, however, only affects those producers who desire to sell their products in the U.S.

In addressing the ozone depletion issue the North American manufacturers of household refrigerators and freezers have accepted HCFCs as the most promising available blowing agent substitutes for CFCs in their polyurethane foam insulations. Over the past few years a great deal of effort has gone into the development of polyurethane foam insulations blown with HCFCs which have the properties required by the North American household refrigeration industry. Between now and 1995 we expect a conversion of the industry from CFC to HCFC blown polyurethane foam insulations.

HCFCs, however, are only transition materials. Since their ozone depletion potentials are not zero, they too are scheduled for production caps and phase-out under the provisions of the amendments to the Montreal Protocol. Thus, it is necessary to begin the development now on the next generation of North American appliance foam formulations which do not use ozone depleting substances as blowing agents.

Our previous work has shown the ability to develop appliance foams blown with HFC 356 which satisfactorily meet the technical requirements of the European appliance industry in many important areas. The design and construction differences between European and North American refrigerated appliances, however, does not allow direct translation of appliance foam technology. The foam flowability, k-factor, density and demold requirements are not the same. Consequently, our development effort has now expanded to address the needs of the North American domestic appliance producer. Results of work done with HFC 356 based foam systems engineered for the North American appliance insulation market are presented with comparisons to known CFC and HCFC blown appliance foams.

TABLE 1
1,1,1,4,4,4 hexafluorobutane (HFC-356)
product properties.

| | HFC-356 | CFC-11 |
|--------------------------------------|--|---------------------|
| Formula | C ₄ H ₄ F ₆ | CFCI ₃ |
| Molecular Weight | 166 g/mol | 137.5 g/mol |
| Boiling Point | 24.6°C | 23.8°C |
| Flashpoint | --- | --- |
| Ignition Temperature | none below 600°C | none below 600°C |
| Explosion Limits | --- | --- |
| Gas Phase Thermal Conductivity, 20°C | 0.0095 W/Km | 0.008 W/Km |
| ODP | 0 | 1 |
| GWP | 0.16* | 1 |

Compatibility with Refrigerator Food Liner Plastics:

| | | |
|----------|--------------|--------------------|
| PS | ++ | - |
| SB | ++ | 0 |
| ABS | ++ | + |
| Toxicity | not complete | TLV/MAK 1000ppm |

*Measured by Prof. Dr. R. Zellner, Göttingen.

EEBSP193

TABLE 2

Appliance Foam Formulation Comparison
CFC 11, HCFC 141b and HFC 356

| | CFC 11 | HCFC 141b | HFC 356 |
|---------------------|--------|-----------|---------|
| Formulated Polyol | 74.00 | 73.85 | 77.04 |
| CFC 11 | 26.00 | | |
| HCFC 141b | | 26.15 | |
| HFC 356 | | | 22.96 |
| | ---- | ---- | ---- |
| Masterbatch Total | 100.00 | 100.00 | 100.00 |
| Polymeric MDI | 106.20 | 124.60 | 116.50 |
| Milliliters gas/gm. | 30.5 | 31.7 | 23.4 |
| Reactivity | | | |
| cream / gel (sec) | 5 / 38 | 8 / 40 | 4 / 27 |
| Hand mix foam | | | |

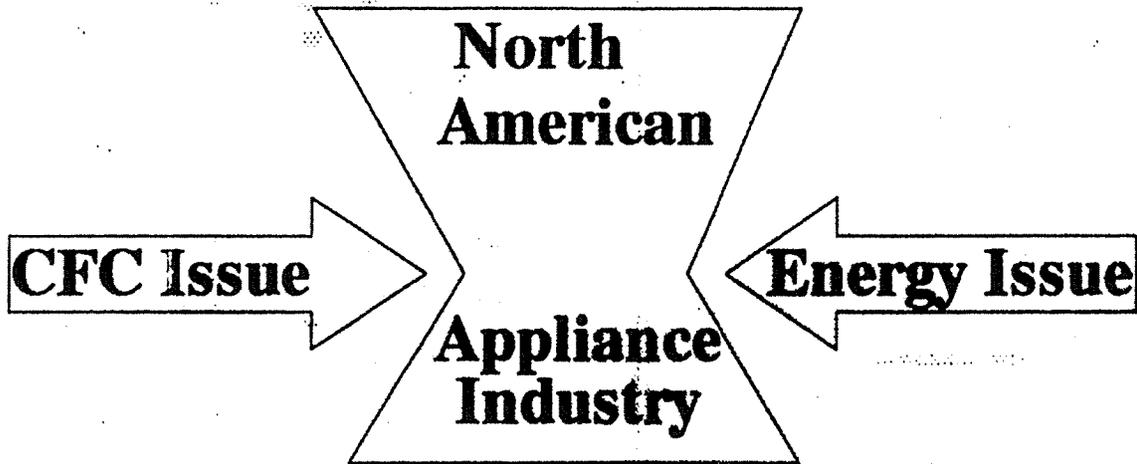
TABLE 3

Appliance Foam Property Comparison
CFC 11, HCFC 141b and HFC 356

| | CFC 11 | HCFC 141b | HFC 356 |
|------------------------------|-------------|-------------|-------------|
| Molded Density | | | |
| pcf (kg/cu.m) | 1.94 (31.1) | 1.74 (27.9) | 2.14 (34.3) |
| Core Density | | | |
| pcf (kg/cu.m) | 1.64 (26.3) | 1.57 (25.2) | 2.00 (32.0) |
| Initial Core K | | | |
| Btu-in/hr ft ² °F | 0.121 | 0.123 | 0.126 |
| mW/m K | 17.4 | 17.7 | 18.2 |
| Avg. Cell Size (um) | 251 | 210 | 132 |
| Freeze Stability | good | good | good |
| Hand mix foams | | | |

HFC 356

**A Zero ODP Blowing Agent Candidate for
North American Appliance Foam Formulations**



356SP101

Blowing Agent Transition to Zero ODP

CFC



HCFC

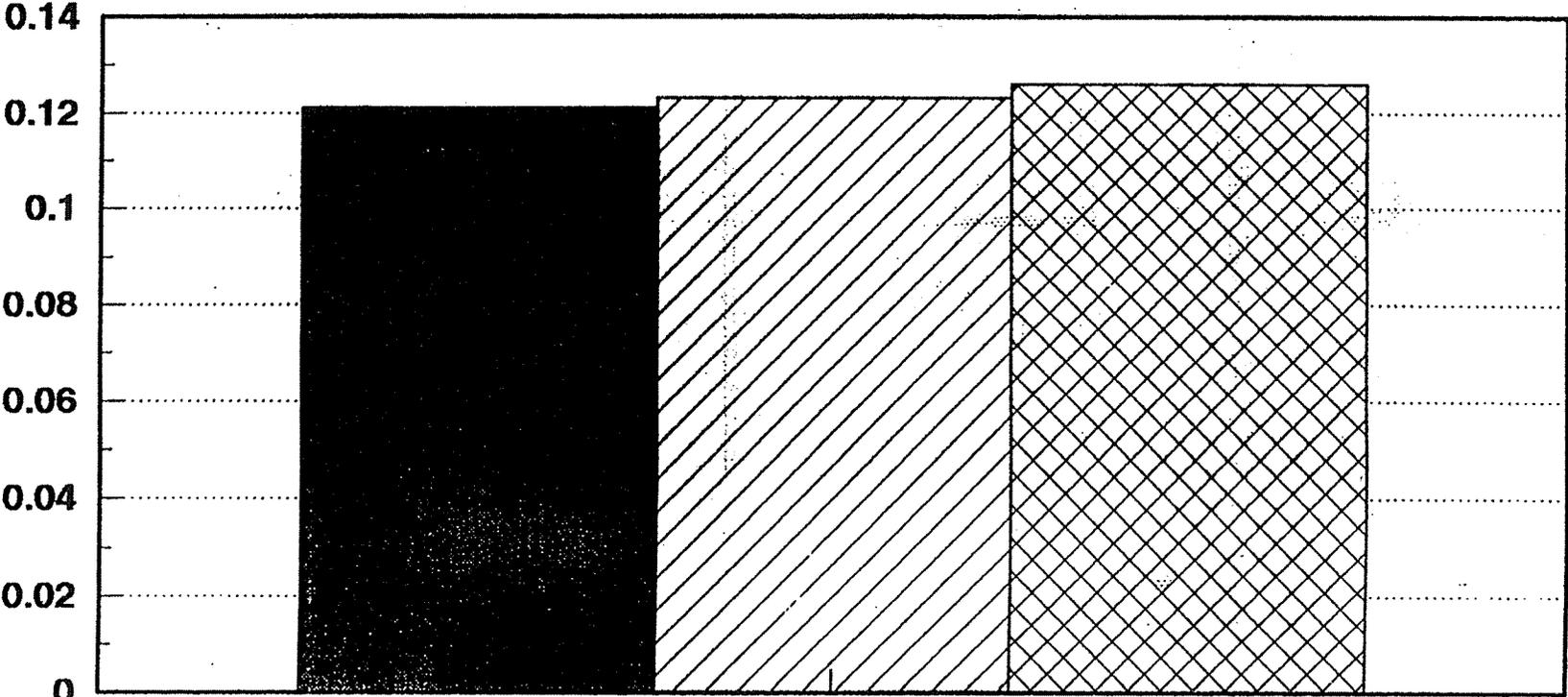


HFC

356SP104

HFC 356
k-Factor Comparison
Handmix Foams

k-factor (Btu in/h ft² °F)

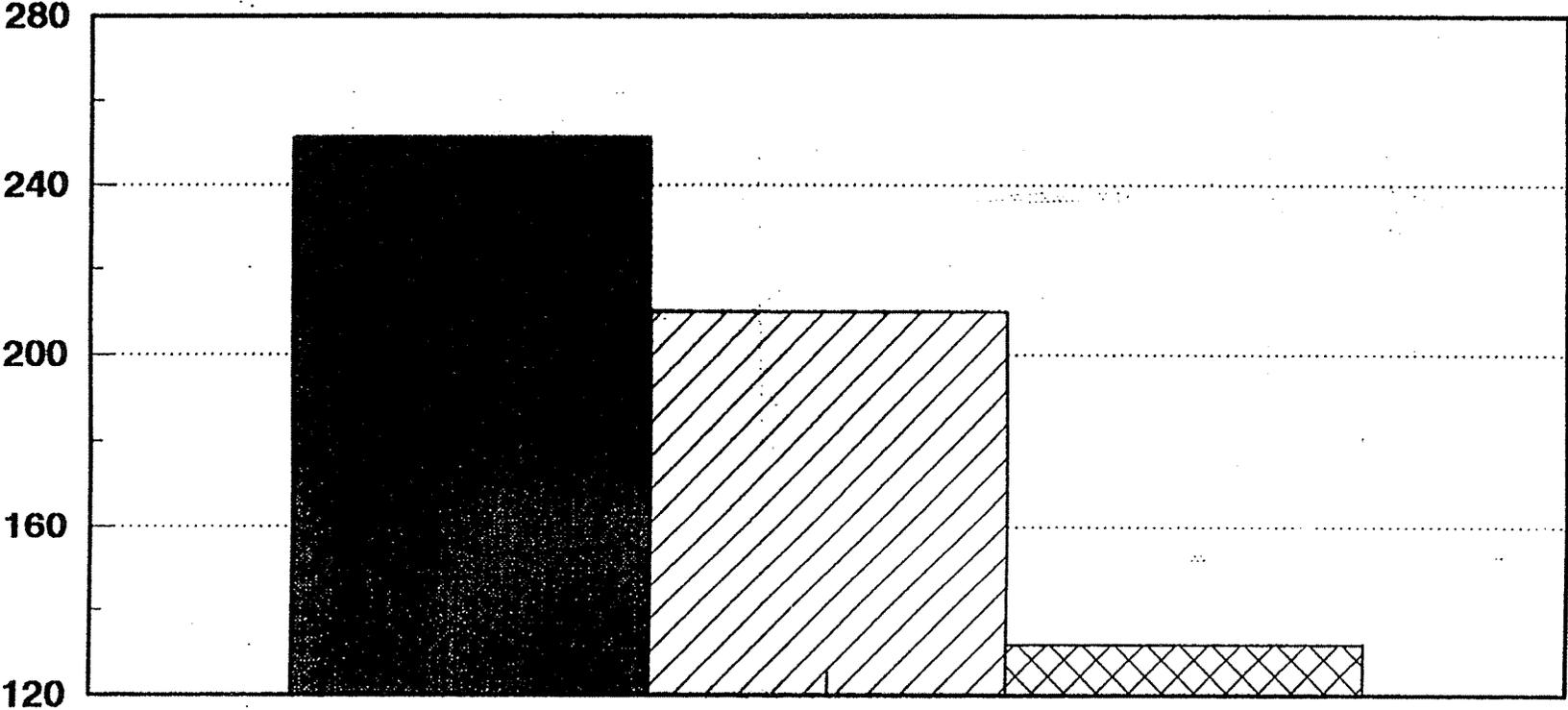


■ CFC 11 ▨ HCFC 141b ▩ HFC 356

50

HFC 356
Cell Size Comparison
Handmix Foams

microns



51

■ CFC 11 ▨ HCFC 141b ▩ HFC 356

Blowing Agents: The Next Generation

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ABSTRACT

It is increasingly recognized that HCFC materials are transitional or interim substances which will have limited commercial lifetimes as foam blowing agents. These materials, which are necessary for a rapid and complete phaseout of CFC blowing agents, will ultimately need to be replaced by even more environmentally benign blowing agents. The purpose of this paper is to discuss some potential options for next generation blowing agents.

The paper addresses two general blowing agent options: the conventional liquid blowing agent, and the lower boiling, so-called gaseous blowing agent. Liquid blowing agents like CFC-11 and HCFC-141b simplify foam processing techniques as well as blowing agent storage, handling and transportation. Optimum properties for this class of blowing agents, such as boiling point, flammability and thermal conductivity are summarized. Chemical classes, for example hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs), from which a next generation blowing agent might be chosen are discussed; physical properties of some model compounds chosen from these families are presented. The model compound data show that retaining the vapor insulation characteristics of HCFC-141b will be a challenge given that the more complicated polyatomic HFCs and HFEs tend to exhibit higher vapor phase thermal conductivities. Nevertheless, HFC and HFE liquids do exist and represent a promising avenue of research for a next generation blowing agent.

There are several HFC gases which are also potential blowing agents, for instance HFC-134a, which is currently being introduced as a commercial product as well as others like HFCs 32 and 125 which are currently under development. Vapor phase thermal conductivity data are presented which show that these species are also poorer insulators than HCFC-141b. Polyol solubility for the HFC gases can be significantly less than even HCFC-22 when compared on a theoretical equivalent (mole) substitution, i.e., a higher vapor pressure is required to maintain an equivalent solution of HFC gas in a polyol than is required for HCFC-22. These and other data presented will impact the choice of the next generation blowing agent.

INTRODUCTION

Hydrochlorofluorocarbon blowing agents such as HCFCs 22, 141b and 142b are now recognized as interim or transitional substitutes for CFC blowing agents used in essential thermal insulation foam applications. Interim use of these HCFC materials is required to achieve as rapid as possible phase-out of CFC blowing agents. The U.S. Clean Air Act currently calls for a phase-out of HCFCs for "nonessential" foam applications by January 1, 1994, and allows the use of HCFCs after the year 2015 only for servicing of existing equipment. HCFCs would be phased out totally by 2030. If prior experience is a guide, this HCFC regulatory scenario will in all likelihood be accelerated, and the time frame available to identify and develop the next generation of blowing agent substitutes could be shorter. Consequently, prudence dictates that the search for this next generation blowing agent(s) begin now given the long lead times required for process development and chronic toxicity evaluation.

In this paper we discuss some of the possible longer term options for blowing agent substitutes. Two general blowing agent options, gases and liquids, are considered as potential substitutes. To a large extent the polyurethane/polyisocyanurate foam industry has employed liquid blowing agents, such as CFC-11 and HCFC-141b, which simplify foam processing as well as blowing agent storage and handling practices. To date, only one zero ozone depletion potential liquid, HFC-356 ($\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$) [1], has been suggested as a long term blowing agent substitute. A number of other hydrofluorocarbon (HFC) liquids are also potential blowing agent candidates and are discussed in this paper. Preliminary physical property data are presented for some of these HFC candidates in order to begin assessing their technical feasibility. Other chemical classes such as hydrofluoroethers (HFEs) are also addressed. Before any of these liquid candidates can become commercial realities, it will be necessary to demonstrate an economically viable manufacturing technology as well as to show that candidates possess low degrees of toxicity and are environmentally acceptable from the viewpoint of global warming, volatile organic compound status and atmospheric fate.

The second general category of blowing agent options are the gaseous candidates. A number of HFC gases such as HFC-152a and HFC-134a are commercially available in limited quantities, while others, such as HFCs 125, 143a and 32, are in various stages of commercial development. These gases are leading candidates to replace HCFC-22, which is currently being used in certain polyurethane foam applications. Properties such as polyol solubility and vapor thermal conductivity are presented and are compared to the corresponding HCFC-22 property.

BLOWING AGENT SELECTION CRITERIA

The optimum blowing agent must be environmentally acceptable as well as economically viable. It must also possess a low degree of toxicity, be nonflammable (or moderately flammable), have a low molecular weight, low vapor thermal conductivity, and a low permeability through the polymer. Other requisites include thermal and chemical stability as well as appropriate materials compatibility, and appropriate solubility in polyols and isocyanates. Further requirements could be specified, but in order to screen potential candidates we propose employing the following simplified set of criteria:

1. Zero ozone depletion potential
2. Nonflammable or moderately flammable
3. 50°C boiling point upper limit
4. Molecular weight less than 180

This list is used to identify potential candidates which would then be narrowed down using other properties such as cost, toxicity, global warming potential, etc.

The first criterion is obvious. Moderate flammability is defined as no flash point in the case of a liquid; vapor flame limits are acceptable as long as there is a relatively high value for the lower flame limit and as long as there is a relatively high minimum ignition energy. Examples of moderately flammable fluids are HCFC-141b and HCFC-

142b. Hydrocarbons and certain HFCs like HFC-152a would not be classified as moderately flammable according to this definition.

An upper limit for the boiling point of a blowing agent is not obvious and the 50°C specified above is to some extent arbitrary. Setting an upper limit for the boiling point is based on aged foam *k*-factor arguments. To illustrate this point a little more clearly, we consider two hypothetical blowing agents, each having identical vapor thermal conductivities, but having significantly different boiling points. Hypothetical foams expanded with these blowing agents are also assumed identical, except that the initial cell gas pressure at ambient temperature in one foam is assumed to be 400 mm Hg for the higher boiling blowing agent (Case 1), while the initial cell gas pressure in the other foam is 700 mm Hg (Case 2). This difference arises because of the different boiling points. The initial *k*-factor for both foams is identical in this hypothetical situation because the vapor thermal conductivity is independent of pressure at these low pressures. However, the aged foam contains an air/blowing agent mixture which will have a greater mole (or relative partial pressure) concentration of blowing agent, and hence a lower thermal conductivity for Case 2. If we assume that the two blowing agents diffuse out of the foams at the same rate and that air enters both foams at equivalent rates, then the foam *k*-factor will change as illustrated in Figure 1. These calculations show that, with all other factors being equal, the foam with the higher initial blowing agent pressure provides better insulation characteristics compared to the lower initial pressure case. There are various means of influencing this initial blowing agent cell pressure; a high boiling blowing agent will result in a lower initial pressure, hence criterion (3) above. This becomes especially important at low service temperatures where the higher boiling point blowing agent will condense leaving ultimately air as the insulation gas. Increased blowing agent pressure can also be obtained by selecting a blowing agent with minimal solubility in the polyurethane polymer.

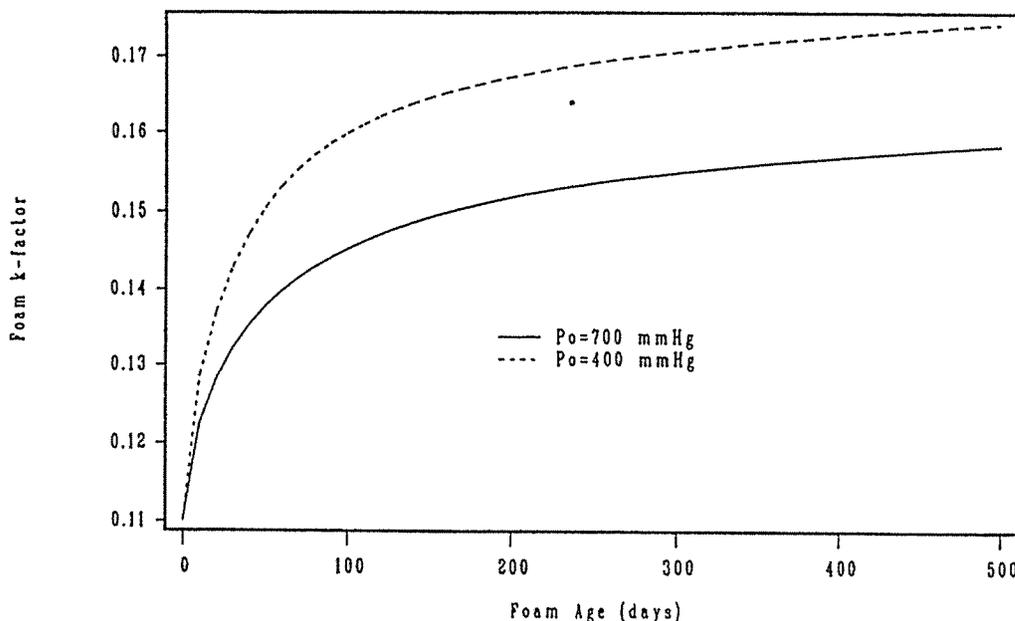


Figure 1. Effect of initial cell gas pressure on aged *k*-factor. Calculations for hypothetical case of identical foams and blowing agents except for different initial cell gas pressures.

If we make the distinction between gaseous and liquid blowing agents then there is probably a minimum boiling point for a fluid to be considered a liquid. Although such distinctions are arbitrary, the National Fire Protection Association (NFPA) defines a liquid as a fluid having a vapor pressure not exceeding 40 psia at 100°F [2]. This vapor pressure criterion translates to a boiling point of about 7°C, i.e., fluids with boiling points greater than about 7°C would be classified as liquids; lower boiling point fluids would be gases. Current U.S. Department of Transportation (DOT) regulations define a nonflammable compressed gas as having a vapor pressure greater than 41 psia at 20°C which is equivalent to a boiling point of about -8°C. For the purpose of this paper we will consider fluids with boiling points greater than 0°C to be liquids. Whether such low boiling liquids can be used as easily as CFC-11 or HCFC-141b depends on the degree of solubility in the polyol and isocyanate.

The molecular weight criterion is again somewhat arbitrary. A better criterion would be the cost of the blowing agent per mole (or theoretical substitution unit). With a molecular weight of 180, the substitution ratio relative to HCFC-141b is 1.54, so even at an equivalent cost per pound as 141b (which is unlikely), the 180 molecular weight substitute would suffer a 54% cost penalty. Obviously minimizing the molecular weight will provide economic advantages.

The list of candidates generated meeting the 4 selection requirements will then need to be honed further using criteria like acceptable manufacturing cost, low global warming potential, low toxicity, and end-use performance. Analysis of global warming impact should be based on a systems approach which accounts for the direct and indirect contributions to global warming [3]. The direct contribution is related to the global warming effect of the blowing agent itself while the indirect contribution is related to CO₂ emissions from fossil fuel based energy generation. Credit must be given for energy saved through use of highly efficient thermal insulation materials, otherwise, less efficient insulation materials, with lower direct contributions, may result in increased CO₂ emissions into the atmosphere and a net increase in global warming.

POTENTIAL CHEMICAL FAMILIES

It is not possible here to give a thorough analysis of what chemical classes or families have members which satisfy the 4 selection criteria, however, similar analyses, albeit for alternative refrigerants, have been reported previously [4]. Suffice to say that there are very few inorganic fluids which satisfy these criteria and which cannot be eliminated immediately for reasons such as toxicity, chemical instability and so on.

Of the organic chemical families, those with active hydrogens (e.g., alcohols, acids, certain amines, etc.) can be eliminated because of their reactivity towards isocyanates. In order to suppress the flammability inherent to most organic fluids, substitution with heteroatoms such as halogens is required. Only fluorine substitution will be generally acceptable because of the zero ODP requirement. In addition, fluorochemicals as a class offer the greatest number of potential candidates which are non-ozone depleting, nonflammable or moderately flammable, and which have at least some members with low toxicity.

The leading fluorochemical class is the fluorocarbon

family due to the relatively well characterized process chemistries and known members with low degrees of chronic toxicity. Of the other fluorochemical families the fluoroethers are probably the most encouraging although there is significantly less known about these chemicals than the fluorocarbons. There is even less known about other fluorochemical families based on other functional groups. Consequently most of this paper will deal with fluorocarbon based candidates.

Perfluorocarbons, as special class of fluorocarbons, are characterized by very long atmospheric lifetimes of the order of hundreds to thousands of years. Hence their global warming impact over the long term could be significant. Consequently, gaseous perfluorocarbons such as FC-14, FC-116, FC-218 and FC-C-318, as well as liquids such as perfluoropentane and perfluorohexane are not considered viable blowing agent options. Cost would also influence the acceptability of these materials as blowing agents. Nevertheless, perfluoropentane and perfluorohexane are useful as foam formulation additives which provide improved thermal insulation properties.

A preliminary literature search for fluoroether candidates did reveal a number of possibilities which meet our 4 simple screening criteria. However, potentially adverse toxicological effects were reported [6-10] for a number of fluoroethers. Although this does not preclude the possibility of low toxicity fluoroethers, it is noteworthy and should be evaluated early on in the development of a fluoroether. Certain fluoroether structures are also likely to be chemically unstable, e.g., so-called E-245, CF₃CH₂OCHF₂, which has been evaluated as a CFC-11 replacement in refrigerant applications. This particular ether was reported [5] as chemically unstable in glass containers at 250°F. Again, the stability of HFEs should be assessed early on in their development.

POTENTIAL GASEOUS HFC BLOWING AGENTS

A number of HFC candidates are currently available in (limited) commercial quantities or are actively under commercial development. Most of these HFCs have been identified as refrigerant substitutes and are being commercialized, at least initially, for this purpose. These materials are HFCs 152a, 134a, 125, 32, 143a and 23, all of which are classified as compressed gases. Atmospheric lifetime and GWP data along with some typical physical properties for these gases and similar data for HCFCs 22 and 142b are summarized in Table 1.

The most attractive of these candidates on an environmental basis is HFC-152a, having a 1.8 year lifetime and a 0.03 GWP. However, 152a is flammable as indicated by the data listed in Table 2. Its minimum ignition energy and autoignition temperature (which measure ease of ignition) as well as vapor flame limits are very similar to methane. Of the other HFC gases only 143a and 32 exhibit flame limits. HFC-143a flame limits are very similar to those for HCFC-142b, while HFC-32 is even less flammable on a flame limit basis, the lower flame limit being 12.7 vol%. HFC-32 is also attractive from the environmental viewpoint having a relatively low GWP, whereas HFC-143a has an atmospheric lifetime and GWP comparable to CFC-11. Only HFCs 152a, 32 and 134a have lower GWPs than HCFC-22.

HFCs 134a and 152a are of lower volatility than HCFC-22; the other HFCs listed in Table 1 all have lower boiling

Table 1. Properties of some HFC gases.

| | HFC-152a | HFC-134a | HFC-125 | HFC-32 | HFC-143a | HCFC-22 | HCFC-142b |
|---|----------------------------------|----------------------------------|-----------------------------------|--------------------------------|---------------------------------|--------------------|-----------------------------------|
| Formula | CF ₂ HCH ₃ | CF ₃ CFH ₂ | CF ₃ CF ₂ H | CH ₂ F ₂ | CF ₃ CH ₃ | CHClF ₂ | CF ₂ ClCH ₃ |
| Atm. Life ¹ (yrs) | 1.8 | 15.6 | 40.5 | 7.3 ² | 64.2 | 15.8 | 22.4 |
| GWP ¹ | 0.03 | 0.25 | 0.84 | 0.17 ² | 1.2 | 0.36 | 0.42 |
| M.Wt. | 66.0 | 102.0 | 120.0 | 52.0 | 84.0 | 86.5 | 100.5 |
| T _g , °C | -24.7 | -26.5 | -48.5 | -51.7 | -47.6 | -40.8 | -9.2 |
| P _{vap} , psia at 70°F | 77.2 | 85.8 | 180.4 | 220.2 | 165.2 | 136.1 | 43.5 |
| Flame Limits, ³ vol.% | 4.2-20.2 | None | None | 12.7-33.4 | 7.0-19.0 | None | 7.2-18.2 |
| Vapor Thermal Conductivity, mW/m/K at 44°C | 14.5 | 15.7 | TBD | 13.8 | 14.0 | 11.5 | 12.4 |

¹UNEP, 1991.

²Preliminary values.

³ASTM E 681-85 method using match ignition source.

points and higher vapor pressures than HCFC-22. Storage tanks and cylinders rated for use with HCFC-22 are not rated to handle pressures associated with HFCs 32, 125 and 143a. Vapor phase thermal conductivity data are also listed in Table 1. None of these HFC gases are as efficient insulators as HCFC-141b or for that matter HCFC-22. This should impact foam insulation efficiency, however the effect may be ameliorated to some extent because of possible lower solubility of these gases in the polymer phase and possibly lower permeability, especially for the more highly fluorinated HFCs. Some of the smaller molecules such as HFC-32 may, however, have a relatively high permeability in the polymer which could affect the aged *k*-factor. These basic blowing agent property measurements are currently underway at our laboratory.

Use of gaseous blowing agents as the sole expansion agent for low density foams generally results in a froth-foam process which is different from the liquid-pour process. The tendency for a gaseous blowing agent to froth is controlled to some extent by its solubility in various foam formulation components. We have evaluated the solubility of most of the HFC gases listed above along with that of HCFC-22 in two test polyols, a sucrose polyether polyol (Pluracol[®] 975, 500 hydroxyl number, manufactured by BASF) and an aromatic polyester polyol (Terate[®] 254, 235 hydroxyl number, manufactured by Cape Industries). We chose these two polyols as test systems after observing that they span the typical solvency range exhibited by polyols towards HCFC and HFC gases, the polyether polyol generally providing good solvency towards gases, the polyester polyol providing poorer solubility.

Polyol/blowing agent solubility measurements are performed in an apparatus depicted schematically in Figure

Table 2. HFC-152a flammability.

| | | |
|----------|--------------------------|----------------|
| HFC-152a | Flame Limits* | 4.2-20.2 vol.% |
| | Minimum ignition energy | <22 mJ |
| | Autoignition temperature | 455 °C |
| Methane | Flame Limits* | 4.8-16.3 vol.% |
| | Minimum ignition energy | 0.3 mJ |
| | Autoignition temperature | 537 °C |

*ASTM E 681, match ignition source, ambient conditions.

2. The apparatus consists of a 126 cm³ stainless steel vessel equipped with a magnetically coupled stirrer which provides a leak-tight stirring arrangement. A large stirring blade is required to ensure rapid equilibrium between the viscous polyol and the gaseous blowing agent. Measurements are performed by loading polyol (or isocyanate) into the vessel to approximately 33% fill by volume. The apparatus is evacuated to remove dissolved air from the polyol; stirring during evacuation prevents the polyol from foaming. Degassed blowing agent is then added from a pre-weighed supply cylinder. Blowing agent remaining in the line after transfer is transferred back to the supply cylinder by freezing the cylinder in liquid nitrogen. The mass of blowing agent added to the solubility cell is determined by re-weighing the supply cylinder. The cell is submerged in a constant temperature bath controlled to ±0.02°C. Equi-

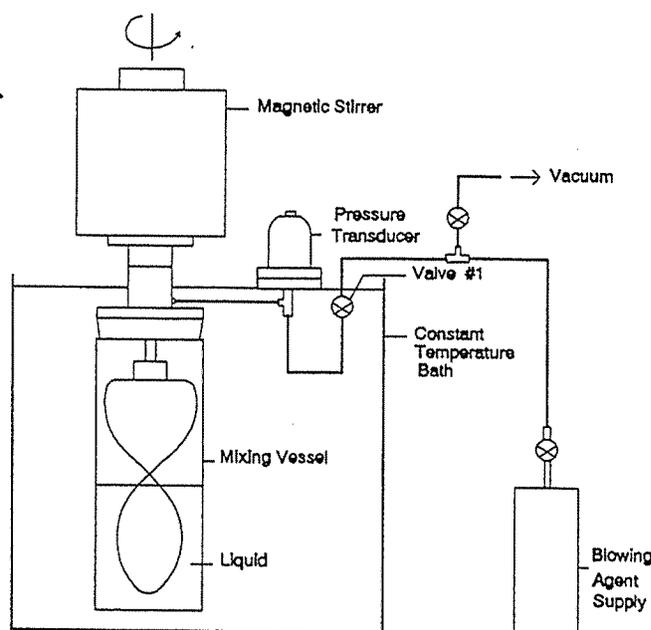


Figure 2. Apparatus for determining blowing agent solubility in polyols.

Table 3a. Solubility of 152a in Pluracol 975.

| T (°C) | P (psia) | Wt. 152a/100 g Polyol | Mole 152a/100 g Polyol |
|--------|----------|--------------------------|------------------------------|
| 25.00 | 5.737 | .9217 | .0140 |
| 25.00 | 13.887 | 2.3557 | .0357 |
| 25.00 | 23.314 | 4.2501 | .0644 |
| 24.99 | 32.157 | 6.3266 | .0959 |
| 50.00 | 8.732 | .8350 | .0127 |
| 50.00 | 21.727 | 2.1237 | .0322 |
| 50.00 | 37.312 | 3.8270 | .0580 |
| 49.99 | 52.587 | 5.6975 | .0863 |

librium is attained after about an hour of vigorous stirring and is indicated by constant pressure readings from the electronic pressure transducer. The amount of blowing agent dissolved in the polyol is determined from the mass of blowing agent added to the cell, corrected for the small quantity of blowing agent present in the vapor space of the cell. This vapor space correction is computed using the blowing agent equation of state from the measured pressure and temperature and the vapor volume (cell volume minus the liquid volume). The solubility is reported as parts of blowing agent dissolved in 100 parts of polyol at the measured temperature and pressure. After completing a measurement the temperature can be varied or an additional quantity of blowing agent added to the cell for the next measurement.

Tables 3-8 summarize solubility measurements of HFCs 152a, 134a, 125, 32, and 143a performed at 25°C and 50°C in the two test polyols. The solubility data are reported as parts by weight blowing agent per 100 parts by weight of polyol as well as moles of blowing agent per 100 g of polyol. Comparing solubilities on the latter basis permits comparison of vapor pressures at equivalent blowing agent theoretical substitution ratios. The results are plotted in Figures 3-6. The polyether polyol data indicate that HCFC-22 is more soluble than any of the HFCs studied at an equivalent mole substitution, e.g., the HCFC-22 pressure at 0.04 moles per 100 g Pluracol 975 (3.5 parts HCFC-22 per 100 parts polyol) is about 6-7 psia at 25°C. HFC-152a at the same mole loading (2.6 pph by weight) exerts a pressure of about 15 psia, i.e., it is less soluble than HCFC-22. The other HFCs are even less soluble than 152a, exerting pressures of about 17 psia for HFC-134a, 27 psia for HFC-32, and greater than 30 psia for HFCs 125 and 143a, all at the same 0.04 moles per 100 g polyol load-

Table 3b. Solubility of 152a in Terate 254.

| T (°C) | P (psia) | Wt. 152a/100 g Polyol | Mole 152a/100 g Polyol |
|--------|----------|--------------------------|------------------------------|
| 25.00 | 6.238 | .8456 | .0128 |
| 25.00 | 14.293 | 2.0118 | .0305 |
| 25.00 | 21.930 | 3.2630 | .0494 |
| 24.99 | 32.240 | 5.1420 | .0779 |
| 50.00 | 9.054 | .7623 | .0116 |
| 50.00 | 21.310 | 1.7989 | .0273 |
| 49.99 | 33.374 | 2.9085 | .0441 |
| 50.01 | 50.224 | 4.5714 | .0693 |

Table 4a. Solubility of 134a in Pluracol 975.

| T (°C) | P (psia) | Wt. 134a/100 g Polyol | Mole 134a/100 g Polyol |
|--------|----------|--------------------------|------------------------------|
| 25.03 | 5.533 | 1.2186 | .0120 |
| 25.03 | 14.484 | 3.3518 | .0329 |
| 25.03 | 22.527 | 5.4117 | .0531 |
| 50.01 | 8.780 | 1.0799 | .0106 |
| 50.02 | 23.804 | 2.9381 | .0288 |
| 50.00 | 37.252 | 4.7425 | .0465 |

Table 4b. Solubility of 134a in Terate 254.

| T (°C) | P (psia) | Wt. 134a/100 g Polyol | Mole 134a/100 g Polyol |
|--------|----------|--------------------------|------------------------------|
| 25.00 | 9.173 | 1.2475 | .0122 |
| 25.03 | 17.944 | 2.4839 | .0244 |
| 25.03 | 28.458 | 4.1317 | .0405 |
| 50.00 | 13.267 | 1.0756 | .0105 |
| 50.00 | 26.214 | 2.1279 | .0209 |
| 50.01 | 41.835 | 3.5408 | .0347 |

Table 5a. Solubility of 32 in Pluracol 975.

| T (°C) | P (psia) | Wt. 32/100 g Polyol | Mole 32/100 g Polyol |
|--------|----------|------------------------|----------------------------|
| 25.08 | 7.861 | 0.6113 | .0118 |
| 24.98 | 18.708 | 1.4732 | .0283 |
| 25.03 | 18.792 | 1.4709 | .0283 |
| 25.03 | 27.348 | 2.1503 | .0414 |
| 25.03 | 34.914 | 3.0595 | .0588 |
| 50.03 | 11.178 | 0.5445 | .0105 |
| 49.99 | 26.859 | 1.3056 | .0251 |
| 50.05 | 39.365 | 1.9002 | .0365 |
| 50.05 | 50.606 | 2.7277 | .0525 |

Table 5b. Solubility of 32 in Terate 254.

| T (°C) | P (psia) | Wt. 32/100 g Polyol | Mole 32/100 g Polyol |
|--------|----------|------------------------|----------------------------|
| 25.04 | 7.932 | 0.5067 | .0097 |
| 25.03 | 19.329 | 1.2613 | .0243 |
| 24.99 | 26.465 | 1.7575 | .0338 |
| 50.04 | 10.510 | 0.4567 | .0088 |
| 50.01 | 26.238 | 1.1215 | .0216 |
| 50.04 | 36.369 | 1.5538 | .0299 |

Table 6a. Solubility of 125 in Pluracol 975.

| T (°C) | P (psia) | Wt. 125/100 g Polyol | Mole 125/100 g Polyol |
|--------|----------|----------------------|-----------------------|
| 25.01 | 9.126 | 1.3045 | .0109 |
| 25.03 | 17.932 | 2.6631 | .0222 |
| 25.03 | 29.006 | 4.4742 | .0373 |
| 50.04 | 13.589 | 1.1070 | .0092 |
| 50.02 | 27.348 | 2.2328 | .0186 |
| 50.01 | 44.591 | 3.7441 | .0312 |

Table 6b. Solubility of 125 in Terate 254.

| T (°C) | P (psia) | Wt. 125/100 g Polyol | Mole 125/100 g Polyol |
|--------|----------|----------------------|-----------------------|
| 25.00 | 16.047 | 1.0756 | .0090 |
| 25.00 | 27.885 | 1.9180 | .0165 |
| 25.00 | 35.343 | 2.4926 | .0208 |
| 50.01 | 19.949 | 0.9103 | .0076 |
| 50.04 | 35.045 | 1.6034 | .0134 |
| 50.02 | 44.675 | 2.0738 | .0173 |

Table 7. Solubility of 143a in Pluracol 975.

| T (°C) | P (psia) | Wt. 143a/100 g Polyol | Mole 143a/100 g Polyol |
|--------|----------|-----------------------|------------------------|
| 25.00 | 5.367 | .3478 | .0041 |
| 25.00 | 14.329 | .8535 | .0102 |
| 25.00 | 22.479 | 1.4051 | .0167 |
| 25.00 | 31.680 | 1.9943 | .0237 |
| 49.99 | 6.608 | .3152 | .0038 |
| 50.00 | 18.135 | .7449 | .0089 |
| 50.01 | 28.696 | 1.2244 | .0146 |
| 50.01 | 40.570 | 1.7349 | .0207 |

Table 8a. Solubility of 22 in Pluracol 975.

| T (°C) | P (psia) | Wt. 22/100 g Polyol | Mole 22/100 g Polyol |
|--------|----------|---------------------|----------------------|
| 24.99 | 10.080 | 4.7901 | .0554 |
| 25.01 | 17.407 | 8.4208 | .0974 |
| 25.01 | 25.283 | 12.4712 | .1442 |
| 50.01 | 19.054 | 4.4312 | .0512 |
| 50.00 | 33.040 | 7.7982 | .0902 |
| 50.02 | 47.849 | 11.5795 | .1339 |

Table 8b. Solubility of 22 in Terate 254.

| T (°C) | P (psia) | Wt. 22/100 g Polyol | Mole 22/100 g Polyol |
|--------|----------|---------------------|----------------------|
| 25.00 | 14.054 | 3.9524 | .0457 |
| 25.00 | 24.138 | 7.1613 | .0828 |
| 25.00 | 32.932 | 10.2924 | .1190 |
| 50.00 | 23.565 | 3.59345 | .0415 |
| 50.00 | 41.047 | 6.52075 | .0754 |
| 50.00 | 56.799 | 9.38544 | .1085 |

ing and at 25°C. Even though HFCs 134a and 152a have lower vapor pressures than HCFC-22 (see Table 1), these HFCs exert higher vapor pressures than HCFC-22 when dissolved in most polyols at equivalent loadings. A possible consequence of this behavior is a greater tendency to froth than is evident with HCFC-22.

Figures 5 and 6 summarize similar data for the aromatic polyester polyol. Again, HCFC-22 is more soluble than the HFC gases of which 152a is the most soluble, followed by HFCs 32 and 134a, which have very similar vapor pressures in this polyol even though 32 and 134a by themselves have very dissimilar vapor pressures (see Table 1). HFC-125 has the lowest solubility of the gases studied in the aromatic polyester polyol. All of the gases exhibit lower solubility in the polyester polyol than in the polyether polyol.

We have also measured the miscibility of HFC gases in Pluracol 975 and another aromatic polyester polyol, Terate® 203 (Cape Industries). Miscibility experiments are performed in sealed, heavy walled glass tubes as depicted in Figure 7. Measurements are performed by adding a known weight of polyol, generally about 2 g, to the tubes then distilling a fixed weight of blowing agent into the tube. The tube is then frozen in liquid nitrogen and the

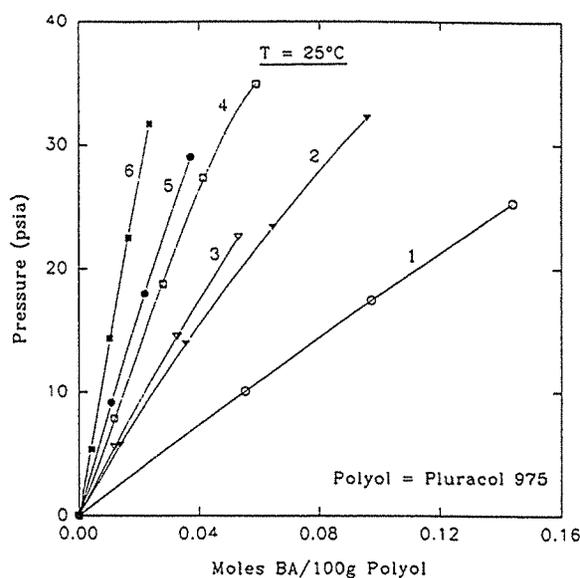


Figure 3. Vapor pressure measurements for various gaseous blowing agents in a polyether polyol (Pluracol 975) at 25°C. Curves: (1) HCFC-22, (2) HFC-152a, (3) HFC-134a, (4) HFC-32, (5) HFC-125, and (6) HFC-143a.

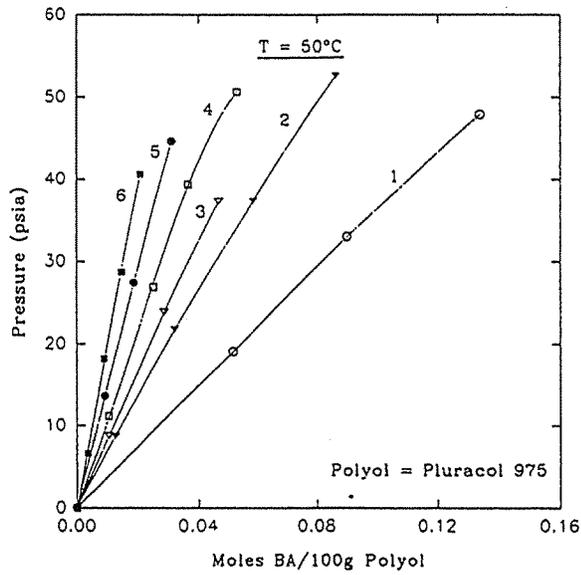


Figure 4. Vapor pressure measurements for various gaseous blowing agents in a polyether polyol (Pluracol 975) at 50°C. Curves: (1) HCFC-22, (2) HFC-152a, (3) HFC-134a, (4) HFC-32, (5) HFC-125, and (6) HFC-143a.

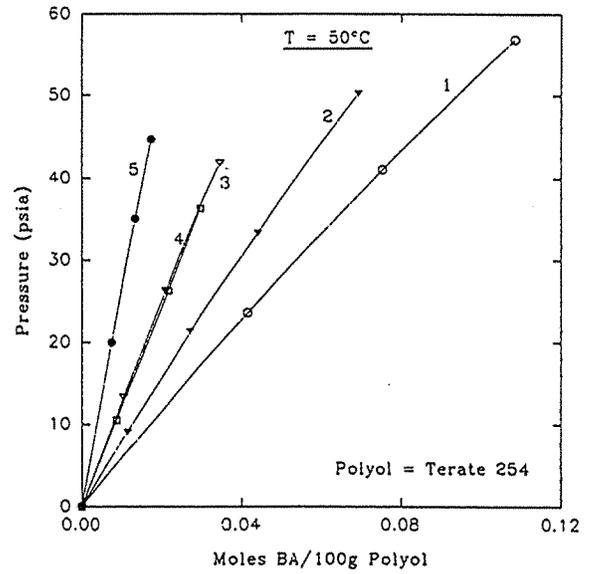


Figure 6. Vapor pressure measurements for various gaseous blowing agents in aromatic polyester polyol (Terate 254) at 50°C. Curves: (1) HCFC-22, (2) HFC-152a, (3) HFC-134a, (4) HFC-32, and (5) HFC-125.

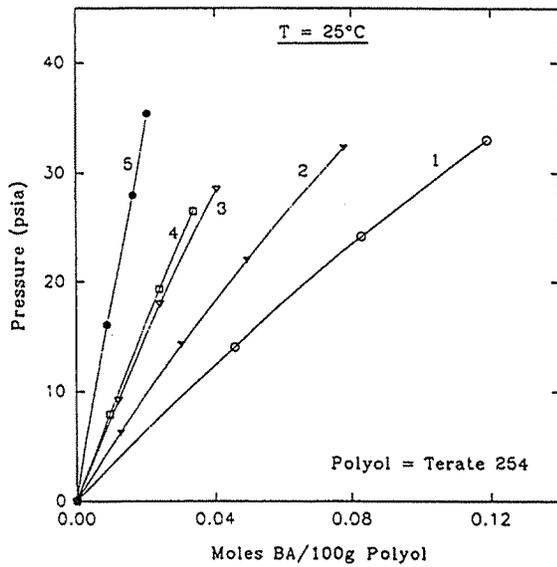


Figure 5. Vapor pressure measurements for various gaseous blowing agents in aromatic polyester polyol (Terate 254) at 25°C. Curves: (1) HCFC-22, (2) HFC-152a, (3) HFC-134a, (4) HFC-32, and (5) HFC-125.

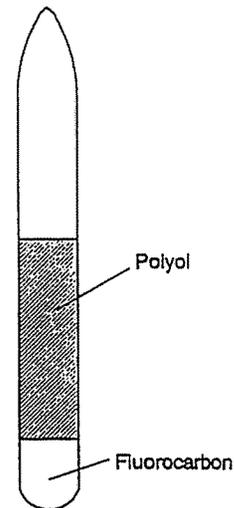


Figure 7. Sealed glass tubes for determining polyol/blowing agent miscibility properties.

Table 9. HFC miscibility^a in polyols.

| Blowing Agent | Terate [®] 203 (Cape Industries) | Pluracol [®] 975 (BASF) |
|---------------|--|-------------------------------------|
| CFC-11 | No | Yes |
| HCFC-22 | Yes | Yes |
| HCFC-141b | Yes | Yes |
| HFC-152a | No | Yes |
| HFC-134a | No | |
| HFC-32 | Yes | |
| HFC-125 | No | Yes |
| HFC-143a | | No |

^aMiscibility determined at the theoretical equivalent of 35 parts of CFC-11 per 100 parts of polyol.

glass sealed using a torch. After thawing the liquid mixture is thoroughly mixed by shaking the tube. Visual observations are recorded after allowing the tube to equilibrate at room temperature for about 24 hours. If separate liquid phases are evident then the blowing agent is immiscible with the polyol at that particular loading. The measurements reported in Table 9 were performed at a single loading theoretically equivalent to 35 parts of CFC-11 per 100 parts of polyol by weight, e.g., this is equivalent to 16.8 parts of HFC-152a per 100 parts of polyol. CFC-11 is

not miscible with Terate 203 at the 35 parts loading. We find that HFCs 134a, 152a and 125 are not miscible with Terate 203 at the same theoretical equivalent loading, whereas HCFCs 22 and 141b as well as HFC-32 are. The different solubility and miscibility characteristics of HFCs versus HCFC-22 may imply different processing requirements for the HFCs versus the HCFC-22.

POTENTIAL LIQUID HFC BLOWING AGENTS

There are literally tens of thousands of HFC isomers if we consider molecules as complex as those based on 5,6,7, etc., carbon atoms. Unfortunately even though most of these compounds are liquids, the majority can be eliminated based on flammability criteria or because their molecular weight is so high as to preclude economic viability as a blowing agent.

If we restrict ourselves initially to branched or linear saturated HFCs, then there are no methane-based HFC liquids and only two ethane-based liquids, HFC-143 ($T_b = 5^\circ\text{C}$) and HFC-152 ($T_b = 30.7^\circ\text{C}$). Recent adverse toxicological findings [11] on HFC-152 essentially eliminates this candidate from contention while HFC-143 exhibits a flash point and would be classed as a flammable liquid. Table 10 summarizes the 28 propane-based HFC structures; these are discussed further below. Most saturated

Table 10. Hydrofluoropropane isomers.

| HFC | Formula | T_b ($^\circ\text{C}$) | M.Wt. | %F | Flash Point ($^\circ\text{C}$) | Flame Limits (vol.%) |
|-------|--|-------------------------------|---------|----|-------------------------------------|-------------------------|
| 218 | $\text{CF}_3\text{CF}_2\text{CF}_3$ | -36.4 | 188.02 | 81 | N | N |
| 227ca | $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$ | -17.7 | 170.03 | 78 | N | N |
| 227ea | $\text{CF}_3\text{CFHCF}_3$ | -18.7 | 170.03 | 78 | N | N |
| 236ca | $\text{CHF}_2\text{CF}_2\text{CHF}_2$ | 10.0 | 152.04 | 75 | N | N |
| 236cb | $\text{CF}_3\text{CF}_2\text{CFH}_2$ | -1.2 | 152.04 | 75 | N | N |
| 236ea | $\text{CF}_3\text{CHFCHF}_2$ | 6.0 | 152.04 | 75 | N | N |
| 236fa | $\text{CF}_3\text{CH}_2\text{CF}_3$ | -0.7 | 152.04 | 75 | N | N |
| 245ca | $\text{CF}_2\text{HCF}_2\text{CFH}_2$ | 25.1 | 134.05 | 71 | N | N |
| 245cb | $\text{CF}_3\text{CF}_2\text{CH}_3$ | -17.6 | 134.05 | 71 | | |
| 245ea | $\text{CF}_2\text{HCHFCF}_2\text{H}$ | | 134.05 | 71 | | |
| 245eb | $\text{CF}_2\text{CHFCFCH}_2$ | | 134.05* | 71 | | |
| 245fa | $\text{CF}_3\text{CH}_2\text{CHF}_2$ | | 134.05 | 71 | | |
| 254ca | $\text{CFH}_2\text{CF}_2\text{CFH}_2$ | | 116.06 | 65 | | |
| 254cb | $\text{CF}_2\text{HCF}_2\text{CH}_3$ | -1.6 | 116.06 | 65 | | |
| 254ea | $\text{CF}_2\text{HCHFCFCH}_2$ | | 116.06 | 65 | | |
| 254eb | $\text{CF}_3\text{CHFCH}_3$ | -1.0 | 116.06 | 65 | | |
| 254fa | $\text{CF}_2\text{HCH}_2\text{CF}_2\text{H}$ | | 116.06 | 65 | | |
| 254fb | $\text{CF}_3\text{CH}_2\text{CFH}_2$ | 29.4 | 116.06 | 65 | -29 | 4.2-ND* |
| 263ca | $\text{CFH}_2\text{CF}_2\text{CH}_3$ | | 98.07 | 58 | Y | Y |
| 263ea | $\text{CH}_2\text{FCHFCF}_2\text{F}$ | | 98.07 | 58 | Y | Y |
| 263eb | $\text{CF}_2\text{HCHFCF}_2$ | | 98.07 | 58 | Y | Y |
| 263fa | $\text{CH}_2\text{FCH}_2\text{CF}_2\text{H}$ | | 98.07 | 58 | Y | Y |
| 263fb | $\text{CF}_3\text{CH}_2\text{CH}_3$ | -13.0 | 98.07 | 58 | Y | Y |
| 272ca | $\text{CH}_3\text{CF}_2\text{CH}_3$ | -0.4 | 80.08 | 47 | Y | Y |
| 272ea | $\text{CH}_2\text{FCHFCF}_2$ | 15.0 | 80.08 | 47 | Y | Y |
| 272fa | $\text{CH}_2\text{FCH}_2\text{CH}_2\text{F}$ | 41.3 | 80.08 | 47 | Y | Y |
| 272fb | $\text{CHF}_2\text{CH}_2\text{CH}_3$ | 8.0 | 80.08 | 47 | Y | Y |
| 281ea | $\text{CH}_3\text{CHFCH}_3$ | -9.4 | 62.09 | 31 | Y | Y |
| 281fa | $\text{CH}_2\text{FCH}_2\text{CH}_3$ | -2.5 | 62.09 | 31 | Y | Y |
| 290 | $\text{CH}_3\text{CH}_2\text{CH}_3$ | -42.1 | 44.10 | 0 | Y | 2.1-9.6 |

*ASTM E 681, match ignition, ambient conditions.

linear or branched HFCs require about 70% by weight fluorine substitution to suppress the flash point. Butane-based HFCs with the general formula $C_nF_nH_{10-n}$, therefore require $n \geq 6$ to achieve about 70% fluorine substitution. For $n = 6$ the molecular weight is 166; these are the hexafluorobutane isomers, one of which is $CF_3CH_2CH_2CF_3$. Butanes with $n \geq 7$ have molecular weights greater than 184 which is tending towards the high side. Hence, the hexafluorobutanes may be the only viable butane-based HFCs. Pentane-based and higher order HFCs having no flash point will require molecular weights greater than about 216 thus are also unlikely candidates based on economic grounds. Therefore, some of the hydrofluoropropanes and the hexafluorobutanes are the most promising HFC liquid candidates.

Table 10 lists the structures of the propane-based HFCs along with boiling point data where available. We have performed flame limit and flash point measurements on some of these candidates and the results indicate that propanes containing 5 or more fluorine atoms will not exhibit flash points, hence, the likely liquid candidates are some of the HFC-245 and HFC-236 isomers. The vapor thermal conductivity of most of these species as well as HFC-356 have been measured at about 44°C using a transient hot wire apparatus [12]. The results of these measurements, summarized in Table 11, indicate that none of these candidates is as efficient thermal insulation gas as HCFC-141b. However, it is likely that other factors will compensate for this loss in vapor insulation efficiency. Most of these candidate liquids are large molecules which will be less soluble and less permeable in polyurethane. Aged foam k -factors should be better than anticipated based on simple vapor thermal conductivity arguments owing to smaller losses of blowing agent vapor due to dissolving in the polymer or diffusing from the foam. Preliminary measurements also show differences between the miscibility of these HFC liquids in polyols and HCFC-141b or CFC-11. Generally the HFCs are less miscible in polyols than HCFC-141b which may impact foam processing.

Ultimate feasibility of these HFC liquids will depend on manufacturing costs, environmental properties and performance characteristics.

SUMMARY

The most promising long term replacements for the HCFC blowing agents are likely to be the HFCs. Although other chemicals such as fluoroethers are feasible, much less is known concerning their toxicological and chemical stability properties. Amongst the HFCs two general op-

tions are possible: liquid blowing agents and gaseous blowing agents. Gaseous HFCs which are already commercially available or are likely to become available in the near future include HFCs 152a, 134a, 32, 125 and 143a. These gases are not as efficient thermal insulators as HCFC-141b or HCFC-22. Nor are they as soluble in polyols on a theoretical substitution basis as HCFC-22 which may have some effect on foam processing characteristics. Although a large number of HFC liquids are known, many of them are impractical because of high molecular weights or are flammable. The more promising HFC liquids are some of the hydrofluoropropanes and the hexafluorobutanes such as $CF_3CH_2CH_2CF_3$. Again these fluids do not have the insulation efficiency of HCFC-141b but this may be offset by the lower solubility and permeability in polyurethane. Further work is required to assess the toxicological and environmental properties of these candidates as well as to develop economically viable manufacturing processes.

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Table 11. Vapor thermal conductivity data.

| | Vapor Thermal Conductivity at 44°C (mW/mK) |
|-----------|--|
| HCFC-141b | 12.1 |
| HFC-236ca | 17.4 |
| HFC-236cb | 15.4 |
| HFC-236ea | 15.6 |
| HFC-236fa | 14.8 |
| HFC-245ca | 13.3 |
| HFC-245eb | 16.0 |
| HFC-356 | 14.7 |

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TECHNICAL PRESENTATION

September 27, 1993
Dr. Stefan Adams
BASF, Ludwigshafen
Abt. HUM/EH - F 500

Cyclopentane as Blowing Agent for Rigid Polyurethane Foam in Refrigerator Insulation

1. Technology Description

1.1 Introduction

Rigid polyurethane (PUR) foam is the major insulation material in household and commercial refrigeration. Production, design and properties of refrigerators, freezers and display cabinets correspond strongly to

- the easy processing of PUR systems,
- their ability to form a light sandwich structure and
- their good insulation values.

Our target was, to look for economical Zero-ODP PUR blowing agents. They must be able to be used in existing production facilities with acceptable efforts in reconstruction. We had to focus on good insulation values, because an increase in energy consumption isn't acceptable at all. For the tight time frame of Chlorofluorocarbon (CFC)-substitution given, we had to look for alternatives which are or can be made available in industrial Quantities in time.

1.2 Zero-ODP Blowing Agents

1.2.1 CarbondiOxide - CO₂

Carbondioxide CO₂ is the oldest known PUR blowing agent. Although CO₂ is a heavy gas with respect to air, it is much lighter than CFCs and other potential substitutes and leads to comparatively poor insulation values. This effect is magnified by a rapid ageing by diffusion leading to an overall thermal conductivity which is only in the range of other plastic foams (e.g. EPS). Therefore the use of CO₂ as sole blowing agent is restricted to applications, where average insulation properties can be tolerated or counterbalanced by thicker insulation layers and diffusion tight facings. Several attempts in refrigeration application have shown, that this blowing agent option is difficult to process resp. needs re-design of cabinets.

1.2.2 PerFluoroAlkanes - PFA

A successful attempt to reach our target of an easy to process PUR foam with excellent insulation values with chlorine-free blowing agents was to use PFAs. They are merely insoluble in PUR raw materials, but with specially formulated PUR systems they can be processed as emulsions on usual metering machines. Foam properties, especially insulation values, are comparable to existing CFC blown systems.

This development was cut off by concern about the relatively high Greenhouse Warming Potential (GWP) of this class of substances. Efforts to reduce their amount in formulations by using other co-blowing agents with low GWP, like pentane, are not honoured by success in the market place.

1.2.3 HydroFluoroCarbons - HFC

Due to their short lifetime in atmosphere, partly fluorinated compounds have a significant lower GWP in comparison to fully fluorinated compounds. We focused our developments on HFC 134a and HFC 227, which are available in industrial quantities now resp. in the next future. Both substances are gases at ambient with low solubility in PUR raw materials at atmospheric pressure. To handle them in an appropriate amount to reach good insulation values, changes in machinery and processing are necessary. By direct comparison HFC 134a shows lower thermal conductivity than HFC 227.

Therefore some appliance manufacturers in Europe took the decision to use HFC 134a as a Zero-ODP blowing agent. But HFCs are still under concern for their remaining GWP and drawbacks in processing.

1.2.4 Hydrocarbons

Hydrocarbons are widely used as blowing agents in the production of plastic foams, e.g. EPS. Especially pentanes, i.e. n-pentane, iso-pentane (2-methylbutane) and cyclopentane are suited to be used as blowing agents for PUR systems. In contrast to other plastic foams, these blowing agents remain in the closed cell structure of PUR rigid foam over a long service time improving its insulation values. Concerning the foam properties, there is no big difference to CFC reduced blown PUR foam. The only drawbacks of these group of blowing agents are caused by their flammability. However, with reasonable changes in PUR system formulation, handling and processing foams with competitive properties are produced.

1.3 CycloPentane - CP

Following a request from refrigeration industry for a blowing agent free of halogens, cyclopentane was identified as the most promising one. Essential foam properties, especially thermal conductivity, remain at desired levels with specially adopted PUR systems.

2. Application

Cyclopentane blown foam is intended to be used as a 1 : 1 substitute for CFC reduced PUR foam with respect to insulation values. Refrigeration industry has clearly stated, that CP blown foam fits their demands.

Other industries are carefully examining cyclopentane or other hydrocarbons as blowing agents.

3. Benefits

In appliance industry there is no re-design of cabinets necessary to stay at the energy efficiency reached with CFC reduced insulation. In addition there is little concern about impacts of this blowing technology on the environment.

4. Technical Issues

However, storage, handling and processing of this flammable blowing agent and its blend with PUR system have to be changed according to the pertinent legal regulations. Intense safety considerations with experts from engineering science solved this problem with reasonable changes on existing production facilities to reach these standards.

4.1 Storage and Handling of Cyclopentane

To reduce the overall handling of flammable liquids to the necessary minimum, it is advisable to blend cyclopentane into the PUR system in the foaming plant. Supply, storage, and transport are subject to the same safety standards that are required, for instance, for gas stations.

4.2 Processing of Polyolcomponents

Flammable blowing agents are metered into the polyol preblend with the help of special, leak proofed or leak controlled pumps. In addition it is recommended, to operate this unit, as well as the second high pressure pump for the polyolcomponent, in a separate, well ventilated chamber. To transport the finished polyol component from a central blending station to the foaming stations permanent installed and leak controlled pipelines represent the state of the art. Automatically to pressure loss responding shutoff valves minimize hazards from line fracture.

The interior space of the working tank of the metering machine has to be rendered inert, for instance with nitrogen. In order to avoid pressure loss through conventional agitator sealings, the content of the tank may also be mixed by a magnetically coupled agitator or by a circulation pump.

To avoid hazard caused by insufficient sealing resp. leakage, suitable gas sensors should in any case monitor the air quality in critical areas. As soon as defined limiting values are reached, warning signals should be given or certain portions of the unit should be cut off. This makes it unnecessary to equip large parts of the unit with explosion protected electrical dashboards. Because static electricity can lead to hidden hazards, all parts of the unit should be grounded.

4.3 Processing of the PUR Foam

The reaction mixture is prepared with usual high pressure pumps, which are equipped with necessary safety measures (see above). Usually small amounts of blowing agents are released during the foaming process. They form a cloud in front of the foaming mixture filling the hollow sphere of the mould. At last they are pressed out of the mold through the venting holes and diluted in the surrounding by air.

To avoid any hazard by building up an explosive mixture in the mould, inertisation of the mould with nitrogen before the shot is necessary.

Alternatively, complete safety may also be obtained by avoiding any ignition, e.g. by static electricity. This can be done by using grounded moulds and antistatic surface materials.

To avoid any hazard by the flammable blowing agent leaving the mould through the venting holes, these have to be diluted by good ventilation. A sufficient safety level is reached, if concentrations in air remain below the given working place exposure levels.

Loss of cyclopentane to the environment stops practically immediately with the end of the reaction between polyol and isocyanate. During completion, storage, transport, and designated use of the refrigerators, no hazards due to formation of flammable gas mixtures are to be expected.

Grinding cyclopentane-containing rigid foams leads to liberation of the cell gases. The amounts depend considerably on the degree of pulverization. At present, measures to minimize the work-related hazard potential at their plants are being discussed with the manufacturers and operators of PUR-recycling units.

5. Economics

Cyclopentane blown rigid PUR foam fits very well into the demands of refrigeration industry:

- No changes of cabinet design, moulds, mould carriers etc.

Investments have to be done mostly on:

- Storage facilities for flammable liquids
- Metering devices
- Safety tools at the high pressure metering machine
- Safety tools at the working place (venting)

Variable costs caused by safety measures are:

- Inertization with nitrogen
- Antistatic treatment of plastic liners

Concerning the variable costs of raw materials

- Cyclopentane is much cheaper than highly fluorinated chemicals.

6. Technology Outlook

The technology is ready available and can be used in appliance production when the necessary safety measures are applied.

First European companies have started production in the first half of 1993. Nearly all European appliance companies have stated to convert to this blowing technology till the end of 1994.

The development is intensely studied by American and Asian companies.

In other industries working with insulation based on PUR rigid foam pentane seems to become the first choice as Zero-ODP blowing agent in the long run.

PUR Foam in Refrigerator Insulation

- Easy processing of PUR systems
- Light sandwich structure
- Superior insulation through CFC

Cyclopentane Blown PUR Foam in Refrigerator Insulation

- Technology
 - Introduction
 - Zero-ODP Blowing Agents
 - Cyclopentane
- Application
- Benefits
- Technical Issues
- Economics
- Outlook

Zero-ODP Blowing Agents

| | GW-Impact (CFC 11 = 1) GWP | Energy Losses | Processing |
|--------------|-------------------------------|---------------|--------------------|
| CO2 | 0.0001 | 1.15 to 1.95 | Difficult |
| PFA | 4 - 5 | 1.00 | Emulsion |
| Pentane/PFA | 0.4 | 1.05 | Emulsion/Flammable |
| HFC 134a | 0.25 | 1.10 | Gas handling |
| Cyclopentane | ≈ 0.001 | 1.06 | Flammable |

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BASF

Polyurethane

Processing of Cyclopentane Blown Foams

- **National regulations for transportation, storage and handling of flammable liquids**
- **Approval by authorities**
- **Certifications by machine manufacturers, consultants and/or engineering offices**
- **Supervision of safety standards**

Processing of Cyclopentane Blown Foams

- Cyclopentane storage at foaming site
- Cyclopentane blending station
- Inertization of working tank
- Gas sensors, ventilation in critical areas
- Electrical grounding
- Inertization of mould or use of antistatic covers

Economics of Cyclopentane Blown Foams

- **No changes of cabinet design**
- **Investments:**
 - **Cyclopentane storage**
 - **Blending station**
 - **Safety at high pressure machine**
 - **Safety at working place**
- **Costs:**
 - **Inertization**
 - **Antistatic plastic liners**
- **Savings:**
 - **Cyclopentane is cheaper than HFCs**

Outlook: Cyclopentane in Refrigerator Insulation

- Technology available
- Production started early 93
- Conversion in Europe 'till end of '94
- Great interest in America and Asia
- In other PUR rigid applications: pentane

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Water-Blown Rigid Urethane Foam for Thermal Insulation

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1993 Non-Fluorocarbon Insulation, Refrigeration and Air-Conditioning Technology
Workshop

September 27 - September 29, Wiesbaden

Water-Blown Rigid Urethane Foam for Thermal Insulation

1 Introduction

Due to low thermal conductivity and good mechanical properties rigid urethane foam (RUF) is often used for thermal insulation applications. The low thermal conductivity of the foam is based on the use of CFC 11, which has the lowest λ -value of all used blowing agents. With the prohibition of CFC 11 (in Germany on Jan. 1st of 1995) industry and research institutes are looking for suitable alternatives. Within the research project "Halonefree Urethane Foam" supported by the German Ministry of Research and Technology, the IKP is optimizing water-blown polyurethane-systems without using halone containing additives and blowing agents.

We use CFC 11-blown foams as a standard reference for foams blown with various blowing agents. Several publications discuss advantages and disadvantages of halone-containing blowing agents /1, 2, 3/. We confine the comparison to properties of water-blown foams.

Tab.1: Comparison of CFC 11-blown and water-blown foams

| Blowing agent | CFC 11 | Water/CO ₂ |
|----------------------------|---|--|
| Thermal conductivity | | |
| Initial value | 0,018 W/m K | ca. 0,023 W/m K |
| Timely course | moderate increase | strong increase |
| Diffusion of cell gas | slow | fast |
| Shrinkage | none | Increase in density to avoid shrinkage |
| Processing | simple | simple |
| Ecology | ODP, GWP | not relevant |
| Reaction, temperature rise | favorable due to consumption of reaction enthalpy for boiling the blowing agent | unfavourable due to production of heat in the water-isocyanate-reaction; danger of core burning; formation of unwanted ureas |

In many applications Water/CO₂-blown RUF can be used successfully. If thermal conductivity or costs are the significant criteria for the use of RUF, the properties of these sort of foams must be improved. With the use of a gas loading unit two aims could be reached.

1. Reduction of density or reduction of the fraction of water required to achieve a determinable density of foam. This reduces the formation of ureas and the temperature rise during the reaction.
2. Improvement of thermal conductivity by reducing the average cell diameter. The cell diameter is influenced by the amount of nucleus in the reaction mixture.

In the following sections basic theory is related to technical equipment. Moreover results of experiments are presented and technical as well as economical aspects are concluded.

2 Basics

2.1 Heat Transfer in RUF

Heat transfer in RUF consists of the thermal conductivity of the polymer, the cell gas, and the radiation heat transfer. Most important is the thermal conductivity of the cell gas. However, the conductivity of the cell gas is fixed and -when using CO₂ as the cell gas- has a high value. The only part of heat transfer we could influence is the radiation part. Radiation decreases when the average cell diameter of the foam decreases (see fig. 1).

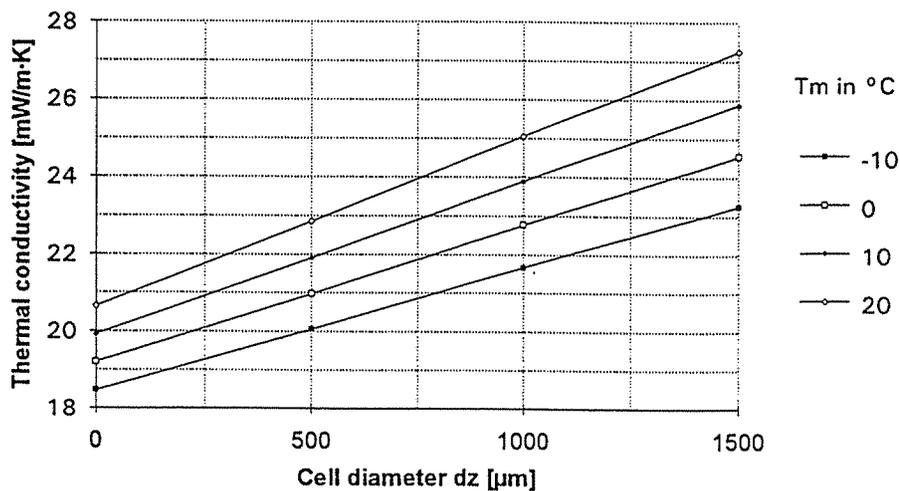


Fig. 1: Calculated thermal conductivity related to the cell diameter for Water/CO₂-foams

2.2 Nucleation of the Reaction Mixture

The aim of the research work is to reduce cell diameter. After mixing the raw materials the water-isocyanate reaction starts and CO_2 is formed. After a short time the emulsion of polyol and isocyanate is supersaturated with CO_2 . This unstable condition can result in two different processes: New bubbles are formed out of the mixture with a diameter larger than the critical one ("self nucleation"). However, a thermodynamical treatment in [4] shows, that in urethane formation self nucleation is an unprobable process. So the second possibility is the way how to stabilize the system: The formed CO_2 diffuses in existing bubbles and enlarges them. To reduce the cell diameter of the foam the number of existing nuclei has to be increased. Some possibilities are shown in fig. 2..

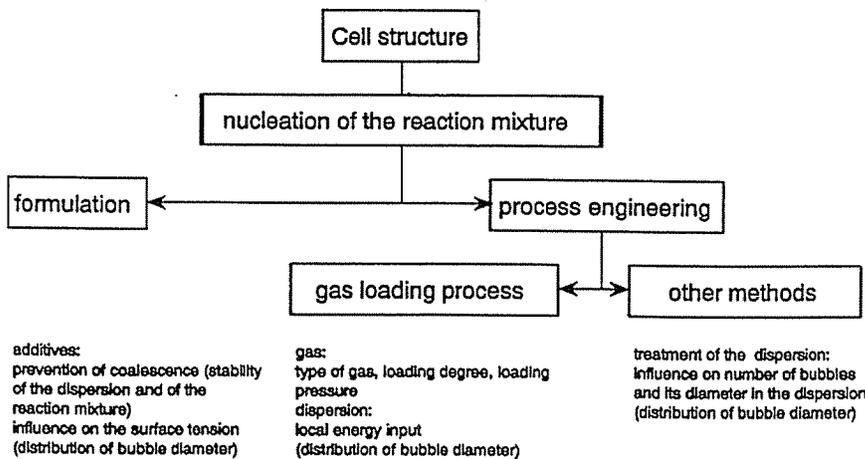


Fig. 2: Influence on cell diameter due to gas loading process

3 Gas Loading in the Production of Rigid Urethane Foams

3.1 Test Stand

The gas loading experiments at the IKP were performed on a high-pressure dosing unit (Cannon Deutschland, Mühlheim). A newly developed gas loading unit was installed parallel to the polyol tank. The so-called Sono-Sonde consists of a quick rotating mixer and a device for ultrasonic admission of the dispersion. This results in local pressure drops in the dispersion in order to improve the efficiency of the process [5]. To compare the new development with the technical standard a second gas loading unit (Cannon AND) was installed at the foaming system. Here the dispersion is made with the help of a rotating roll. The gas loading degree was measured and controlled by a decompression method (Air Nucleation Detector). The diagram of the test stand is shown in fig. 3.

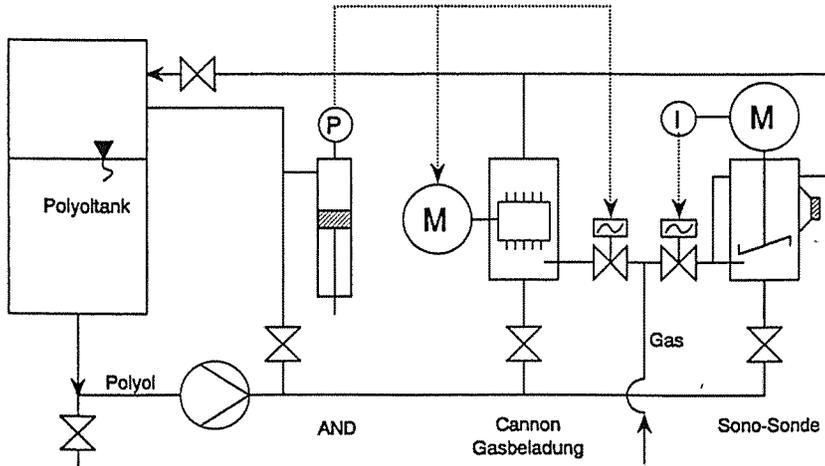


Fig.3: Diagram of the gas loading units

The reactive mixture was injected through a hose line in the mould(1000 mm x 800 mm x 100 mm) . The distribution along the length of the mould is provided by a guide bar with constant speed.

3.2 Evaluation

Gas loading degree

To measure the gas loading degree the density of the expanded dispersion (ρ_D) was determined. Therefore a sample of the dispersion was taken from the polyol tank. The gas loading degree X_G^V is defined (according to /6/) as the ratio of gas volume at normal conditions to the liquid volume. Equally good is the gas volume fraction ε_G (like it is used in /7/), defined as the ratio of gas volume at normal conditions to the volume of the dispersion at normal conditions.

The gas loading degree X_G^V is calculated according to:

$$X_G^V = \frac{\rho_P - \rho_D}{\rho_D - \rho_G} * 100\% \quad \left[X_G^V \right] = \frac{Nm^3G}{m^3L} \quad (\text{eq. 1})$$

ρ_P : polyol density [kg/m³]

ρ_D : dispersion density [kg/m³]

ρ_G : gas density [kg/m³]

Cell structure

In order to determine the average cell diameter of the foam, a thin slice of rigid foam was cut with a microtome. Micro-photographs were taken from which the average diameter of the cells was obtained.

3.2 Results

Gas loading and foam density

The polyurethane system used for the experiments was the Vorracor CM 205 of Dow Chemicals (NL). In several test series the maximum of the gas loading degree was determined, using Carbon dioxide as the loading gas. The average value of gas loading degree, divided by the absolute pressure was

$$X_G^V = 150 \frac{\text{Nm}^3\text{G}}{\text{m}^3\text{L} \cdot \text{bar}} \%$$

The loaded carbon dioxide, dispersed and solved in the polyol, reduces foam density. The expected reduction of the foam density agrees well with the observed. The results show that partly blowing with loaded gases is possible. However, foams blown at high gas loading degrees show a worse cell structure and have shrink holes due to the frothing effect.

Nucleation

Nucleation with solid particles or fluids leads to foams with improved cell structure. For example, water-blown foams nucleated with fluoro carbons like Perfluoro-hexane show a very fine cell structure. By using grinded rigid foam as a solid nucleation agent in laboratory experiments at the IKP the average cell diameter could be distinctly reduced compared with the standard formulation. In the following results of gas nucleation are described.

In cooperation with the Erich Rühl AG, Friedrichsdorf, the influence of various additives on the cell structure of rigid foams was tested. Various surface-active agents were added to the polyol formulation. The foams produced at the foaming machine were analyzed with regard to their cell structure. A positive influence of gas loading is evident in the following two pictures.

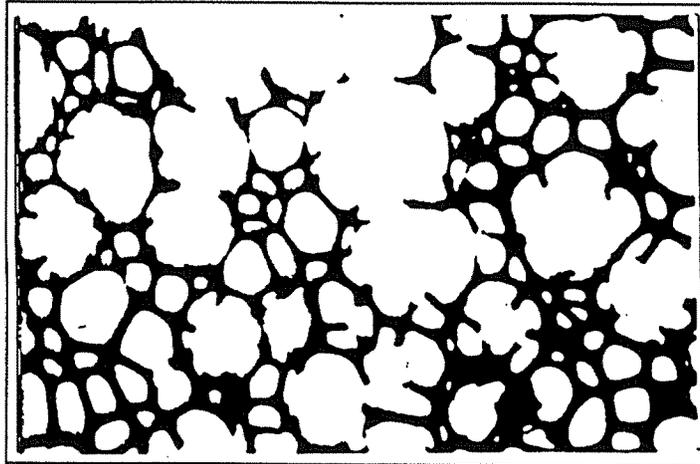


Fig. 5: Additive 3 (1,5 %) without gassing

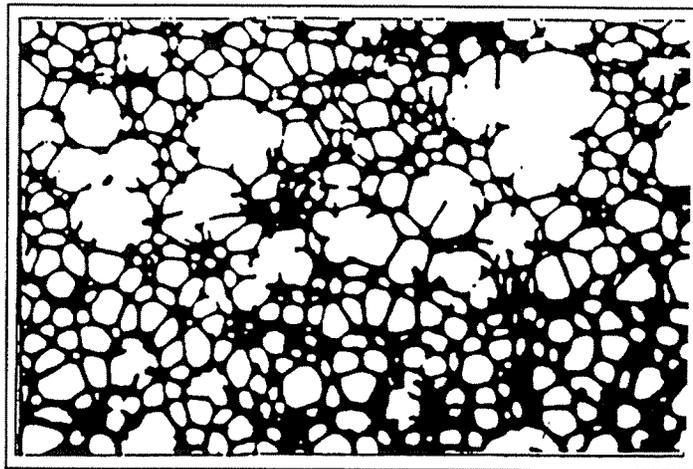


Fig. 6: Additive 3 (1,5 %), gassing with argon, Cannon AND, 2 bar

4 Summary, Conclusions and Outlook

1. Gas loading in the production of water-blown rigid foams improves their properties. It is a possibility to get a finer cell structure of the foams and therefore a lower thermal conductivity. However, to avoid shrinkage, the minimum foam density is about 40 kg/m³. Alternative blown rigid foams have lower densities. E.g. pentane-foams can be produced with a density of 34 kg/m³. The difference in the specific weight rises the weight and this in the manufacturing costs of 1 m³ insulating panels. The use of Water-blown foams is limited to applications where the foam density is high anyway due to

required mechanical properties. E.g. in the production of sandwich panels for refrigerator bodies with foam densities ranging from 50 to 80 kg/m³.

2. HCFC like R141b must be avoided due to their Ozon Depletion Potential (ODP) which is not equal zero.

[H-]FC is used in the production of insulating panels with a low thermal conductivity. Especially unsolvable fluoro carbons like Per-fluoro hexane nucleate the polyurethane formation, improve cell structure and thermal conductivity. The application of such insulating panels reduces energy consumption of insulating systems and consequently the emission of carbon dioxide and the Global Warming Potential. But the [H-]FC itself have a high value for the GWP. Their benefit for the reduce of GWP-relevant emissions must be proved by Life Cycle Analysis.

3. At the moment Pentane is the favorite blowing agent and it is - without doubt - a progress in environmental protection. But there are disadvantages:

- Flammability of the blowing agents and of the foams
- Explosion-proof equipments and waste air purification are required
- Moreover, pentane is a volatile organic compound which causes photo smog. Perhaps this is a topic for discussions in the year 2003.

4. Return to the first known blowing agent: CO₂ out of the water-isocyanate reaction.

- Combined with pentane, CO₂ or other inert gases could nucleate the foam formation in order to improve cell structure and thermal conductivity.
- In larger amounts CO₂ or other inert gases could act as a co- or main-blowing agent for RUF-systems.

We want to discuss these two possibilities on the background of the research work at the IKP.

To improve the nucleation process a large amount of nuclei in the beginning of the foam formation is necessary. By gassing the polyol component we found an improvement in nucleation. However, experiments indicated that at high gas loading degrees the nucleation deteriorates because gas bubbles in the dispersion and in the reaction mixture are no longer stable. We want to optimize the gas loading process by treating the dispersion after the gas loading unit.

1. Big bubbles will be separated from the dispersion. This improves stability of the dispersion and has only little influence on the amount of nuclei in the dispersion.

2. The amount of small bubbles will be increased by concentrating the dispersion.

Both is done with a separator, where the distribution of bubble diameter and gas loading degree can be controlled. First experiments with the separator technology were done in cooperation with Westfalia Separator AG (Oelde) and show the predicted effects.

The second problem to be investigated is blowing with loaded gas. Large quantities of gas could not be loaded when using a low-pressure-unit. Tests were made with a high-pressure unit injecting the gas directly in the high pressure loop of the foaming machine. Mixing was done with a static mixer. First tests with that technology showed interesting results. Combining CO₂ with compounds whose diffusion rate out of the foam is low (other gases or physical blowing agents) could solve the problem of shrinkage of water-CO₂-blown foams. To optimize the fraction of co-blowing agents an exact prediction of the ageing of the foams is necessary. A FEM-program was installed at the IKP in order to calculate the timely course of partial pressure of the cell gas components and the total pressure in the cells.

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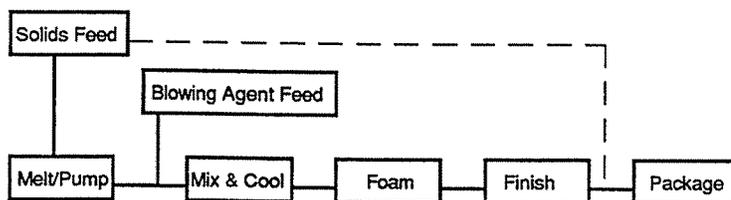
POSSIBLE FUTURE DIRECTIONS FOR EXTRUDED POLYSTYRENE FOAM INSULATION

J. Godfrey Abbott and John H. Minsker
The Dow Chemical Company
27 September 1993

TECHNOLOGY DESCRIPTION:

Extruded polystyrene foam has been used as an insulation product for several decades. Over that time, the volume of product sold and the number of manufacturers around the globe has increased dramatically. Because of the relatively high capital requirements for such a plant, the technology of extruded foam manufacture for boardstock, unlike many other foam types, has developed primarily through proprietary processes. This has limited the amount of information available regarding process details and future developments. Nonetheless, some general information is available¹.

Extrusion foaming uses thermoplastic resins which are processed by melting, foaming with one or more blowing agents (BAs) and solidification by cooling. A simplified process flow diagram is shown below.



Most components in the formulation, except blowing agents are solids at room temperature. These are fed as powders and pellets to the extruder where they are melted. The extruder also acts as a pump to develop pressure sufficient to contain the blowing agents and to forward the material through the process. In addition to the resin pellets, other solid additives might include fire retardant additives, colorants, nucleators and other processing aids. Trim and other scrap is also returned to the process at this point.

Blowing agents are then pumped under high pressure and at a precise rate into the molten polymer stream. Mixing and cooling to bring the molten mass to a uniform consistency and temperature is accomplished either in a second extruder or in

¹For a more comprehensive review of extruded polystyrene foam technology and applications, the reader may refer to the following or other numerous sources:

a) Report of the Flexible and Rigid Foams Technical Options Committee, Montreal Protocol 1991 Assessment, December 31, 1991

b) Suh, K.W. and Webb, D.D., Cellular Materials, Encyclopedia of Polymer Science and Engineering, Vol. 3, 2nd Ed., pp 1-59, 1985, John Wiley & Sons, Inc.

specifically designed devices. Uniformity of the melt at this point is critical to production of a consistent foam product of constant thickness, density and cell size, all of which are important to meeting the property requirements of various applications.

Foaming is accomplished by the melt passing through a die into atmospheric or reduced pressure. At this point, the blowing agents vaporize creating a foam structure. The vaporization and expansion of the BAs takes heat from the melted polymer causing the foam to solidify almost instantaneously. In a boardstock extrusion process the die opening is generally rectangular and adjustable to make products of various thickness. This is in contrast to the extruded foam sheet process which uses an adjustable annular die to create a thin tube of foam which is subsequently slit to form a thin (< 6 mm) sheet.

The foam is now a continuous board of the thickness desired and with a skin formed in the process. Finishing operations can include slicing to make thinner boards, lamination of films or paper, removal of the skin surface, printing, trimming to length and width and cutting various edge treatments, such as a tongue and groove or shiplap. Finally, the product is packaged for shipment.

Originally, the blowing agent of choice for extruded polystyrene foam boardstock (XPS) was CFC-12. Beginning in 1989, the industry began converting to HCFC-142b alone or in blends with HCFC-22. This conversion process is complete in developed countries and nearing completion elsewhere.

The purpose of the CFC or HCFC blowing agent is two-fold. In addition to producing foam in the process, it is retained in the foam structure and acts to provide greater insulation value to the product. This is due to its thermal conductivity, which is lower than that of air. Because of this important role, insulating gas choice is limited to those gases which will permeate only slowly from the foam. Auxiliary blowing agents, which help produce low density foams, are used. With the exception of HCFC-22, these are not ozone depleting substances. One process uses a vacuum foaming technique to replace the need for auxiliary blowing agents.

Selection of a zero ozone depleting substance as an insulating gas/blowing agent is limited by the criteria of the process and the final product. Specifically, a low boiling gas is required which has acceptable solubility in both the molten and solid polymer, flammability characteristics that can be handled in the plant and applications, low thermal conductivity and slow permeability from the foam. Few choices exist. HFC-134a has been considered but is too expensive for use in this competitive market. HFC-152a, hydrocarbons, alcohols and carbon dioxide have all been considered but have permeabilities which are too high and are not acceptable as insulating gases. Industry is working with potential suppliers to identify and develop other blowing agents with the desired properties.

Insulation value can be modified somewhat through reduction in cell size or addition of materials to block radiant energy transfer through the foam. However, no producer has

demonstrated a commercial product which will maintain the insulation value of today's products.

APPLICATION:

Nearly all applications for extruded polystyrene foam boardstock are as insulation in various construction methods. XPS is used to insulate roofs, walls and below-ground structures of a residential, commercial and industrial nature. The primary characteristics of XPS which lend themselves to these applications are high insulating efficiency, strength, dimensional stability, moisture resistance and ease of handling. Products are available in a wide variety of thicknesses, widths, lengths, density, surface and edge treatments and in composite structures with other materials to meet the needs of individual applications.

A significant portion of residential and commercial wall insulation is XPS. Its high moisture resistance leads XPS to be selected as the preferred below-grade product in applications as varied as insulation of residential basement walls to light-weight insulation and fill over underground structures. XPS is used to protect frozen tundra, highways, airport runways and taxiways and railroad tunnels. XPS is used in inverted roofing systems in which the insulation is applied above the membrane, thus protecting it from the weather. Sandwich panel constructions with XPS cores take advantage of its strength and ease of fabrication as well as insulation performance.

BENEFITS:

The DOE/AFEAS study on the global warming impact of various insulation materials showed the net benefit of using high efficiency foam insulations using HCFCs or HFCs. In most cases, the net total global warming effect was found to be less with high efficiency insulations than in substitution with lower efficiency insulation products containing no global warming gas.

The long continued and growing use of XPS insulation around the globe speaks to its desirability in many construction systems. It is often used in conjunction with lower cost insulation materials such as mineral fibres or moulded polystyrene foam where the properties of XPS are needed in the composite structure.

TECHNICAL ISSUES:

Because of a desire to minimize and ultimately eliminate the use of ozone depleting substances the XPS industry has aggressively searched for suitable blowing agents which meet all criteria. Working in concert with potential suppliers, the industry is today researching and evaluating candidate materials.

As noted above, the search is hampered by the strict criteria of the process and applications and by the difficulty of identifying suitable materials which also meet environmental, toxicological and economic demands. The candidates identified to date, and discussed briefly above, all have significant drawbacks which limit their effectiveness.

The process of identification, evaluation, foam and BA process development, foam product development, toxicology testing, government approval, BA plant construction/modification, and foam product/process conversion is a long and complicated one. It has been estimated to be as long as 10 years². Negative results at any step can doom a possible candidate. Consequently, industry will need the full lifetime of HCFCs allowed under the Copenhagen Amendments to the Montreal Protocol in order to continue supplying products with today's insulation value at competitive prices.

Alternatively, industry can look to ways of providing insulation power without the use of insulating gases. Such an approach, if successful, would open the possibility of using blowing agents without ozone depletion or significant global warming effects.

Since heat transfer through a foam occurs via radiation, solids conduction and gaseous conduction, some means must be therefore found to reduce either of the first two routes in response to an increase in gaseous heat transfer caused by use of a more thermally conductive (non-insulating) gas. Solids conduction represents only a small portion of the total energy transfer so most efforts are related to minimizing radiation heat transfer. Reduced cell size is one approach but has technical limitations in the process. Inclusion of infrared blockers such as carbon black, or reflectors like mica, have also been suggested in the literature. However, inclusion of significant quantities of non-melting solids to an extrusion process is difficult to say the least. To date, no commercial XPS products are available with the necessary properties identified.

ECONOMICS:

XPS insulation has found wide use because of its price for performance. Competition with other insulation materials can be significant. Consequently, large additional costs cannot be borne without loss of markets and availability of products.

The Copenhagen Amendments stipulate a consumption ceiling ("cap") for HCFCs. Along with insulation foams other user industries, predominantly refrigeration, compete for the supply of HCFCs. Once this ceiling is reached, insulation foams, because blowing agents represent a considerable fraction of the formulation, cannot successfully bid for HCFCs, whose price will, under the effect of market forces, rise relentlessly.

²Shankland, Ian; presentation to UNIDO representatives, University of Detroit, February 2, 1993

TECHNOLOGY OUTLOOK:

The extruded polystyrene insulation foam industry made an early conversion from CFCs to HCFCs at least in part because of a desire to minimize ozone depletion potential. Research and development efforts did not stop with that conversion as the industry recognized the need for the ultimate elimination of all ozone depleting gases. Because no commercially available or developmental products have been identified to date, it is expected to be a decade or so before a complete conversion can be made out of HCFC-142b while maintaining current thermal performance.

ORNL Workshop Wiesbaden September 1993

Jürg Nipkow, ARENA, Zürich, Switzerland

SWISS ECO REFRIGERATOR PROJECT

0. Introduction

The Swiss "Eco Refrigerator" project was initiated by BUWAL and a group of experts who have been closely involved in the problem of CFCs for a long time. The project is sponsored by the Federal Office for Environment, Forests and Landscape (BUWAL). The project group comprises, besides BUWAL, the Energy Systems Laboratory of the Federal Institute of Technology (ETH), Zurich, the Laboratory for Thermodynamics and Refrigeration Technology of the New Buchs Technical College (NTB), and Greenpeace Switzerland. Project management is at IET energy consultants.

Goal of the project is to develop and produce some refrigerator/freezer prototypes with respect to later series manufacturing, which should achieve the following requirements:

- Electricity consumption less than 0.48 kWh per day for a 240 litre refrigerator with integrated freezing (***) compartment (i.e. < 0,2 kWh/100 l)
- No halogenated organic substances used
- Reducing the environmental impact of manufacturing by
 - content of non-renewable resources as low as possible
 - using recycled raw materials
 - energy use for manufacturing as low as possible
 - harmful emissions as low as possible
 - service life longer than 15 years
- Reducing of the environmental impact in the dismantling step by
 - using raw materials which can be re-used or recycled
 - design for easy dismantling
- Life cycle costs not higher than refrigerators presently on market

1. Technology Description (see also paper of L. Schilf)

At the state of project in June 1993 several decisions on technical options are already made: The refrigerant will be a mixture of Propane (70%) and Iso-Butane (30%), a Vacuum-Super-Insulation (kieselgur/steel-Technology) will be applied (patents by Mr. Schilf, manufacturing of prototype by Mannesmann under negotiation).

Cooling Process

An evaluation of various cooling processes has resulted in choosing the cold vapour process as efficient, available and technically well-known. Optimization seems possible by longer running-cycles. Therefore cold storage materials can be put at the evaporator and control is eventually to be adapted.

Hydrocarbons as Refrigerants.

Due to their thermodynamic properties close to CFC-12 Propane and Isobutane require minor design changes compared to HFC 134a. Pioneer on the field of CFC-free cooling appliances is FORON, a refrigerator manufacturer in the eastern part of Germany. FORON in cooperation with Greenpeace launched the first refrigerator totally free of CFCs and HFCs on the market in march 1993. FORON used a mixture of 50% propane and 50% isobutane as refrigerant. It was proved by TÜV, that the inflammability of the some 20 grams of hydrocarbons in a domestic appliance is no problem.

Insulation

In traditional refrigerator/freezers 70 - 80% of the CFCs are applied in the insulation foam. In the course of 1993 many European refrigerator/freezer-producers have switched away from CFC 11 to a substitute as foam blowing agent. The first totally CFC and HFC-free refrigerator from FORON still uses a polystyrene foam insulation. Thermal conductivity of polystyrene foam does not allow a reduction of heat transfer unless at insulation thicknesses which reduce significantly the net cooling volume.

Insulation technologies were evaluated in an early phase of the project. Requirements to thermal conductivity λ were set $< 0,2 \text{ W/mK}$ to achieve a good relation of insulation thickness and thermal losses. Further requirements are: no Ozone Depletion Potential (ODP), no or low Global Warming Potential (GWP), easy dismantling and recycling, serial manufacturing at sensible costs to be expected. "Stone and iron" were mentioned as ideal material types!

Table 1 shows some of the examined technologies and their respective data (λ = thermal conductivity). VSI was evaluated as best suitable technology.

| Insulation technology | λ W/mK | Resources | Recycling | Environm. impacts | Technology availability | suitability for project |
|------------------------------------|----------------|-----------|-----------|-------------------|-------------------------|-------------------------|
| Non organic fibers | 0,04 | + | - | - | + | - |
| WDS (special silica) | 0,02 | + | +/- | ? | + | - |
| Natural organic fibers | >0,04 | + | + | + | + | - |
| EPS (exp. Polystyrene) | 0,032 | +/- | +/- | - | + | - |
| XPS (extruded PS) | 0,028 | +/- | - | - | + | - |
| Polyurethane | 0,02 | +/- | - | - | + | - |
| New Systems | | | | | | |
| Gas-filled Panels (Krypton) | 0,012 | +/- | +/- | +/- | +/- | +/- |
| Aerogel Panels (non vacuumized) | 0,012 | + | + | +/- | - | - |
| Silica/sheet plastic vacu. Panels | 0,006 | + | +/- | +/- | + | +/- |
| <i>kieselgur/steel vacuumized.</i> | 0,005 | + | + | + | + | + |
| Fibers/steel vacuumized | 0,003 | + | +/- | ? | ? | ? |
| Spacers/steel (hard vacuum) | 0,001 | + | + | + | - | - |

Vacuum Super Insulation

VSI technology works with Cr-Ni-steel casings (V2A) and with kieselgur (SiO_2 , diatomee silica) as filling material. The gas-tight connection of inner and outer casing will be made by membranes (thin sheet metal). For the casing an "integrated construction" is foreseen. This means, that the assembled casing has to be vacuumized. In contrast to an integrated construction, the construction with panels causes higher transmission losses on the edges and gives less mechanical stability.

Up to now, in the VSI technology there are only experiences with kieselgur as filling material. Kieselgur is a natural occurring material and is therefore quite cheap. Under atmospherical conditions Kieselgur has a thermal conductivity of about 0,05 W/mK. Under a vacuum of 0,1 mbar this value decreases below 0,005W/mK. A disadvantage is the relatively high density of about 0,4 to 0,5 kg/dm³. Filling materials in form of powder can be processed in large series much better than any fibrous or layered materials, although the vacuumized thermal conductivity may be not quite so excellent.

As we expect controlling problems, if more than 50% of the refrigerating capacity is needed for the freezing compartment, the necessary foam insulation thickness might become 80 mm and more. Therefore a slide-in VSI freezing box is foreseen, eventually with foamed lid.

3. Benefits, efficiency

User Net Capacity

The wall thickness of 25 mm allows a user net capacity of more than 260 litres (freezing compartment included), compared to 240 litres of the conventional model of the same outer dimensions. Therefore a significantly reduced energy consumption and an enlargement of the user net capacity will be possible at the same time. Insulation volume, user net capacity and kieselgur weight of our R/F model are, depending on wall thickness:

| Insulation thickness [mm] | 20 | 25 | 30 |
|---|------|------|------|
| Casing insulation volume [dm ³] | 61,1 | 75,6 | 89,7 |
| Freezing box insulation vol. [dm ³] | 10,6 | 13,0 | 15,3 |
| Remaining user net capacity [dm ³] | 289 | 272 | 256 |
| Kieselgur weight [kg] | 35,8 | 44,3 | 52,5 |

Duration of life

The duration of life of the vacuum insulated casing is assumed to be about 30 years. This is due to fully metal enclosed vacuum. Sheet metal parts may not be thinner than 0,05 mm to ensure gas-tightness.

Transmission losses, Energy use

Calculations of the transmission losses of our R/F result in a daily energy consumption of 0,395 kWh (0,15 kWh/d per 100 l) which is significantly lower than the preliminary requirements of the project (0,2 kWh/d per 100 l). Therefore energy cost savings might be even higher than mentioned hereafter.

The application of kieselgur and steel changes the thermal characteristics of the refrigerator: The thermal capacity of 0,96 kJ/kg makes the refrigerator react slowly to fluctuations of the temperature. After the refrigerator is put into operation, it takes about 4 hours to reach the desired temperature inside. On the other hand an increase of temperature in case of a power failure is very slow.

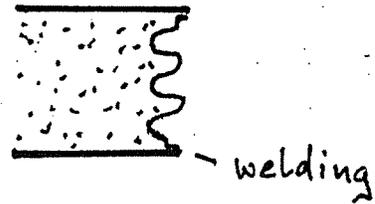
4. Technology issues and eventual problems

Thermal conductivity

Thermal properties are described above and explained in detail by L. Schilf. Alternative filling materials (to kieselgur) may be considered later, when lower costs are to be expected. Aerogel might be a promising option.

Thermal bridges

Most important thermal bridges are the front and door edges. These are optimized by thin metal sheet material with high thermal conductivity, such as CrNi-steel, and a long resulting thermal width by forming waves. Lead-in holes for refrigerant tube and lighting are made of ready-made corrugated tubings.



Weight of the casing

The weight of the casing is determined by the steel walls and the filling material (see also kieselgur weight, above). The complete 10/6 prototype R/F will weigh between 60 and 70 kg. For the serial manufacturing the weight shall be reduced by optimising the wall thickness and the density of the filling.

Stability

During distribution and operation the refrigerator will be charged in different ways. Calculated tests with different load conditions pointed out, that the chosen concept can be realised.

Manufacturing

An "integrated" construction due to minimal thermal bridges needs an accurate joining and welding process of assembly. This may cause more costs than assembling many pre-fabricated parts. Our calculations indicate that a comparable over-all thermal insulation is hardly to be reached by panel constructions.

5. Economics

First costs of VSI technology are rather high compared to conventional foaming technology. This is essentially caused by two extra manufacturing steps: gas-tight welding of the integral casings and the special vacuumizing equipment. As both of these can be adapted to different types of refrigerators (or other devices), their first cost is to be distributed on as high charge as possible, to reduce unit costs. In construction work for prototype manufacturing a cost assessment was made for a 10/6 refrigerator (SINK-Norm) with integrated deep freezing compartment. This is presented by Mr. Schilf.

Concerning the cooling system, hydrocarbons as refrigerant instead of HFC 134a will result in lower handling costs. An eventual two-loop coolant circuit (for R/F) as well as an electronic temperature control will on the other hand result in higher unit costs.

Considering our lifetime requirements and comparing lifetime costs with conventional refrigerators, the market price of our eco-refrigerator may be significantly higher: Economising 50% electricity consumption of a conventional refrigerator (with freezing compartment; 1 kWh/day) over a lifetime of 15 years means 2737 kWh and, at 0.20 SFr/DM or 15 cents, 547 SFr/DM or 410 \$ savings to the consumer.

6. Technology outlook

Development status

The manufacturing procedure of the VSI technology is already practised and is suitable to serial manufacturing. District heating tubes are manufactured in Germany as well as cooling boxes for health service applications in Japan. Up to now, large series manufacturing has not yet been realised. Therefore a timetable to VSI commercialization cannot yet be given.

Cooling devices with hydrocarbon refrigerant are being manufactured by FORON, working in one-temperature refrigerators. A refrigerator-freezer cooling system will soon be on the market. Optimization steps for this application are worked at in several places, as well in our project.

Market penetration

The present status of eco-refrigerator technology does not allow to speak of market penetration prospects. Similar developments, e.g. electric cars, let assume a potential demand for high-tech, relatively expensive products that promise benefits in energy use and environmental impacts. First economic guesses indicate, that the goal of lower (or not-higher) life cycle costs of our eco-refrigerator may be reached.

The MBB-Vacuum Super Insulation (VSI)*

L. Schilf
Dipl. Phys.

1. SUMMARY

RESUME: Systèmes d'isolation thermique évacués représentent l'état d'art actuel dans la technique du froid. Ce rapport présente un système d'isolation thermique évacué qui possède des habitudes additives comme la capacité de résister à grandes pressions, de changer les attitudes thermiques moins vers les températures chaudes, d'avoir une vie longue, d'être complètement inflammable et de ne pas coûter cher. Des différentes applications sont présentées.

2. INTRODUCTION

Vacuum Super Insulations represent the state of the art for very effective insulations for the purpose of thermal control of space crafts and also for specific terrestrial applications like cryogenics. The principle of all of these vacuum super insulations is the following: To prevent for instance the solar radiation from a satellite structure heat shields of reflecting foils are used which are separated by filament nets (see fig. 1).

This way heat losses by radiation are reduced dramatically. Due to the fact that the foils are perforated the air which is enclosed in the spaces between the foils can evade into the ambient vacuum of space during the launch of the space vehicle. Thus the heat losses due to gas convection is also dramatically reduced.

Fig. 2 shows a satellite structure which is insulated by such a foil package.

This principle of insulation has been used under atmospheric conditions since many years. But in contrast to the space application the foil package must be enclosed into a pressure bearing, gas tight vacuum envelope which then has to be evacuated in a manner so that the vacuum remains stable over a long period.

In addition there are systems in which the foil shield package is replaced by a powder package which also reduces radiation and convection effectively.

All these systems have certain disadvantages in common:

The fact that the vacuum envelope has to withstand the external pressure or other forces which are applied to the insulation demands great wall

* Symposium on CFC Restriction & Inhibition Strategy
(Qiandao - 23-25.04.90 P.R.C.)

3. The VSI

That is why has been looking for ways to realize a vacuum insulation in a manner which would enable to reduce the cost and by that way broad the field of applications.

The principal solution is shown in fig. 1.

The vacuum envelope consists of welded foils or thin metal sheets. The envelope is filled by a compressed porous material which withstands the applied external pressure or forces.

Fig. 2 shows an electron beam microscopic picture of the applied powder.

The remaining spaces within the porous material are evacuated sufficiently so that convection and intermolecular energy exchange are prevented or reduced dramatically.

The remaining solid state heat conduction is minimized by the fact that the contact areas between adjacent powder particles are very small due to the powder morphology. Heat transfer by radiation can be reduced further by adding reflecting particles.

Fig. 3 shows the heat conductivity of the evacuated compressed powder as a function of the applied vacuum.

The edge losses can be kept small by a proper design and small thickness of the vacuum envelope at the edges.

The heat conductivity in the undisturbed area of VSI elements is between

$$\lambda = 5 \times 10^{-3} \text{ W/mK} \text{ and } 1 \times 10^{-2} \text{ W/mK}$$

depending on the pressure resistivity (up to 40 - 50 bar at temperature differences up to 200 K).

At temperature differences of 400 K the heat conductivity is about 1.5×10^{-2} W/mK at a pressure resistivity of 10 bar.

The VSI is completely non-inflammable because no organic material is used. In addition the steel qualities used for the vacuum envelope can be chosen that way that the elements are food clean, sterilizable and custom designed for extreme environmental conditions.

During the recent years prototypes for different applications have been developed, constructed and tested and from today's the excellent fitness of the VSI-technology for applications in

- piping construction
- vessel construction
- industrial plants
- low temperature technology
- logistics
- industrial engineering
- home appliances

can be taken as proven.

Fig. 4 demonstrates the application of VSI in pipes.

Because of the high pressure resistivity of the VSI it appeared senseful to position the VSI on the inner side of the pipe and to use the pressure pipe as a part of the vacuum envelope. Thus the pressure pipe is exposed only yet to the temperature variations of the ambient temperature. The stainless steel inner pipe has only a wall thickness of 1 mm compared to the wall thickness of the pressure pipe.

For the VSI-district-heating pipe the advantage that the pressure pipe remains nearly at ambient temperature is very important. For by this fact there is no need for measures against thermal elongation of the pipeline.

This leads to low construction cost. In addition the energetic savings make this a very attractive application.

These advantages convinced the German company Mannesmann to sign a licence contract for the pipe application and to install a production facility which is in operation since the beginning of this year.

Besides of the pipe applications storage vessels in VSI-technology have been developed. (For instance a 4,5 m³-vessel (see fig. 7)). It has a 100 mm thick internal VSI-insulation. By the modular design from separated ground and ceiling segments by inserting of cylindrical segments which are similar to the pipe design there is the possibility to produce vessels of up to some 10 m³ volume.

In addition a 450 l-storage has been developed and constructed (see fig. 6). The wall thickness of the insulation in that case is 60 mm. The sketch in fig. 6 shows the cooling down behaviour of such a vessel.

Fig. 7 shows a standard VSI-flat element which can be used for instance for the construction of cooling containers, thermal boxes and for applications in industrial engineering (cold houses, power plants etc.)

Fig. 8 shows an ISO - 10'Container of VSI panels.

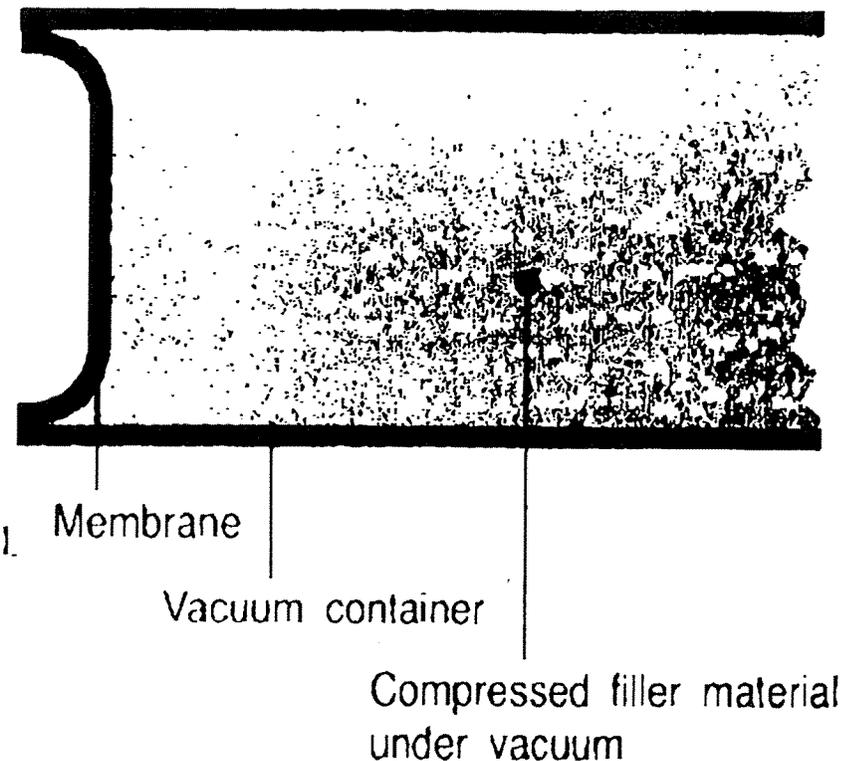
The cold house shown in fig. 9 has been constructed from similar panels. The cold house is completely non-inflammable and is in operation since 4 years successfully.

Besides of the flat panels, pipes and vessels, there is a great variety of special applications for which the VSI-technology is very advantageous, but which cannot be listed all in the available space.

Among others the design of home appliances like refrigerators and freezers have been investigated with excellent results. This field would be a very promising task because a VSI refrigerator would not emit CFC's from the insulation and due to its excellent insulation figures would reduce dramatically the consumption of electrical current which results in the saving of fuel and thus lead to a reduction of CO₂ emission which is necessary to avoid the growth of the greenhouse effect.

Principle of the Insulation System

- VSI is a vacuum-powder insulation
- The insulation container consist of a double wall, the edges of which are sealed vacuum-tight by a membrane.
- The gap between the walls is filled with a powder and then evacuated.
- The powder bears not only the pressure of the atmosphere, but high compressive forces far in excess of atmospheric pressure as well.
- The powder has good thermal-insulation properties.



**Vacuum
Super Insulation**

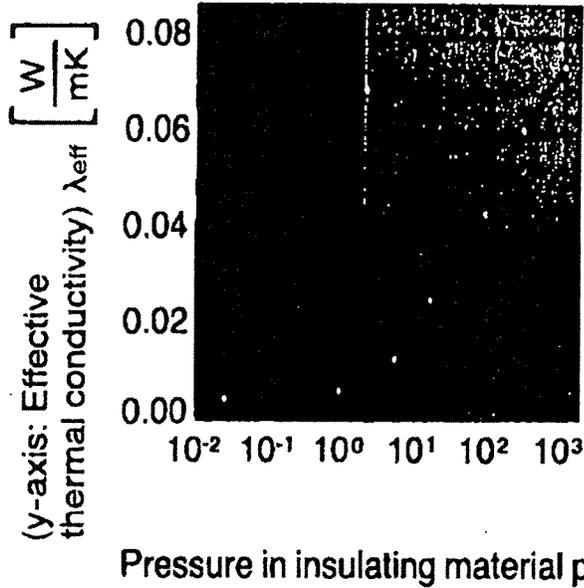
- With fine-grain powder the effective distance is small, making it possible to achieve low thermal conductivity while expending little effort for evacuation.
- Diatom earth is used as the powder in VSI.
- Diatom earth is very fine-grained, thus taking benefits from the Smoluchowski effect and limiting thermal conduction through radiation.
- Diatom earth has low specific thermal conductivity.
- Diatom earth can bear pressure.
- Its pressure resistance can be affected by compression.



Diatom earth under a surface electron microscope

Properties of Diatom earth

■ Thermal conductivity in relation to residual gas pressure



■ Thermal conductivity

| | |
|-------------------------|---------------------|
| Air (1 bar) | 0.0257 W/mK |
| Glass wool | 0.03 ... 0.06 W/mK |
| Cork | 0.03 ... 0.07 W/mK |
| PU foam | 0.03 ... 0.035 W/mK |
| Silicic acids (roasted) | 0.116 W/mK |
| VSI (0.01 mbar) | 0.005 ... 0.01 W/mK |

Source:
University of Dortmund study
conducted for BEWAG

**Vacuum
Super Insulation**

MBB Energy- and
Industrial Technology

VSI Pipes



District-heating pipe

- DN 400
- Length: 6 m
- Max. temperature: 180°C
- PN 20
- k value: 0.17 W/m²K

■ Development models available

Fig. 4

**■ Vacuum
Super Insulation**

MBB Energy- and
Industrial Technology

VSI Tanks

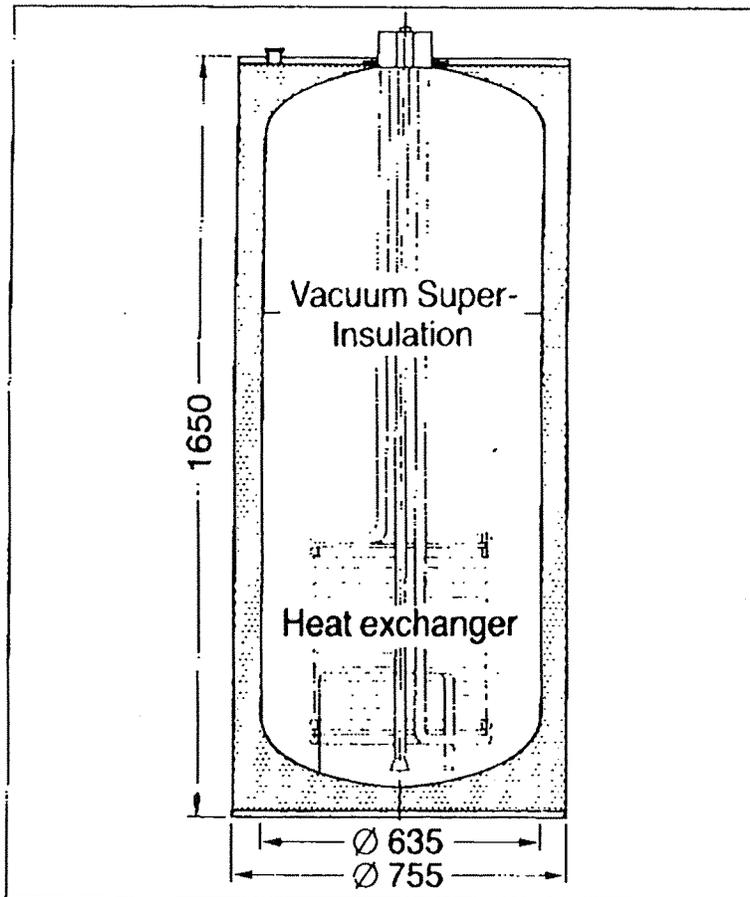


4.5 m³ vessel

- Usable as heat accumulator or for product storage
- 2.9 m x 1.8 m in diameter
- Materials: outside - St 37
inside - 1.4541 stainless steel
- k-value: 0.09 ... 0.12 W/m²K

■ Development models available

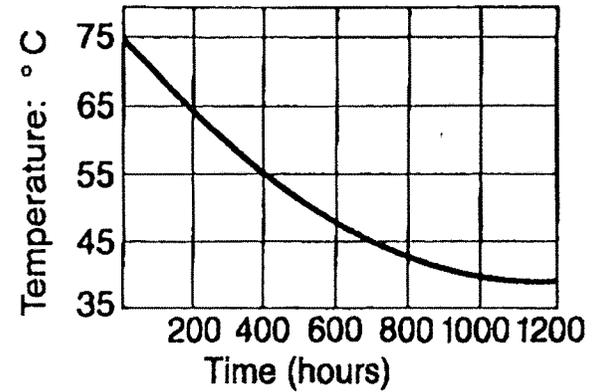
VSI Vessel



Vessel for heat accumulators

- 1700 mm x 755 mm in diameter volume of 450 l (gross)
- Material: 1.4541 stainless steel
- Weight: 282 kg
- k value: 0.18 W/m²K
- Permissible operating pressure: 6 bars

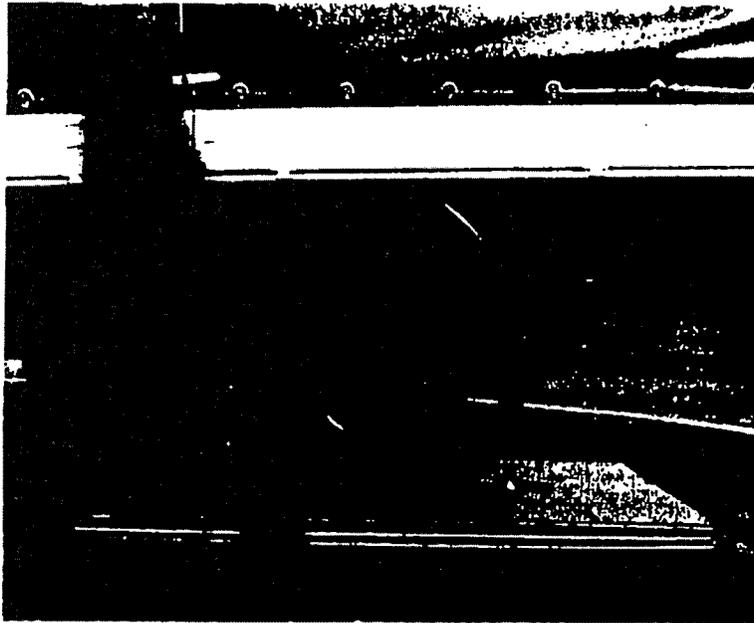
Temperature decay test on VSI accumulators



- Development models available

Fig. 6

VSI Panels



Panels

- Dimensions: 2500 x 1250 x 102 mm
- Material: metallic, selected according to application
- $\lambda = 0.005 \text{ W/mK}$ in the undisturbed area
- Pressure loadability: 10 bars

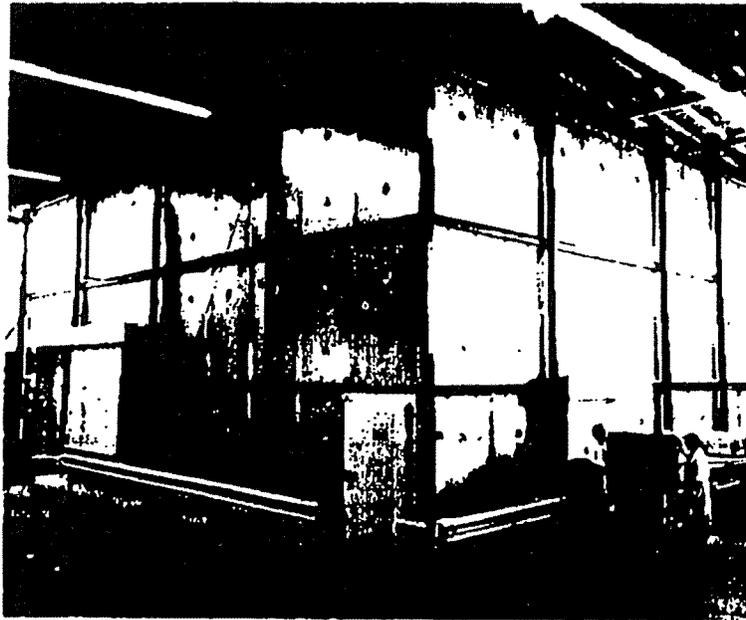
VSI Panels



10-foot thermal container (test model)

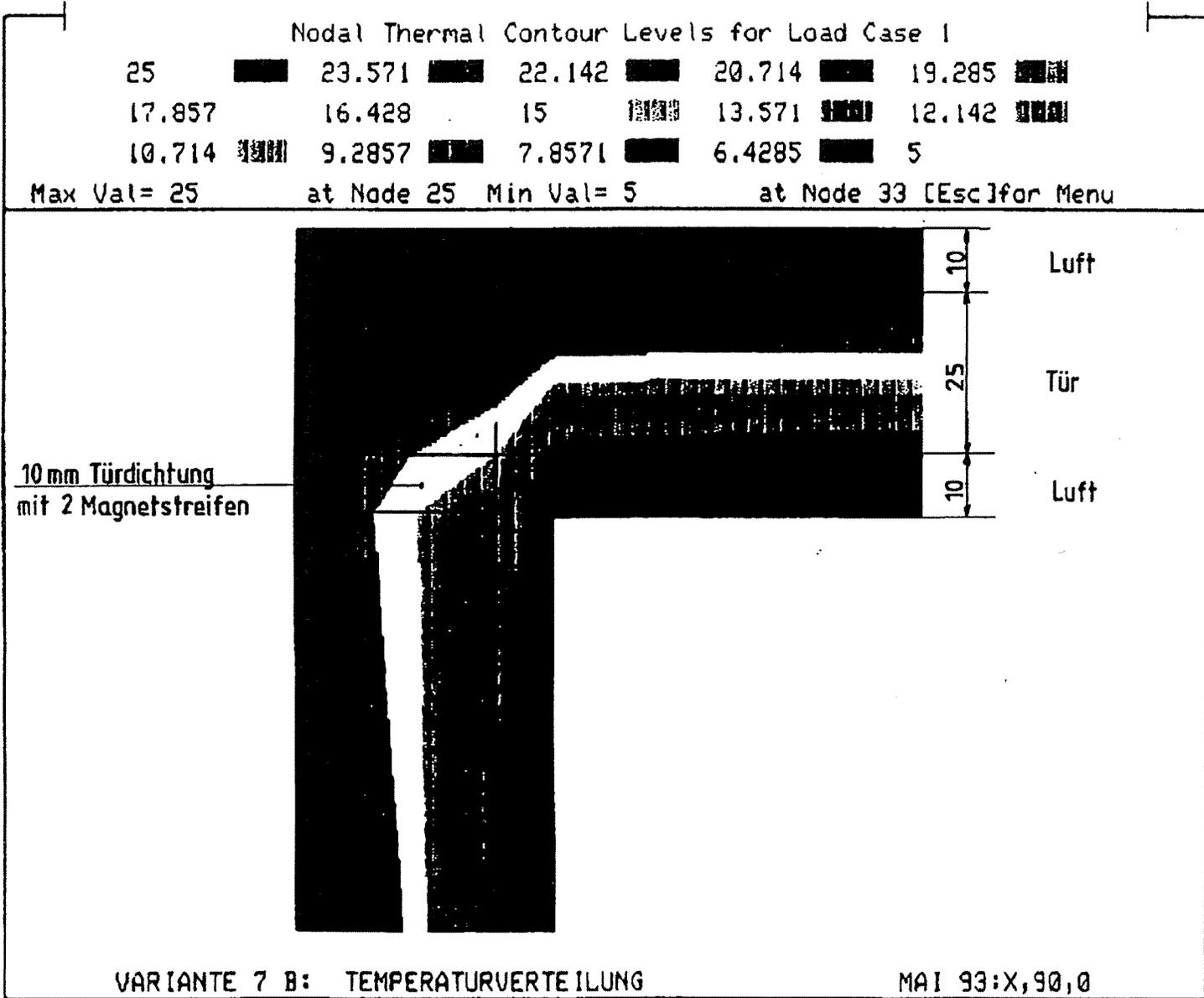
- Experimental model for thermal and mechanical tests
- Dimensions conforming with ISO, panels with various dimensions, 65 mm thick
- Material: 1.4541 stainless steel
- k value = $0.325 \text{ W/m}^2\text{K}$
- ATP approval by the Bavarian TÜV (244 IR)
- Panels also play a role in the structure's statics

VSI Panels



Cold-storage facility for pre-preg material (CFK)

- Volume: approx.
19.0 x 16.5 x 7 m (L x W x H)
229 panels, mostly
2450 x 1500 x 100 mm
- Material: 1.4541 stainless steel
- k value = 0.12 W/m²K
- Temperature: -20° C
- Noncombustible
- Special equipment: vacuum sensors



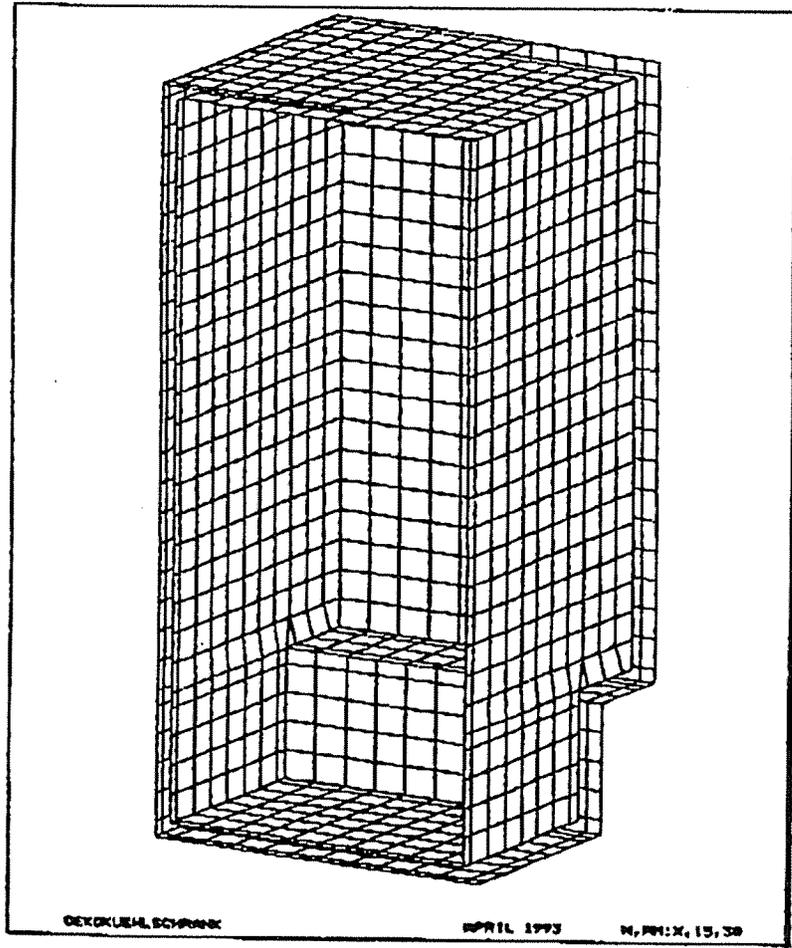


Abb. 2

Development of Evacuated Panel Thermal Insulations

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Report ZAE2-0993-2 (1993)

1. Technological Description

Conventional insulations like rock wool or glass fiber boards have typical thermal conductivities in the range 0.03 W/mK to 0.04 W/mK. Insulations based on fumed silica like Microtherm^R have conductivities in air of > 0.02 W/mK. As they are rather expensive, however, they are mainly used for special applications at higher temperatures. Closed cell polyurethane foams, which are blown with environmentally hazardous CFC gases or their chlorine-free substitutes also have conductivities around 0.020 W/mK. Due to diffusion of atmospheric gases into and effusion of the blowing gases out of the closed cell polyurethane foam, this value increases with life time.

A complete suppression of gas conductivity only is possible with evacuated devices. Evacuated superinsulations based on highly reflective multi-foils have been used since a long time for cryogenic tasks as transport and storage of cold, liquid gases. Thermal conductivities as low as 10^{-5} W/mK at 300 K can be achieved. For these superinsulations cylindrical or spherical vessels with thick walls are necessary in order to sustain the atmospheric pressure load, which is equivalent to 10 tons per squaremeter. Also loose evacuated powders are employed as cryo-insulants, however their thermal conductivity is of the order of 10^{-3} W/mK.

Flat evacuated panels can only be constructed with a filling material which sustains the external atmospheric pressure load. A load bearing filling has the advantage that the vacuum-tight envelope may be made of comparably thin, flexible materials.

Suitable filling materials for load bearing insulations are fibers, powders or gels. At ambient temperature the conductivity of a load bearing evacuated glass fiber board is typically in the range between 0.003 W/mK and 0.005 W/mK, for optimized fiber materials a value as low as 0.002 W/mK is possible. Evacuated fiber boards are used for the insulation of the sodium-sulphur high energy battery which runs at 300 °C and is under development at ABB, Mannheim.

The thermal conductivity of evacuated, compressed powders varies between 0.003 W/mK and 0.010 W/mK. Further optimization of powder materials may also lead to values of around 0.002 W/mK.

Transparent gels like silica aerogel are especially suitable for transparent superinsulations for window applications. Thermal transfer coefficients as low as 0.5 W/m²K can be achieved with a 20 mm thick evacuated aerogel panel.

As the thermal conductivity of the evacuated insulating material depends on the gas pressure, control of air leakage of the insulation envelope is of importance. Nanoporous materials like aerogels tolerate internal air pressures up to 10 mbar without any onset of gaseous thermal conduction. This is due to their extremely fine pore structure with pore diameters below 100 nm which impedes the movement of the air molecules. Fiber and powder insulations due to their much coarser structure have to be kept at internal gas pressures at or below values of 0.1 mbar in order to suppress air conduction completely, while for multi-foil insulations with their relative large spaces between the foils of typically 0.1 to 0.5 mm the pressure has to be kept below 10⁻⁴ mbar.

The vacuum-tight envelope of the insulation has the task to keep the internal air

pressure below the above stated values during the whole lifetime. It may be constructed from thin metal sheets, glass and multi-component plastic foils.

2. Application

Evacuated flat panel superinsulations are a promising alternative to CFC-blown polyurethane foams used in home appliances like refrigerators, freezers and hot water storage tanks. Further applications are the thermal insulation of large mobile or stationary storage systems for frozen food. Even a thermal superinsulation of house walls is conceivable with evacuated flat panels.

3. Benefits

Load bearing superinsulations provide a thermal conductivity up to ten times lower than the CFC-, HCFC- or HFC-blown PU-foams. Thus insulations with smaller thickness, which then enclose a higher utility volume, are possible. Furthermore the reduced heat loss will save energy and thus diminish CO₂ emission. The powder material of the insulation is 100% recycable, in contrast to PU-foamed insulation systems where the disposal or recycling costs may be considerably higher than the production costs.

4. Technical Issues

While the development of high efficiency insulants is a task for material research, the construction of the vacuum tight envelope for the flat insulation panels is a technological problem. The internal gas pressure has to be kept below 1 mbar during the lifetime of the insulation, which typically can range between 5 and 20 years, depending on application.

One difficult item also is to minimize heat losses through the rim sealing.

Materials with the required very low gas penetration properties are metal or glass sheets. Aluminum foils provide a vacuum-tight barrier, due to their high thermal conductivity, however, they are not suitable for superinsulation envelopes. Also multi-layered plastic foils with low gas and water vapour permeability and high thermal resistance are in development.

Powders are most suitable for load bearing vacuum insulations, as they are relatively cheap and handling and recycling is considered easier than for fiber or foam boards.

The technology of filling the powder into the envelope, evacuation and sealing the envelope remains the most important issue to be solved. As the powder usually contains adsorbed water it has to be dried at sufficiently high temperatures and need not to be exposed to ambient air before evacuation. Desorbing water otherwise would degrade the vacuum and the insulation performance of the panel.

The sealing of the envelope has to be done in such a way that it is in compliance with the filling and evacuation process. The rim seal also should not enhance the gas penetration into the insulation volume.

Thin envelope foils are to be protected against mechanical rupture by additional covers which also form and strengthen the evacuated panel.

5. Economics

Production costs of opacified silica aerogels, which provide the lowest thermal conductivity (0.003 W/mK) of filling materials up to now, are in the range of several thousand DM per cubic meter. Cheap powders like diatomite also have been proposed as filling material. It has a relative high conductivity in the order of

0.007 W/mK, however. Providing low cost powders with low thermal conductivity is a concern of future research and development.

The costs of the panel construction are not easy to estimate. The aim of future development must be to decrease the production costs to a level of 3 DM/m² for a heat transfer coefficient of 1 W/m²K. For a coefficient of 0.2 W/m²K, which is typical for a well-insulated freezer, the cost of the evacuated insulation panel should not exceed the range of 15 DM per square meter. The thickness of the panel then could be as low as 20 mm compared to a 100 mm CFC-blown PU foam insulation.

6. Technology Outlook

Evacuated superinsulations based on multi-foil systems and - especially for large storage tanks - loose powder fillings have been successfully used for cryogenic applications since decades. Many attempts have been made to establish load bearing superinsulation systems for mass applications. Up to now, however, no development has reached broad commercialization. At the Bavarian Center of Applied Energy Research (ZAE Bayern) one concern of our research is to develop cheap powders with thermal conductivities below 0.003 W/mK. Furthermore promising technologies for both high quality and low cost envelopes will be investigated.

The goal is to develop load bearing evacuated superinsulations which have a sufficiently large life time at costs which are not considerably higher than the ones for CFC filled PU foam insulations. All components of the superinsulation panel should be recyclable, have as low environmental impact and low health risks as possible.

Aerogels - A Foam Alternative

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ABSTRACT

Aerogels offer a thermal performance unattained by any other class of material.

For a long time aerogels have been of little interest for big volume applications such as domestic appliances because of lack of availability, technical barriers and cheap energy prices. They have only become viable for some small scale specialist applications.

However, during recent years BASF has successfully embarked on a program to build up a pilot production plant for granular inorganic aerogels (Basogel[®]) comprising amorphous SiO₂. So, an advanced thermal insulation material can be provided which seems to meet tough future performance and regulatory needs.

Big scale industrial processing of the material has proven possible. Growing interest for application of aerogels in the home appliances manufacturers industry (boilers, refrigerators, freezers, ovens, etc.) may be expected, as excellent quality of aerogel fillings bring remarkable 20 % improvement over conventional foamed insulation systems in terms of energy consumption. Additional optimization could be expected by application of vacuum techniques.

INTRODUCTION

Expected fast growing costs for energy and the upcoming phase out of CFC blown foams have led to a search for alternative high performance thermal insulation materials. It is generally acknowledged, that they should not only meet performance requirements of appliances as for instance the 1993 DOE standards but conform to environmental rules governing energy consumption/1/.

® = registered Trademark of BASF

Some countries such as Germany are pressing for an ordinance that will force appliance makers to take back and recycle their products. This development requires materials which can be recycled easily.

It has been shown by several authors that aerogels might be able to provide fundamental solutions to these problems. Since their invention in the early 30's silica aerogels have been well known because of their excellent thermal insulation capacity/2/.

As a result of their high content of micropores with diameters in the range of nanometers, their thermal conductivity is even lower than the values of argon or air. In addition silica aerogel is characterized in particular by its optical transparency and its suitability for recycling.

For several years BASF has been engaged in a program to develop aerogels for large scale applications. Figure 1 presents the history of this program by a pyramid of development, where each stage refers to a milestone. After having successfully gone through the R&D level focussing on basic properties, an area of major concern in the development of an advanced aerogel such as Basogel® was the moisture resistance of the material (second level). Specifically exposure to moisturized atmospheres are known to cause pronounced detrimental effects on the materials structure and properties. Therefore, a fair amount of work and time has been devoted to develop with Basogel® a hydrophobic version of an aerogel.

The higher levels represent recent developments of glazing components for daylighting and trombe wall elements of buildings going along with further adjustment of the production technique. At the end some very positive experience was the reason for entering a precommercial phase for such elements.

Today, a specified silica aerogel is available in limited volumes for a phase of investigation of further selected key applications, which generally seems to meet the requirements for a general industrial application. It has proven its excellent properties in a series of tests and pilot applications.

It is the subject of this paper to comprehensively discuss the properties and quality of Basogel®. Technical developments, feasibility studies and pilot projects for different applications in the construction and home appliances industry are reported subsequently. Finally, special emphasis in the discussion is placed upon the ecological effects of a broad application of aerogels.

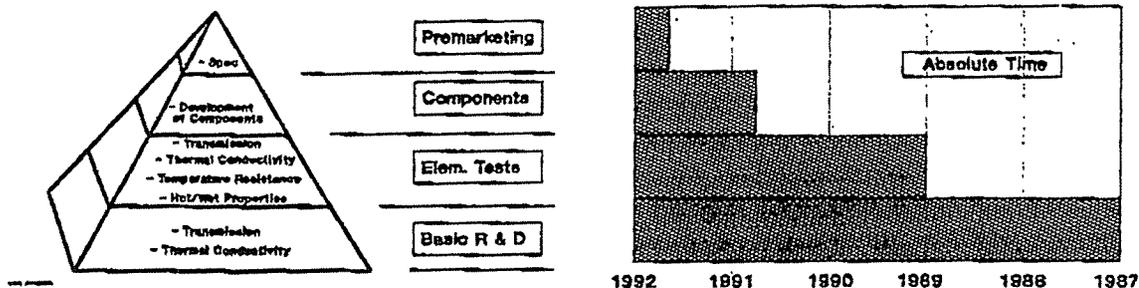


Figure 1: Basogel[®], Pyramid of Development

MATERIAL PROPERTIES AND QUALITY

Product Line

Based upon a production process by spraying mineral acid and water glass solution through a mixing jet conus into a basin, where the hydrogel pellets obtained are washed and hypercritically in dried the final product Basogel[®] is a transparent granular material with diameters between 1 and 6 mm allowing optional compositions of diameter distributions. Densities are scattered between 130 and 140 kg/m³.

Under the same specification of diameter and specific weight, carbon particle loaded (opacified) Basogel[®] has also been developed. This type of aerogel exhibits a lower intrinsic conductivity and a higher infrared extinction coefficient than transparent silica aerogel, resulting in a significantly lower overall thermal conductivity.

From both transparent and opacified Basogel[®] a powder can be produced. As the powder with its microgranular consistence allows narrow air spaces to be filled this material can serve as thin wall insulation as well as an optimized insulation technique by 40/60-powder/bedd mixtures with the powder filling the spaces between large diameter granules.

Thermal Conductivity

The thermal conductivity λ - continuously monitored for QC purposes - is given by values between 0.016 and 0.022 W/mK (mean temperature 10°C). An analysis of the possible improvement by powder/bedd mixtures yielded a 15 % reduction of the heat transmission coefficient.

By the opacifying process the IR extinction coefficient can be increased by a factor of almost four over unloaded silica/3/. This goes along with an apparent reduction of the average pore size by the carbon particles and provides a dual benefit which leads to an improvement of the total heat conductivity especially at elevated temperatures of 13 % (50°C) /28 % (100°C). Figure 2 summarizes test results up to 200°C and compares them to air and translucent Basogel®, which should not be considered for service temperatures above 50°C.

Vacuum Application

For monolithic aerogels already a low vacuum of 100 mbar is sufficient to achieve heat transmission coefficients of 7.5 mW/mK. As such a vacuum is to be achieved and maintained relatively easily the further use of these materials can be expected for evacuated systems.

For granular aerogel the large air-filled spaces between the beads are the reason that similar conductivities cannot even be achieved with pressures below 0.1 mbar.

Figure 3/4-6/ puts the two materials into relation to each other at different pressure levels and compares them with the results of powdered opacified Basogel®. The comparison reveals clear advantages for the latter material over granular aerogel. Although not performing as well as monolithic aerogel the picture provides evidence for the excellent performance of the opacified Basogel® powder under low vacuum.

However due to the statistical nature of these properties further tests including different Basogel® batches and types are in progress to substantiate these values.

Moisture and Temperature Resistance

As communicated earlier the detrimental effect of moist environments is also a factor of prime concern in the utilization of aerogels.

Trough the hydrophobic performance of Basogel® the granules even swimm on water many days without getting damaged. Exposure tests with Basogel® in a climate chamber at 70°C/80 % r.h. showed the material is resistant to this climate over more than 5 months. Suveying transmission, conductivity, density and volatile content of Basogel® exposed to normal building conditions over a period of 12 months the material's performance has been stable.

To obtain information on the behavior of Basogel[®] at elevated temperatures an evaluation of DSC and DTGA analysis has been performed over a wide range of temperatures. With respect to the hydrophobic quality of the Basogel[®] the following recommendations can be obtained:

Max. service temperature of a hydrophobic material: 170°C
 Max. short term temperature resistance: 200°C

At temperatures above 200°C the hydrophobic protection of the material gets impaired. As long as dry environments and conditions can be maintained silica aerogel is able to bear temperatures of up to 750°C/5/.

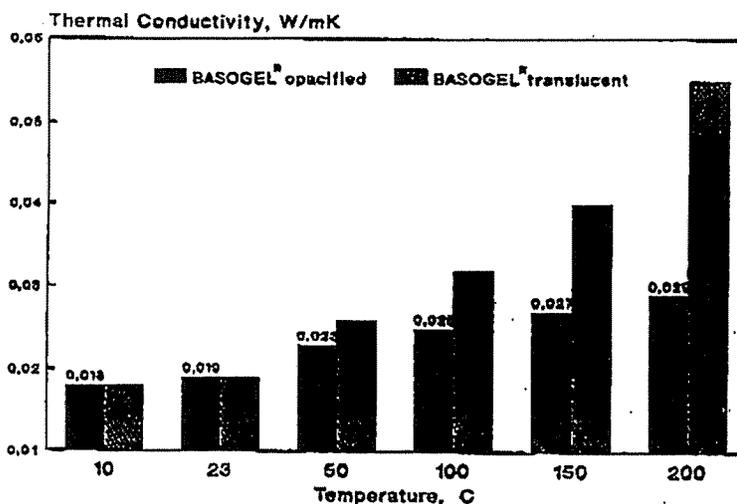


Figure 2: Thermal Conductivity of Basogel[®] at elevated Temperatures

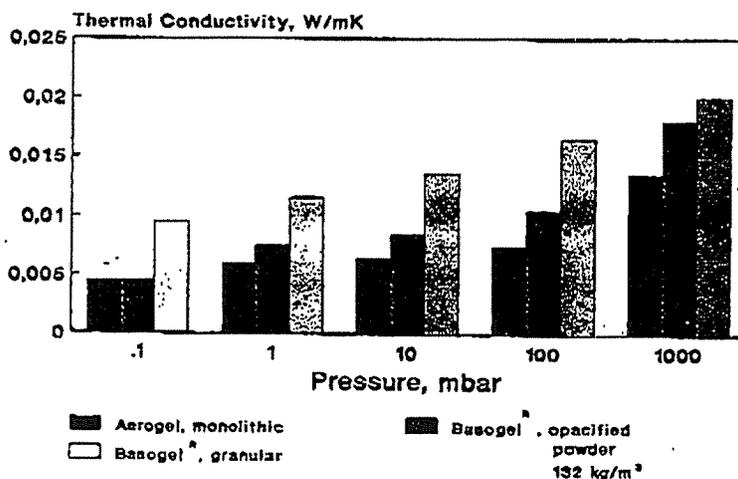


Figure 3: Aerogels under Vacuum

Outlook

A promising analysis of the sol-gel process has been started, as it is well known that the optimization of effective pore sizes and specific weight of the aerogels leads to improved thermal insulation values /3/. The structure and density of aerogels can be influenced by the pH value, the temperature and the concentration of the ingredients employed in the sol-gel synthesis. So far this method has been the most efficient means for approaching optimum/minimum conductivities as they are calculated by different authors and measured with several laboratory scale samples /2,3,7/. As figure 4 shows opacified silica aerogels perform equivalent to aerogels with organic matrix.

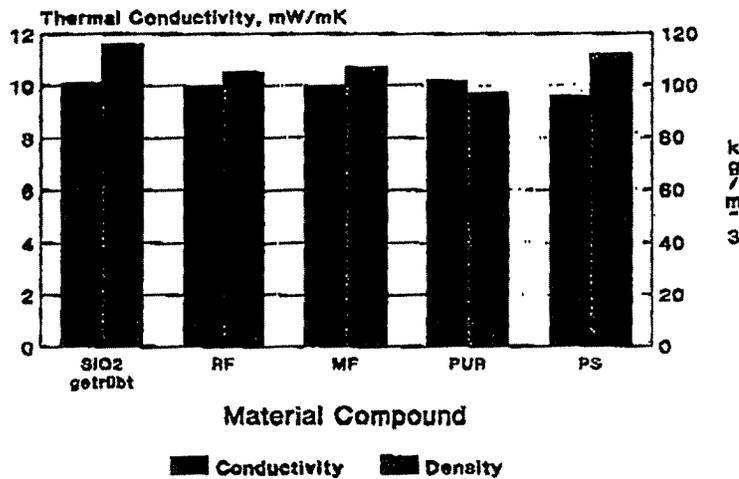


Figure 4: Silica vs Organic Aerogels, Calculated Optimum Densities for Lowest Thermal Conductivity (300 oK, Air Filled) /3/

MAJOR APPLIANCES

The introduction of aerogels into 100.000 t of insulation material consuming industries requires extensive development efforts for new design concepts and material evaluation and qualification work.

As recent developments in the home appliances industry indicate, there is a general desire by manufacturers to incorporate alternative insulation systems to enhance insulation of all kind of major appliances and for ecological reasons.

Namely the silica vacuum panel technology with its 300 to 400 micron thick multilayer halogen-free vacuumformed and silica filled plastic shells has created remarkable attraction /1,9/. They can reduce refrigerator energy consumption by 15 to 25 % over energy use levels of appliances with conventional insulation.

As Basogel® could cut refrigerator and boiler energy consumption by the same amount without needing vacuum and facing leakage and other problems, extensive feasibility studies have been performed during the last few months.

In table 1 the appliances which have been investigated are listed together with the corresponding types of Basogel®.

Table 1

| Application | Basogel® Powder | Basogel® Powder/Granules | Basogel® Granules |
|-------------------------------------|--------------------|-----------------------------|-----------------------|
| Refrigerators | | transparent/opacified | transparent/opacified |
| Freezers | | transparent | transparent |
| Boilers | | opacified | |
| Heat storage systems/Heat batteries | opacified | | |

The essential elements of the test program considered here are listed briefly:

1. Physical (and mechanical) tests to determine the materials' performance profile. The test matrix includes for example tests of conductivity, emissivity, density, porosity as well as the determination of hydrophobic properties.
2. Environmental tests to check the durability of Basogel® under various climate conditions.
3. Processability tests to determine the behavior of Basogel under industrial conditions and filling cycles.
4. Subcomponent and full scale test for investigation of real service conditions.

Most of the elementary tests (1., 2.) have been discussed previously.

Figure 5 shows the values for improvement of the energy consumptions of different appliances. Surprisingly the values for the refrigerators and boilers are higher than could be expected from the elementary test results. The reason is the dense packing of the aerogel granules caused by a special filling technique derived from processability tests (3.) which applies a high frequency vibration to guarantee the absolute consolidation and compression of the insulation.

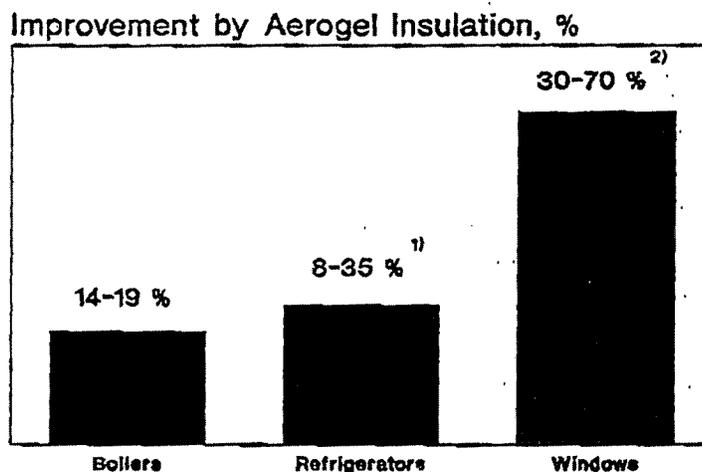


Figure 6: Basogel[®] Insulated Systems, Cut Back of Energy Consumption
 1) Extrapolation from Refrigerators with Basogel[®] insulated doors
 2) Improvement over Commercial Standard Products

EFFECTS OF BROAD APPLICATION

Extensive life cycle analysis identifying the energy and raw materials used and wastes generated in the manufacturing, distribution, use, recycling and disposal shows that aerogels do not cause any ecological problems /6,12/. Therefore the demand for increased product responsibility and closed production cycles is satisfied particularly well. With a primary energy consumption between 48 and 72 GJ/t, /6/, 70 GJ/t, /12/ respectively a comparison of granular aerogel with conventional insulating materials comes out in favor of aerogels. The shorter the life cycle of the insulated product the bigger the advantage of aerogel is. Granular aerogel performs far better than monolithic aerogel with its primary energy consumption between 175 and 215 GJ/t, /5/.

Research and demonstration projects have proved that aerogels offer interesting techniques to reduce the energy consumption of buildings. The favorite applications for such transparent insulation are elements described above.

Simulations predict a high potential for solar energy conservation. Solar gains between 50 and 250 kWh/m²y for south facing walls are possible. Measured results are somewhat lower, ranging between 40 and 80 kWh/m²y/11/. A comparison of recent and actual German standards with the performance of transparent insulated buildings brings a more than 50 % advantage in the annual heating energy consumption/5/. Even the Swedish standard is 30 % lower.

As continuously performed quality control monitoring of Basogel® shows the material is 100 % amorphous. In addition to the nontoxic nature of silica dioxide the material has no potential for any health or waste hazard.

SUMMARY

The characteristics and the property profile of Basogel®, the silica aerogel of BASF have been summarized. The product is currently being produced successfully in a pilot plant in Ludwigshafen/G.

Typical for the overall performance of Basogel® are its excellent thermal insulation properties and its moisture resistance, both of which are significantly improved over existing materials of this type. But it is the combination with further properties such as its easy recyclability and ecological balanced production process which ultimately makes this aerogel even economically attractive and feasible.

An opacified material yields significantly reduced u-values at temperatures above 50 °C.

The effects of vacuum on thermal insulation values are currently under evaluation.

It is obvious that the further development of Basogel® requires close cooperation between the material supplier and the major appliances industry. The mutual supportive relationship between the two partners is a prime requisite not only for the definition and carrying out of the task in a cost effective manner but also for the technical and timely completion of the development effort.

ACKNOWLEDGEMENTS

We are grateful to Mr. Gall and Mr. Schelling of the BASF Technical Development Department for their cooperation throughout the course of the development phase. The support of Mr. Schulze and Dr. Vogelsang of the BASF business unit Foam Plastics is also gratefully acknowledged.

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Vacuum Insulation Panels (VIPs)

by Roland Reuter and Gerhard Sextl
Degussa AG, Hanau / Germany

0. Introduction

Degussa has developed silica based Vacuum Insulation Panels (VIPs) that, based on their low thermal conductivity make it possible to create both non CFC and energy saving insulation materials.

1. Technology Description

Vacuum Insulation Panels are manufactured from silica, non-woven and barrier film. Silica is first pressed to a board and then sealed under vacuum into gas- and water-tight film envelope. The choice of a highly structured silica facilitates thermal conductivities of between 6 and 7 mW/m/K, at a panel's internal pressure of approx. 1 mbar. Maximum dimensions available at present are 800 x 600 x 25 mm. Symmetric panels show the circulatory welding seam in the center of the panel (Fig 1), whereas asymmetrical panels have that welding seam in level with the aluminium-lined film serving as the panel's top cover.

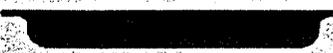
| Vacuum Insulation Panels (VIPs) Construction and Properties | |
|--|--|
| CONSTRUCTION: | Filler compressed to form a board, evacuated and subsequently sealed in gas and water tight barrier films. |
| SHAPES: | symmetric:  asymmetric:  <div style="text-align: right; margin-right: 50px;">sealing edges</div> |
| FILLER: | highly structured silica |
| THERMAL CONDUCTIVITY: | 6 to 8 mW/mK |
| INTERNAL PRESSURE: | 1 to 2 mbar |
| PANEL DIMENSIONS: | max. 800mm x 600mm x 25mm |
| LIFE EXPECTANCY: | appr. 15 y (In this time period increase of thermal conductivity to 8 mW/mK) |

Figure 1 Construction and properties of VIPs

Besides low thermal conductivity, a favorable longterm-behaviour is another decisive factor governing the choice of silica. As per Fig 2, silica 1 exhibits an almost stable thermal conductivity over the entire pressure range of between 1 to 20 mbar, remaining relatively unharmed by gases and water vapour diffusing into the panel during it's life-span. In comparison, similar fillers such as perlite or silica 2 show a remarkable different behaviour in the same pressure range. Combinations of appropriate silica with appropriate barrier films present the optimum with regard to durability and longterm-behaviour.

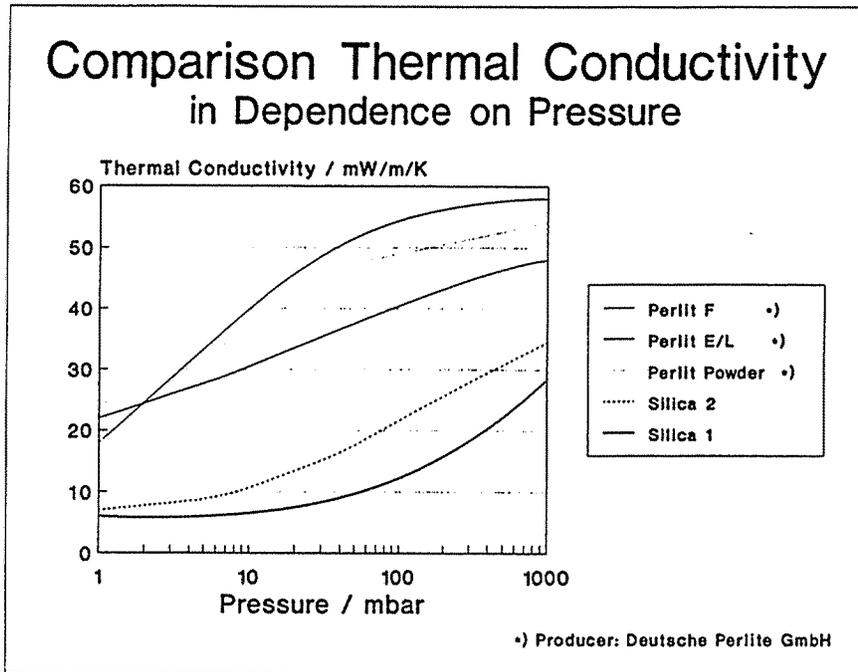


Figure 2 Comparison of thermal conductivity of different filler-materials

2. Application

PUR-foam is the insulation material of the choice for most conventional refrigerators/freezers. Besides its insulation properties, it lends stability to the unit. The first commercially available freezer (Fig 3) is an example of how PUR-foam is combined with VIPs. The panels are attached to the metal casing, before the remaining space between inner and outer casing are filled with PUR-foam. In this case insulation is mainly due to the VIPs, while the foam still improves mechanical properties.

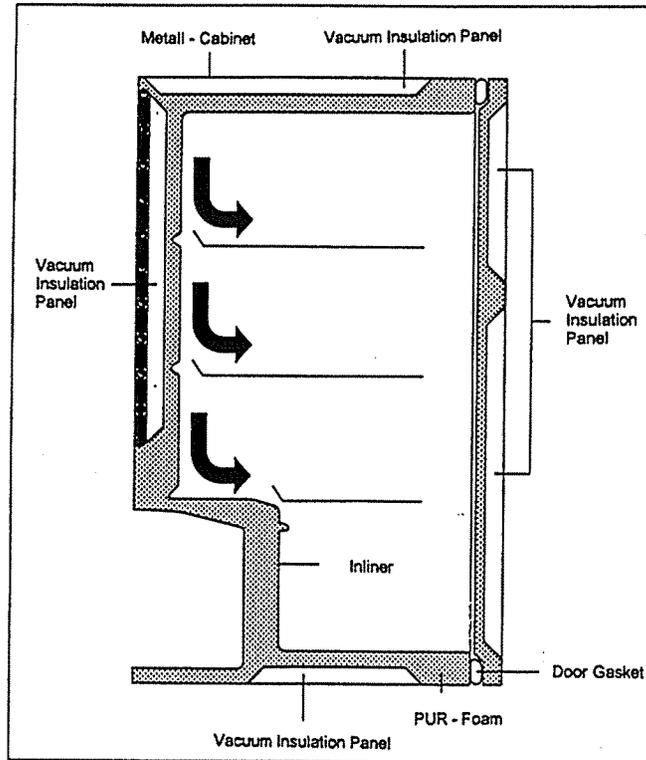


Figure 3 VIP insulated built-in freezer (Fa. AEG, Kassel Type: Öko-Arctis 1352i)

3. Benefits

The joint ZVEI/Degussa program comprised evaluation of four different classes of R/F's: refrigerator cabinet, freezer cabinet, R/F combination cabinet, and chest freezer. All cabinets were foamed with R11 (50% reduction) blown PUR. The relative energy saving for VIP insulated cabinets are in the range of 20 - 25 % without any optimization.

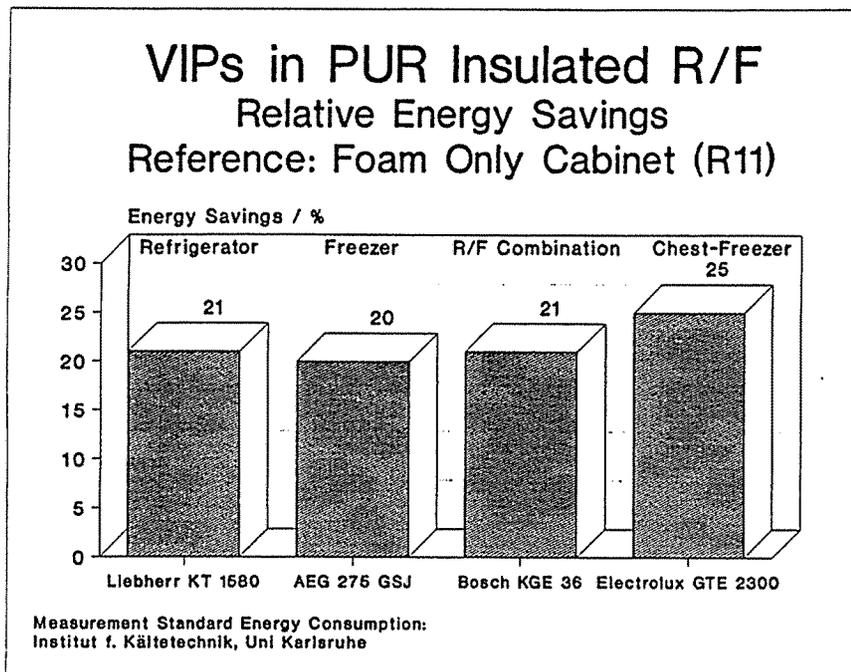


Figure 4 Relative Energy Saving Potential

VIPs used in refrigerators/freezers have a significantly favorable impact on the Global Warming Potential. Since they help to lower the energy consumption of the entire cabinet and, hence, to reduce the total carbon dioxide emission, they are a major factor in the "Total Equivalent Warming Potential" (TEWI) concept. The TEWI is the sum of the direct equivalent (e.g. chemical emissions) and the indirect global warming effects (e.g. energy use). It is an interesting fact that in the present case, the TEWI saving potential from VIP insulation is considerably higher than the TEWI contribution due to the blowing agent. (Fig 5). In the commercially available AEG freezers (type AEG 275 GSJ) 600 g of HFC-134a are used as blowing agent. The contribution of the "Direct Equivalent Warming Potential" of the blowing agent on TEWI is less than half of the reduced carbon dioxide emission (indirect warming potential) due to the electrical energy savings of vacuum insulated freezer.

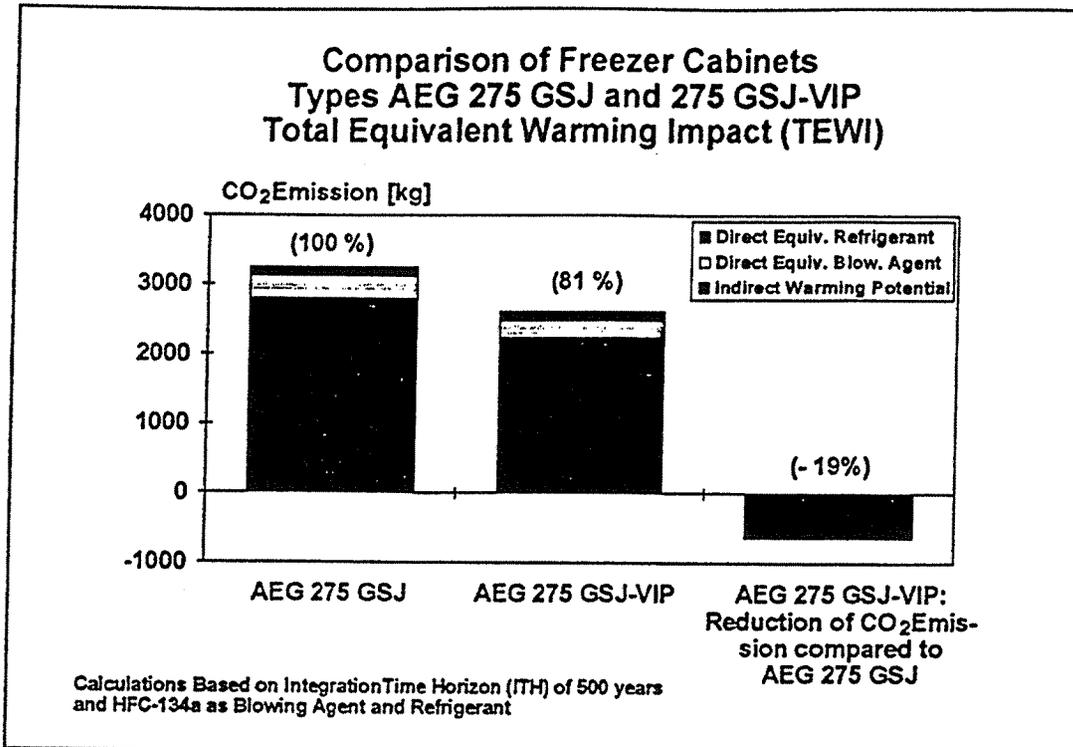


Figure 5 Comparison of Freezer Cabinet's Impact to TEWI

4. Technical Issues

The following technical issues (Fig 6) have been addressed over the last 7 years of Degussa's development. All of the mentioned items have been solved by practical testing at Degussa or at our partners in the appliance manufacturing industry.

| Technical Aspects on VIPs | |
|--|-------------------|
| • Product Film Filler Thermal Conductivity | ✓ |
| • Application Mounting Foaming of VIP-Cabinets | ✓ |
| • Energy Saving | ✓ |
| • Life-Time Expectancy | ✓ |
| • Waste Management of VIP-Cabinets | ✓ |
| • Quality Assurance | ✓ |
| • Production on Pilot Scale | ✓ |
| • Production on Large Scale | Start UP Mid 1994 |

Figure 6 Technical Questions on VIPs

Electrolux Siegen, a German subsidiary of the Swedish Electrolux AB group, will operate the first large scale VIP production starting the mid of 1994.

5. Economics

Past experience has shown that the production costs per sqm VIP from a commercial plant will be in the range of 50 to 70 DM. 2.4 sqm of VIP, as used in the AEG unit, would cause between 120 and 170 DM of production costs. The increase in selling-price of commercial available VIP insulated refrigerators or freezers will be higher than the given cost figures. On the one hand additional costs for retooling and assembling have to be added and on the other hand companies have to work profitably.

Fig 7 shows that the life-time energy savings of the AEG GSJ 275 freezer are in the range of 300 DM.

Converting the German cost figures into US\$, the VIP cost will be in the range of \$ 2.50 and \$ 3.80 per sqft.

26 sqft of VIP insulation for a 10 sqft freezer cabinet would add additional \$ 72 to 96 panel production cost. On the other hand 1200 kWh of energy can be saved over 15 years.

Depending on the cost per kWh of 8 to 15 cts., the energy cost savings would be in the range of \$ 96 and 180.

| VIP ENERGY BALANCE | | | |
|---|--------------------|------------------------|-------------------|
| Comparison of Freezer Cabinets | | | |
| Type AEG 275 GSJ and AEG 275 GSJ-VIP (with VIPs) | | | |
| Cabinet: | AEG 275 GSJ | AEG 275 GSJ-VIP | Difference |
| <i>Electric Power Consumption (Operation):</i> | | | |
| Time Period: 24 h: | 1.11 kWh(el) | 0.89 kWh(el) | - 0.22 kWh(el) |
| Time Period: 15 y: | 6078 kWh(el) | 4872 kWh(el) | - 1206 kWh(el) |
| <i>Electric Power Cost *</i> | | | |
| Time Period: 15 y: | 1519.50 DM | 1218.00 DM | - 301.50 DM |
| * DM 0.25 / kWh(el) | | | |

Figure 7 Comparison of Freezer Cabinet's Consumption and Cost of Electrical Power

6. Technology Outlook

As shown in Fig 6, Degussa has developed VIP technology to commercial scale. It is an important feature of our technology that due to its modular design, it can easily be scaled up. Starting point of any commercial plant is the project phase to determine individual requirements e.g. dimensions and capacity, to be followed by detailed engineering and construction. The time frame for the entire project including start up is expected to range between 2 and 2 1/2 years.

Degussa is prepared to grant a technology licence to interested parties, before individual contracts will cover respective engineering concepts. These concepts might include for engineering services as well as detailed basic engineering provided by Degussa AG.

On account of its worldwide network, Degussa AG has started to enter into negotiations in Europe, North America and the Far East, indicating a strong commercial interest in Vacuum Insulation Panels.

AURA™
A Fiberglass Based Vacuum
Insulation Panel Technology

Presented at

**"1993 Non-Fluorocarbon Insulation,
Refrigeration and Air-Conditioning
Technology Workshop"**

Wiesbaden, Germany
September 27-29, 1993

Author: Ralph D. McGrath
Owens-Corning Fiberglas
Science and Technology Center
Granville, OH

ACKNOWLEDGEMENTS

I want to acknowledge the entire Owens-Corning Aura² project team without whose dedication there would not have been the breakthroughs that made this paper worthy of note.

I want to especially draw attention to Stan Rusek, a senior engineer, whose persistence and diligence brought about the first Aura² panels.

DESCRIPTION OF TECHNOLOGY

AURA insulation is an "evacuated panel insulation" that combines a thermally crafted FIBERGLASS media with a STAINLESS STEEL vacuum envelope, (see figure 1) to provide unsurpassed thermal insulating performance over a broad range of operating temperatures.

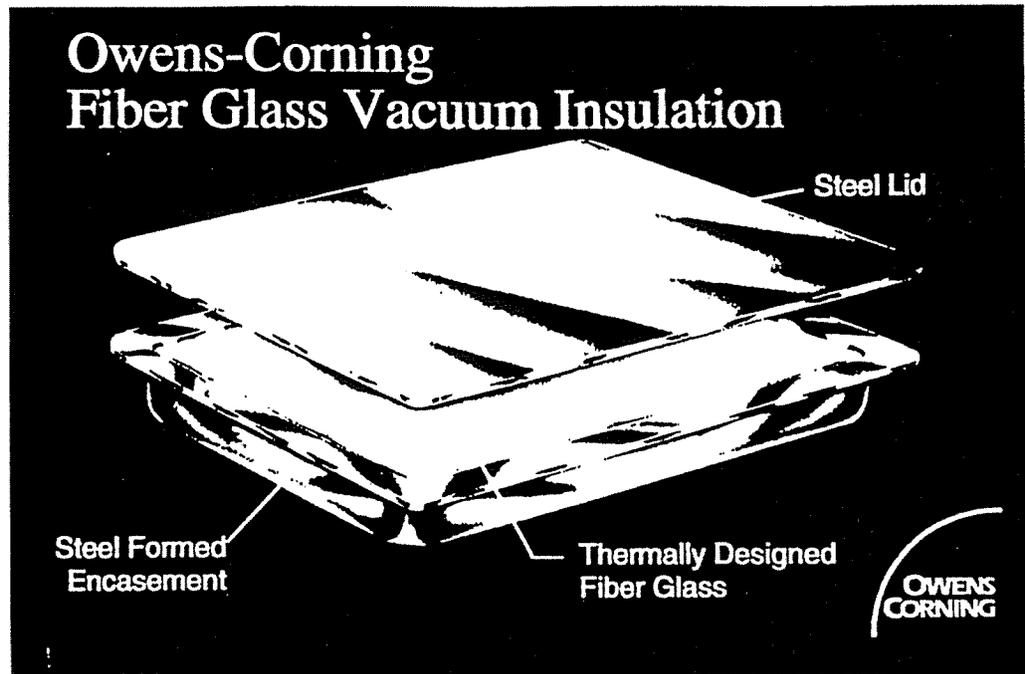


FIGURE 1

The selection of the materials of construction in the first instance was made with full regard not just to the anticipated demands of the targeted applications, but also to the Environmental impact of the total insulating system. Working within those parameters, Owens-Corning's Research & Development effort was characterized by a pronounced bias towards an arrangement that would result in an insulation product with excellent longevity of performance (particularly retained thermal performance), ease of recyclability, durability, and a wide operating temperature band.

Fiberglass Media

Several past articles have expounded upon the utility of fibrous glass in evacuated panel arrangements, and the fundamental attributes of a glass fiber media can be readily determined upon review. In summary, it was understood that the fiberglass media would outperform "powder" at higher levels of vacuum, and the incentive was therefore to develop an enclosure that could maintain this vacuum level over a typical product lifespan.

The fiberglass media developed for AURA insulation is a unique departure from previous teachings and can truly be described as being crafted solely for the purpose of its usage in a "hard vacuum environment".

In basic terms the fiberglass media is a relatively heavy density arrangement of discrete glass fibers that is pre-fabricated to completely fill the stainless steel panel. Extreme care is given during the fiber forming stage and the media fabrication process to ensure that the resulting arrangement of fibers is highly uniform. This construction is critical to achieving the remarkable high levels of thermal performance achieved for this product.

Stainless Steel Envelope

The selection of stainless steel came after extensive experimentation with many alternative barrier materials, including several polymeric film systems as well as glass and various metallic foils.

In choosing stainless steel over the other candidates Owens-Corning's research effort gave full regard to the previously described "fitness for use" for the delivered AURA insulation panel, namely:

- Stainless steel had obvious advantages with its proven track record in vacuum systems specifically designed for "long life" and "durability". Stainless steel thermos bottles and cryogenic containment vessels are two excellent examples of products that have been manufactured with proven reliabilities for some fifty years. No other candidate material satisfied either criteria in a satisfactory manner;

- The desired "broad band" of operating temperatures for the finished panel is readily achievable with stainless steel, and correspondingly limited with the alternatives;

- Extensive technology for stainless steel panel fabrication exists which should provide the required flexibility in panel design to satisfy anticipated customer needs. An example of this flexibility can be seen in figure 2 which reveals a panel fabricated for use on the top of a water heater (note the cut outs).

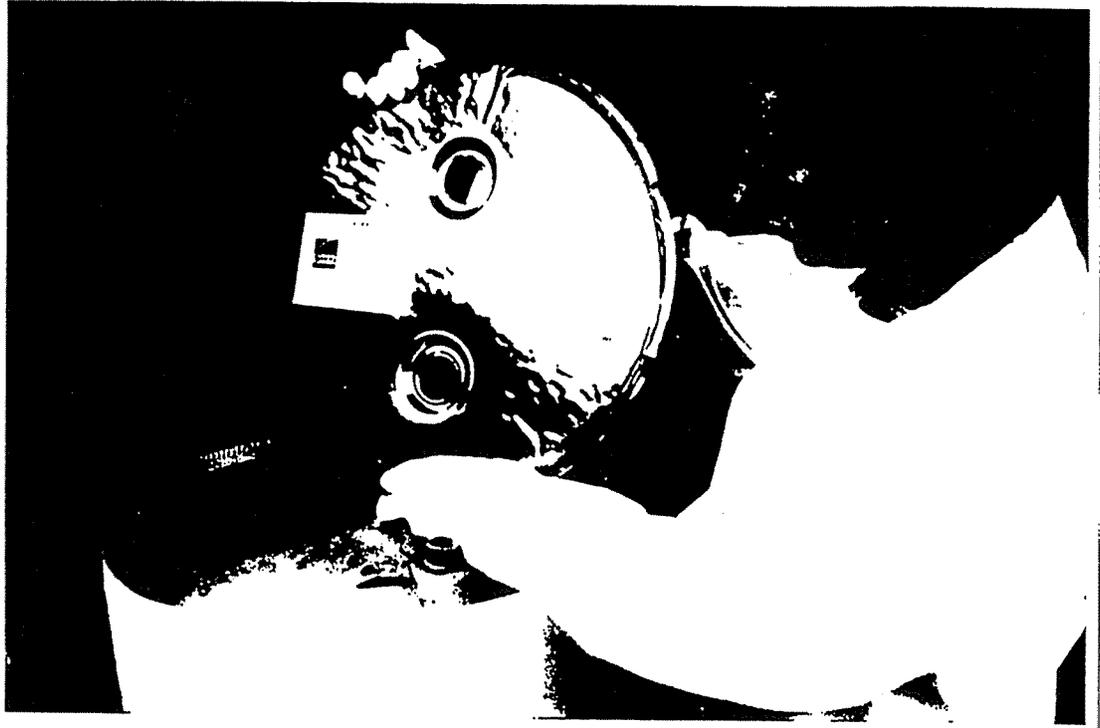


Figure 2

AURA PANEL PERFORMANCE

The success of synergism between the fiberglass media and the stainless steel envelope becomes most apparent in terms of achievable AURA panel performance, (see figure 3) and the realization that this performance can be provided over a long time.

R/inch vs. Vacuum Level

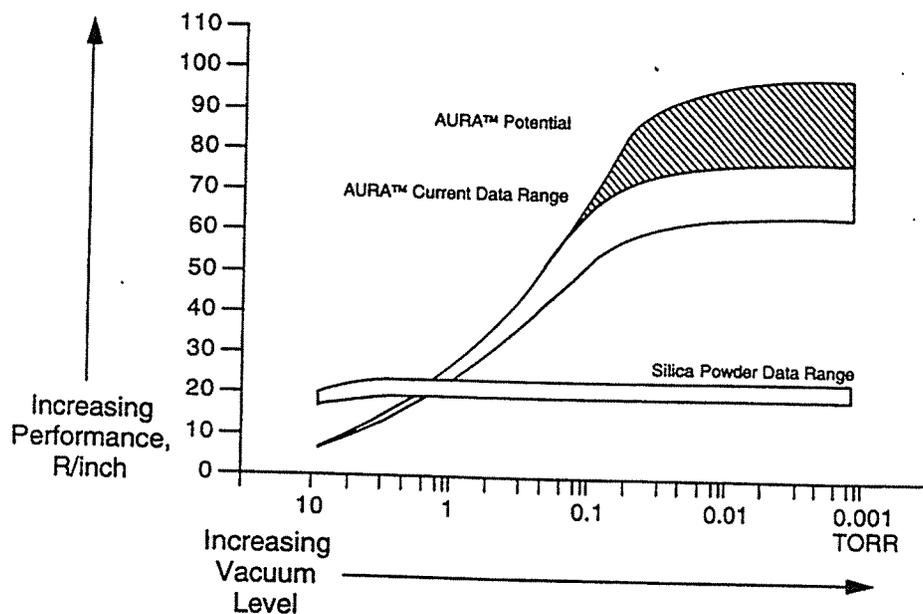


Figure 3

Thermal Performance Comparisons

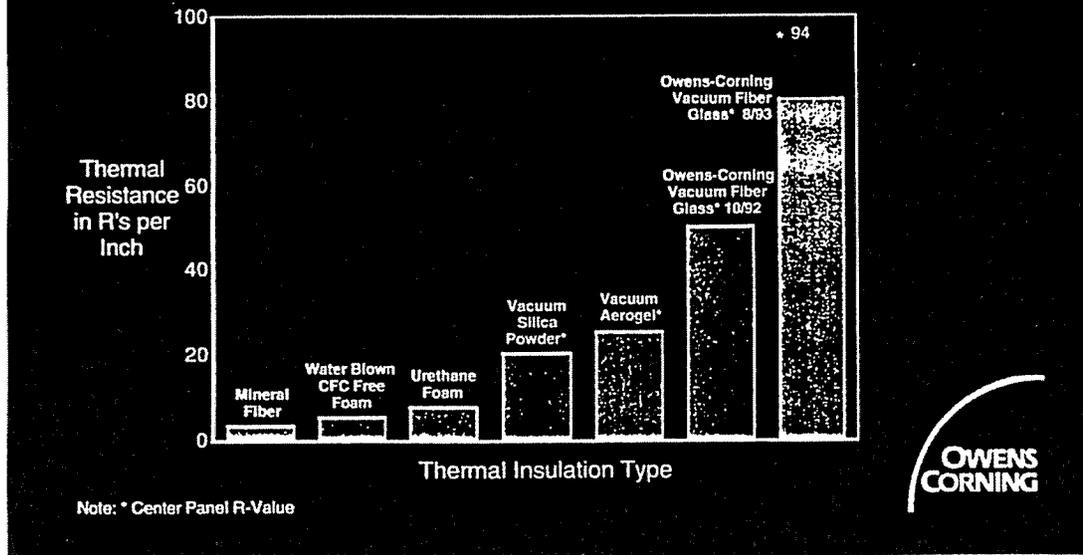


Figure 4

In comparison with other known insulation products, (see figure 4) there is no doubt that the overall thermal insulation potential of the AURA panel stands out significantly from its competition in standard tests, (center of panel measurement).

It is worth noting that for most practical arrangements of insulation, these "center of panel" values must be transformed into "installed" or delivered insulation performance. Owens-Corning has made significant progress in devising "insulation system" designs that effectively optimize AURA insulation for use in energy efficient product designs.

R-Value vs. Mean Temperature

AURA™ vs. Current OC Products

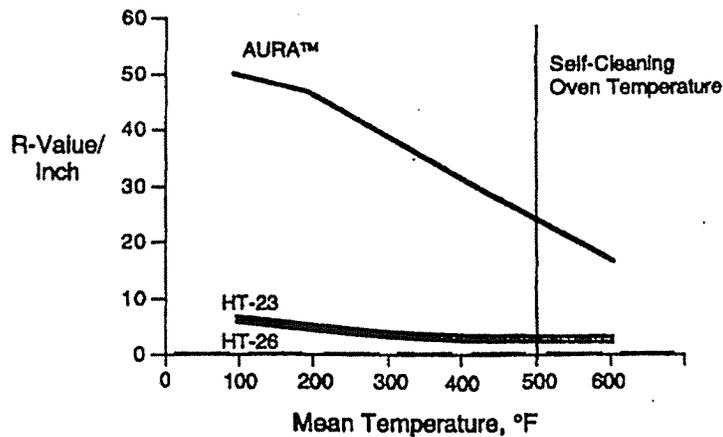


Figure 5

The uniqueness of the AURA insulation panel becomes still more pronounced when consideration is given to its "high temperature" capabilities, (see figure 5). This temperature range is very important for oven and range applications, and the data shown was taken from actual installed product tests.

TARGETED APPLICATIONS

Primary focus for continued AURA insulation development will be to secure its application in refrigerators. The ongoing attention being given towards improving the "energy efficiency" of such systems would appear to provide an excellent opportunity to introduce AURA insulation.

Beyond refrigerators several other applications are being evaluated to exploit AURA full performance capabilities. These include ovens/ranges (high temperature), and refrigerated transport (thermal and durability).

BENEFITS TO THE USER

Two applications can be considered to generally describe the benefits assignable to AURA insulation, these are residential refrigerators, and ovens/ranges.

Residential Refrigerators

In terms of AURA insulation use in Residential Refrigerators, Owens-Corning research findings and independent testing has successfully demonstrated that the

installation of AURA insulation can substantially improve the overall energy efficiency of the unit in which it is installed. The resultant benefit will obviously depend upon the amount, and the location of AURA insulation incorporated into a particular unit.

Tests are ongoing with various US refrigerator manufacturers, but these programs have already revealed that AURA insulation, properly installed in just the door assemblies alone, can lead to reductions of between 10 to 15% overall unit energy consumption.

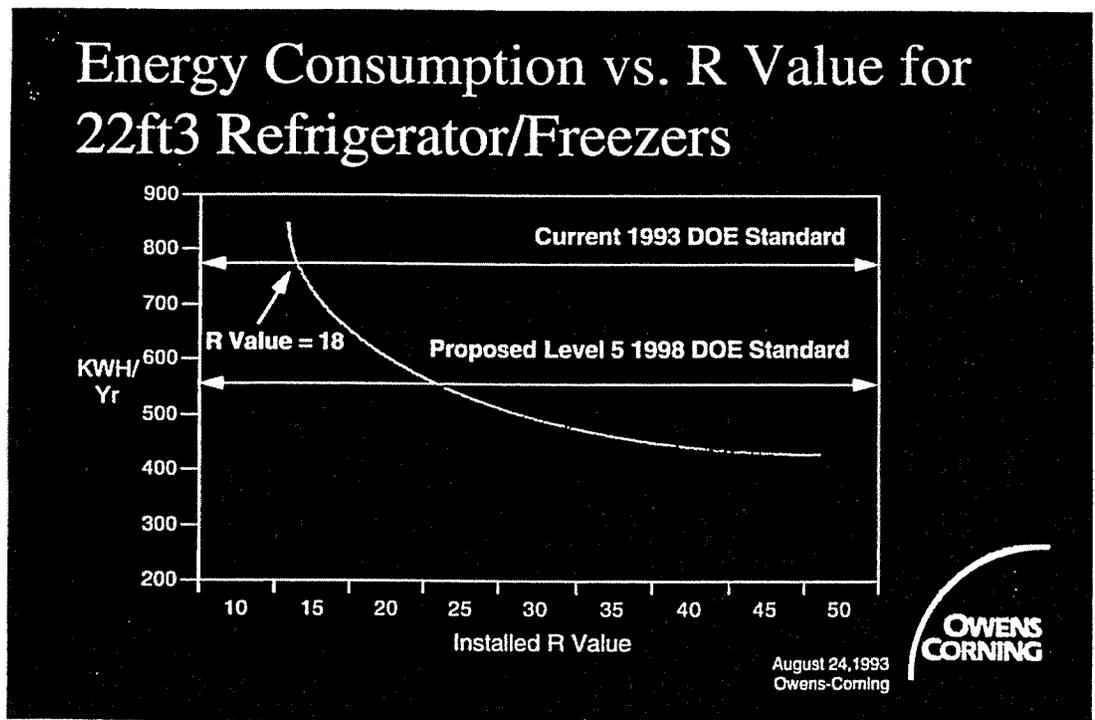


Figure 6

Based on results to date from several levels of testing Owens-Corning's research team now believes that for refrigerators fully converted to AURA insulation, (cabinets & doors), energy consumption could be reduced by realistically 40% beyond the present US 1993 Standards.

In terms of total US refrigerator energy consumption realization of that reduction could amount to approximately 2,400 MW of power saving per year.

Ovens/Ranges

Many of the advantages stated above, apply equally well to this HOT application, but beyond energy savings, AURA insulation has the potential to dramatically improve the user safety of these devices by providing cooler outside surface temperatures. Regulatory bodies are becoming increasingly strict in this matter with future codes proposing oven door surface temperatures be held to 49 degrees Celsius, during appliance use, a tall task for a self cleaning oven.

Benefit Summary:

- # Substantial Energy Savings.
- # Thinner Walls can equate to more useful internal volume.
- # Elimination of CFC's, HCFC's, and HFC's.
- # Reliability & Longevity of Stainless Steel.
- # Totally Recyclable
- # Application for both HOT & COLD use.
- # Improved SAFETY for OVENS & RANGES

TECHNICAL ISSUES ASSOCIATED WITH AURA INSULATION

Some of the outstanding technical issues with AURA insulation are associated with the selection of appropriate methods to facilitate effective incorporation of AURA insulation into the targeted applications. Essentially this entails the development of installation methods which maximize the Insulation potential as measured by "center of panel" tests.

Owens-Corning's AURA insulation development efforts have acknowledged this situation and ongoing panel developments are closely engaged with the efforts of several prospective customers. The ultimate aim of this work will be the creation of a catalogue of methods revealing the usage options available and the provision of instructions on how to optimize installation in terms of thermal efficiency and cost effectiveness.

The technical issues from a refrigerator manufacturer's perspective are complicated to a some extent by the fact that the Urethane Foam used in most refrigerator assemblies serves not only as an insulation but also as a STRUCTURAL ELEMENT. The urethane foam in fact links together the thin gauge steel outer shell and lightweight thermoplastic inner liner to provide the required structural integrity.

Any replacement insulation system must therefore find a way to either retain the urethane foam, at least for structure, or come packaged with an

alternate means to provide structural integrity. AURA insulation development is currently proceeding along a route that should provide a range of installation options, some options could utilize foam in combination with AURA insulation while others will feature assemblies devoid of foam.

ECONOMICS OF AURA INSULATION

In the context of the targeted applications, AURA insulation should not be thought of as a simple substitution for existing foam insulation materials and systems. One should instead think in terms of what overall benefit can be assigned to AURA insulation that cannot be realized with other Insulations.

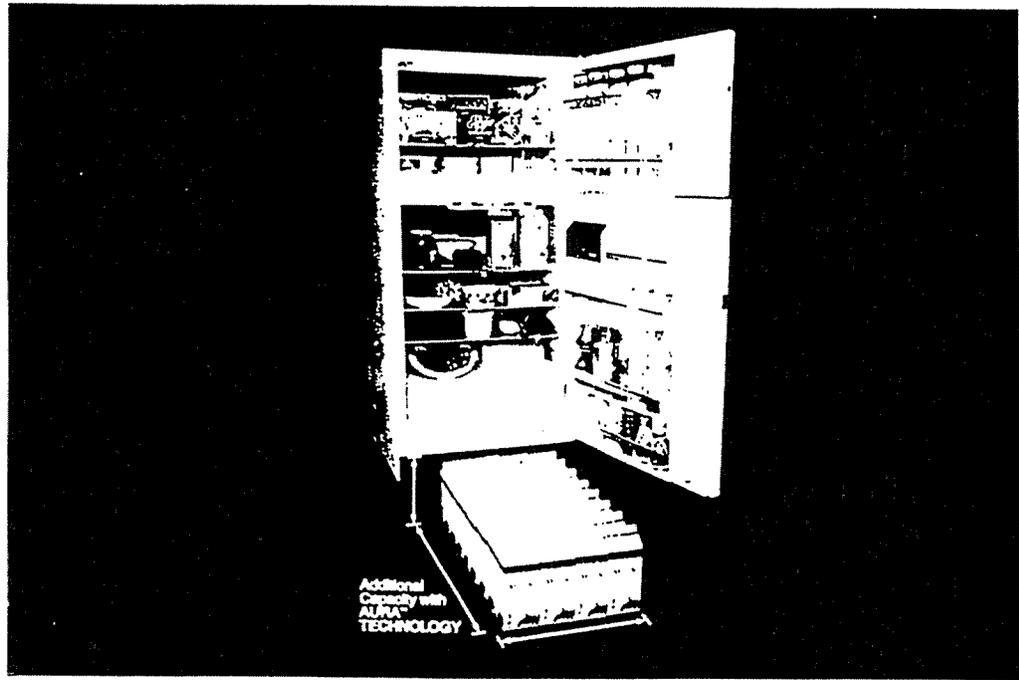


Figure 7

For domestic refrigerators, it has been determined that AURA insulation's performance is powerful enough to allow it to be exploited not only in terms of "energy efficiency" but also to provide additional usable storage volume in the same unit footprint. This volume shift can be achieved by substantial reduction of wall section, for example the featured illustration, (see figure 7) highlights a volume increase from 18 cu.ft. to 22 cu.ft.

TECHNOLOGY OUTLOOK FOR AURA INSULATION

Current Status

Manufacturing capability will be in place for the commercial production of AURA insulation panels by mid year 1994.

Several development projects involving prospective customers are well advanced, with actual product testing underway.

Owens-Corning has also chosen to work with certain leading edge development projects, including refrigeration storage systems for NASA's space programs.

Overall, the outlook for the AURA technology is very encouraging with practical usage in several application areas anticipated for 1994.

Longer Term Outlook

Beyond the immediate development activities, the future looks very exciting for AURA technology, with continuous improvements expected in all related areas from basic panel performance through to panel fabrication and related manufacturing methods.

MARKET OPPORTUNITY

Domestic refrigerator sales stand at approximately 8MM units in the US with similar levels in Europe, associated insulation requirements on a global basis currently exceed 1 BILLION square feet and will continue to grow as the world-wide standard of living improves.

The opportunity for AURA insulation should be substantial, because AURA insulation offers the most cost effective INSULATION solution to an industry faced with EVER INCREASING ENERGY STANDARDS, and the demand for ENVIRONMENTALLY CORRECT refrigerator systems.

A recurring theme encountered with the enquiries made to Owens-Corning concerning AURA insulation is the interest from people involved with alternative or innovative cooling technologies. These parties engaged with such items as thermoelectric cooling modules or photovoltaic power generation systems, appear to see AURA insulation as a potential key to enlarge their presence in world markets.

One quote from a NASA scientist even went as far as to compare the emergence of AURA technology in the insulation field to the shift from vacuum tubes to transistors in the electronics industry.

Absorption Technology

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ZAE Bayern e.V.

Abteilung: Energieumwandlung, -speicherung
D-85748 Garching/München

(1) Technology Description

Principle and state of art for basic cycles is widely known. For advanced cycles see:

G. Alefeld
R. Radermacher
Heat Conversion Systems
CRC Press - Boca Raton, Ann Arbor, London, Tokyo
ISBN 0-8493-8928-3

(2) Applications

Chiller, air-conditioners, ice-maker etc., heatpump applications; use in systems with waste heat, use in systems for combined heat-power and/or refrigeration

(3) Benefits

For energy efficiency and for CO₂ emission reduction consult figures 1-8.
Absorption technology is as efficient as compression technology.

(4) Technical Issues

- (a) Efficiency can strongly be increased by advanced cycles like triple-effect cycles, combined power and refrigeration or combined heat and refrigeration cycles.
- (b) Chillers must be usable as heatpumps in winter.
- (c) Chillers must be developed for district cooling applications.
- (d) Corrosion inhibitors, which permit application of temperatures beyond 180°C, are needed.

(5) Economics

First cost are usually higher than for compressions technology. Not necessarily so for systems producing combined heat and refrigeration. Total cost can be lower for absorption systems, depending on the price for heat versus electricity. The tariff structure quite often favours absorption systems. Cheap labor available now in Eastern Europe will bring down first cost.

(6) Market and Technology Outlook

In Japan absorption technology holds 85% of the air-conditioning market for units larger than 100 kW. A 50 Mio US \$ programme has been launched to develop cost effective units with about 10 kW. In Korea, India and China the production of equipment and market penetration are expanding very fast. In USA a comeback of absorbers is anticipated. In Europe the absorption market is small but growing rather fast.

Primary energy PE for one unit power and H units heat

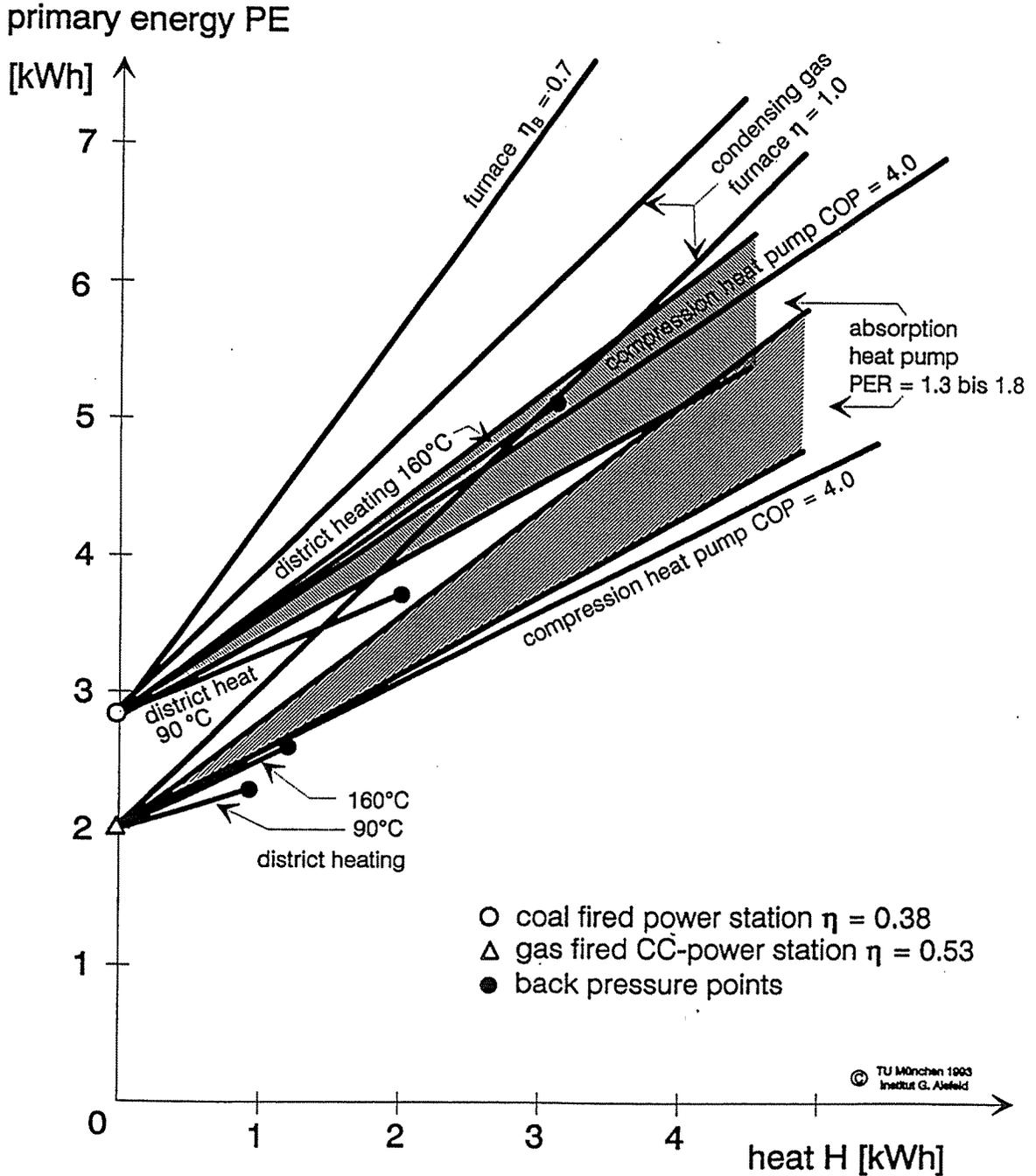


Figure 1: Primary energy need for the production of one kWh power and H kWh heat

SDLW072E

ALEFELD, München

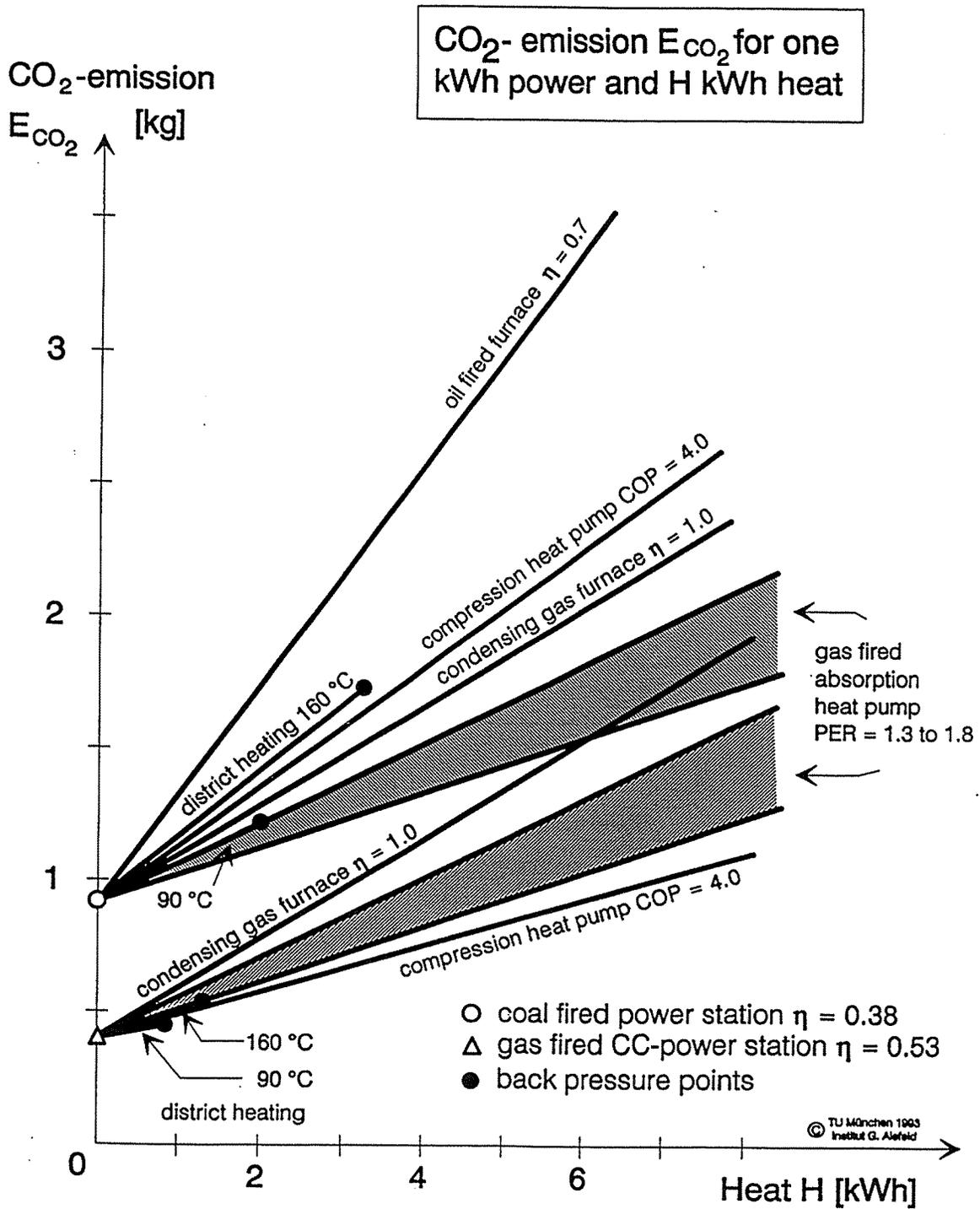


Figure 2: CO₂-emission for the production of one kWh power and H kWh heat

ALEFELD, München

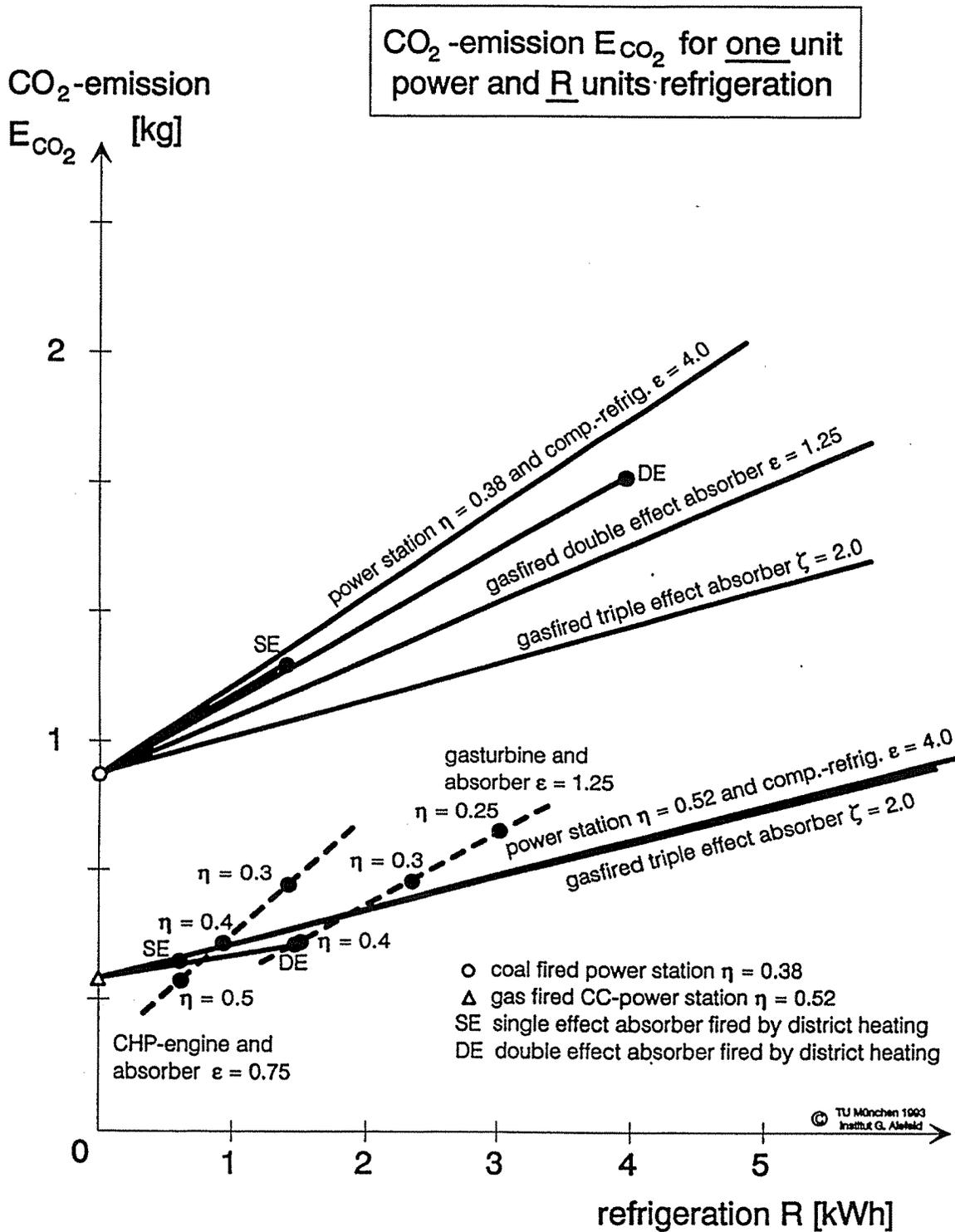


Figure 4: CO₂-emission for the production of one kWh power and R kWh of refrigeration

SOLC103E

ALEFELD, München

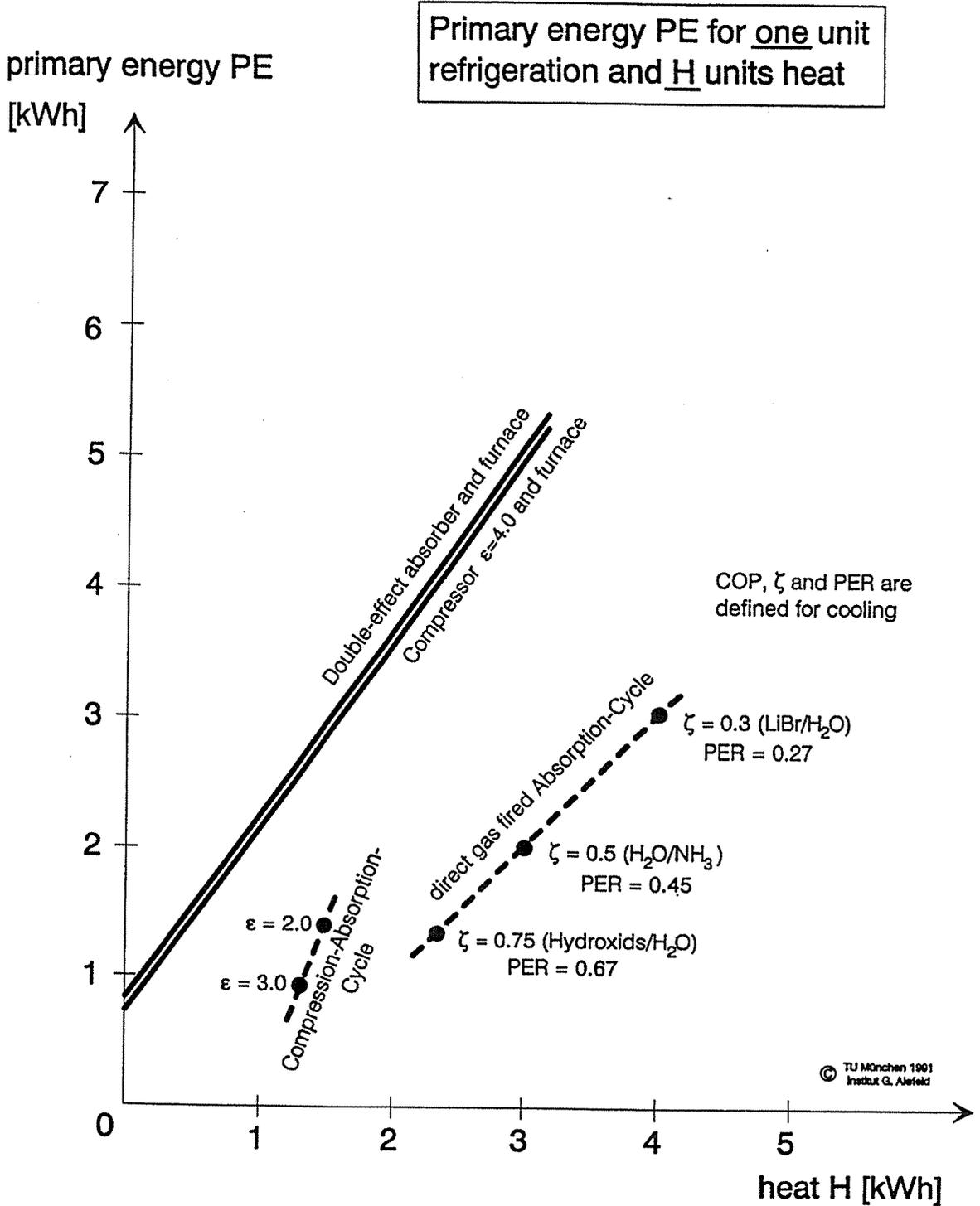


Figure 5: Primary energy need for the production of one kWh refrigeration and H kWh heat

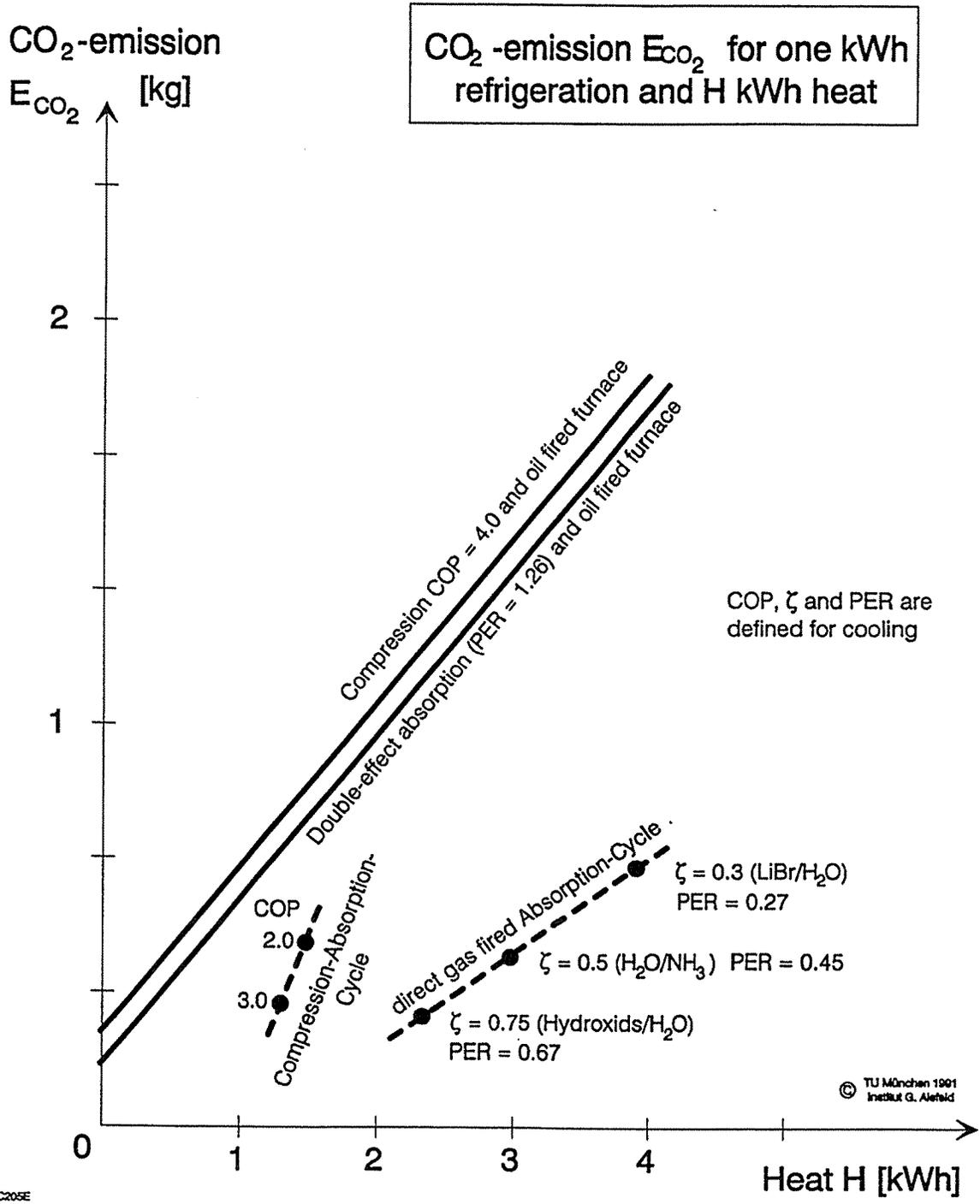


Figure 6: CO₂-emission for the production of one kWh refrigeration and H kWh heat

ALEFELD, München

Primary energy demand in kWh for 1 kWh heating

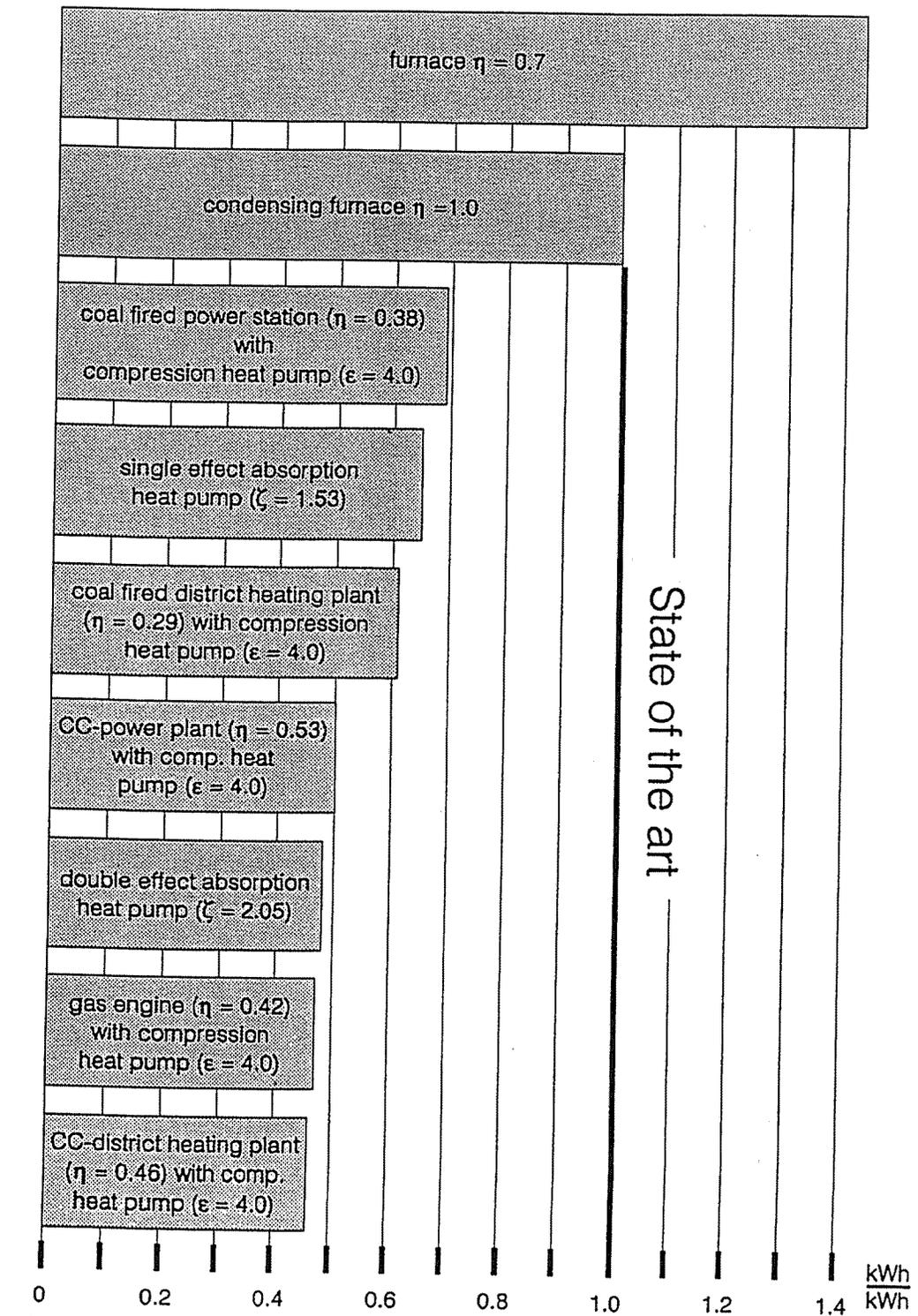


Figure 7: Primary energy demand in kWh for 1 kWh heating

ALEFELD, München

Primary energy demand in kWh for 1 kWh air-conditioning

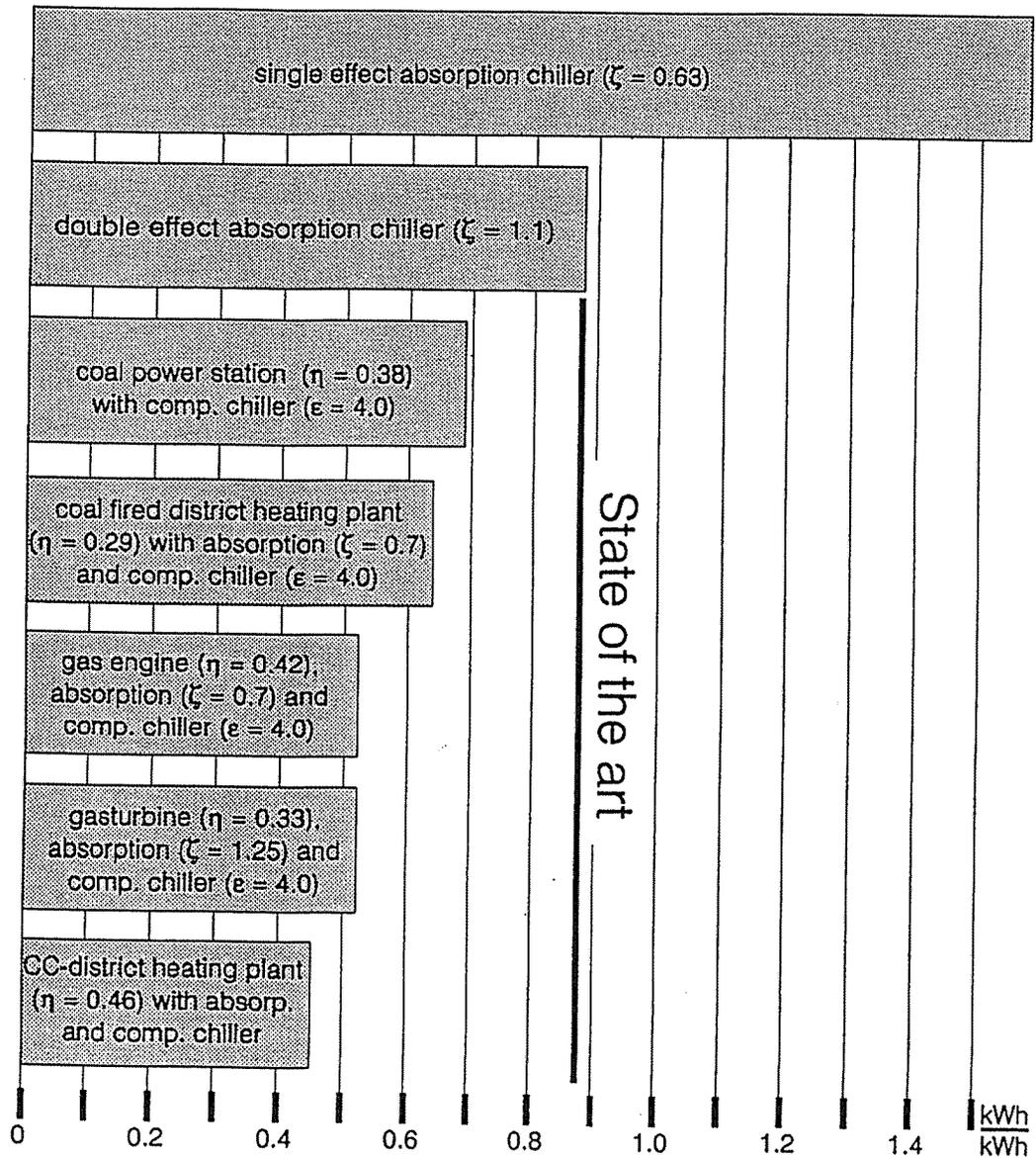


Figure 8: Primary energy demand in kWh for 1 kWh air-conditioning

ALEFELD, München

Gas cooling—a worldwide overview

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Paper presented at the 58th Autumn Meeting, 24th November 1992

John Chapman graduated in physics from Hull University in 1972. He worked on aero-engine acoustics at Rolls-Royce before joining British Gas Midlands Research Station in 1978 as a noise consultant.

Subsequently he moved into the field of gas-fired building energy services where he was particularly involved in the field trials of gas engine driven heat pumps. More recently he has worked on the utilisation of gas in the low temperature process industries such as liquid heating and drying. He is currently responsible for the R&D programme on building energy services for the industrial and commercial market.



Paul Welsby graduated in chemical engineering at Salford University in 1981 and subsequently gained a PhD from the same department for research work on heat pump systems. He joined the British Gas Midlands Research Station in 1984 to work on gas engine driven heat pumps.

In 1992 Paul Welsby moved to the British Gas National Market Development Team, where he became the Air Conditioning Development manager. In this role, he is responsible for all aspects of developing the market for gas air conditioning.



Dave Whitman joined British Gas Midlands Research Station in 1978 after graduating in Physics from Aston University. He worked initially on fundamental studies of combustion noise, before moving on to the mathematical modelling of combustion systems.

Subsequently he entered the field of gas-fired building energy services, where he was particularly involved in radiant space heating systems for industrial premises and the development of absorption technology for cooling commercial buildings.

Following a short period recently when he worked on best practice design procedures for industrial furnaces, he now leads a team in Thermal Engineering Division which is concerned with gas-fired conditioning systems.



1. Summary

Gas has only a small proportion of the air conditioning market worldwide. Cooling equipment is usually electrically powered, although environmentally superior gas alternatives are commercially available or under development.

Economic factors in Japan have given gas over 25% of the air conditioning load. In Great Britain, Europe and the USA the market share is considerably lower, although the growth of demand for air conditioning and environmental pressures present market opportunities for gas. This paper reviews the world air conditioning market, current technologies, the environmental advantages of gas cooling, and the gas developments and research in progress.

2. Introduction

Human comfort is a desirable and hence marketable commodity. Heating, to provide comfort, has been a widespread practice from primitive times to the present day. The technology of cooling, however, is essentially a 20th century capability. The purpose of air conditioning is to control the temperature, humidity, purity and movement of air in order to maintain a comfortable internal atmospheric environment within a building, irrespective of the outside conditions.

Before the invention of mechanical refrigeration plant, the only methods available for cooling involved the use of evaporation or ice. A vast international trade in naturally produced ice existed for several centuries, ending around 1930.¹ The first patent for mechanical refrigeration, which formed the basis for most current cooling equipment, was filed by Perkins in 1834. This type of refrigeration equipment was used commercially to produce artificial ice from about 1890.² A different design of ice maker, the predecessor of the modern gas-fired absorption chiller, was patented by Nicolle in 1861.³

Modern air conditioning is based largely on the work of Carrier in the early 1900s. The first office air conditioner was installed in 1912, and the first home air conditioner in 1914. Air conditioning is used extensively now and can be found in industrial, commercial and residential buildings worldwide.

The cost of modern cooling technology is high, and currently its use is mainly restricted to the developed economies, particularly North America, Europe and Japan. Even in these developed economies, the requirement for greater comfort levels continues to grow. Demand for this technology could be more than three times its present magnitude if the viable

market could be extended to encompass all the hot countries of the world.

This paper describes some aspects of the worldwide air conditioning market. The environmental problems associated with air conditioning are discussed and the particular advantages of gas powered equipment are explained. Finally, international research on gas powered cooling systems is reviewed, and this includes work being undertaken by British Gas.

3. The worldwide air conditioning market

The international market in air conditioning systems is expanding rapidly, under the influence of a number of factors. In all the major markets for air conditioning, changes are occurring in building design, including for example, increasing levels of thermal and acoustic insulation. This is accompanied by higher levels of heat gains within buildings caused by growing densities of both people and electronic equipment. At the same time increases in people's expectations, especially in the work place, heighten the demand for comfort. Modern work practices, requiring mental concentration from the workforce, make these demands a question of practical importance to employers.

Types of air conditioning plant

Air conditioning systems are conventionally split into two major categories.

The most commonly found systems are packaged units, which include two types of small air conditioner. Firstly there are room units, which are small self contained units serving individual rooms or small groups of rooms. Secondly, there are split systems which are distinct in that one part of the system is located outside the building and the other part inside, with the refrigerant being pumped some distance between the two parts. Most of the equipment that falls into the packaged air conditioning category tends to be reverse cycle heat pumps, which are single units providing both chilling and heating duties.

Central station systems are larger, generally being located in a plant room, and use refrigeration machines to cool water or air for distribution to a building through a pipe or ductwork system.

The demand for air conditioning

The small packaged air conditioner market is the sector where the most recent market data exists. According to research carried out by the Japan Refrigeration and Air Conditioning Industry Association⁴ the total number of packaged air conditioners sold throughout the world amounted to some 21.8 million units. The two biggest markets for this small, often residential equipment, are the USA and Japan with 43% and 26% respectively of total world sales. In fact, in Japan 70% of all houses have air conditioning.

The lack of any substantial residential demand in Europe means that the European market for packaged units is only 3% of the world total. The climate of much of Southern Europe is such that there is real discomfort during the summer months if no cooling is available. Nevertheless, sales of air conditioning equipment are in part linked to ability to pay for it and so air conditioning is generally restricted to the commercial sector. The sales of packaged air conditioners in the UK run at a tenth of the European total, some 73,000 units,⁵ which are mainly in small commercial applications. Some authorities are, however, predicting growth in home air conditioning in both Europe and the UK.⁶

Up to date information on the world demand for central station chillers is not as readily available in such a cohesive form. Nevertheless, information from a variety of sources can give some indication of the scope of the demand for these larger systems. In Japan, the demand for central air conditioning is estimated at some 25,000 units during 1991. Sales in the USA are thought to be of a similar order. Information from the Building Services Research and Information Association (BSRIA) indicates that the European market is also at a similar level, with sales of some 22,000 units. Within Europe, the biggest demand for central systems comes from Italy followed by Spain and UK.⁵

The Impact of Gas Air Conditioning

The key fact that this information conceals, is that in most cases it refers to electric air conditioning. What of the inroads made into this market by gas technology?

The country where gas air conditioning has had most success is Japan. In 1977, the Japanese government, the gas utilities and several manufacturers collaborated to develop high efficiency industrial and commercial gas-fired chillers. The main drivers behind this move were the need to reduce dependency on oil, the need to minimise summer electricity usage and the requirement to even out seasonal gas usage. This latter point is important because for two months, very hot humid conditions prevail, making air conditioning essential in commercial buildings. This situation leads to a marked trough in the use of gas during the summer months, and a large peak in electricity usage, giving rise to higher prices for electricity in summer.

In 1980, the Japanese government set the target of capturing around 30% of the central air conditioning market with gas by 1991. In 1991, this share actually stood at some 27% or 2.64 million kW of cooling. R&D on gas cooling technology in Japan is strongly influenced by a number of government and other agencies including the Ministry of International Trade and Industry (MITI), the New Energy and Industrial Development Organisation (NEDO), and the Heat Pump Technology Centre of Japan.

The gain of such a large market share has been assisted by both the government, through tax incentives and accelerated depreciation, and by the gas utilities, providing manufacturers with development subsidies and customers with favourable gas tariffs.

The story in the USA is similar, if a little behind Japan. In the early 1970s relatively inefficient gas air conditioners were selling well because of low gas prices. Towards the end of the 70s, with increasing gas costs customers turned to the more efficient and lower cost electric alternatives. However, during the 1980s, the US government began to promote more widely the use of gas and the utilities began to attempt to re-establish the market with the new generation of high efficiency gas-fired air conditioners.

A number of gas utilities now offer incentives to encourage the use of gas for air conditioning. These include special rates, low interest loans, capital rebates and the provision of specialised service. In fact, in the USA, some electric utilities are also providing incentives for the installation of gas cooling equipment to assist them with their demand management.

The American Gas Association (AGA), in their 1990 Commercial Gas Cooling survey, estimates that the total commercial gas-fired cooling installations amounted to some 2.1 million kW. This equated to an 86% increase over 1989 installations. In terms of overall market, this means that gas provides 5% of all the cooling requirements in commercial buildings.

The market for gas air conditioning in Europe is very much in its infancy. Several European gas companies, and indeed many around the world, view gas air conditioning as a potential element of national or regional energy policy. By supplying an energy demand in a growing sector, the need for additional electric power generation capacity can be offset. In some situations, financial assistance from governments or energy utilities towards the purchase of gas-fired equipment, is more economic than building a new power station.

A number of European gas utilities are attempting to develop the market for gas air conditioning, in particular those in Italy, Spain, France and the United Kingdom.

In the UK, the present market share for gas stands at less than 1%. British Gas has recently initiated a strong marketing drive to increase the penetration of gas further into this traditional electric stronghold. One element of the marketing plan is the evaluation and development of new, more efficient and more effective gas technologies for air conditioning. An awareness of research and development across the globe is fundamental to this work programme.

The following sections outline the current status of worldwide developments in four key technologies, and detail British Gas work in each of these areas.

4. Vapour compression chillers

The vast majority of air conditioning equipment currently installed uses electrically powered refrigeration plant that works on the same principle as the domestic 'fridge'—the vapour compression cycle. This is a closed cycle containing refrigerant fluid, comprising of two heat exchangers, a compressor and an expansion device. The cycle is illustrated in Figure 1.

Heat from the building is taken in by an evaporator which contains liquid refrigerant. The heat causes the liquid refrigerant to vaporise, giving a low pressure gas. This refrigerant vapour is pumped via a compressor, which raises the pressure, to the condenser. At this point in the cycle, the high pressure gas condenses back into a liquid and in the process heat is rejected outside the building. The liquid is still at high pressure, and passes through an expansion valve which reduces the pressure and temperature. The resulting low pressure liquid refrigerant finally flows back to the evaporator, where the reduced pressure assists the evaporation process and completes the cycle. The major energy input to the system is to the electric motor which drives the compressor.

Refrigeration unit efficiency is generally expressed as a Coefficient of Performance (COP), defined as:

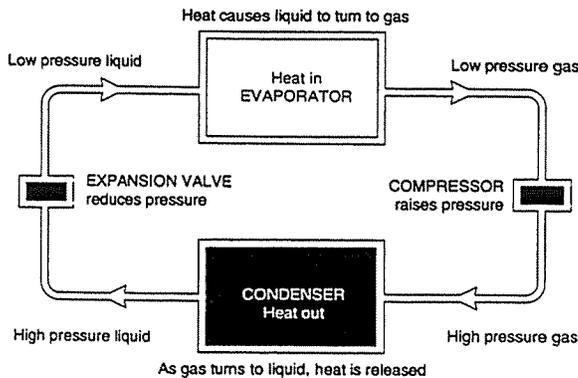


Figure 1. The principle of the vapour compression cycle.

$$\text{COP} = \frac{\text{Heat transferred (cooling obtained) kW}}{\text{Work required (e.g. shaft power) kW}}$$

and because of the thermodynamic nature of the system. COPs are not constrained to be less than one. In fact, manufacturers' specifications for electric chillers are generally in the range 3–5. Monitored data for several large electric chillers in the field, however, indicate actual COPs between 2.5 and 3.3⁷. Smaller electric chillers have been found to be slightly less efficient.

The heat pump is another important type of equipment based on the vapour compression cycle. A simple heat pump system makes use of the heating from the condenser, rather than the cooling from the evaporator. For air conditioning, however, a reverse cycle heat pump may be used, in which the evaporator and condenser functions are interchangeable. Thus a reverse cycle heat pump can be used to either cool or heat a building.

Any vapour compression cycle needs the input of shaft power to drive the compressor. This does not necessarily have to be from an electric motor; an engine is capable of providing the required input. Gas fuelled engines in heat pump systems have significant advantages. Not only is heating or cooling available as with any heat pump, but in heating mode additional heat is available from the engine cooling system. Thus, gas engine chiller heaters (GECHs) represent a very efficient way of using energy.

In Japan small gas engine heat pumps have moved from the R&D stage to the market place. A group of 21 manufacturing companies and three gas companies, with funding from MITI, developed a range of units with duties of five to 17kW. Fourteen models of this type are now on the market in Japan, supplied by Yamaha, Aisin Seiki, Yanmar and Sanyo. In 1990 over 20,000 were sold. A typical example is shown in Figure 2.

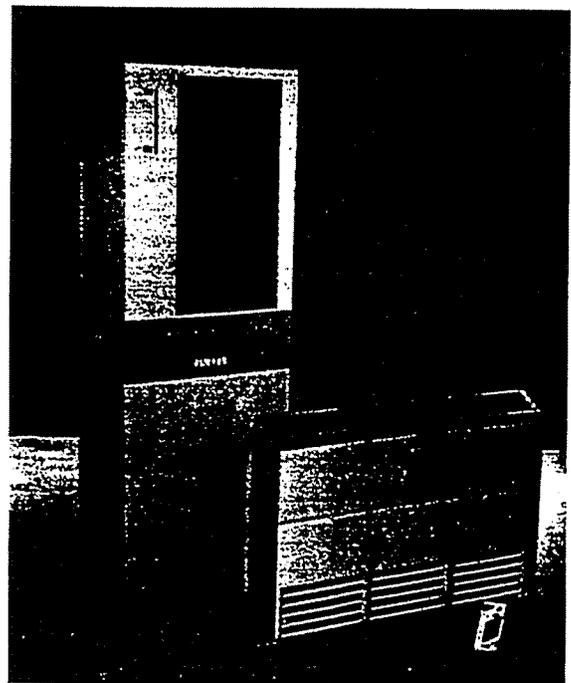


Figure 2. 5kW Yamaha gas heat pump unit.

Environmental aspects

Atmospheric emissions are becoming a major issue, and governments are legislating as part of a general anti-pollutant stance. In any comparison of cooling provided by different fuel sources, it is not only emissions at the point of use which must be taken into account; analysis of electric powered air conditioning must also include those emissions occurring during the generation process.

Possibly the most serious environmental problem is global warming, or the greenhouse effect. One major 'greenhouse gas' which contributes to this is carbon dioxide which is produced whenever a fossil fuel is burnt. For each unit of cooling, gas engine driven air conditioning produces less than half the amount of carbon dioxide that electric equipment would produce (see Table 1).

Table 1: Reductions in emissions by the use of gas chilling.

| | Reductions of emissions | | | |
|-----------------------------|---|-----------------|-----------------|--------------|
| | CO ₂ | SO _x | NO _x | Particulates |
| <i>Absorption chillers:</i> | | | | |
| AGA calculation | 57% | 100% | 68% | 97% |
| BG R&T calculation: | 57% | 100% | 50% | |
| <i>Gas engine chillers:</i> | | | | |
| BG R&T calculation: | 65% | 100% | 98% | |
| Assumptions: | | | | |
| AGA | — electricity is from an oil fired power station | | | |
| BG R&T | — electricity is from a coal fired power station | | | |
| | — gas engine is fitted with a catalytic converter | | | |

Lower emissions of oxides of nitrogen (NO_x) and virtually no oxides of sulphur (SO_x) are produced by modern gas engine powered systems (Table 1). As these pollutants are responsible for acid rain problems, lower emissions are a major advantage for gas.

Another serious problem is the depletion of the earth's ozone layer. The use of a range of chemicals called chlorofluorocarbons (CFCs) is now considered proven as the major cause of this depletion. The chlorine atoms in these compounds attack the ozone layer when CFCs are released into the atmosphere and breakdown. In addition, CFCs are also strong greenhouse gases. Until recently these refrigerants, such as R12, have been used extensively in nearly all vapour compression chilling equipment. The refrigerants escape into the atmosphere when equipment is serviced or scrapped.

There is a worldwide move toward the phasing out of these chemicals, with an almost unprecedented level of agreement amongst governments which led to the United Nations Environmental Programme Montreal Protocol of 1987. Signatories to this Protocol have now agreed to cease production of CFCs in 1995. Some alternative refrigerants are available for vapour compression systems, but there are still major problems. Less damaging are the hydrochlorofluorocarbons (HCFCs), such as R22, with an ozone depletion potential of around 5% that of CFCs. Nevertheless their use is likely to be restricted or banned in the future.

Refrigerants with zero ozone depletion potential, the hydrofluorocarbons (HFCs), have been developed by companies such as ICI and Du Pont, but are as yet unproven and are expensive. The most promising of these, R134a, is still undergoing toxicity testing.

International research

Gas engine systems have been the focus of significant world-

wide research over the last three decades. Development effort now is largely concentrated on reducing cost, minimising unwanted exhaust emissions and extending maintenance intervals.

Japan

In 1984 the Japanese government—through MITI—initiated a huge R&D programme, on large scale gas engine heat pumps. One aim of this was to produce a pilot demonstration of a 1MW heat pump for an integrated urban district heating system by 1992.

Japan also has an extensive R&D programme on other gas engine heat pumps such as those based on the Stirling cycle and its derivatives. Stirling engines are external combustion engines, the movement of the engine pistons being effected through the application of heat from an external source such as a gas burner. Because combustion is continuous, much more complete combustion is possible, giving lower emissions and the possibility of high efficiency. Tokyo Gas, Toho Gas and Osaka Gas⁸ have been involved with Mitsubishi and Aisin Seiki in developing a heat pump driven by a Stirling engine instead of a conventional internal combustion engine.

A further development carried out by the same three gas companies and Sanyo, is the use of the Stirling derived Vuilleumier cycle. This cycle has been employed to build a direct drive heat pump. The working fluid is moved around a set of compartments which form part of the engine itself, and as the engine repeats the thermal compression and expansion cycle, heat is continuously absorbed and rejected. The system can thus produce hot and cold water simultaneously. The working fluid is helium, and so in addition to the environmental benefits of external combustion, there is the advantage of CFC free cooling.

The USA

In the USA there are large scale gas cooling programmes being carried out by the Gas Research Institute (GRI), the American Gas Association (AGA) and the American Gas Cooling Centre (AGCC). The AGCC works with both AGA and GRI and over 30 individual gas companies have joined the Centre. Additionally, some gas utility companies, such as Brooklyn Union Gas, have their own development programmes.

The gas engine heat pump is a major element of these programmes. GRI and AGCC have been involved with York International in developing a 10kW (cooling) gas engine heat pump which has now been successfully field tested in 10 locations.⁹ The unit is about to enter a 50 unit field demonstration programme. GRI and AGCC are also involved in the development of a 17.5kW unit with Aisin Seiki. This should also go into a demonstration phase towards the end of 1992.

On a more commercial basis, AGCC is working with Trane to introduce a larger, 200–280kW range of gas engine chillers to the US market, and with Tecogen to assist in the marketing of a 500kW chiller. GRI are working with another refrigeration manufacturer, Thermoking, to establish a 52.5kW chiller in the market place. This unit is shown in Figure 3.

There is also some work on Stirling engine systems in the USA, with companies such as Mechanical Technology Incorporated and Stirling Power Systems Corporation working with GRI. Most of the work is concerned with developing the engines. The US Department of Energy (DoE) has taken an interest in some of this work, but is now thought to view it as a long term development.

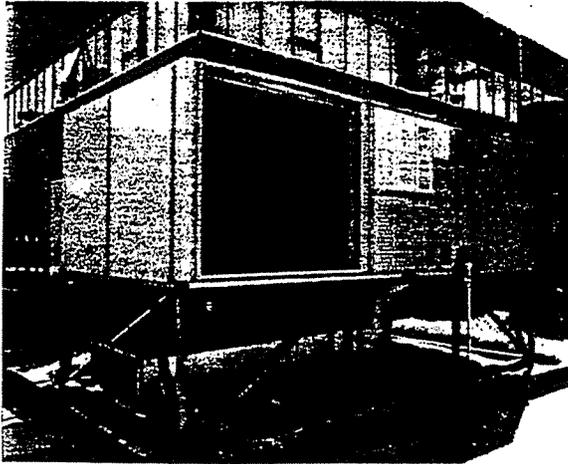


Figure 3. The Thermo King 53kW chiller under test.

Europe

In the early 1980s, British Gas carried out a large scale programme of installing and monitoring gas engine heat pumps in a number of sites. Much practical information was gathered concerning reliability and it became clear that robust and efficient equipment could be constructed, but capital cost was a major issue. This programme has subsequently evolved with the aim of developing a range of packaged gas engine chiller heater units, the first model being available for field trials in 1992.

The initial work has concentrated on two different 70kW packages for roof top and plant room application. The British Gas work in this area is strongly oriented towards commercial exploitation and links were established with potential manufacturers of the units at a very early stage. Two specialist refrigeration companies were used to assemble the two prototypes, and as the field trial programme commences, commercialisation of the units is viewed as a crucial issue by British Gas. Discussions are now continuing with a number of potential manufacturers to evaluate options and arrive at the most effective method of commercial exploitation.

British Gas also obtained five of the small gas engine heat pumps from Japan for testing and evaluation in the UK. Results indicate that these units have an average heating effectiveness (ratio of heat transferred to gas input) of just over 1.0 and a cooling effectiveness of about 0.7. Although this is not as efficient as larger gas engine systems, these units can be comparable with electric equipment on running costs, due to the high cost of electricity.

British Gas is also investigating Stirling engine systems. This work has included the design and construction of a small Stirling engine, in conjunction with Cambridge University. The main application is seen as a small domestic CHP unit providing 3kW of electricity. A commercially available unit from TEM in Sweden is also under consideration. Additionally, an economic feasibility study has highlighted an alternative Stirling concept, already used in limited application for cooling, for further study.

In Spain, large gas engine chillers, above 150kW, are being imported from Tecogen in the USA and trials of the small units from Japan are underway. Development work on small gas engine chillers has been carried out by Gas Natural (formerly Catalana de Gas) and Johnson, one of Spain's largest air conditioning companies. This work originally concentrated on a 15kW unit driven by a two stroke engine, but it is understood there were problems with oil emissions from

this unit. Subsequently, a more successful collaboration has led to a unit providing 20kW cooling and 25kW heating, using a conventional SEAT engine.

Gas Natural are also working with an Italian company Climaveneta to produce 100kW and 170kW systems which are now available in both chiller or reverse cycle heat pump versions. The first commercial installation of one of these units is at Barcelona's main railway station, for air conditioning in its restaurant. Italgas has also been involved in the development of the Climaveneta units. Another Italian air conditioning company, Marelli-Clima has developed a range of gas engine chillers and heat pumps offering 100–300kW of cooling, and have sold some of these units to Italgas.

5. Absorption chillers

Absorption chillers use a different process from the vapour compression cycle. The general principle is shown in Figure 4. Two fluids are used: one is a refrigerant which carries heat around the system, and the other is an absorbent. A common combination, or fluid pair, uses water as the refrigerant and lithium bromide (LiBr) as absorbent.

A pump is used to deliver LiBr solution to the generator, where heat is added causing the water to boil off from the solution. The vapour passes to the condenser where it liquefies, giving out heat, while the more concentrated solution in the generator is reduced in pressure and piped back into the absorber. Meanwhile, the water expands into the evaporator, where it vaporises and removes heat from the building. To complete the cycle, the water vapour enters the absorber and mixes with the strong solution. The major energy input to these chillers is simply heat, which is used to separate the fluid pair in the generator and drive the refrigerant around the system. This heat can come from a gas burner, hot water or steam.

The original design of this type of system used only one generator and is known as a 'single effect' system. Until recently, the only absorption chillers promoted in the UK were ammonia-water, single effect chillers. These have been developed mainly in the USA, where they have been in use since the 1930s. Development work was carried out in the late 1960s and they were popular in the USA until the energy crisis of 1973–74 caused a rise in running costs, with sales peaking at 75,000 per annum.¹⁰ They are now manufactured by Robur, and have claimed COPs around 0.6. With this current performance the units are competitive and selling in increasing numbers. Elstree Air Conditioning has been marketing these

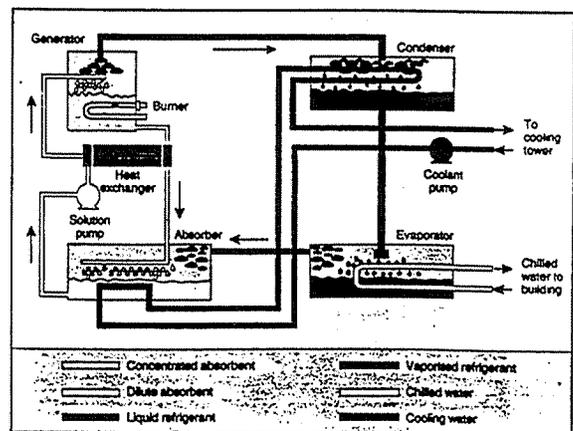


Figure 4. Basic absorption refrigeration cycle.

devices in the UK for around 20 years, and there are around 1,300 units installed in the UK at present, with installations now running at about 250 annually. Further development of these units by the manufacturer is taking place.

Some later designs of absorption chiller use a second, low temperature generator to increase efficiency, and these are known as 'double effect' chillers. Over the last two decades, these chillers have been developed extensively in Japan. Gas-fired double effect units are claimed by manufacturers to have COPs of 0.95, and monitoring of Japanese double effect units in British Gas premises has shown that in practice this can be achieved.⁷ A wide range of gas-fired double effect chillers are now available in the UK. These include products from all the leading US companies, such as York, Trane and Carrier, as well as equipment from the major Japanese companies such as Sanyo and Mitsubishi.

At Southbank University, a study has been carried out¹¹ to investigate the feasibility of using gas-fired absorption chillers in UK climatic and economic conditions. The study concluded that 'absorption chillers are in a very good position to compete with centrifugal (conventional) chillers' and also that the environmental advantages of absorption units offer 'substantial improvement' over other chilling systems.

In some instances, heat may be available in the form of steam or hot water from a Combined Heat and Power (CHP) system. CHP system use a gas fuelled engine or turbine to drive an electricity generator, and provide heat recovered from the prime mover. If CHP is combined with absorption chiller technology, a complete gas-fired building energy system can be obtained, giving electricity, heat and cooling.

A number of manufacturers supply single and double effect, hot water and steam driven chillers which are suitable for use in combined CHP/absorption chiller installations. The British Gas North Western Regional HQ at Altrincham has one of these systems providing cooling for the offices and computer installation. Other major combined systems that have recently been, or are being installed include the Wellcome Foundation and the new Westminster & Chelsea Hospital.¹²

All chillers must reject the heat they have extracted from a building. For double effect and large single effect absorption chillers, a cooling water system is used, often incorporating a wet evaporative cooling tower. This type of heat rejection, which is also common in large conventional vapour compression systems, has been associated with the problem of Legionnaires Disease. If the water system is kept clean, well maintained, and dosed with bactericides, the problem is avoided but this adds to the running costs. There is also room for human error or bad workmanship, and there is now a move away from wet cooling towers altogether. Alternatives include dry, or wetted surface air blast coolers. The gas-fired Robur single effect chiller incorporates a dry air cooled condenser, needing no further cooling, and therefore avoids problems with Legionnaires Disease altogether.

Environmental aspects

In common with gas driven vapour compression systems, absorption chillers show good environmental performance on emissions of CO₂, SO_x and NO_x, see Table 1. In addition they do not have the CFC problems, discussed earlier as they contain none of these damaging chemicals. The environmental advantages of gas-fired absorption chillers are therefore not compromised by the nature of the absorption fluids. The CFC and HCFC issue is likely to become increasingly important as pressure mounts to reduce their usage in refrigeration systems. Absorption systems represent an existing energy efficient solution to this problem.

International research

Internationally, there is a large amount of research into absorption technologies, particularly because of their inherent environmental advantages.

Japan

In Japan, absorption chillers are now commercially accepted, with sales of over 6,500 units in 1991. Research work in Japan is therefore aiming to extend the range of application in the large commercial sector. Tokyo Gas, Toho Gas and Osaka Gas are involved with Kawasaki in developing a 'hyper-efficiency' double effect chiller/heater,¹³ which uses a condensing heat exchanger to recover latent heat from the burner exhaust gases. This heat is used, in cooling mode, to preheat the absorbent before it enters the second, low temperature generator. Modifications to the absorber and evaporator, to enhance heat conductivity, are also utilised to improve cooling efficiency. In heating mode, the exhaust gas is used to vaporise refrigerant before it enters the absorber. The new design achieves cooling and heating COPs of 1.3 and 0.95 respectively.

The three gas companies, along with Hitachi, have also investigated the use of air cooling for water-lithium bromide double effect units.¹⁴ Air cooling is not as efficient as conventional water cooling, having a lower heat transfer coefficient. Temperatures within an air cooled machine are thus increased, which can lead to over concentration of the LiBr solution, especially at high load. This can cause crystallisation when the solution is subsequently reduced in temperature. To obtain a practical temperature range in an air cooled machine with standard finned tube heat exchangers requires a much larger heat transfer area, resulting in a bulky machine. To deal with these problems, the absorber and condenser were redesigned to improve the heat transfer characteristics, using novel 'super slit fin' heat exchangers. A prototype has been shown to operate with outside air temperatures up to 35°C, without any crystallisation problems.

The USA

In the USA, the Gas Research Institute, American Gas Cooling Center and the American Gas Association are all involved in absorption chiller studies. As with the gas engine chillers, there are also several gas utilities carrying out R&D programmes. GRI and AGCC are both in partnership with three major air conditioning manufacturers—Carrier, Trane and York International—in development of large absorption chillers for the commercial market. Carrier and Trane are now selling double effect units developed by the Japanese companies Ebara and Kawasaki respectively. A Trane chiller is shown in Figure 5. York have recently set up a manufacturing facility for Hitachi designed double effect chillers. York have also, with GRI sponsorship, licensed a triple effect system design from Oak Ridge National Laboratory, introducing a third generator into the absorption cycle.

There is also significant effort on smaller scale systems. GRI has supported the development, by Columbia Gas, of a double effect absorption heat pump using ammonia as the refrigerant and sodium thiocyanate (NaSCN) as the absorbent.¹⁵ A prototype achieved a COP for heating of 1.65, and for cooling, 0.82. GRI has also supported work on a dual-cycle concept thermally links two conventional single effect subsystems. One of these is a high temperature cycle, using lithium bromide with water as refrigerant, while the other, low temperature, subsystem uses water with ammonia as the refrigerant. This technique extends the operating temperature range.

The US DoE has sponsored an independent company, Phillips Engineering, in its development of an advanced absorp-

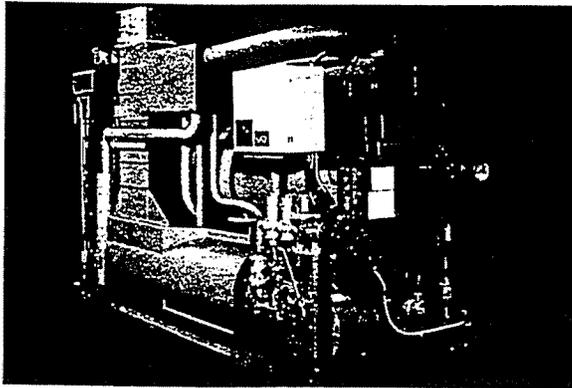


Figure 5. Trane Thermachill direct gas-fired absorption chiller.

tion heat pump which uses generator/absorber heat exchange technology (GAX).¹⁶ This approach gives simplicity of design, and reduces the heat exchanger area needed. This ammonia water system has been demonstrated to have a COP for heating of 1.8, and for cooling, 0.9.

The adsorption system is a novel process which is similar to the absorption cycle. GRI has funded work on two absorption heat pump projects and one of these involves the Wave Air Corporation, a company in which British Gas has invested through a North American venture capital fund.

Europe

British Gas is carrying out work to investigate the performance of CHP/absorption chiller combinations. The systems being examined use commercially available CHP packs and chillers. Further development work is planned to improve the integration of such systems, with a major test facility currently being commissioned (Figure 6).

CHP/absorption chiller applications tend to be mostly for very large systems, and so each case must be individually assessed. A computer programme, CHEEP, has been developed by British Gas to assist its engineers in carrying out a feasibility study and selecting appropriate plant for a potential site. Figure 7 illustrates the software available to British Gas engineers.

For small applications, such as houses or small shops, the new absorption concept known as Rotex has been identified by British Gas as particularly promising. It offers reductions

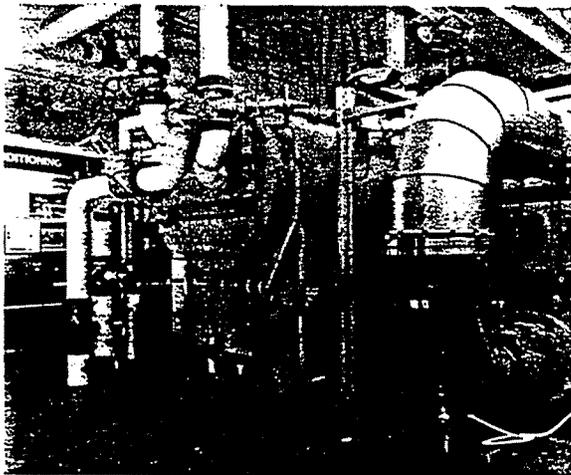


Figure 6. Chiller test facility at British Gas.

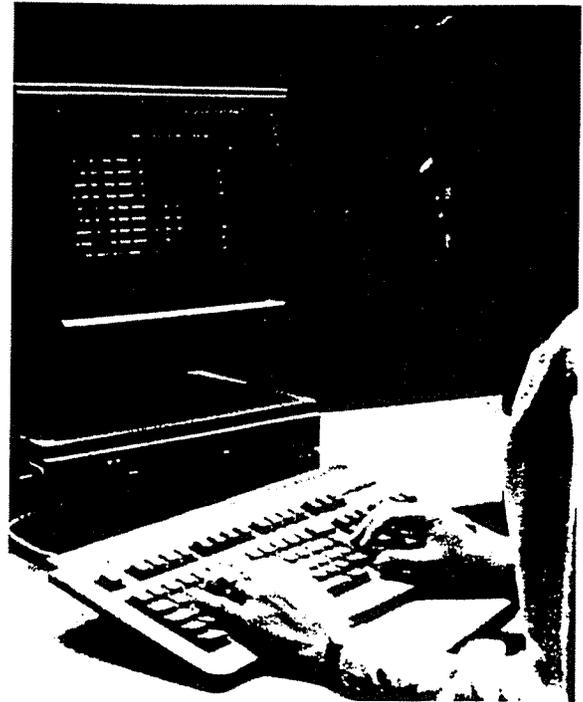


Figure 7a. Entering data into the Cheep program.

in size, weight and cost over more conventional design approaches, as well as improvements in efficiency. It is based on a technique known as process intensification which has been developed by ICI for increasing rates of heat and mass transfer in chemical plant and which has been applied to heat pumps in collaboration with MB Caradon. In the Rotex system, the heat exchangers are rotated at high speed, subjecting the working fluid to a high centrifugal force thus creating a high rate of shear in the fluid. This has the effect of dramatically reducing the resistance of the fluid to both heat and mass transfer, thus enhancing heat transfer. Rotex uses a recently developed working fluid pair comprising water and a mixture of metal hydroxides which allows the unit to provide heating as well as cooling. This represents an advance over conventional water-lithium bromide units which are unable to act as heat pumps. British Gas is now involved with Spanish companies in a joint project to develop Rotex and bring it to the market, with support from the European Eureka Programme.

| | UTILIZED (MJ) (Therms/h) | | AVAILABLE (MJ) (Therms/h) | |
|-----------------------------|-----------------------------|------|------------------------------|------|
| ELECTRICAL LOAD (Mwe) | : 635 | | 645 | |
| GAS CONSUMPTION | : 2138 | 72.9 | 2165 | 73.8 |
| HEAT AVAILABLE FROM JACKET | : 426 | 14.5 | 431 | 14.7 |
| HEAT AVAILABLE FROM EXHAUST | : 389 | 12.9 | 386 | 13.1 |
| ELECTRICAL EFFICIENCY (%) | : 29.69 | | 29.79 | |

| | WINTER | SPRING | SUMMER | AUTUMN |
|------------------------|---------|--------|--------|--------|
| REQUIRED HEAT (MJ) | : 1289 | 898 | 369 | 688 |
| SUPPLIED HEAT (MJ) | : 572 | 367 | 228 | 117 |
| REQUIRED CHILLING (TR) | : 39 | | 99 | 79 |
| SUPPLIED CHILLING (TR) | : - | 1 | | |
| TWO-HOUR CHILLING | : 76020 | 71069 | 191639 | 76650 |
| HEATED HEAT (MJ) | : 0 | 0 | 0 | 0 |

Figure 7b. A Cheep data output information screen demonstrating heating and chilling base-load levels.

Elsewhere in the UK, there is work from the academic institutions. Professor Riffat at Nottingham University has been investigating hybrid systems based on the absorption cycle, but incorporating a compressor to recompress vapour into the generator. This allows heat which would otherwise be rejected to be upgraded and used by the absorption cycle.^{17,18}

There is also activity on the European mainland. For example Spanish and Italian gas utilities are beginning to address the market for gas in air conditioning. There are a number of R&D projects in the absorption field, and some of these involve collaboration with other European countries. Gas Natural and Italgas are involved in a project, supported by the European Joule Programme, to develop a 100kW ammonia water absorption heat pump with Rendamax of the Netherlands. The heat pump design does not need a recirculation pump. Rendamax, whose speciality is the design of high efficiency gas boilers, are also involved in developing a system similar to the GAX technology described above, and are investigating compact heat exchanger designs.

There is considerable academic expertise in absorption cycles in Europe. Steimle, in Germany is noted for work on alternative absorption pairs.¹⁹ Professor Lazzarin at the University of Padova in Italy has carried out research since the 1970s on solar powered absorption systems. Professor Prevost at the University of Toulouse in France has worked on an absorption type heat pump which uses a reversible chemical reaction, the hydrogenation and dehydrogenation of alcohols. Much of the academic work does not appear to progress to commercial applications, which may be due to the lack of European manufacturers willing to enter the absorption field with the enthusiasm demonstrated by Japanese industry.

6. Desiccant systems

Most air conditioning systems carry out some dehumidification. This is usually done by using the refrigeration plant to condense moisture out of the air. This adds to the chilling load, and hence with most systems increases energy usage. With this traditional type of dehumidification, the cooling coils have to be regularly defrosted, and air which has its relative humidity decreased in this way must generally be reheated to maintain comfort conditions in the building.

A more radical approach is to absorb moisture from the air into a desiccant material, which must then be heated to remove the moisture. A convenient way of arranging this as a continuous process is to have the desiccant material on a honeycomb structure arranged as a slowly rotating wheel, as illustrated in Figure 8. British Gas, in conjunction with Munters plc, has been active in developing a gas powered version of this system.

Field trials of gas-fired desiccant wheels have been conducted in a variety of applications including warehouses, swimming pools, and an ice rink. A further field trial is in progress in a supermarket, where there is great interest in maintaining more comfortable conditions around the frozen food areas, and also in preventing airborne moisture freezing onto the produce. In all these applications, the desiccant technology is being used solely to create a sufficiently dry atmosphere for the normal use of the building.

Additionally, desiccant wheels may be used as the dehumidifier part of a conventional air conditioning system. Such systems are already in use in the USA and in the UK Romag, a glass manufacturer, uses this type of system to control the

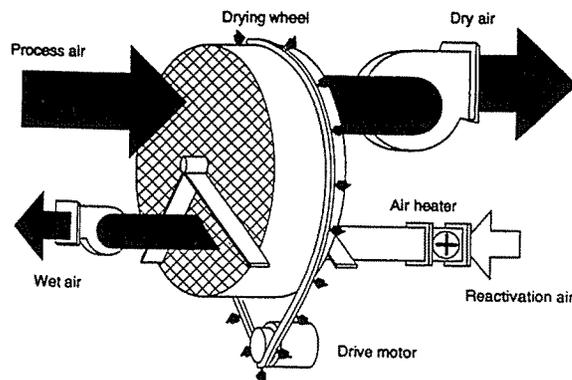


Figure 8. Operating principle of desiccant wheel.

atmosphere in an industrial clean room. In the USA, ICC Technologies is selling a dehumidification system using solid desiccant technology—the 'Desi/Air latent air conditioner'—which is designed to supplement conventional air conditioning.

International research

The main thrust of international research is to combine desiccant technology with an evaporative cooling system, giving another approach to completely gas powered air conditioning.

In the USA, ICC is now developing a combined solid desiccant/evaporative cooler using a new desiccant material.²⁰ This material, which contains silica and alumina, acts as a molecular sieve, straining water molecules out of the air. The air is dehumidified to a very low moisture content, and as the airborne moisture is absorbed, heat is released which is rejected from the system. The dry air then has a small amount of water evaporated back into it, and as the water vaporises it provides the cooling effect.

A programme started recently by British Gas, in conjunction with a manufacturer, is developing a liquid desiccant air conditioner using a similar evaporative cooling approach. This work is in conjunction with Albers Air Conditioning, and has been described in a recent IGE communication.²¹ The unit is shown in Figure 9.

7. Air conditioning systems

Most of the gas cooling research work around the world is concerned with the actual cooling devices, and has been described previously. There is some work, however, which relates more to the whole air conditioning system, and how this interacts with buildings and their inhabitants.

There is significant R&D work in Japan, including effort from Tokyo Gas, Osaka Gas and Toho Gas. All three companies are involved in a joint programme investigating thermal comfort and its assessment, to be used as a basis for developing improved air conditioning equipment. Tokyo Gas have been investigating a total energy system for buildings, incorporating CHP, fuel cells and absorption heat pumps. They are also interested in air conditioning systems for factories.

GRI has extensive R&D programmes in both residential and commercial space conditioning, which includes both heating and cooling. A large part of the programme is directed at 'multi-functional' space conditioning systems integrating air

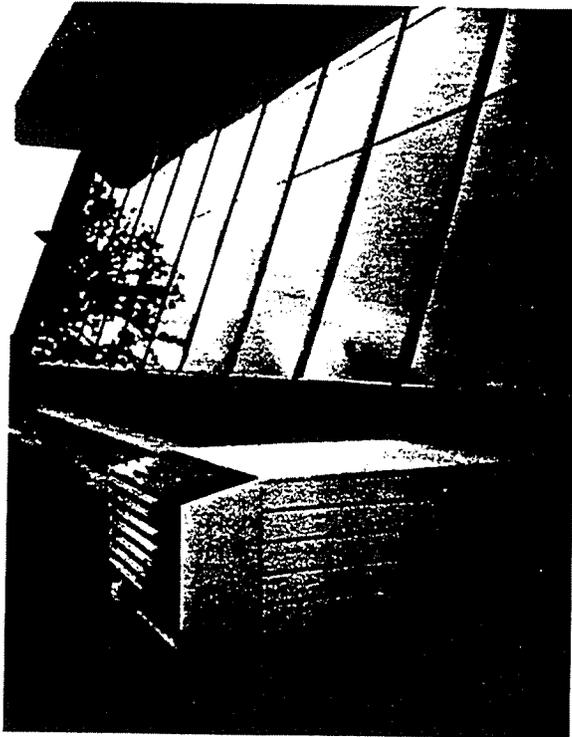


Figure 9. Liquid desiccant air conditioner.

treatment, boilers and liquid desiccant air conditioners, to produce 'total-comfort' systems.

In Europe, Gaz de France has a five storey, 25 apartment unoccupied experimental building in which whole air conditioning systems may be tested. One system that has been investigated in this building uses only evaporative cooling plus night time ventilation to cool the building.²²

British Gas has also had an involvement in studies of thermal comfort in buildings, although to date this has been more concerned with heating systems.

A further British Gas work programme is concerned with the mathematical modelling of energy usage in buildings. This involves two distinct approaches. For the more straightforward designs of many buildings, British Gas has developed the Energy Audit package. This simulation, which approximates dynamic conditions, estimates both heating and cooling loads for a range of buildings.

For more complex applications, British Gas studies have shown that the use of traditional sizing methods can lead to an oversizing of cooling equipment. Advanced mathematical models which rigorously simulate the dynamic energy flows in buildings have been investigated and applied to various buildings. One example was the sizing of the gas-fired absorption chiller currently used to cool the administration building at the Midlands Research Station. The use of a model led to a much smaller unit being installed than suggested by the traditional methods, and yet this unit has been successfully operating for four years, with good client satisfaction.

Another application was to simulate the Company's new Gas Research Centre at Loughborough, where state of the art gas powered systems, incorporating CHP and absorption chillers, are being installed to provide electricity, cooling and heating for the large, purpose built complex.

8. Conclusions

1. The air conditioning of industrial, commercial and residential buildings is widely practised in the world's three main markets: Japan, USA and Europe.

2. This worldwide demand is increasing, which presents opportunities for gas-fired equipment, with its inherent environmental advantages over conventional electric systems.

3. Gas air conditioning, particularly through the use of absorption chillers, is well established in Japan where, because of economic factors, gas accounts for over 25% of the air conditioning demand. Gas is also advancing in the USA where it has a 5% share of air conditioning for commercial buildings.

4. The search for even more effective gas air conditioning is the basis of much commercial and academic R&D work throughout the world. This work centres on four main technological approaches:

- gas engine driven chillers and heat pumps
- improved absorption chillers
- desiccant based air conditioners
- computer simulations of building energy usage

5. The main emphasise of work for the small to medium range of chilling duties is the development of gas engine driven devices. On this front, Japan, the USA and the UK, through British Gas, all have major work programmes in progress.

6. Most of the R&D work on absorption chillers, particularly at the larger scale, relates to increasing applications for this now well proven technology. Some novel cycles, however, are being developed for smaller, residential sized applications.

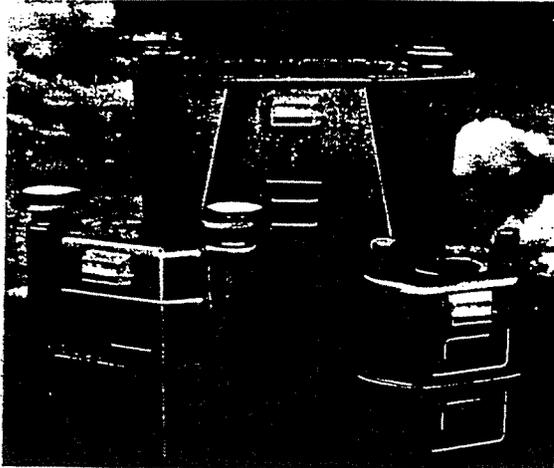
7. Gas-fired, desiccant air conditioning technology is an exciting prospect for the future. Major programmes of development work on both solid and liquid desiccant systems are underway in the USA and in the UK through British Gas.

8. There is a worldwide impetus toward developing and applying building energy models. This will ensure that air conditioning systems are sized and designed so as to give optimum efficiency and effectiveness in operation.

9. British Gas have recently initiated a strong marketing drive to increase the penetration of gas in the UK air conditioning market. An important element of the marketing plan is an R&D programme to develop new equipment and techniques in each of the four key technologies.

Acknowledgements

The authors would like to thank British Gas plc for permission to publish this paper. They also thank their colleagues in Research & Technology and Marketing for supply of information and much helpful discussion.



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Cooling and Air Conditioning with Water/Zeolite

J. Schwarz, P. Maier-Laxhuber, R. Wörz

The natural substances water and zeolite can be combined in an adsorption process for the concurrent production of heating and cooling power and for the efficient storage of thermal energy. Of the large variety of resulting engineering applications three well developed types are described in more detail.

The three applications are:

- ♦ an electricity-independent icemaker for which only a small hand-operated vacuum pump is required.
- ♦ an automobile air conditioner which draws its power largely from the hot exhaust gases of the combustion engine and thus can serve to reduce the world-wide green-house effect
- ♦ a combination of electric water heater and refrigerator which does not draw additional power for the refrigeration part.

Fundamentals of the Water/Zeolite Sorption Technology

With zeolite, a substance with similar chemical composition as sand, and water, one can produce cooling power in a refrigeration cycle. Zeolite has the property to attract (adsorb) water and to release heat while binding the water in the zeolite's crystalline structure. If this process is started in a vacuum (see fig. 1), the attraction of water by the zeolite is so forceful, that the internal pressure drops dramatically. The water in an attached vessel cools down and freezes immediately due to the heat of evaporation. The ice generated can be used for cooling and air conditioning while the heat of adsorption which is generated on the side of the zeolite vessel can be utilized for heating purposes. If a valve is introduced between the two vessels, then the cooling or heating effect can be interrupted indefinitely without loss of energy.

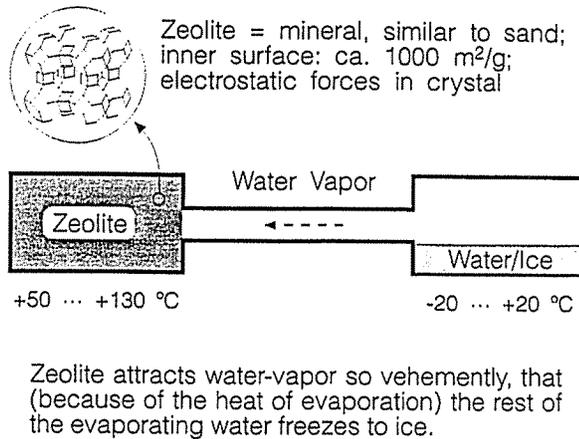
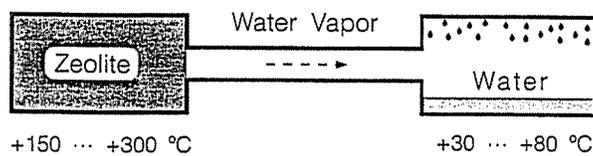


Fig. 1: Adsorption = Refrigeration



Heating the zeolite bed at high temperature desorbs water vapor out of the zeolite. The water vapor then condenses.

Fig. 2: Desorption = Regeneration

The first step of this discontinuous energy transformation continues to the point where the zeolite is saturated with water. In a consecutive second step the water can be removed (desorbed) from the zeolite by application of heat and the whole process is reversed. The water vapor leaving the zeolite is condensed in the water vessel and can be re-used. In the next cycle the water is again evaporated and cools down due to the rapid vapor adsorption in the zeolite.

A nearly continuous production of cooling power can be accomplished if two or more such sorption devices are applied in a phase-shifted manner. The regeneration of the zeolite can be performed with electrically generated heat or – more efficiently in terms of energy usage – with the waste heat of a combustion process.

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Thermodynamics of the Adsorption Process

The actual performance of different types of zeolite has been determined by pressure/temperature measurements for different water concentrations. Fig. 3 b shows the results of the measurements for zeolite of type Na-A. The x-axis shows the invers of the (absolute) temperature and the y-axis shows the water vapor pressure (logarithmic scale). With the axes scaled in this way, the curves of the water vapor pressure of zeolite with a constant water concentration ξ_i appear as nearly straight lines, so-called isosteres. Using a device shown in a schematic way in fig. 3a, we describe an ideal low-pressure sorption process between 10 and 100 mbar and the related path of the system state in the vapor pressure diagram of fig. 3a:

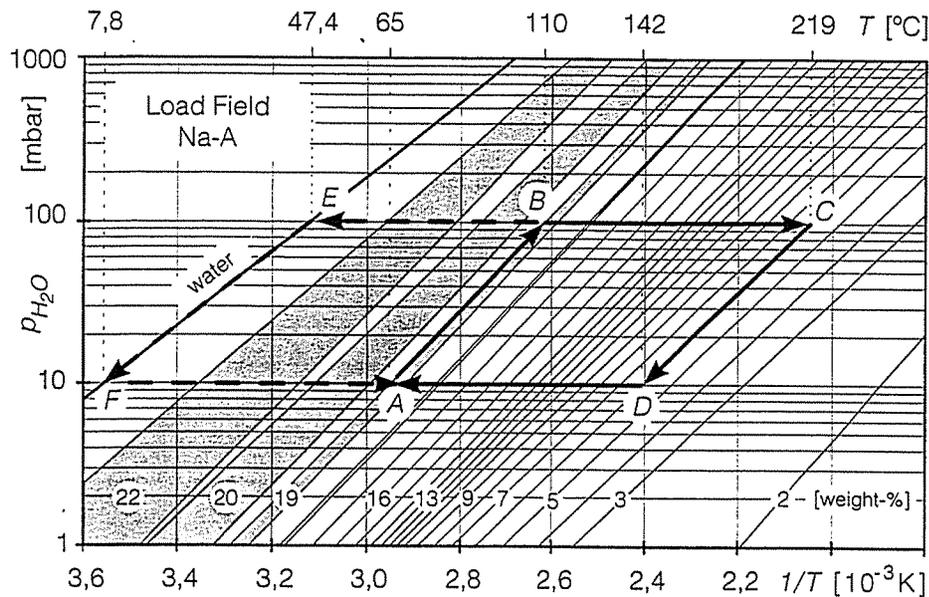
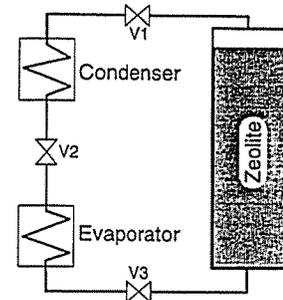


Fig. 3: Sorption Process

- ♦ (A-B): Temperature increase in the zeolite from 65 degree Celsius to about 110 degree Celsius and pressure increase from 10 to 100 mbar,
- ♦ (B-C): temperature increase from 110 degree Celsius to 210 degree Celsius at constant pressure,
- ♦ (E-F): Release of water vapor from the zeolite and condensation of water vapor at 47 degree Celsius and cooling of water (liquid),
- ♦ (C-D): Cooling off the zeolite from 219 to 142 degree Celsius and decrease of the pressure from 100 mbar to 10 mbar,
- ♦ (D-A): Decrease of the temperature from 142 to 65 degree Celsius; attraction of water vapor (from F) and thus evaporative cooling action in the evaporator.

This completes the thermodynamic cycle and the process can start again. Three heat flows at different temperature levels can be utilized:

- ♦ heat released at the condenser (E) in the desorption phase
- ♦ heat released in the adsorber ($C-A$) in the adsorption phase and
- ♦ heat uptake (=cooling power) at the evaporator (F) during the adsorption phase.

Theoretical Coefficient of Performance

The calculation of the COP for this theoretical, ideal process gives $COP = 0.55$ for cooling and $COP = 1.5$ for heating. These values are the theoretical maximum values. For actual devices the heat capacity and the heat transfer efficiency of the heat exchangers have to be taken into account. Further, throttling in the water vapor ducts and thermal losses by radiation in the desorption phase lead to a reduction of the theoretical COP.

ICE-Quick

ICE-Quick is an icemaker which operates independent of the electrical network. It can freeze a small amount of water within seconds.

ICE-Quick consists of a small hand-held vacuum pump which is connected by a hose to an adapter and a zeolite-filled cartridge. This cartridge with the adapter is set on top of a glass with water to form an air-tight lid. The whole arrangement

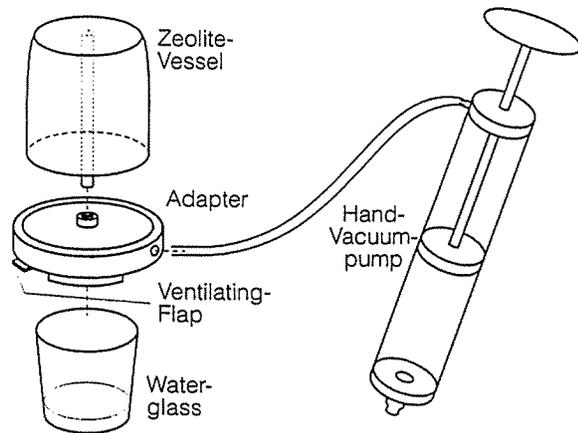


Fig. 4: ICE-Quick

is then evacuated with the pump.

After a few strokes with the pump plunger the inside pressure is reduced below the vapor pressure of the water at ambient temperature and the water begins to boil. The more air is removed from the system by the vacuum pump, the stronger becomes the adsorption of water vapor. The vapor above the water surface is adsorbed in the crystalline structure of the zeolite. As a result the remaining liquid water cools down. After a few further strokes the water freezes.

This process can be repeated several times with arbitrary intermediate periods until the suction action of the zeolite is exhausted. Then the contents of the zeolite cartridge can be regenerated by heating it to 250 degree Celsius in the oven.

Adsorption Air Conditioner

Fig. 5 shows in a schematic way an automotive air conditioner based on the sorption principle. Two sorption cartridges with together 5.4 kg zeolite are built into a special muffler. The zeolite cartridges work alternately as adsorber and desorber. The muffler is mounted in the exhaust system of a passenger car downstream from the catalytic converter.

One zeolite cartridge of this special muffler is heated by the hot exhaust gases from the engine in one compartment, while air is blown through the other compartment by a fan in order to cool the second zeolite cartridge. With the position of the flap as shown in fig. 5, the external air is blown through the right compartment, in which the included zeolite acts as the adsorber. The heat of adsorption generated in the zeolite is taken up by the air which keeps the zeolite temperature low. The preheated air flows over to the other compartment and leaves the muffler together with the exhaust. As soon as the temperature of the left zeolite cartridge, the desorber, reaches 200 degree Celsius the flap is pneumatically switched to reverse the roles of adsorber and desorber. The external air cools down the hot left cartridge to a temperature where adsorption can take place internally, mixes with the exhaust (now in the right chamber) and leaves the muffler. The air conditioning effect is accomplished in the evaporator, where the water vapor extracts heat via evaporation. The passenger compartment air is cooled via heat exchange with the evaporator. The valves of the evaporator/condenser unit are switched in phase with the exhaust flap in order to reverse the role of condenser and evaporator according to the switching of adsorber and desorber.

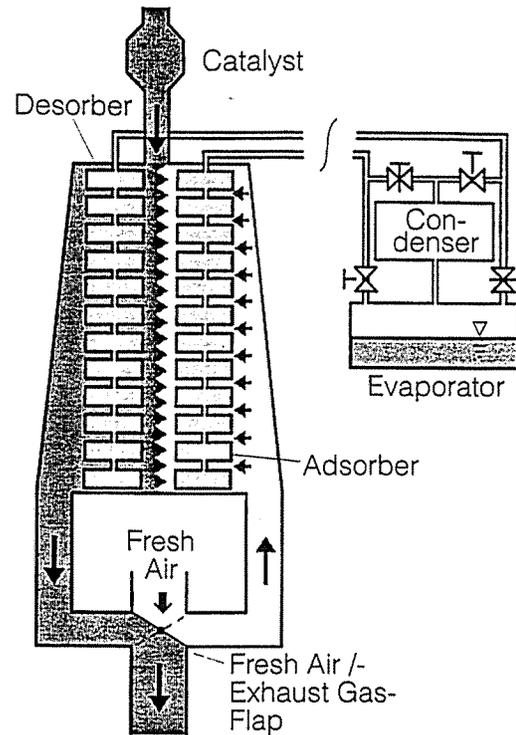


Fig. 5: Scheme of an adsorption air conditioner.

Air Conditioning without Starting the Motor

In normal operation the air conditioner will be turned off together with the engine and the evaporator/condenser valves will be closed to prevent the adsorption of water in the zeolite. Thus the device stores the ability to cool air. Therefore

the air conditioner can be turned on to cool air without the engine by opening the valves. Only if the air conditioner is operated without the engine for longer periods until both zeolite containers are saturated then a certain startup period will be required when turning on the engine before cooling can start again.

Testing

During tests the hot exhaust gases were simulated by a blower with an electric heater. The energy required for heating the ambient air was measured and the exhaust heat required for the operation of the device was determined. During tests the evaporator temperature, the cycle time, the temperature and the volumetric flow rate of exhaust and ambient air as well as the valve positioning times were varied.

Cooling Power versus Time

The cooling power is generated – as explained above – alternately by the two compartments. During the switching period between the two sorption containers both evaporator/condenser valves are closed for a short time. The previously active adsorption vessel does not adsorb any more and the previous desorber does not yet adsorb. During this time – about 15 seconds – the evaporator is inactive and the cooling effect is interrupted. The interruption of adsorption action and cooling power is normally compensated by the »buffer-effect« of the ice which builds up in the evaporator. Fig. 6 shows the cooling power curve of the system versus time. The power reduction introduced by the short interruption during switching effectively reduces the average cooling power to about 85% of the maximum power. Further, the curves show, that the two adsorbers (marked by 1 and 2) differ somewhat in the cooling power delivered. By reducing the switching period and with equal performance of both sorption containers the delivered net cooling power can be increased considerably.

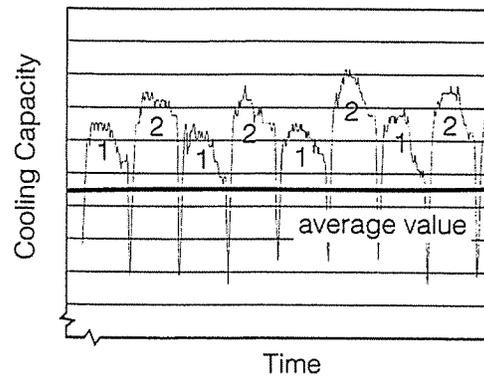


Fig. 6: Cooling power versus Time

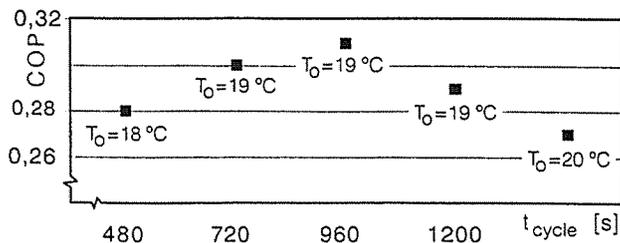


Fig. 7: Coefficients of Performance

COP

With the first prototype the cooling power (operating at high evaporator temperatures) is to a certain degree dependant on the evaporator temperature and the cycle time. After a reduction of the flow rate of hot air at the be-

gin of the half-cycle and a reduction of the ambient air flow rate at the end of the half-cycle a maximum COP of 0.31 at a cycle time of 960 seconds was accomplished. Of course this first optimum is dependant on many other parameters, like construction details, materials, zeolite type, temperature levels etc, which are not described here. The first optimum therefore is merely a starting point which will be improved in the future.

Results of Testing

The adsorption air conditioner with zeolite/water has demonstrated the principal functionality. The targeted COP of 0.3 was accomplished. The first prototype built is still too voluminous but there is ample potential for a significant reduction of mass and volume. A further potential for improvement is in the geometry of the air passages, which should be adapted such that the temperature versus time curves in the zeolite are independent of the position in the device. This will allow to utilize the maximum concentration change in the zeolite.

Ecological Aspects

The technical functionality of an automotive air conditioner is not the only selection criterion. A further, very important criterion is the environmental compatibility all the way from raw material production, final product manufacturing, application and disposal. The most important aspect today is the energy consumption of future automotive air conditioners and the related carbon dioxide emission respectively the contribution to the overall greenhouse effect.

Contribution to the Greenhouse Effect

The energy necessary for the powering the water/zeolite air conditioner in an automobile is normally provided by the rest-energy contained in the exhaust gases. Only the electrical energy for an air circulation blower of about 125 W has to be spent in addition. However, there are operating ranges in which the exhaust energy does not suffice to drive the sorption process. For example, this is the case during city stop-and-go traffic or during extremely slow driving. For these cases the missing exhaust heat will be supplied via a small commercial gasoline heater. The related fuel consumption for these operating modes is small compared to a conventional air conditioner.

Conventional automotive air conditioners indirectly contribute to the greenhouse effect due to the additional fuel consumption and the related carbon dioxide emission. Compressor airconditioners inherently leak small quantities of refrigerant. The refrigerant to be used in the future, R134a, is a contributor to the greenhouse effect. Therefore these devices additionally contribute directly to the greenhouse effect through the leaking of refrigerant, which can be measured in CO₂ equivalent mass.

For evaluation purposes of the environmental compatibility we compare the CO₂-equivalent of future R134a air conditioners and of water/zeolite automotive air conditioners (both optimized for efficiency).

Boundary Conditions for a Compressor Air Conditioner

According to experience it is necessary to refill an air conditioner twice during a period of ten years of operation. We assume, that the refrigerant and the contained lubricant are disposed in a controlled way when the vehicle is dismantled. The mechanical power of an air conditioner is about 3.5 kW. For an optimistic average engine efficiency of about 20 percent and for a COP for cooling of 1.8 the primary energy usage is 9.7 kW. Experience has shown, that on a worldwide average basis automotive air conditioners are used for about 150 hours per year (in Europe this figure is lower, however). The resulting direct contribution to the greenhouse effect for a period of 20 years is (in relative CO₂ units) 3200 for R134a refrigerant and 7100 for R12 refrigerant.

Boundary Conditions for a Sorption Air Conditioner

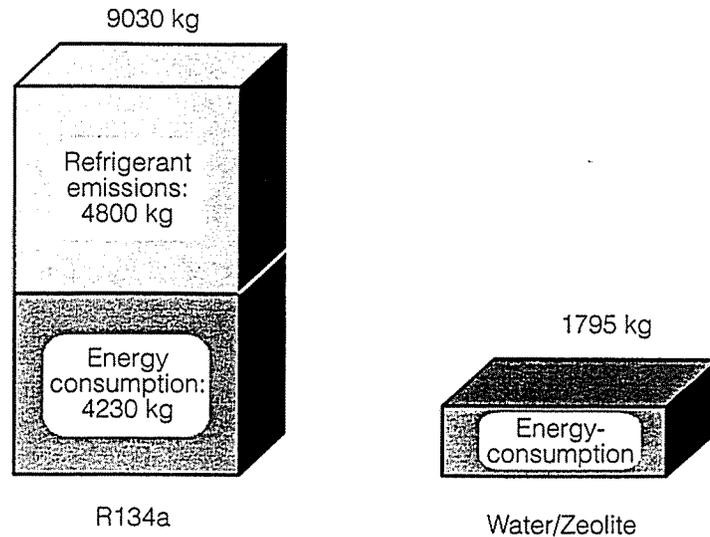
The period of operation and the lifetime of the device correspond to the values defined above. Further, the mass of the system and the delivered cooling power are about the same. The water/zeolite air conditioner has an average thermal power input of about 9 kW. We assume, that during about 40 percent of the time an auxiliary gasoline heater is used to supplement the exhaust heat of the engine. The electrical power of the blower is assumed to be 125 W. For an engine efficiency of 20 percent the related primary energy is 625 W.

Total Equivalent of Warming Impact

As shown in the following diagram, the total CO₂ equivalent for a future R134a air conditioner is 9030 kg. 53% of this are related to the direct greenhouse effect from refrigerant leakage. The remaining 47% result from the additional energy usage. Energy consumption for manufacturing and disposal of the system as well as the refrigerant leakage during disposal were not considered in this calculation. For a water/zeolite system the leakage of refrigerant (=water) does not contribute to the greenhouse effect. Therefore the overall greenhouse equivalent is given by the additional energy consumption related to the use of the air conditioner. The CO₂ equivalent of the water/zeolite system is about 20 % of the value calculated for the R134a system. If the water/zeolite system can be operated solely with exhaust heat, then the CO₂ equivalent is near zero.

Results: Ecological Aspects

With respect to the total CO₂ equivalent for a 10 year operating period definite advantages have been found for a sorption air conditioner in comparison to a conventional compressor air conditioner using R134a. Similar advantages result in



rel. GWP_{20a/CO_2} (R134a) = 3200, $COP = 0,4$; $\dot{Q}_0 = 3,5 \text{ kW}$
 Emissions in 10 years: 1,5 kg, $P_{Fan} = 125 \text{ W}$
 $\epsilon = 1,8$; $\dot{Q}_0 = 3,5 \text{ kW}$, $\eta_{Mot} = 20 \%$, Additional burner time: 40 %
 Disposal after 10 years: 100 %, Running time: 1500 h $\hat{=} 10 \text{ a}$
 Spec. emissions: 0,29 kg CO_2/kWh ,
 Running time: 1500 h $\hat{=} 10 \text{ a}$

Fig. 8: TEWI of future air conditioners

the areas raw materials production, manufacturing and, finally for the disposal (after reaching the intended lifetime) of the airconditioners:

- ♦ the manufacturing process of zeolite is a cyclic process which does not produce unwanted byproducts and for which only three raw materials are required: sand, sodium hydroxide and aluminumhydroxide. In addition, water and steam for process heating are required in this low energy process.
- ♦ the overall energy consumption for the manufacturing of the basic materials and the manufacturing of the device is about 100 kWh. This corresponds to an equivalent CO_2 mass of 46 kg. Thus the manufacturing-equivalent is small in comparison to the CO_2 -equivalent related to the operation of the air conditioner.
- ♦ the use and disposal of zeolite has been evaluated with positive result by the German Umweltbundesamt and the Federal Ministry of Environment. The evaluation was performed in connection with the replacement of phosphates in laundry detergents by zeolites.

The cooler/boiler

The cooler/boiler is an electricity powered combination of refrigerator and boiler. The energy for heating the water consists to a large part of the heat which is removed from the refrigerated container. The advantage of such a system is that the refrigeration is provided without additional energy expense compared to a boiler. The operation of the refrigerator is thus free of cost, while the operation cost of the boiler is about 35% cheaper than for conventional boilers.

Construction and Operating Principle

The system consists mainly of two zeolite adsorber containers, a buffer/collection chamber which also acts as a heat exchanger, a steam collection manifold, a water boiler, a vacuum pump, one-way valves as well as solenoid checkvalves, and the refrigerated storage container.

To heat the water to the desired temperature in the boiler the adsorber, e.g. in container no. 1, is heated via an electric heating coil to 250 degree Celsius at a time of low electricity tariff (e.g. at night). The cooling water which is still in the zeolite heat exchanger evaporates in the pipes and collects in the buffer/collection vessel above the adsorbers (see fig. 9). Simultaneously the zeolite releases water vapor which was adsorbed in a previous phase. The generated water vapor flows via the one-way valve into the buffer/collection vessel and condenses immediately. The heat of condensation is transferred through the wall of the container to the water in the boiler. The evaporator of the refrigerator is supplied with water from the buffer/collection vessel. The heating time is about 1.5 hours, during which time the boiler water is heated by heat from adsorber 2 or by the heat of condensation resulting from steam coming from adsorber 1.

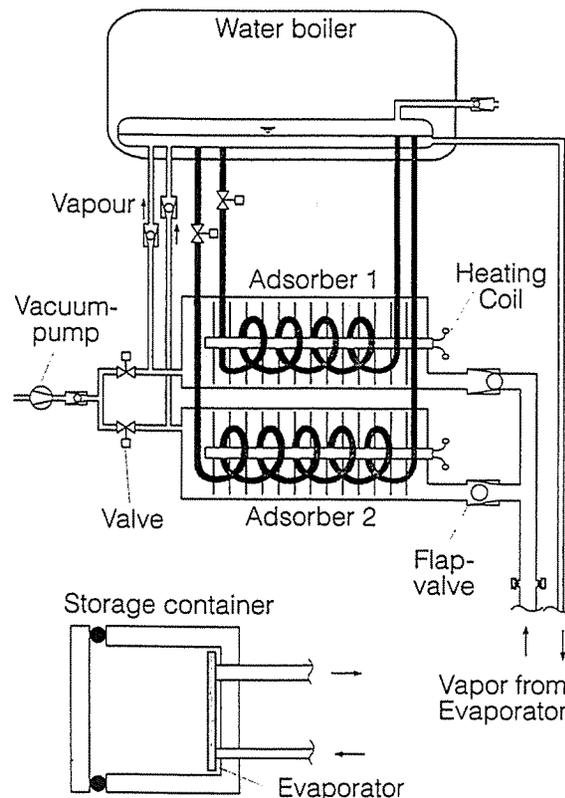


Fig. 9: Cooler/Boiler-scheme

Subsequently adsorber 2 is heated in the same way. In order to supply heat the solenoid check-valve at the buffer/collection vessel is opened at the adsorber 1.

Cooling water (temperature of the boiler) flows into the very hot heat exchanger of adsorber 1, evaporates there and condenses in the buffer/expansion container. This process continues until the temperature of the zeolite bed has decreased to the temperature of the boiler water. This process cools adsorber 1 enough to allow the adsorption of water vapor which is sucked in through the collection manifold. The rapid adsorption of water vapor generates cooling power via the pressure reduction and resulting water evaporation from the evaporator in the refrigerated storage chamber. The evaporated water is drawn from the buffer/collection vessel. During the adsorption adsorber 1 releases the heat of adsorption which is transferred to the boiler water. After three more hours the heating phase in adsorber 2 is completed. Adsorber 2 is cooled in the same way as soon as the boiler requires heat. By this process the whole boiler water can be heated to the required temperature in a few hours. The consumption of electrical energy can thus be limited to the low tariff period.

The construction includes two adsorbers and thus ensures a continuous refrigeration. During desorption of adsorber 1 the adsorber 2 (not yet saturated with water) provides for the cooling effect. Adsorber 1 takes over the cooling action as soon as it cools down, while adsorber 2 is being desorbed. If adsorber 1 saturates at some point during the day, the valve in the steam collection manifold is switched such that adsorber 2 can ensure the cooling effect up to the point when the next desorption phase starts.

Energy Considerations

The annual contribution of a cooler/boiler to the greenhouse effect in comparison to a conventional combination of refrigerator and electrically heated boiler of equivalent cooling and heating capacity is shown in fig. 10. The use of the conventional combination results in 60% higher energy consumption and thus more CO₂ than with the water/zeolite-cooler/boiler.

The cooler/boiler requires more equipment in the form of zeolite, heat exchangers, vacuum pump, valves and control devices. However, the compressor with all its parts is eliminated, which leads to potentially smaller overall dimensions of the system. The amortisation of the system is estimated to be well within the expected lifetime. More detailed calculations are dependant on the tariffs for electricity and have to be carried out on a case by case basis.

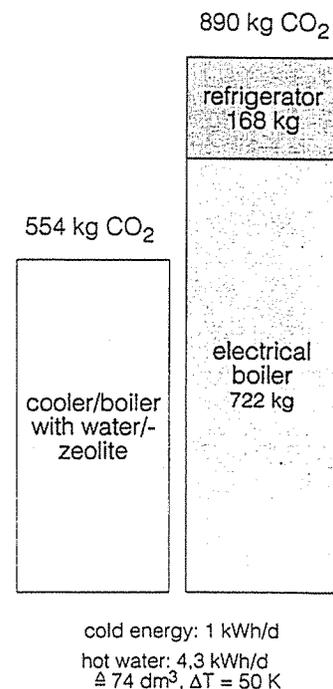


Fig. 10: CO₂ equivalent of Cooler/boiler

Summery and Outlook

The principal functioning of the water/zeolite sorption technology has been demonstrated with a multitude of devices and systems, some of them under public funding. The sorption technology available facilities refrigeration and energy storage with natural materials. These materials are compatibel with today's and future environmental regulations with repect to their production, use and disposal.

The energy to drive the discontinuous sorption process is applied in the form of heat. The coefficient of performance with respect to heat input is today more than 30 % for cooling and can be optimized to yield more than 40 % via internal heat exchange.

The unusually large range of applications reaches from cooling, air conditioning to storage heat and cooling capacity as well as ice-producing.

This ensures a very good technology and economic potential.

ZEO-TECH GmbH is dedicated to the research and development of sorption technology based on water/zeolite and owns a comprehensive patent rights. For production and marketing of final products ZEO-TECH is open for cooperation.

STIRLING CYCLE REFRIGERATORS AND HEAT PUMPS

by

Dr. Per G. Lundqvist

Department of Energy Technology
Div. of Applied Thermodynamics and Refrigeration,
The Royal Institute of Technology
s - 100 44, Stockholm, Sweden

1. Technology description

There are no Stirling machines, engines or refrigerators that operate according to the *Ideal Stirling cycle*. Still we name these machines after this cycle. The ideal cycle is of course named after the inventors Robert and James Stirling whose machines definitely not worked according to the ideal cycle. The definition of what kind of machine that is *worthy* the name Stirling machine has been proposed by several authors. The perhaps most clearly written is taken from the very first paragraph of prof. Walkers book - *Stirling Cycle machines* (1973):

"A Stirling-Cycle machine is a device which operates on a closed regenerative thermodynamic cycle, with cyclic compression and expansion of the working fluid at different temperature levels, and where the flow is controlled by volume changes, so that there is a net conversion of heat to work or vice versa."

This definition captures most of the typical Stirling machine characteristics without the almost impossible heat transfer demands necessary for isothermal expansion and compression. There are other cycles which operate with a regenerative heat exchanger but the gas flow is either controlled by valves, as in Ericsson-cycle machines, or without cyclic compression and expansion such as in a closed, regenerative, gas turbine cycle (Joule-Brayton cycle).

Figure 1.1 Illustrates the function of an ideal so called β -type Stirling refrigerator in a pressure vs. volume diagram. The heat exchangers are omitted and the regenerator is placed inside the displacer (the cross-hatched piston). This ideal diagram bear little resemblance to practical machines due to, mainly, two reasons:

- non-isothermal heat exchange ($d \rightarrow c$ and $b \rightarrow a$ in figure 1.1)
- continuous piston movements. The displacement of gas from the cold to the warm side, and vice versa, is not undertaken at constant volume ($c \rightarrow b$ and $a \rightarrow d$).

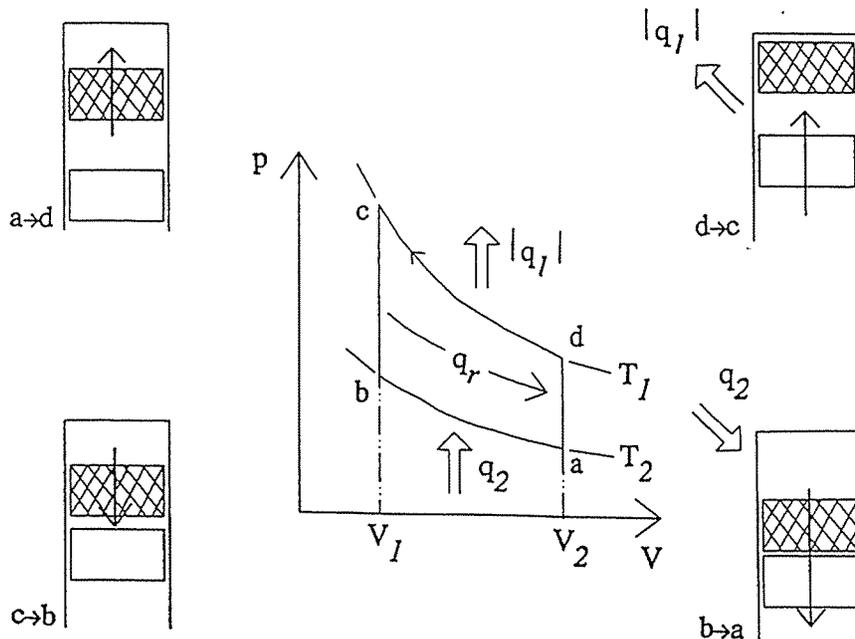


Fig 1.1 Ideal β -type refrigerator illustrated in a pressure vs. volume diagram. The cooling capacity, q_2 , is obtained at constant temperature during the expansion ($b \rightarrow a$). Heat is exchanged in the regenerator during phase $c \rightarrow b$ and $a \rightarrow d$.

A Stirling cycle machine can also be designed as α -type. Figure 1.2 shows a typical α -type machine. The displacer and the work piston pair is here replaced with an expansion and a compression piston (ep and cp). The thermodynamic cycle is essentially the same. The difference is that the expansion work has to be recovered by the expansion piston and transferred to the compression piston via the crank mechanism. The components in figure 1.2 are: Warm heat exchanger (3), Regenerator (4), and Cold heat exchanger (5).

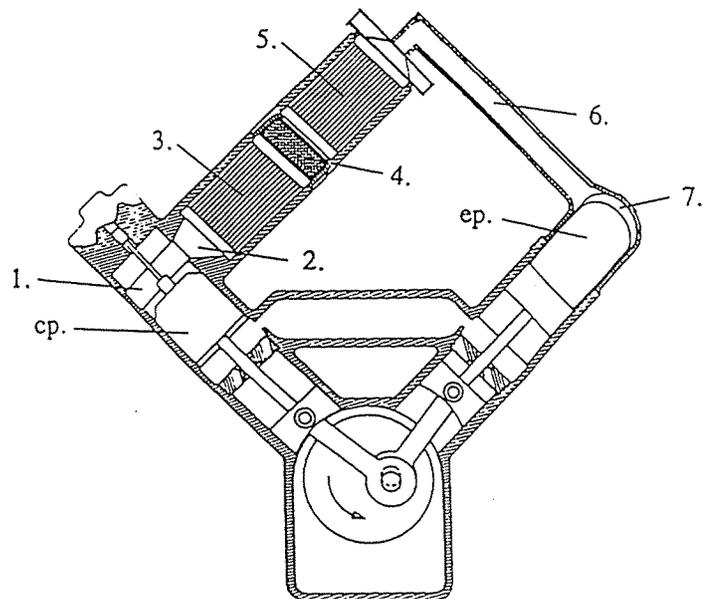


Fig 1.2 A typical α -type Stirling cycle machine (V160 Stirling engine modified to a refrigerator).

2. Application

The potential in replacing current refrigeration technology with alternatives based on the Stirling cycle increase with the temperature lift. The reason for this is explained later in the paper. It is therefore realistic to expect an initial breakthrough at temperature levels between 173 to 243 K (with heat rejection to ambient at 313 K). The Stirling cycle is already commercially used at cryogenic temperature levels in, for example, air liquefaction and infrared optics. Work by many researchers have showed that the Stirling cycle may compete with the vapour compression cycle for temperature lifts higher than 60 K with the current technology status.

3. Benefits

The Stirling cycle may operate with either helium or hydrogen as working fluid. Hydrogen gives slightly more favourable characteristics but the flammability may be an issue. The amount of working medium in a small hermetic refrigerator is however small. The efficiency of a Stirling system remains reasonable constant when the size of the machinery is decreased. Stirling cycle coolers for infrared sensors is available at capacities as low as 0.25 Watts! Modulation of capacity is readily achieved by adjusting the operating speed, the operating pressure or the stroke of the pistons. All methods are used in practical machinery. Figure 3.1 is an example where the cooling capacity is modulated by adjusting the working pressure. The data is taken from experiments with the V160 refrigerator showed in figure 1.2.

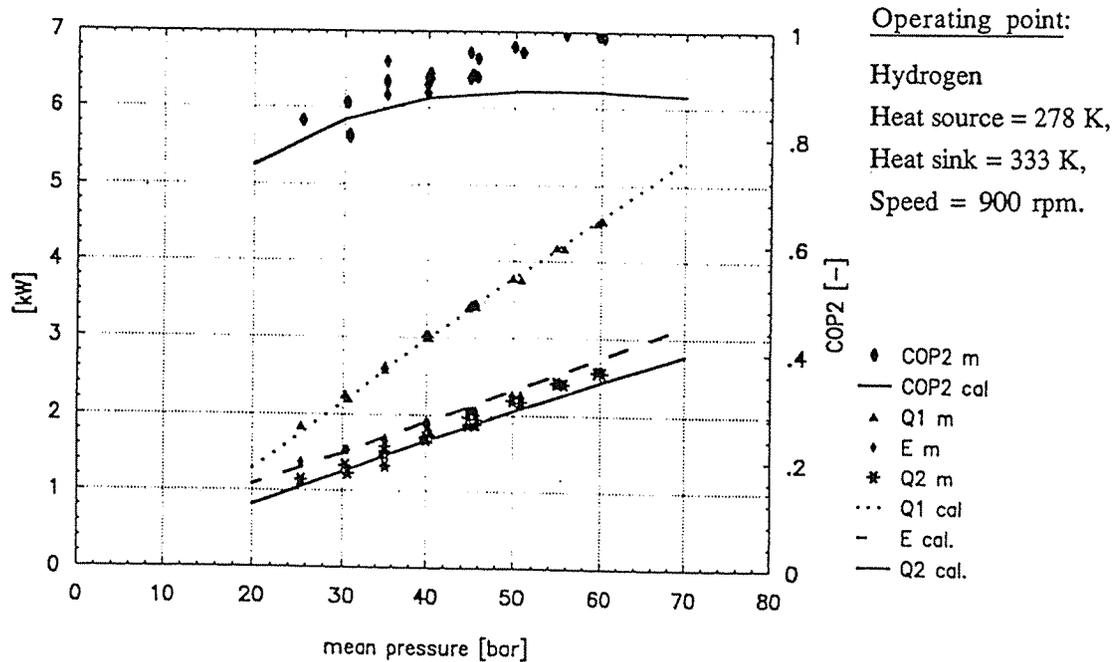


Fig 3.1 V160 refrigerator. Cooling capacity, input work and rejected heat as a function of mean operating pressure (symbols: measured - lines: simulated).

4. Technical issues

The art of Stirling engine design has been refined during the last 30 years. The same is valid for low temperature lift Stirling refrigerators. The influence of the different losses that occur in the cycle affect the design strategy in a similar way for these two applications. The basic design rule is to avoid unnecessary dead volumes and use as good regenerator as possible.

The optimum design of a refrigerator or heat pump, based on the Stirling cycle, differs substantially from the design of a Stirling engine or a low temperature Stirling refrigerator. It has been shown, experimentally as well as theoretically, that the temperature lift strongly influence the importance of the design parameters. Figure 4.1 is an attempt to illustrate the relative influence of the losses in a Stirling refrigerator operating over a low temperature lift. The machine in the figure is by no means optimal.

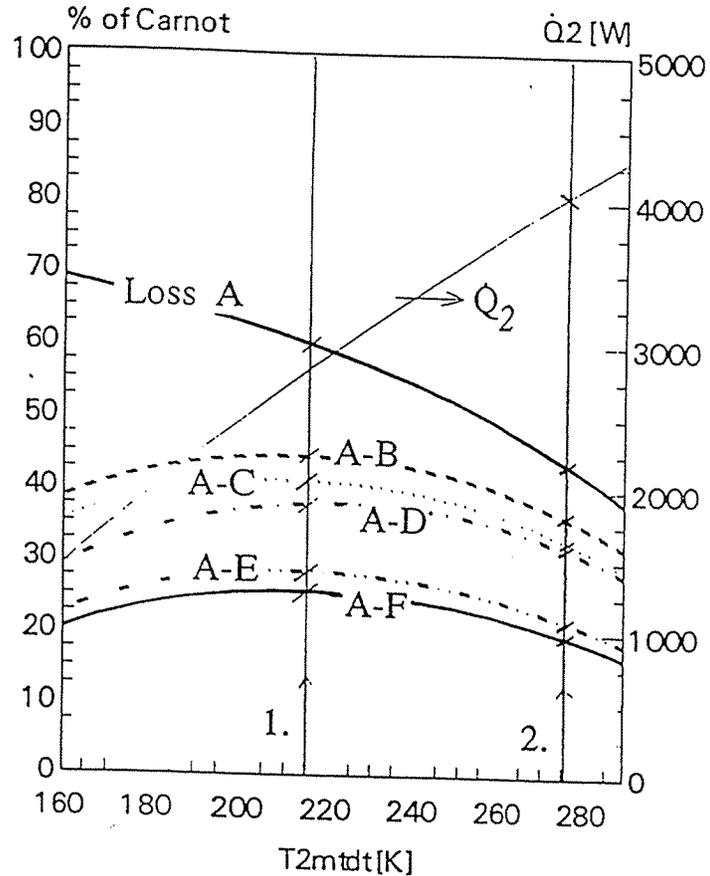


Fig 4.1 Impact of different losses as a function of the temperature lift for a modified V160 Stirling machine operated as a refrigerator. The losses may be identified with the below table. Heat is rejected at 330 K. Compare the distribution of losses at line 1 and 2!

The losses in a Stirling refrigerator or heat pump may be divided in six main groups (as presented in figure 4.1):

- Heat transfer related losses - "Loss A"
- Regenerator losses (thermal efficiency and pressure drop) - "Loss B"
- Flow losses (regenerator losses excluded) - "Loss C"
- Heat conduction losses - "Loss D"
- Friction losses - "Loss E"
- Other losses (electric motor efficiency etc.) - "Loss F"

The relative influence of the losses is strongly dependant of the temperature lift. Figure 4.1 show the relative influence of these groups of losses for a V160 refrigerator that have been thoroughly tested at the laboratory of Applied Thermodynamics and Refrigeration, KTH, Stockholm.

The most important losses in a low temperature lift Stirling refrigerator or heat pump are:

- temperature differences in the heat exchangers,
- adiabatic cylinder losses (internal cycle temperature differences).

It can be shown that mechanical friction and unwanted heat conduction set a limit for the design changes necessary to avoid these losses. Any optimization process therefore needs to take these phenomena into consideration at an early stage.

Figure 4.2 illustrates the influence of one of the temperature difference related losses shown in figure 4.1. I have as an example chosen the temperature differences in the heat exchange with the surroundings for an, otherwise, ideal refrigerator. The temperature on the cold side is varied from 30 to 300 K. The heat rejection temperature is held constant at 313 K (+40 °C). A heat exchanger temperature difference of 6 K (dotted line) means 75 % of the ideal efficiency at 270 K on the cold side. The same temperature difference gives approximately 90 % of the ideal efficiency at a cold side temperature of 170 K.

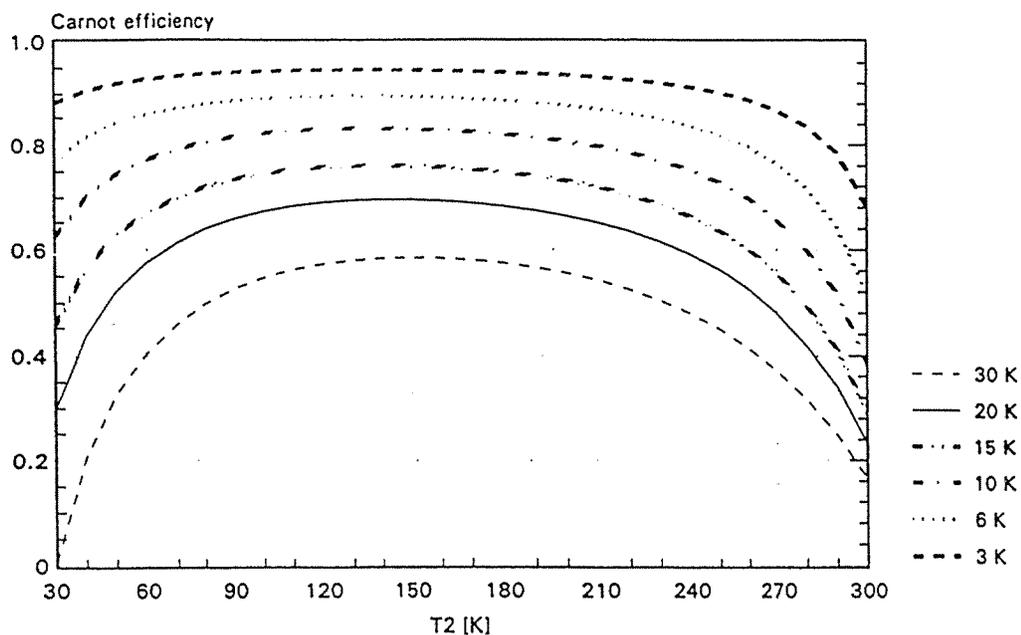


Fig 4.2 Deviation from the the ideal Carnot efficiency due to temperature differences in the heat exchangers. The heat rejection temperature is 313 K (+40°C).

Many of the temperature difference related losses are a function of the pressure ratio in the cycle (p_{max}/p_{min}). A machine with low pressure ratio will have low temperature difference related losses but, unfortunately, also low cooling capacity. Mechanical friction and unwanted heat conduction, as mentioned above, are the parameters that influence to what level the pressure ratio can be lowered. The pressure ratio is for example lowered by increasing the size of the heat exchangers.

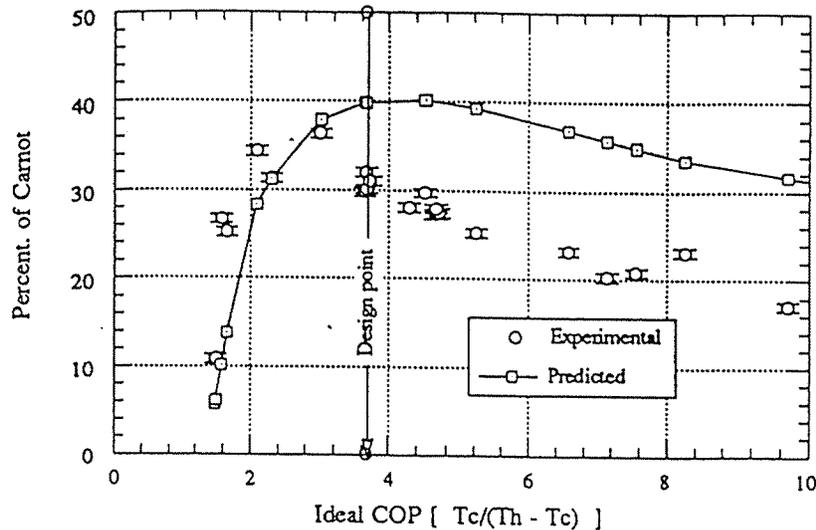


Fig 4.3 Data for Sunpower demonstrator free-piston Stirling cooler for domestic refrigeration as presented by D. M. Berchowicz at the 6th International Stirling Engine Conference.

Figure 4.3 shows some results from one of the leading Stirling developers. The graph illustrates experimental and predicted values for the efficiency for a *Demonstrator Free-piston Stirling Cooler* for domestic refrigeration. The figure shows the percent of ideal Carnot efficiency (y-axis) for different values of the ideal Cop (x-axis). Values to the right corresponds to low temperature lifts. An ideal COP value of 4 correspond to a temperature lift of $\approx 60\text{K}$ if the heat rejection temperature is 313 K ($+40^\circ\text{C}$). The experimental points indicate that the optimum performance is obtained at higher temperature lifts. The best percentage of Carnot is obtained at a temperature lift of $\approx 78\text{K}$ (with the same heat rejection temperature as above). The design goal is to move the curve for the percentage of Carnot *to the right*, towards lower temperature lifts.

The way of doing this is to further eliminate mechanical friction and unwanted heat conduction and thus enhance the possibilities to reduce the heat transfer related losses (losses A in figure 4.1).

5. Economics

Many attempts have been made to estimate the costs for various types of Stirling engines. A Stirling refrigerator or heat pump share many components with the engine but lacks the material constraints due to high temperatures. The heat exchangers should therefore be cheaper than for the corresponding Stirling engine (although the heat exchanger area may be increased). A simplified regenerator with sufficient thermal efficiency (random fibers instead of wire nets is an example of essential future cost reductions).

6. Technology outlook

Mechanical friction and unwanted heat conduction set a limit for the design changes necessary for a low temperature lift Stirling refrigerator. It is also important to avoid large temperature differences in the heat exchangers. The relative influence of the losses in a low temperature refrigerator differs from typical Stirling engine or cryogenic refrigerator characteristics. Further development of existing computational aids therefore need to be done with careful modeling of the temperature difference related losses.

The important work therefore need to be directed towards:

- Better drive mechanisms with less mechanical friction and longer life
- Cheaper heat exchangers with sufficient thermal performance
- Continued Stirling heat exchanger studies (theoretical as well as practical)
- Simulation code development with close cooperation with experimental work

7. Suggested reading

There is a wide variety of literature on the subject. The following list is an attempt to list some books or conference papers that cover the subject of low temperature lift Stirling refrigerators in a critical and comprehensive way (from my personal point of view).

Books:

- Hargreaves, C.M., 1991, *The Philips Stirling Engine*, Elsevier Publishing Company, Amsterdam, London, New York, Tokyo.
- "Energy efficient alternatives to Chlorofluorocarbons", revised final report, Prepared for U.S. dept. of Energy by A.D. Little, reference 66384.
- Lundqvist, P., 1993, "Stirling Cycle Heat Pumps and Refrigerators", Doctoral dissertation, ISRN KTH/REFR/R-93/9-SE, Trita REFR Report No93/9, ISSN 1102-0245
- Urieli, I., Berchowitz, D.M., 1984, *Stirling Cycle Engine Analysis*, Adam Hilger Ltd., Bristol, U.K.
- Walker, G., 1989c, *Miniature Refrigerators For Cryogenic Sensors and Cold Electronics*, Clarendon press, Oxford.

Conference papers:

- Berchowitz, D.M., 1991b, "Experimental performance of a Free-piston Stirling cycle cooler for non-CFC domestic refrigeration applications", Proc. of the XVIIIth International Conference of Refrigeration, August 10-17, Montreal, Canada.
- Berchowitz, D.M., 1992, "Free-piston Stirling coolers", Proceedings from the Xth International Refrigeration Conference, Purdue pp. 327-336.
- Berchowitz, D.M., 1992, "Free-piston Stirling coolers for intermediate Lift temperatures", ", Proceedings from the 27th IECEC, pp 5.115-5.121
- Lundqvist, P., 1991, "The reversed Stirling cycle - A comparison of theory and test results", Proc. of the XVIIIth International Conference of Refrigeration, August 10-17, Montreal, Canada.

Thermoacoustic Refrigeration and Acoustic Compression

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ABSTRACT

Resonant high amplitude sound produces two significant phenomena; thermoacoustic refrigeration and sonic compression of gas. In this report, experimental studies on thermoacoustic refrigeration recently done in Japan were briefly shown, and a few discussions on acoustic compression refrigerator were also made. Few researchers in Japan have been interested in thermoacoustic refrigeration. Acoustic compressor is supposed not to have been experimented in Japan. Recently not a few designers of refrigeration are gradually interested in the results of experiments of both thermoacoustic refrigeration and acoustic compressors. When we can break through some problems (heat exchangers, valves, drivers and so on), their efficiencies will be expected to be equivalent to conventional compressors.

Thermoacoustic Refrigeration

Resonant high amplitude sound produces two significant effects; thermoacoustic Refrigeration phenomena and sonic compression of refrigerant[1]. We will discuss them here separately.

Technology Description

Thermoacoustic refrigeration, one of sound refrigeration technology, has been studied by many researchers recently[2]. It is one of phenomena in thermoacoustics.

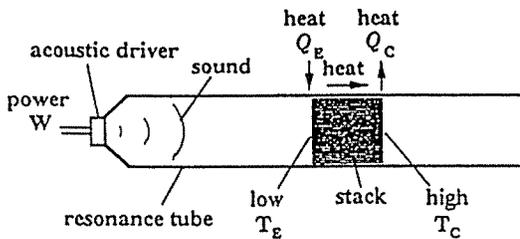


Figure 1 Schematic Diagram of Thermoacoustic Refrigerator

A schematic diagram of a simple, one-quarter wavelength, $\lambda/4$, thermoacoustic refrigerator is shown in Figure 1. The loud speaker (acoustic driver) at the left sets up the standing wave within the gas-filled tube. Its frequency is chosen so that the loud speaker excites the fundamental ($\lambda/4$) resonance of the tube. The termination at the right-hand end of the tube is rigid, so the longitudinal particle velocity at the rigid end is zero (a velocity node) and the acoustical pressure variations are

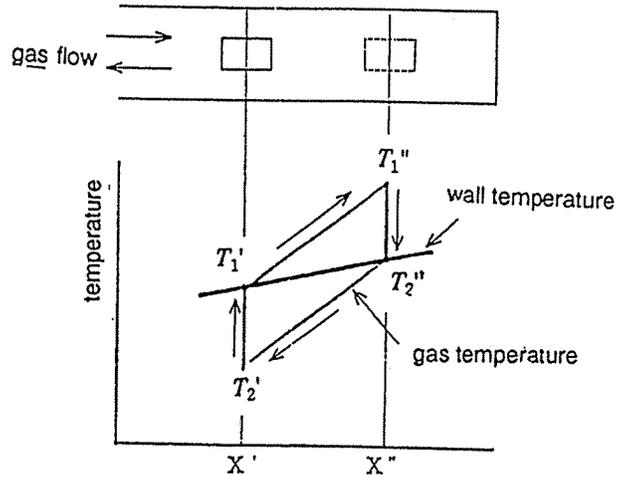


Figure 2 Principle of Thermoacoustic Refrigeration

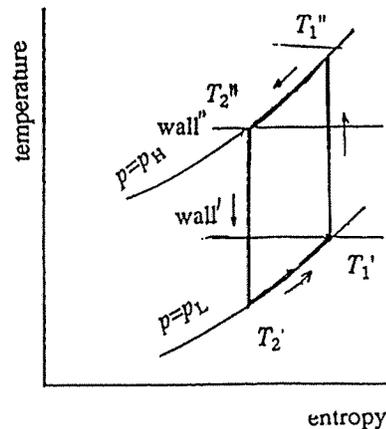


Figure 3 Temperature-Entropy Diagram

maximum (a pressure antinode). At the loud speaker end of the tube, there is an acoustic pressure node and a particle velocity antinode. To the left of the termination is a stack of plates (the "stack") whose spacing is chosen to be a few thermal penetration depths.

In the upper half of Figure 2, a small portion of the stack has been magnified and a parcel of gas undergoing an acoustic oscillation is shown. The four steps in the cycle are represented by the two boxes which are shown as moving simply back and forth for clarity. As the fluid oscillates back and forth along the tube, it undergoes changes in temperature due to the adiabatic compression and

expansion resulting from the pressure variations which accompany the standing sound wave. The compressions and expansions of the gas which constitute the sound wave are adiabatic if they are far from the surface of the tube.

Figure 3 shows temperature-entropy diagram of the thermoacoustic refrigeration cycle. It is one of Braton cycle and obeys the limit of Carnot efficiency. It shows that cycle efficiency can be predicted by the theory of gas cycle.

Experiments in Japan

1) Measuring axial temperature distribution[4]

This experiment was aimed to understand thermoacoustic phenomena for the first step of our research. Fig. 4 shows experimental apparatus for study of thermoacoustic refrigeration. The driver is a 20W full-range speaker obtained from local electronics supply stores. Thermocouples are 0.2mm diam Copper and Constantan wires with insulation. The apparatus was simply constructed so that it can be easily assembled and readily inserted a small stack of plates, the thermocouple to measure axial temperature distribution. Pressure transducer was set at the right end of the tube to measure dynamic pressure amplitude.

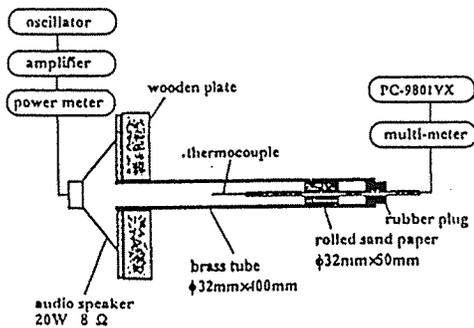


Figure 4 Experimental Apparatus for Thermoacoustic Refrigerator[4]

Axial temperature distributions, of air at the center of the tube without stack were shown in Figure 5. They are lowered with the decrease of sound frequency, and lowest temperature was gained at 180Hz of frequency which is equivalent to the relation tube length was about same as one-quarter wavelength. Lowest temperature was gained at the right hand side of the tube. Temperature gradually decreased right way.

Figure 6 shows axial temperature distributions when stack was inserted in the tube at the position where lowest temperature was gained at the precedent experiment. When we compare Figure 5 and 6, temperature difference with-stack is about four times larger than that of without-stack. Lowest temperature was measured at the left side of stack. In the sack, temperature sharply increased at the right way.

When stack is improved, operating pressure is increased, and Helium is inserted instead of air, we

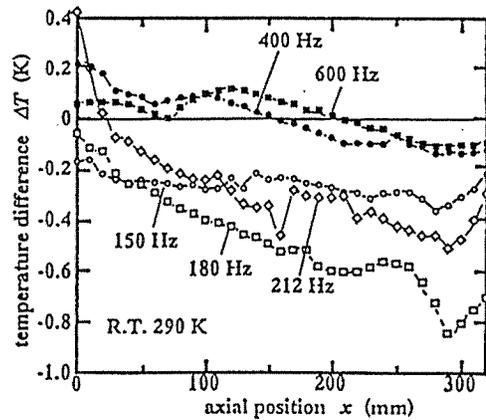


Figure 5 Axial Temperature Distribution[4] (without Stack)

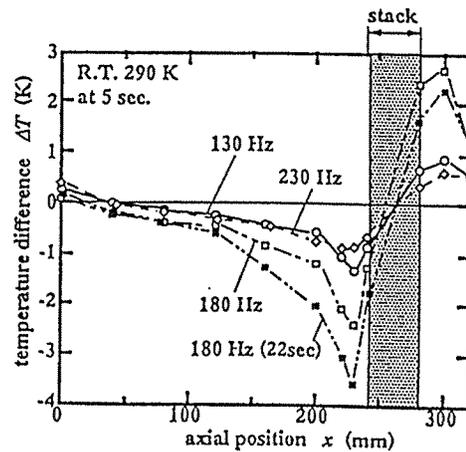


Figure 6 Axial Temperature Distribution (with Stack)[4]

think to be able to get high refrigeration capacity.

2) Relation of stack temperature and sound frequency[5]

This experiment was made to estimate the performance of thermoacoustic refrigeration cycle. Figure 7 shows an experimental apparatus to investigate a relation of stack temperature and wide-range of sound frequency. It was made as same size as Wheatly's acoustic refrigerator[6]. In the Figure, upper part is an acoustic driver and lower part is a resonator. The driver is conventional 50W input full-range speaker.

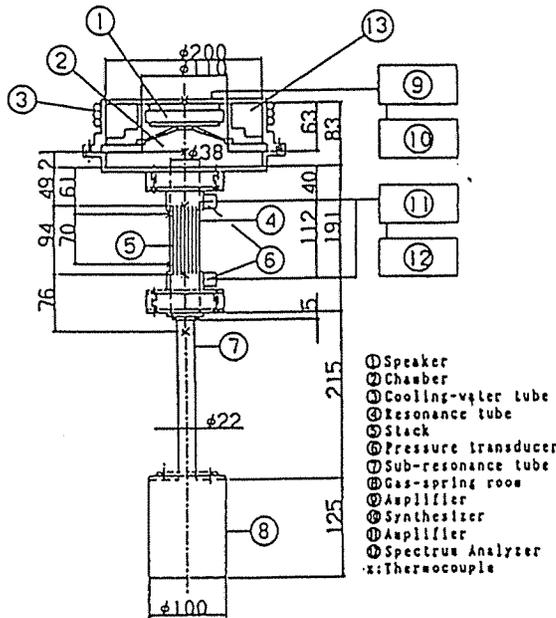


Figure 7 Experimental Apparatus for Thermoacoustic Refrigeration in High Pressure[5]

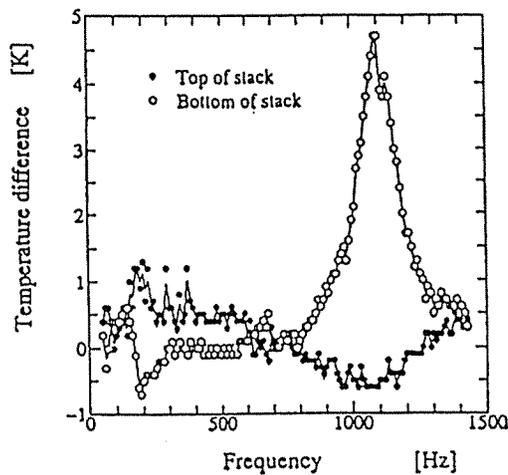


Figure 8 Relation of Stack Temperature and Driving Frequency[5]

Temperature difference between top and bottom of stack were measured, as shown in Figure 8. With another date of pressure amplitude and frequency, which is not shown, heat transfer phenomena occur when pressure amplitude varies along axial direction, and heat is transferred from low amplitude to high amplitude.

3) Thermally driven acoustic refrigerator[7][8]

An experimental apparatus was made to evaluate the usefulness of thermoacoustic refrigeration for cryogenics in space. The apparatus was made on the basis of the apparatus at Los Alamos National

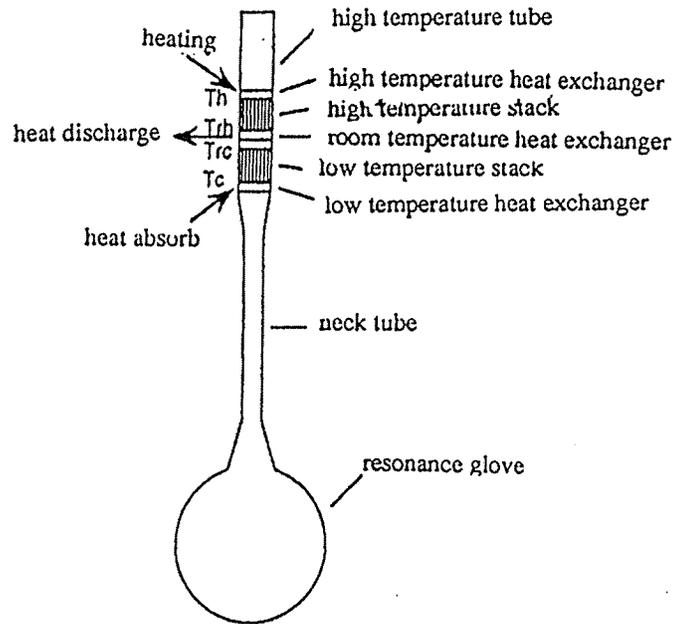


Figure 9 Thermally Driven Thermoacoustic Refrigerator[7]

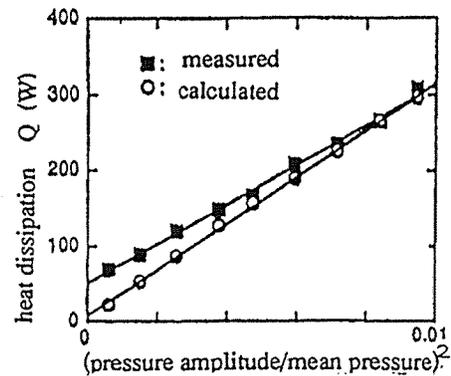


Figure 10 Relation of Pressure Amplitude and Heat Dissipation[7]

Laboratory.

Figure 9 shows a schematic diagram of experimental apparatus of thermally driven thermoacoustic refrigerator. Stack was constituted stainless steel plates. The length of the refrigerator was about 800mm. Helium gas inserted in the tube. High temperature heat exchanger was heated up to 570-670K. Generated frequency was around 300-400Hz.

Figure 10 shows experimental and analytical results of exhaust heat and pressure amplitude. Experimental results are well agreed to calculated results. This shows performances of thermoacoustic refrigerator can be predicted by theory.

Application

- cryogenics
- refrigeration in space
- home refrigerator
- air-conditioner

Benefits

- no-moving part
- oil free
- non-CFC
- compact
- light weight

Technical Issues

- acoustic driver
- high density stack
- compact heat exchanger
- insulation
- noise control
- large volume

Economics

Technology outlook

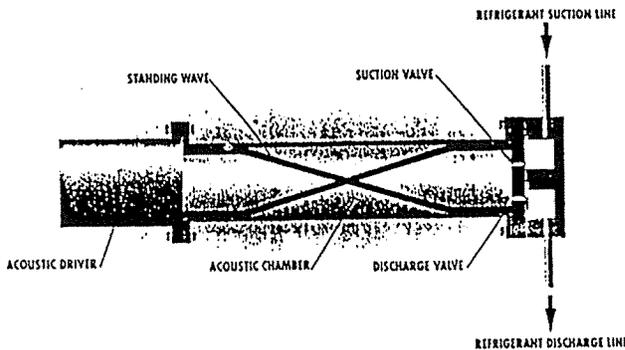


Figure 11 Acoustic compressor for refrigerator[1]

ACOUSTIC COMPRESSION

Any reports could not be seen in Japan. We just began to study sound resonator by our experimental apparatus. We are now in operation.

Technology Description

Figure 11 shows a schematic diagram of acoustic compressor for refrigeration cycle[1]. An acoustic driver sets up a sound wave that is converted into usable gas compression by the valves between the chamber and refrigerant lines. Refrigerant circulates to the condenser and evaporator through discharge and suction lines.

Figure 12 shows a refrigeration cycle using acoustic compressor[9]. It includes thermoacoustic refrigeration for subcooling of condensate refrigerant at the inlet of capillary tube. It is useful for the increase of refrigeration capacity. As is shown in Figure 13, enthalpy difference of evaporator increases from Δi_e to $\Delta i_e'$.

Application

- home refrigerator
- air-conditioner

Benefits

- oil free
- non-CFC
- no-moving part
- compact
- light weight

Technical Issues

- acoustic driver
- valves
- noise control
- large volume
- compact heat exchanger

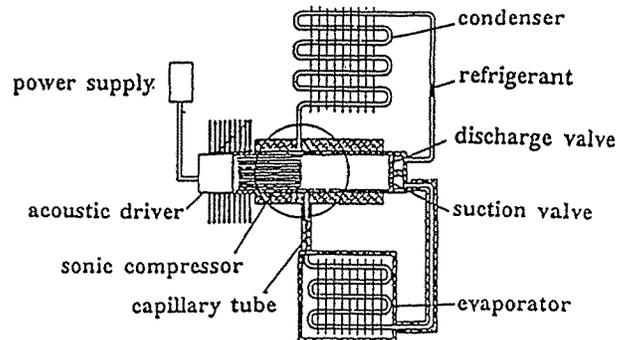


Figure 12 Refrigeration System with Acoustic Compressor[9]

WATER AS REFRIGERANT AND SECONDARY REFRIGERANT TECHNOLOGIES FOR THE PRODUCTION OF CHILLED WATER AND ICE-SLURRIES

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1. TECHNOLOGY DESCRIPTION

1.1 WATER AS REFRIGERANT ("ECOCHILLER")

The increasingly intense discussion about future refrigerants is creating headaches for manufacturers of refrigeration equipment, installers and especially for end-users. Whatever decision is taken today, the result may prove to be wrong at a later stage. There is a threat to many substances and no-one can really forecast the eventual solution.

The German "Umweltbundesamt - UBA" in Berlin (Federal Authority of the Environment) - has published a list some 3 years ago, which lists refrigerants according to their impact on the environment and this "hit-list" shows clearly, that among all substances only the following can be rated to be "safe" in the long run: **Water, Air, Ammonia, Carbon-Dioxide and Hydrocarbons.**

The other refrigerants have "unsafe" qualities, mainly in respect of ODP (Ozone Depletion Potential) and GWP (Greenhouse Warming Potential). The Montréal-Protocol covers the ODP only and although reduction of GWP is not yet mandatory it is generally agreed that further refrigerants will be eliminated. The question therefore is, what can be done to overcome the threats of phasing-out or restricting the use of certain refrigerants in the future? A perfect choice when it comes to environmental friendliness and safety is "WATER AS REFRIGERANT".

General Principle:

In this case the process needs no refrigerant of the conventional kind, but the water from the process itself is used to generate cooling. This means, that **water is itself the refrigerant!** This is certainly eye-catching and incorporates many of the considerations about the future of refrigerants. The process with "Water as Refrigerant" is similar to conventional cycles with the only difference, that subatmospheric pressure prevails (vacuum). This vacuum-process can be used to cool water, to generate (pumpable) ice-slurries or to operate as a heat pump.

Evaporation:

Water subjected to a low enough pressure evaporates and water is cooled or ice eventually produced by extracting the evaporating enthalpy from the water. The evaporation can best be described as "flash-evaporation". Since the flash-vapour and the water to be cooled or frozen are of the same origin, a heat exchanger is not necessary, which makes the evaporator an empty vessel without need of heat transfer surfaces.

Compression:

The generated vapour must be removed by using either mechanical compressors with electric motors or thermal compressors working with steam as driving energy source. The compressed vapour is liquefied in the condenser. The compression-ratio of the compressor must be high enough to meet the necessary condensing pressure. Since the specific volume of water vapour is extremely high, centrifugal machines or ejectors are commonly applied, since positive displacement compressors will be too small.

Condensation:

The condenser can be cooled either by

- cooling-water or by a
- conventional refrigeration plant.

Indirect condensation can be achieved by either using a conventional refrigeration plant or by cooling water in a surface condenser. Direct condensation can be achieved by spraying cooling-water directly into an (empty) condenser vessel, thereby avoiding this heat exchanger completely. Depending on the application this is the most advanced and energy-efficient method to produce chilled water or ice. Expensive heat exchanger surfaces can be omitted completely, neither the evaporator nor the condenser require such installations, fouling is completely avoided and heat transfer-losses will not occur.

Further Remarks:

Since no heat exchanger on the "dirty" evaporator-side is needed, any kind of water can be cooled or transformed into Binary Ice, there is no problem even with sewage water! The condenser-side with or without heat exchanger does not suffer from contaminated water, since the evaporation is at the same time a distillation process which yields pure, distilled water on the condenser-side and keeps it clear.

The vacuum-process works at subatmospheric pressure which means at the same time, that no pressure-vessel regulations apply. This makes the operation of the vacuum-machine simple and easy, since testing and repeated inspections are unnecessary. In order to maintain the pressure in the system and to remove non-condensable gases (NCGs), a vacuum-pump is connected to the condenser.

1.2 ICE-SLURRY AS SECONDARY REFRIGERANT ("BINARY ICE®")

Binary Ice® is a suspension of small ice-crystals in water. These ice-crystals show a "binary" behaviour, i.e. they are either in the *frozen* or in the *melted* state. The typical size of such crystals is between 0,1 and 0,5 mm, mainly depending upon water quality, generation temperature and other side-effects. Binary Ice has unique properties as a secondary refrigerant (coolant). Regardless of the technology to generate Binary Ice, this fluid combines the advantages of direct expansion cooling with a refrigerant, and the easiness and simplicity of water- or brine systems. Binary Ice has a very high energy density, superior heat transfer properties and is environmentally "safe".

Looking at the macroscopic properties of Binary Ice, this fluid at low concentrations (abt. 20 %) has the properties of pure water showing, however, an energetic density which is already some 450 % better than of chilled water at 12/6 °C. At 40 % concentration (energetic density already abt. 700 % higher), Binary Ice still flows like a fluid, however with a higher "virtual" viscosity. From 40 % concentration upwards, the fluid becomes increasingly "richer" and turns into heavy slush at abt. 70 %. This concentration is too high for transportation with normal pumps. From 90 % upwards, the ice is "dry" and can be used like ordinary ice.

Binary Ice can be produced with the

- **VACUUM-ICE** Process ⇒ *Water as Refrigerant*
- **FLO-ICE®** Process. ⇒ *Working with any Refrigerant*

Any process to generate Binary Ice needs a small amount of a substance to depress the freezing point of the solution. These substances can be found in the water itself (NaCl and other minerals) or must be added (e.g. glycol, minerals). The quality of the ice/water-mixture depends on the type and amount of such substances, which enables the user to "adjust" the ice-quality within certain limits.

2. APPLICATION

2.1 WATER AS REFRIGERANT ("ECOCHILLER")

The ECOCHILLER-concept can be applied for any kind of

- Water Cooling *Chiller*
- Ice-Generation *Binary Ice Machine*
- Heat Generation *Heat Pump*

The majority of refrigeration installations above 0 °C is working as water chillers which can be realized with "Water as Refrigerant".

2.2 ICE-SLURRY AS SECONDARY REFRIGERANT ("BINARY ICE")

BINARY ICE is an ideal secondary refrigerant (coolant) for transportation of cold energy, storage of ice and efficient heat transfer. Refrigeration plants will not use direct expansion in a large number of evaporators any more (refrigerant charge and/or quality of refrigerants s.a. ammonia, hydrocarbons etc.) but rather perform indirect cooling with a secondary refrigerant for distribution of "cold" energy.

Fig. 1 shows the design principles of refrigeration plants in relation to the above statements. The indirect systems with a coolant and systems using substances as mentioned under 1) will have the biggest potential. Together with hermetic design and small refrigerant charge, the TEWI will be lowest and the choice of such a plant will most likely prove the best. For bigger capacities, water as refrigerant shows unique properties when it comes to energy consumption, environmental friendliness and flexibility.

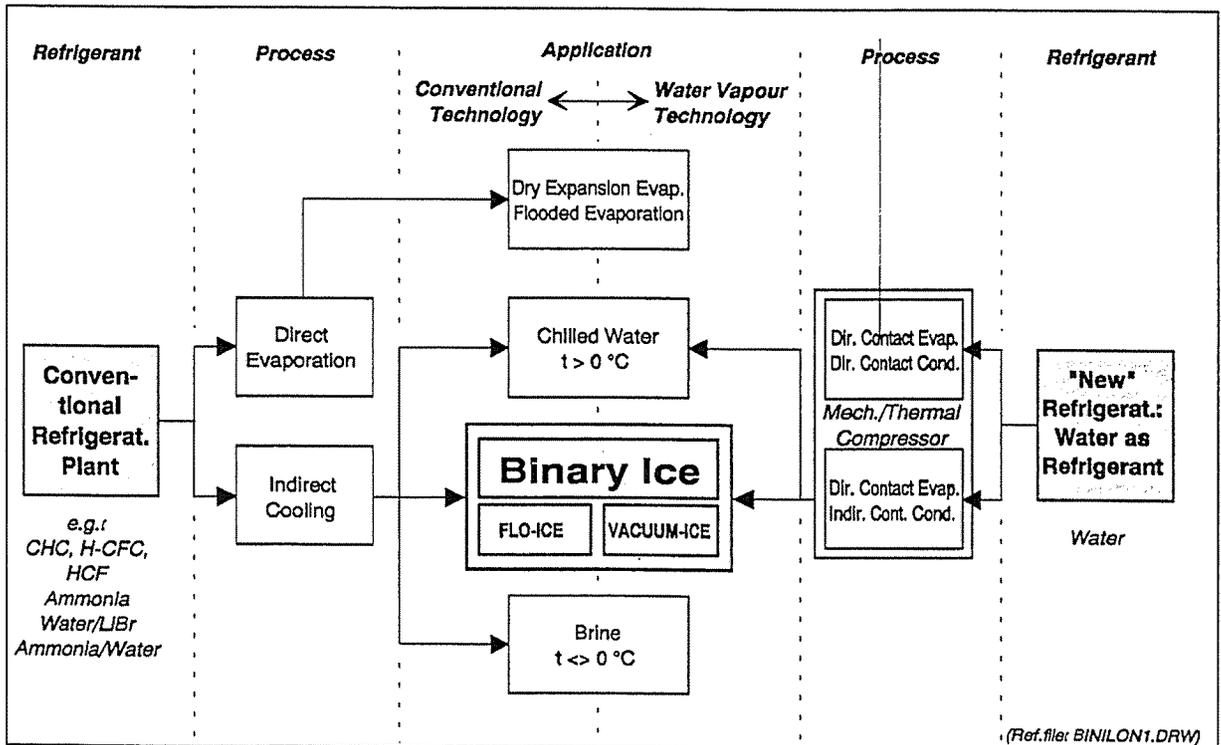


Fig. 1: Ways to Generate Cooling

3. BENEFITS

3.1 WATER AS REFRIGERANT ("ECOCHILLER")

Water is an excellent refrigerant whose virtues cannot be neglected. Water shows superior qualities which can be expressed as:

- unmatched environmental friendliness
- unlimited availability
- insensitive to water-quality and water pollution
- insensitive to leakages (vacuum)
- generation of pumpable ice-slurry is possible at $\sim 0^{\circ}\text{C}$
- wide operating range (ice, chilled water, high-temp. heat pumps)
- absence of heat exchangers and pressure vessels
- simple operation, few moving parts
- excellent energy efficiency.

However, some of the drawbacks should also be mentioned. These are:

- space requirements (high specific volume)
- high volumetric flow and high pressure ratio.

The **energy efficiency** of "Water as refrigerant" is very good. The absence of heat exchangers reduces heat transfer losses. This is an intrinsic value of the process, saving some 10 K in temperature lift. Furthermore, scaling or fouling cannot occur which assures over the plant's service-life unchanged heat exchange qualities without "fading" of operating temperatures.

3.2 ICE-SLURRY AS SECONDARY REFRIGERANT ("BINARY ICE")

Binary Ice is an efficient secondary refrigerant which is superior to chilled water or brine. The main virtues are:

- high energetic density
(approx. 3 - 7 times higher than of water)
- only small pumps and small pipes are needed for transport
- very good heat transfer properties, smaller heat exchangers
(3 - 6 times better than of water)
- storage of cold energy is easily and cheaply possible
- reduction of installed refrigerating capacity possible
(reducing size and - in the case of FLO-ICE - refrigerant charge)
- lower condensing temperature during night operation
- use of latent energy makes heat exchanger calculations simple
(no oversizing of heat exchangers)

The **energetic balance** of Binary Ice systems can be improved significantly, if the following points are taken into consideration:

- colder air requires less volume and therefore less fan power
- thermal losses are smaller
- night-operation results in lower condensing temperature
- no ON/OFF operation, part-load does not occur
- special "NIMI"-arrangement assures during discharge operation a high evaporating temperature
(NIMI = "Non Ice Making Ice Generator" - Pat. Pending)

4. TECHNICAL ISSUES

4.1 WATER AS REFRIGERANT ("ECOCHILLER")

The process of using "Water as Refrigerant" is straight forward and basically not too complicated. The main component is the mechanical compressor, which is not readily available on the market. Its volumetric flow and the pressure ratio are very high. The following figures give a brief impression:

| Operation: Temperature-Range: | Binary Ice Maker 0/40 °C | | Water Chiller 6/32 °C | | Heat Pump 40/70 °C | |
|----------------------------------|-----------------------------|-------------------|--------------------------|-------------------|-----------------------|-------------------|
| • Volumetric Flow: | | | | | | |
| for 10 kW: | 3.000 | m ³ /h | 2.000 | m ³ /h | 300 | m ³ /h |
| 100 kW: | 30.000 | m ³ /h | 20.000 | m ³ /h | 3.000 | m ³ /h |
| 1.000 kW: | 300.000 | m ³ /h | 200.000 | m ³ /h | 30.000 | m ³ /h |
| 5.000 kW: | 1.500.000 | m ³ /h | 1.000.000 | m ³ /h | 150.000 | m ³ /h |
| • Pressure Ratio: | | | | | | |
| | 7,5 | | 5,3 | | 4,0 | |

Table 1: Specification of Water Vapour Compressors

Such compressors can be built in many different ways. Size, arrangement(s), weight and sensitivity towards droplet carry-over determine the basic design features of such machines. It is a major demand to size such compressors in a way that they - together with the evaporator and condenser - fit into existing machine-rooms.

Another technical issue is the height of the installation. Vacuum equipment is generally "bulky" and needs therefore space. On the other hand - since these vessels are "empty" - no reserve space has to be foreseen to clean (non existing) tubes or to cater for space to replace such tubes. This is an advantage. Since the pumps extract the chilled and the cooling water from vessels which are under vacuum, the NPSH is very small, for which provisions have to be taken.

4.2 ICE-SLURRY AS SECONDARY REFRIGERANT ("BINARY ICE")

As already mentioned, Binary Ice machines can be divided into two different processes which are:

- VACUUM ICE or
- FLO-ICE.

Both machines produce in principle the same kind of pumpable ice-slurry and the only difference is the capacity of the machines. Vacuum-Ice is produced with "Water as Refrigerant" for capacities from some 500 kW on, whereas FLO-ICE has today a refrigerating capacity of some 100 kW and soon up to 500 kW. The range of capacities is then covered from very small (starting at 1 kW) to very large (approx. 5 MW) and today's biggest ice-maker supplies 3 MW of cooling (660 TR = tons of ice per day).

Technical issues for the Vacuum-Ice machine are in principle the very same as for "Water as Refrigerant" (see above). The development and enlargement of available capacities for FLO-ICE machines are merely a design question and are not worth being mentioned under the headline of this chapter. On the other hand, properties of Binary Ice, storage and handling issues as well as additives for the fluid are not yet fully investigated and are worth to be considered further.

5. ECONOMICS

5.1 WATER AS REFRIGERANT ("ECOCHILLER") AND VACUUM-ICE MAKERS

Water Chillers:

It is difficult to compare first costs of Ecochiller-plants at the present state-of-the-art and to standard chillers with many decades of development incorporated in today's design. The target price is clear: Standard chiller level.

Since both Ecochillers and standard chillers need evaporators and condensers, the major component to deal with is the compressor which is different from those transporting refrigerant. Today's price level for vapour compressors is certainly many times too high.

The following table summarizes briefly figures for main components indicating today's price level and the forecast for future components:

| | Standard Chillers | Ecochillers (Water as Refrigerant) | |
|--------------------------|----------------------------------|------------------------------------|-----------------|
| | <i>Conventional Refrigerants</i> | <i>today</i> | <i>tomorrow</i> |
| • Evaporator | 100 | 50 | 40 |
| • Condenser | 100 | 50 | 40 |
| • Electrics and Controls | 100 | 200 | 150 |
| • Piping, Insulation | 100 | 300 | 250 |
| • Assembly, Steel-work | 100 | 200 | 200 |
| • Compressor | 100 | 800 | 300 |
| • TOTAL | 600 | 1.600 | 980 |

Table 2:
First Costs for Standard Chillers and Ecochillers ("Water as Refrigerant")

As can be seen easily from table 2, the main target is the compressor which governs the whole issue of first costs. Such machines are not readily available and must be developed.

Vacuum-Ice Makers:

If it comes to ice makers the target price is higher, since other ice-makers need also additional equipment and the specific price is therefore higher. On the other hand, the pressure ratio for the vapour compressor and its swept volume is necessarily bigger. This issue is not investigated in more detail in this paper.

5.2 FLO-ICE AS SECONDARY REFRIGERANT ("BINARY ICE")

The statements made here refer only to FLO-ICE makers in the lower capacity range. For this technology a wealth of practical experience is already available and it has shown until now, that the calculation of first costs looks different to the one in table 2. In principle, Binary Ice machines do not compete with chillers directly but must be evaluated differently when it comes to first costs and operating costs. Ice machines are mainly installed to cut down installed refrigerating capacity and to store thermal energy. Therefore the comparison between installed capacities would be wrong and "useful" refrigerating capacities must be compared instead.

There is hardly a difference between chillers and FLO-ICE installations, since the higher specific first costs are compensated by the smaller installed capacity. If e.g. coolers, pipework, energy costs etc. are taken into account, FLO-ICE installations have always shown a very competitive position.

6. TECHNOLOGY OUTLOOK

6.1 WATER AS REFRIGERANT ("ECOCHILLER") AND VACUUM-ICE MAKERS

"The future has already begun". Ecochillers and Vacuum-Ice makers have already been installed and withstood competition. However, since the specific price is high today such installations have been of interest to customers where the benefits of the technology were dominating the decision making.

After having gained experience in design and operation of plants with "Water as Refrigerant" the development aims now at the compressor. A "Development Team" incorporating external experts with international reputation has been formed. "Launching Customers" (as aircraft manufacturers call an airline involved in the definition of design criteria) assist in the project. The following table lists the development team's set-up and the development plans:

| Development Team | Development Plan |
|--|--|
| <ul style="list-style-type: none">• INTEGRAL• Research Institutes• Design Experts• Material Experts• Scientists• Manufacturers• "Launching Customers" (Users)• Contractors• Utilities• Consulting Engineers | <ul style="list-style-type: none">• Evaporator Design• Condenser Design• Compressor Design<ul style="list-style-type: none">• Fundamental Design• Detailed Design• Cost Analysis• Electric and Controls• Auxilliary Equipment• Documentation, Computer Programs• Market Analysis |

The project is on its way and in different stages. Further details cannot be released. However, a qualified contractor's application for participation in the project can be considered.

6.2 FLO-ICE AS SECONDARY REFRIGERANT ("BINARY ICE")

FLO-ICE is already in the commercialization phase for the smaller capacity range (up to approx. 100 kW). Development for capacities up to approx. 500 kW is on its way and shall be finished in 1994. There will still be ongoing projects for the handling of ice and for peripheral equipment s.a. concentrators, ice-concentration meters etc. Again, qualified contractors are invited to apply for cooperation.

(BINIORNL.DOC)

Binary Ice® is the Trade Mark of INTEGRAL Technologie GmbH/Flensburg, *FLO-ICE*® is the Trade Mark of Solmecs FLO-ICE Systems/London.

OUTDOOR AIR AND GROUNDWATER AS NATURAL SOURCES FOR COOLING.

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Danish Energy Analysis A/S

Introduction.

The purpose of this paper is to discuss ideas and proposals for cooling without the use of refrigerants as CFC's by the utilization of the natural changes in outdoor air temperature during a day and the uniform temperature of groundwater during the year. The cooling methods mentioned in the paper can be used for air-conditioning, chillers and process cooling at moderate temperatures, but they can not be used to replace freezers and other cooling machinery with evaporation temperature below 0 deg. C.

The use of alternative cooling sources as outdoor air and groundwater means at the same time a reduction in the use of refrigerants and a reduction in the electricity consumption in comparison to cooling compressors. As a consequence of the reduction in electricity consumption there will be a reduction in CO₂-emission to the atmosphere in case of power production based on fossil fuels.

Technology Description

In zones of climates with average air temperature during a year below appr. 16 deg. C there is a potential for a direct utilization of outdoor air and groundwater as a replacement or supply to traditional compressor cooling. Roughly spoken, it will be possible to utilize such natural cooling sources north of the Tropic of Cancer and south of the Tropic of Capricorn as illustrated in figure 1, but outdoor air cooling can also be used in climates with large temperature differences between day and night in combination with cold storage. In relation to cooling, groundwater has the advantage to outdoor air, that the temperature of the groundwater in the upper reservoirs is constant throughout the year and equal to the average air temperature at the surface of the ground. In figure 2 the temperature profile is shown for a typical danish soil. The variation in temperature as a function of depth is almost died away 10 meters below surface.

Groundwater situated more than 10 meters below surface therefore has a constant temperature throughout the year. The geothermal gradient has no significant influence on the groundwater temperature in near surface aquifers.

Similar temperature profiles are valid for the most of earth soils.

Cooling with outdoor air.

In figure 3 a traditional air conditioning system is shown. The air is cooled by a CFC cooling compressor installation with e.g. R22 as refrigerant.

In figure 4 the air conditioning system is supplied with a cooling tower or a dry-cooler with the intention of utilize the outdoor air as coolant. When the outdoor air temperature is sufficient low the circulation pump in the outdoor circuit is switched on and the cooling compressor is stopped. The procedure is reversed when the outdoor air temperature is too high. The cooling compressor installation can be provided with a very small amount of coolant by using water cooled evaporator and condenser. In disadvantage, the electricity consumption for the compressor increases in consequence of the extra heat exchangers.

Cooling with outdoor air in combination with cold storage.

Figure 5 shows a cooling system with a demand for cooling only in daytime. In such cases the outdoor air system can be combined with a water tank or a water bassin to utilize cold outdoor air at night, to cool down water in the storage for daytime use. Hereby it is possible to avoid the use of traditional CFC compressor cooling.

Cooling with groundwater.

A compressor installation for process cooling is shown in figure 6.

For process cooling (and air-conditioning) groundwater is however a promising alternative to compressor chillers.

The uniform temperature of the groundwater can be used when the demanded cooling water temperature is above the groundwater temperature. A groundwater based alternative to the chiller installation in figure 6 is shown in figure 7. The groundwater is pumped from a well to a heat exchanger, where the groundwater is heated some few deg. C by heat exchange with the return process cooling water. After warming up, the groundwater is returned to the reservoir through another well some distance apart from the pumping well. Because of returning the groundwater into the aquifer there is no net use of groundwater.

In addition, aquifers situated in sand formations are normally good as heat and cold storages both on short term and seasonal basis, which can be used in connection with outdoor air cooling when the cooling demand varies throughout the day or throughout the year.

Figure 8 shows a plant where the aquifer is charged with groundwater cooled by outdoor air in nighttime or in wintertime.

In daytime or in summertime when there is a cooling demand for air-conditioning or process cooling the cooled groundwater is recharged from the aquifer by reversing the flow direction (figure 9). As a consequence of this operation mode a thermal balance situation can be achieved within a small reservoir volume.

Applications.

Cooling based on outdoor air and groundwater can be used for air-conditioning and process cooling with moderate demands for the temperature of the process cooling water (>0 deg. C). In addition groundwater cooling can be combined with heat- and

cold storage in buildings, when there is a need for both heating and cooling.

Benefits.

The described alternatives give a possibility to replace traditional compressor cooling with cooling systems without the well-known CFC refrigerants. In the same time the alternatives represents an important potential for energy savings. At danish climate conditions the reduction in electricity consumption can be reduced with more than 50% for e.g. computer mainframe cooling in comparison to compressor cooling. For installations based only on groundwater cooling the savings in electricity can be more than 75%. The electricity savings furthermore means a reduction in emission of CO₂ where the power production is based on fossil fuels.

Technical Issues.

Cooling with outdoor air.

An increased use of outdoor air as coolant hardly gives difficulties in a technical or environmental matter. However, limitations in the placing possibilities and noise reduction of fan blowers can be the major obstacle for a widespread use in densely populated areas.

Cooling with outdoor air in combination with cold storage.

Technical or environmental issues will properly not create major obstacles for a more widespread utilization of outdoor air cooling plants with cold storage. By outdoor placing of cold stores e.g. steel-tanks there can be some problems in finding sufficient space for the installation and there can be some aesthetic conditions that must be taken into consideration.

By indoor situated open water bassins it can be nessesary to add some chemicals to the water to prevent scaling and corrosion. Indoor placing of storage tanks or bassins is of practical reasons most attractive in combination with new building construction. Bassins normally will be more expensive than steel tanks.

Cooling with groundwater.

A more widespread use of groundwater for cooling and cold storage means a thermal impact of the used aquifers, caused of the temperature difference in comparison to the natural groundwater temperature.

A rise or lowering of groundwater temperature with a few deg. C will not cause any difficulties in a technical matter with respect to groundwater circulation.

Injection of heated groundwater means a theoretical possibility in growth of the original population of microorganism in the aquifer around the wells. However, investigations of different soils samples have shown, that the problem do not arise if no feed for the microorganism is added to the aquifer. The technical installations and well casings therefore must be kept airtight.

Growth of microorganism as a consequence of temperature rise will not give technical or environmental problems when no food for the microorganism is added to the circulated groundwater.

Every groundwater well penetrates the layers of soil above the aquifer. Groundwater wells therefore create a direct contact between surface and groundwater reservoirs. Surface pollution nearby wells gives of that reason a greater potential for groundwater pollution. Therefore drilling of wells and completions of wells must be carefully carried out to prevent percolation of surface water along the outside of well casings. Another obstacle is the local availability of groundwater regarding the depth to usable groundwater and the chemical composition of the groundwater. Of these reasons groundwater cooling will not be a technology, which can be used everywhere, but must be considered with respect to the hydrogeological possibilities and other local interests in each single case.

From investigations and practical experiences it must be concluded that the use of outdoor air and groundwater for cooling will not give special technical problems for a more widespread use.

Economics

Cooling with outdoor air.

In case of air cooling systems which are in operation throughout the year e.g. computer cooling (figure 4) the simple pay-back time in Denmark is 1.5 to 2 years by adding dry coolers to existing compressor cooling installations. The savings in electricity consumption in comparison to compressor cooling is about 50%.

Cooling with outdoor air in combination with cold storage.

By replacing existing cooling compressors with an outdoor air cooling system in combination with a tank storage the pay-back time for the investment is strongly dependent of the driving temperature difference that can be achieved between "cold" and "warm" water in the tank. In addition, the pay-back time depends of the specific price on storage volume, electricity pricing, efficiency of pumps, cooling yield and Coefficient Of Performance (COP) for the cooling compressor installation which the alternative installation can be compared to.

In case of replacing a CFC cooling plant for air-conditioning (figure 3) with a system based only on outdoor air with cold storage (figure 5) the investment costs mainly depend on installation of the storage tank (when the air cooler for the condenser can be reused).

Figure 10 shows the result of an analysis concerning the profitability of storage tank installations depending on temperature difference between cold and warm water in the store. The system analysed has an operation time for cooling and cold storage of 4380 hours/year.

By new construction of buildings when it is possible to choose between the installation of traditional compressor cooling or cooling with outdoor air in combination with cold storage tanks the extra investment costs in the latter alternative approximately reduces the pay-back time to 50% of the values in figure 10.

The economics in open basin stores have not been analysed in this work, but they will probably be more expensive than tank stores.

Cooling with groundwater.

The costs of drilling wells for a groundwater cooling system are depending on the local hydrogeological conditions. The necessary depth of drilling is an important parameter for the profitability. Investigations for Danish hydrogeological conditions have shown specific, total installation costs of about 250 to 400 US\$ per kW cooling yield in case of larger groundwater cooling systems (above 1 MW cooling performance). The costs are comparable to installation costs for compressor cooling systems.

When groundwater cooling is established as a supplement to a compressor cooling plant the simple pay-back time in Denmark is 2-4 years due to the saving in electricity. Electricity price for industrial use is approx. 0.06 US\$ per kWh in Denmark.

Technology Outlook.

Cooling with outdoor air.

Cooling with outdoor air in addition to cooling compressor operation is established in a number of commercial and industrial plants. The technology is developed and accessible PLC- and PC-based regulation systems are in the market. The concept is therefore commercial available. In relation to the use of CFC the solution normally means no direct reduction, because it is in the most situations necessary to retain a compressor cooling installation. The market penetration is relatively low but greater for commercial use than for industrial use. The potential for new installations seems to be large.

Cooling with outdoor air in combination with cold storage.

The technology is in use in e.g. Saudi Arabia. The concept is commercial available but the current market penetration is low because of the high establishment costs. The potential seems to be large and will probably be largest for air-conditioning installations because most process-cooling plants demand continuous cooling.

Cooling with groundwater.

The concept is used in several countries e.g. U.S., Canada, Holland, Sweden, and The Public Republic of China. The market penetration is low for the moment, but largest in commercial cooling (building and computer cooling). Only few plants are established for industrial cooling processes.

The market penetration is low. The market potential seems to be large, but plants can not be situated everywhere.

A number of the established plants have been in operation for a number of years without major difficulties.

List of references.

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- 2) "Free Cooling in Refrigeration Plant for Comfort Purposes". Holtze, B. VVS Denmark, April 1992, Vol. 28, no. 5.
- 3) International Energy Agency (IEA): "Implementing Agreement for a Programme of Research and Development on Energy Conservation through Energy Storage". Annex VI: "Environmental and Chemical Aspects of Thermal Energy Storage in Aquifers and Research and Development of Water Treatment Methods", July 1991.

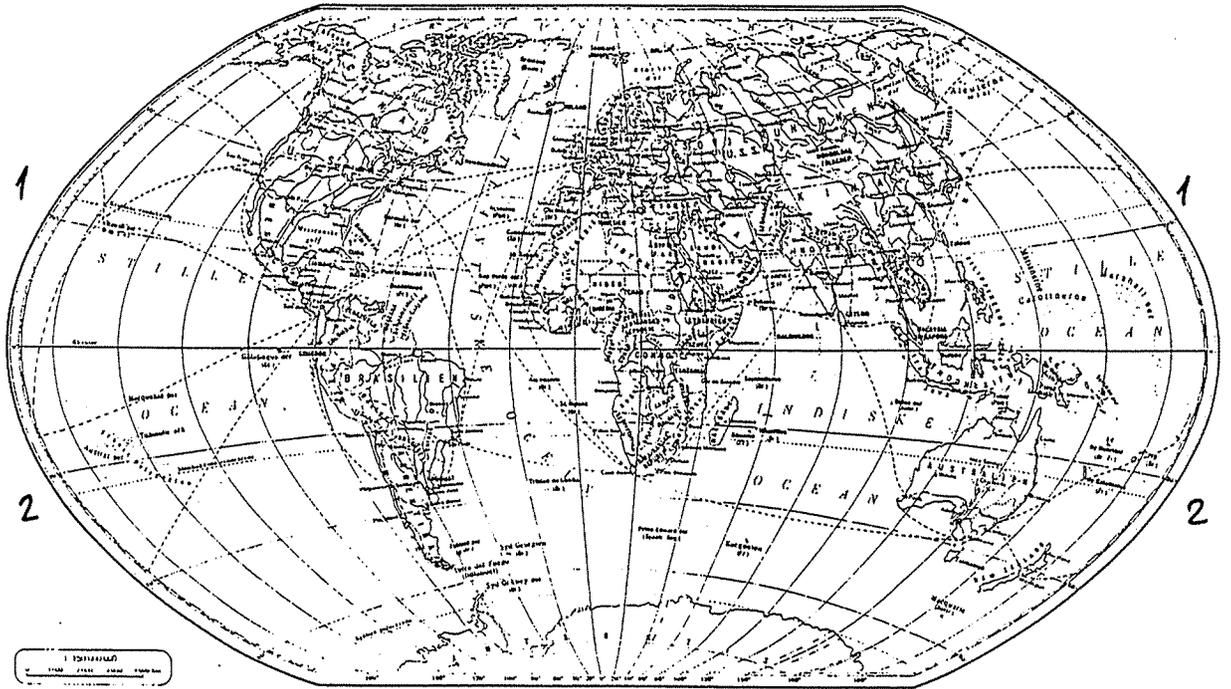


Figure 1. Possibilities of a direct use of outdoor air and groundwater for cooling. 1) Tropic of Cancer. 2) Tropic of Capricorn.

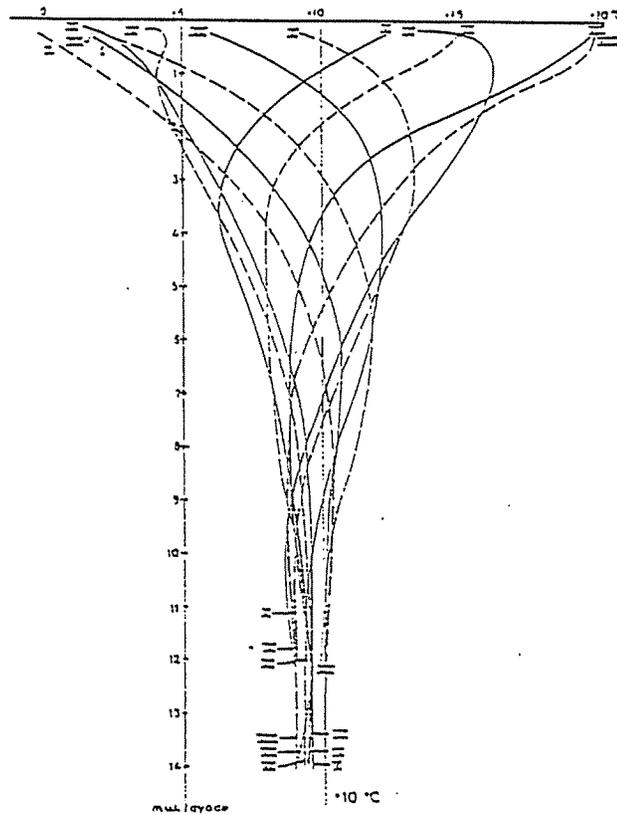


Figure 2. Temperature profile in a danish soil.

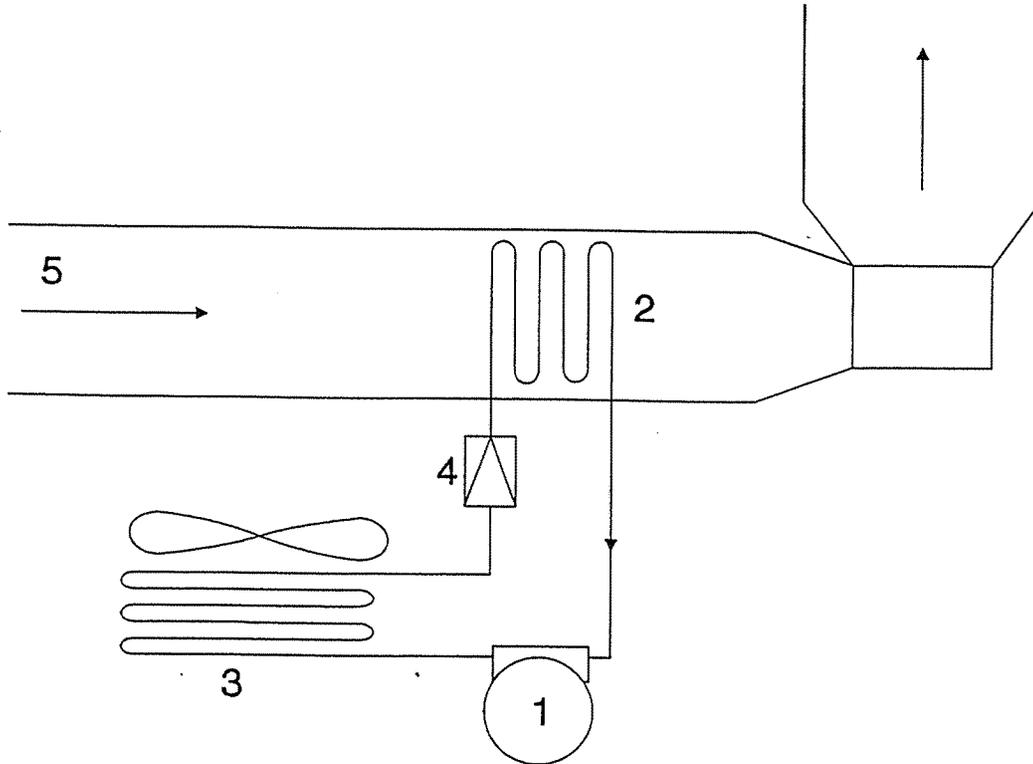


Figure 3. CFC cooling plant for air conditioning. 1) compressor. 2) evaporator. 3) air-cooled condenser. 4) expansion well. 5) ventilation air.

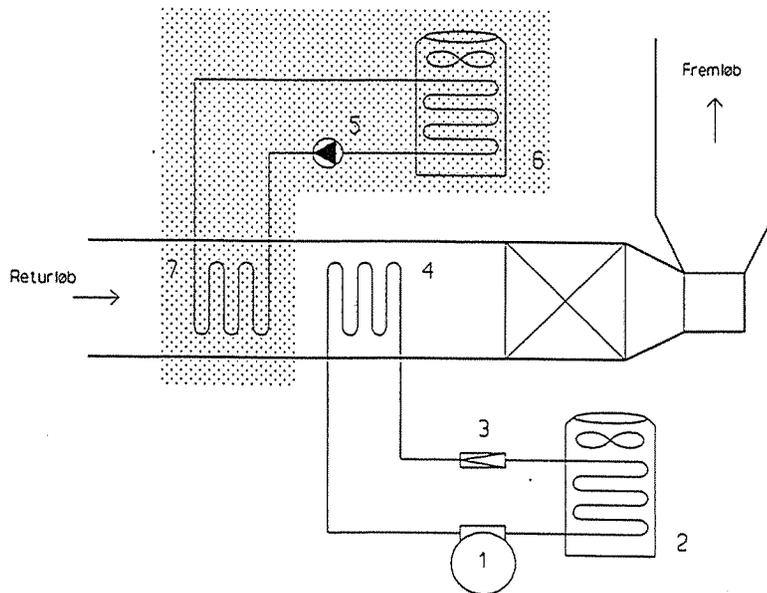


Figure 4. CFC cooling plant for air-conditioning in combination with outdoor air cooling. 1) compressor. 2) air-cooled condenser. 3) expansion valve. 4) evaporator. 5) circulation pump. 6) dry-cooler. 7) heat-exchanger.

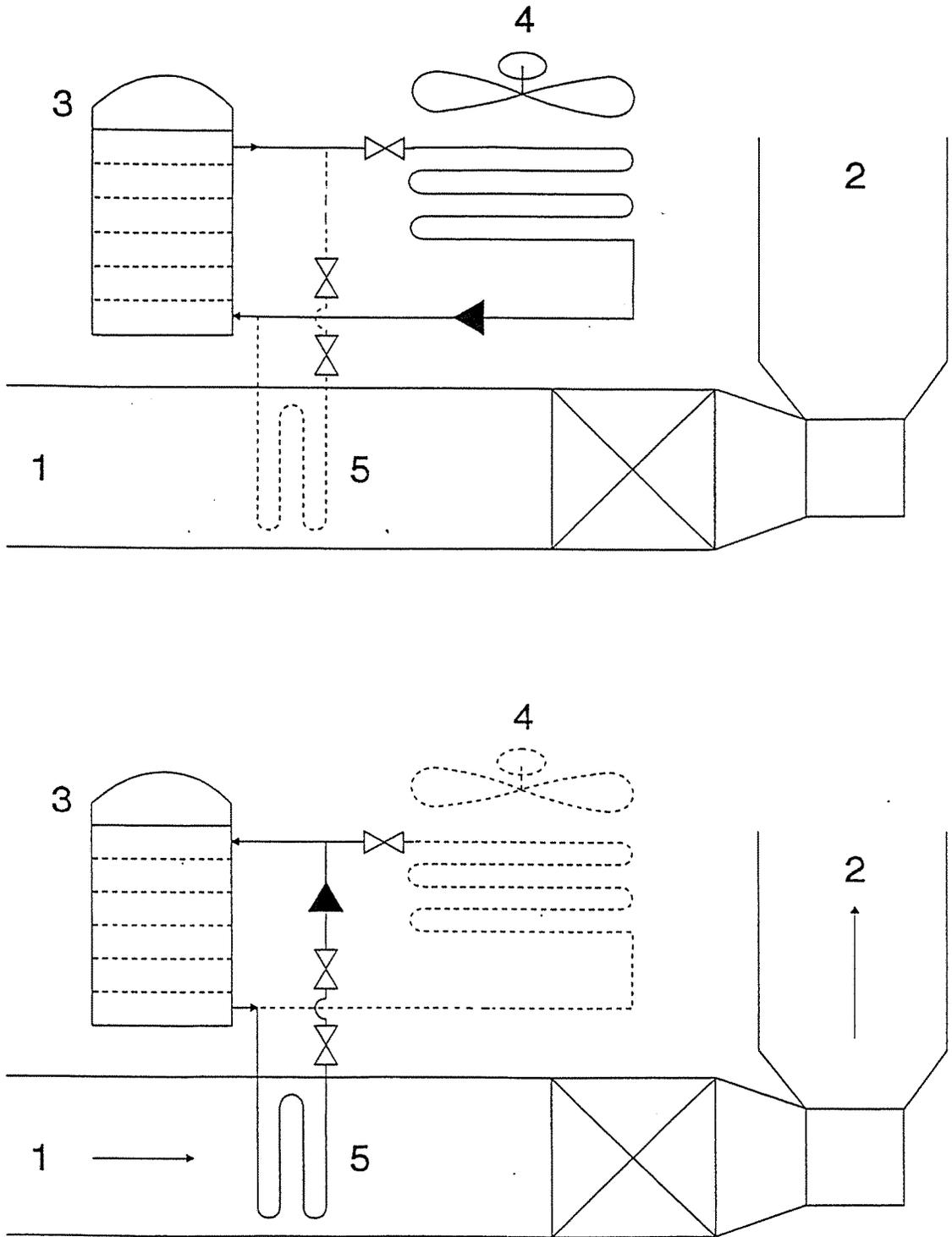


Figure 5. Outdoor air cooling without CFC compressor cooling. 1)+2) ventilation air. 3) water storage. 4) fan. 5) heat exchanger.

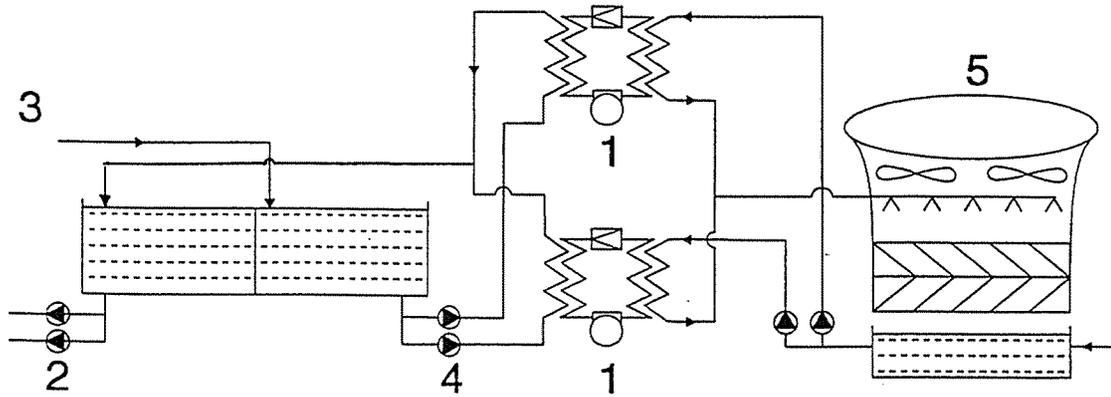


Figure 6. CFC cooling plant for process cooling. 1) compressors. 2) process cooling water pumps. 3) process cooling water return. 4) water circulation pumps. 5) cooling tower.

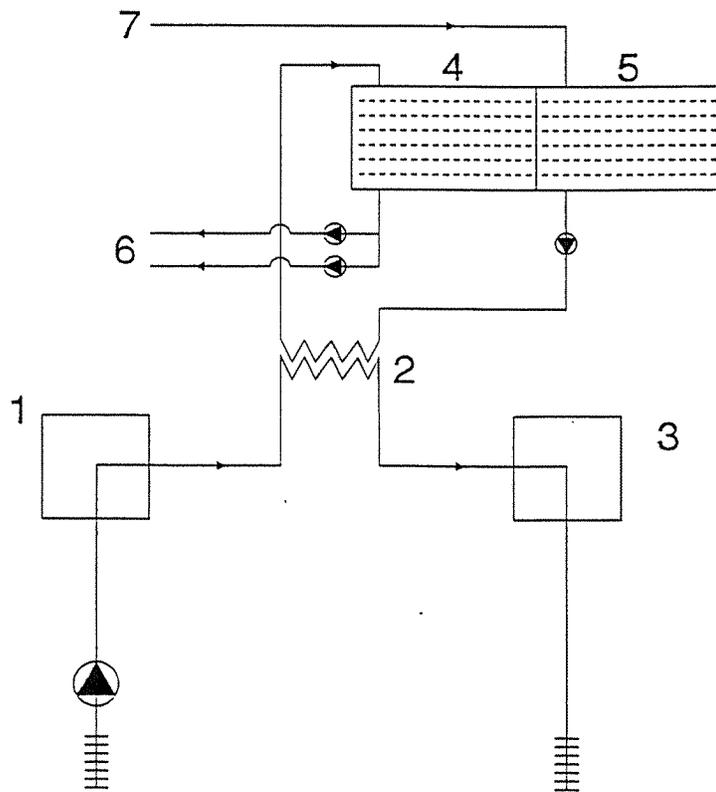


Figure 7. Groundwater used for process cooling. 1) pumping well. 2) heat exchanger. 3) return well. 4) cold water storage. 5) warm water storage. 6) process cooling water. 7) process cooling water return.

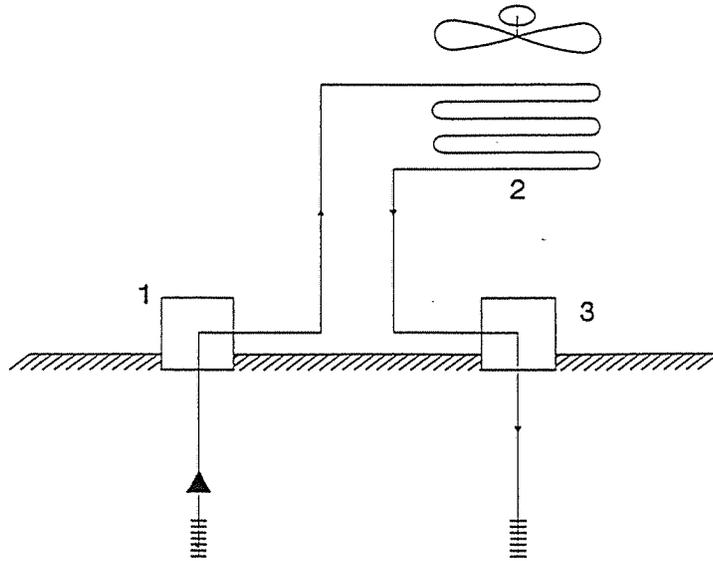


Figure 8. Loading the aquifer with outdoor cooled groundwater: 1) pumping well. 2) dry cooler. 3) return well.

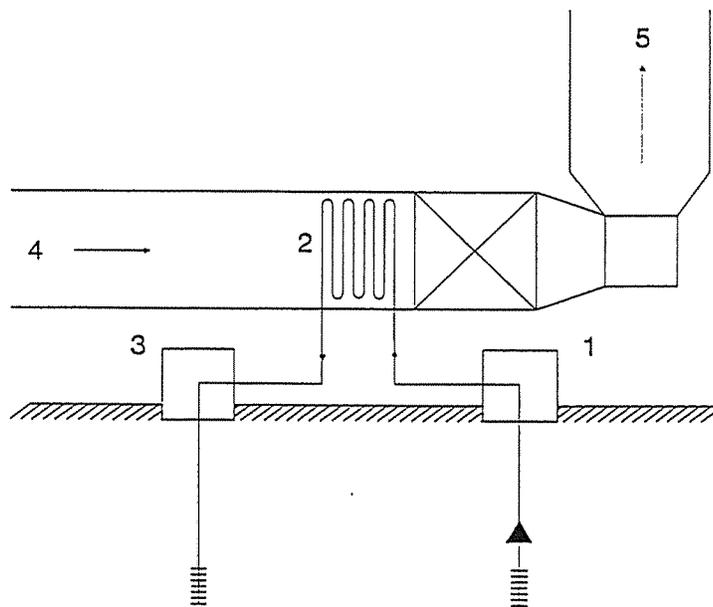


Figure 9. Unloading cooled groundwater from the aquifer. 1) pumping well. 2) heat exchanger. 3) return well. 4)+5) ventilation air.

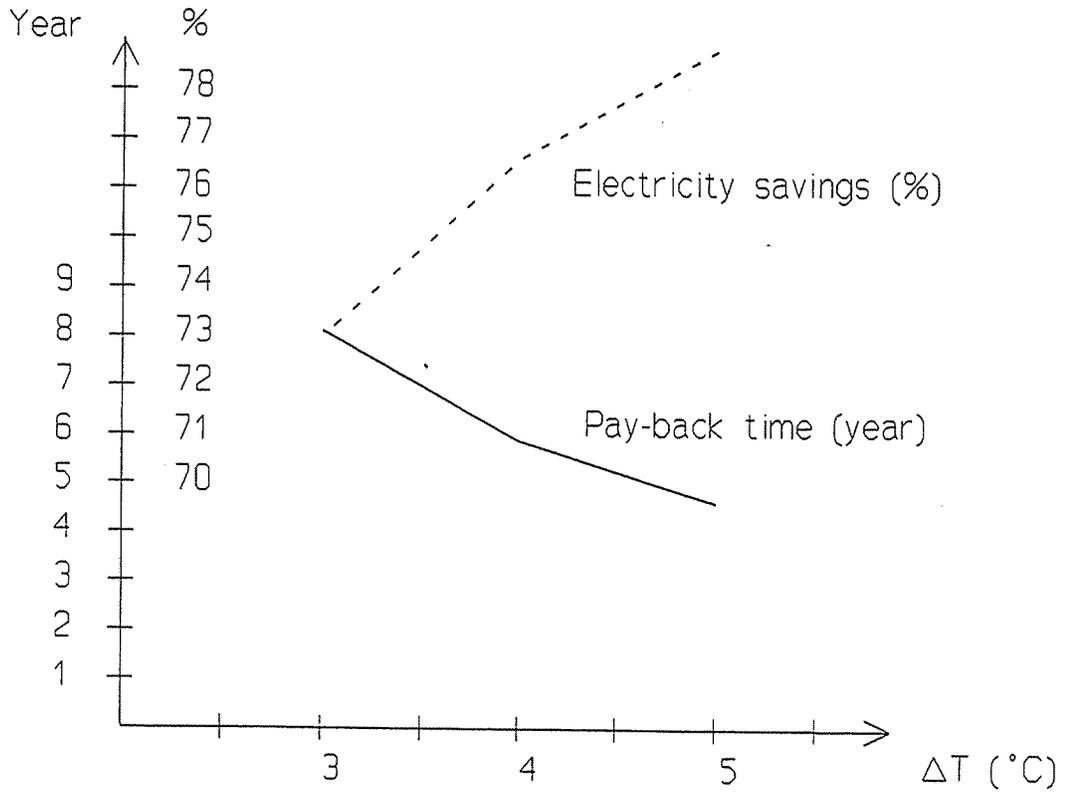


Figure 10. Profitability (simple pay-back time) and electricity savings by adding cold storage steel tank and outdoor air cooling to a CFC air conditioning system. The results of the analysis are shown as a function of temperature difference between "cold" and "warm" water in the storage tank. Electricity savings are based on a compressor load of 10 kW. Circulation pump efficiency (total): 50%. COP: 4,5. Electricity pricing 0.06 US\$/kWh. Steel tank installation price: 125 US\$/m³.

High Density Energy Storage For Desiccant Cooling Systems

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1 Technology Description

The objective of our development is an **open cycle liquid desiccant cooling system** designed to provide cooling and dehumidification for air conditioning purposes as well as efficient energy storage within the desiccant (up to 1000 MJ/m³ of diluted solution).

A schematic of the system is shown in Fig. 1. Ambient air (1) is dehumidified in a sorption reactor by a concentrated hygroscopic salt solution, e.g. Klimat 3930¹ or LiCl-H₂O, supplied from a plastic storage tank. The heat of absorption is transferred to a cooling tower by a cooling water loop to achieve an almost isothermal absorption process, required for optimal air dehumidification and optimal energy storage capacity. The salt solution is diluted in the absorption process and pumped to a second tank.

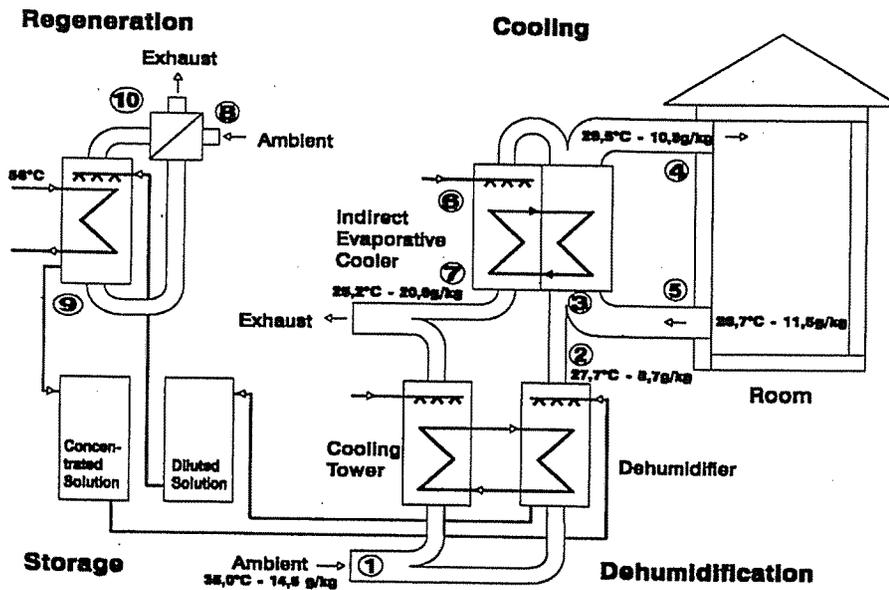


Fig. 1: Experimental open cycle liquid desiccant cooling system.
(ARI Standard Conditions, 20% latent cooling load)

The dehumidified air (2) is mixed (3) with indoor air of state (5), cooled in an indirect evaporative cooler (4) and supplied to the room. A part of the air flow (6) is humidified in contact with a wet heat exchanger surface and provides indirect evaporative cooling. The exhaust air temperature and dewpoint (7) are close to room temperature.

A separate operation mode or a separate sorption reactor is used to reconcentrate the salt solution. The heat for regeneration can be supplied via a heating water loop by any heat source of about 65 °C or higher.

1.1 Indirect Evaporative Cooler

The indirect evaporative cooler is the key component for a thermal coefficient of performance well above 1.0 in single effect systems. It exploits the cooling potential of the room air in an optimal way.

¹an aqueous solution of CaCl₂ and Ca(NO₃)₂, patented by Solvay Deutschland GmbH

An ideal indirect evaporative cooler has the potential to cool air to its dewpoint instead of its wet bulb temperature, which is the potential of a direct evaporator. Even more essential is its capability of exhausting air at a temperature **and dewpoint** close to room temperature. Therefore, under ARI standard conditions², the difference in enthalpy of dry inlet air and humid exit air is almost doubled compared to, e.g., a Pennington Cycle or Ventilation Cycle, which use direct evaporators in inlet and exhaust air flow and conventional heat exchangers between them.

Indirect evaporative coolers are already in the market (e.g. Drycon, Australia and Menerga, Germany), but their ratio of wet to total exchanger surface has to be improved with respect to auxillary electrical energy consumption.

1.2 Sorption Reactor

The sorption reactor used as dehumidifier is the key component for effective air dehumidification and energy storage in the desiccant. It is not a standard component. A new design has to meet the following demands:

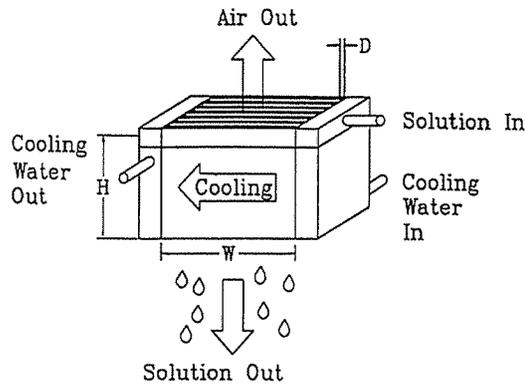
- Cool the hygroscopic solution sufficiently to achieve low humidity ratios.
- Distribute a small solution flow of high viscosity of about 0.2 ltr/h/m² uniformly over an exchange surface to achieve a large difference in salt concentration of diluted and concentrated solution, which results in a large energy storage capacity.
- Provide a high ratio of wet to total exchanger surface to reduce the required exchanger area and electrical energy consumption for fans.
- Withstand the corrosiv forces of the salt solution
- Must be build of inexpensive materials, easily to be manufactured.

According to these requirements, a new sorption reactor has been developed at the Ludwig-Maximilians-Universität München and the ZAE Bayern (Bayerisches Zentrum für angewandte Energieforschung e.V.) in cooperation with ISE (Fraunhofer Institut für Solare Energiesysteme, Freiburg) and Solvay Deutschland GmbH.

The design shown in Fig. 2 proved to be appropriate. Cooling water circulates through thin walled polypropylen double plates (0.5 mm) in cross current to an upward air flow and a downward solution flow. A solution distribution element and a coating of the surface of the exchanger plates care for a stable micro flow of salt solution, which covers more than 90% of the surface. The deviation of the flow rate of the mean value is less than 15% at specific flow rates of 0.2 ltr/h/m². Spacers between the plates provide mechanical support, turbulence within the air flow for better mass transfer and support solution distribution.

Based on the results of experiments with small reactors, an experimental open cycle liquid desiccant cooling system with a rated cooling power of 8 kW under ARI conditions has been build and started up. First test runs of the sorption reactor PSR-1000 have been successfully performed and design calculations have been verified.

²Standard conditions of the American Institute of Refrigeration, ARI, for desiccant cooling systems: outdoor 35 °C , 14.5 g/kg, 40% r.h., indoor 26.7 °C , 11 g/kg, 50% r.h.



Sorption Reactors built:

| | TSR-50 | PSR-1000 | |
|--------------------|----------------|----------|-------------------|
| Number of Channels | 6 | 29 | |
| Distance | D | 8 | mm |
| Reactor Width | W | 280 | 1000 mm |
| Reactor Height | H | 475 | 960 mm |
| Surface | A | 1.8 | 56 m ² |
| Air Mass Flow | M _a | 50 | 1000 kg/h |
| Solution Flow | M _s | 0.5 | 10 kg/h |

Fig. 2: Sorption reactor design

2 Application

Open cycle desiccant cooling systems provide air dehumidification and cooling for residential or commercial air conditioning purposes as alternative or additive to conventional air conditioning systems driven by vapor compression cooling devices.

Systems using solid desiccants are already commercially available and begin to penetrate into U.S. niche markets, especially in applications with high latent cooling loads e.g. super markets.

Hybrid systems using vapor compression for cooling and desiccants for dehumidification have also been installed. In some applications the compressor heat has been used for desiccant regeneration.

The system under development provides in addition an efficient and nondissipative energy storage in the liquid desiccant, which enables the use of waste heat sources remote from the air conditioning system in time or location.

Heat sources as industrial waste heat, heat from cogeneration, district heating, solar energy or, in hybrid systems, from the compressor of a vapor compression device shall be used for desiccant regeneration.

3 Benefits

- Designed to be driven by low temperature heat instead of electricity, desiccant cooling systems can achieve substantial fossil energy savings by utilizing heat sources as described above, which otherwise would not be used.
- The applicability of waste heat or solar energy is improved by energy storage within the regenerated desiccant, or by long distance transportation of the desiccant. Especially low cost aqueous solutions of hygroscopic salts, e.g. CaCl₂ or LiCl, are suitable for decoupling energy supply and air conditioning demand in time and location.
- The proposed system does not use any CFC, toxic materials or volatile substances other than water.

- Construction materials for the reactors are plastics as polypropylen or polyethylen, which are environmentally harmless and suitable for mass production.
- Desiccant cooling systems can be operated in an overdrive mode. The cooling power can be increased by about 40%, while the COPs are deteriorated. Peak loads can be covered for a short time. Therefore, the system size is determined by average load rather than by peak load, which results in a positiv effect on initial costs.
- A thermal COP_{th} of about 1.5 and an electrical COP_{el} of 10 to 15 under ARI standard conditions ³ are achievable with a single effect system. Double effect systems can be used if higher temperatures are available.

4 Technical Issues

Open cycle systems are attractive for air conditioning because the thermodynamic potential of the atmosphere or the room air, which are not saturated with water vapor, can be exploited easily.

In these systems, however, air is the natural carrier of heat and water vapor. Therefore, care has to be taken to keep the required electrical energy for fans low. High air velocities have to be avoided and sufficiently large exchanger area has to be provided in order to compensate for smaller transfer coefficients.

Wherever wet exchanger surfaces are required, in sorption reactors or evaporators, it is essential to ensure the surfaces to be wetted almost completely, in order to save electrical energy for fans.

Low temperature applications are attractive for air conditioning because low temperature heat is available as waste heat or facilitates solar energy use. But low temperature technology requires small temperature differences for achieving good coefficients of performance. Again large exchanger areas are required to compensate for that, whenever given thermal power has to be transfered.

So, if low temperature and open cycle technology are considered, the main question is: Is it possible to produce the necessary exchanger area sufficiently inexpensive?

The development of an energy economic micro flow technique on thin walled (0.5 to 0.3 mm) plastic surfaces is a first step into that direction.

5 Economics

Depending on ambient and room conditions and regarding presently achievable transfer coefficients, a specific total heat and mass exchanger area of about 20 to 30 m²/kW is necessary for air conditioning systems of the proposed type.

Estimating a mean price of 60 DM/m² for micro flow wet exchanger surfaces, corresponding to about 1.5 the price at which conventional wet plastic heat exchangers surfaces are sold, a specific price of 1200 to 1800 DM/kW results. The price will increase to about 1700 to 2300

³Coefficient Of Performance: $COP_{th} = (\text{latent and sensible heat removed from the room})/(\text{heat for desiccant regeneration})$

$COP_{el} = (\text{latent and sensible heat removed from the room})/(\text{electrical energy used for fans and pumps to drive the fluids through the system components, not through the piping of a buiding})$

DM/kW for small systems (10 to 50 kW), if additional equipment as pumps, filters and fans is regarded.

Initial costs of 700 to 1100 DM/kW are calculated in Germany for small systems if conventional vapor compression cooling is installed.

At present status there is a considerable economic disadvantage for open cycle cooling systems compared to conventional systems if first costs are considered, even if a bonus of about 40% is given for installing average instead of peak cooling power.

The operating costs for cooling systems offer a pay back potential if the electricity saved can be substituted by heat economically. Table 1. lists the roughly calculated heat and electricity consumption of different systems.

Table 1. Heat and electricity consumption:

| type | vapor compression | open cycle sorption | |
|--|----------------------|---------------------|---------------|
| | | single effect | double effect |
| cooling power output | 100 % | 100 % | 100 % |
| electricity input | 25 % | 7 % | 8 % |
| heat input for electricity generation, fossile ca. 500 °C | 72 % | 20 % | 23 % |
| heat input regener. 70 °C | 0 % | 66 % | 0 % |
| heat input regener. 110°C | 0 % | 0 % | 40 % |
| total heat input | 72 % | 86 % | 63 % |

About 68 ... 70% (20/72 or 23/72) of the fossile energy and CO₂ emission for electricity generation can be saved. It depends on the price for electricity and (waste) heat wether it can be done economically.

A part of the electricity input of 18% (17%) of the cooling power can be substituted either by 66% of low temperature heat (70 °C) or by 40% of higher temperature heat (110 °C).

6 Technology Outlook

An energy economic micro flow technique on thin walled plastic surfaces has been developed, suitable for sorption reactors or indirect evaporative coolers. The desired function has been realized within an experimental desiccant cooling system of a rated power of 8 kW. The reliability of the distribution element, for water or liquid desiccants, has to be improved.

The next steps in technical developement will be:

- Improvement of reliability
- Developement of exchanger surfaces and manufacturing technology suitable for mass production.
- Component developement: sorption reactors, indirect evaporative coolers, cooling towers, integrated subsystems, double effect regenerator.

A CO₂ VAPOUR COMPRESSION SYSTEM FOR VEHICLE AIR CONDITIONING

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Conditioning Technology Workshop (ORNL/DoE/AFEAS)
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Abstract

A new, efficient and environmentally benign automobile air conditioning system "MAC-2000" has been developed at The Norwegian Institute of Technology, in cooperation with Hydro Aluminium. The new system is based on a vapour compression cycle with carbon dioxide as the refrigerant. Although working pressures and component design are different, the basic principle of the CO₂ system is similar to present CFC/HFC units. By development and testing of a laboratory prototype, it has been documented that the CO₂ system is highly competitive to present CFC-12 and HFC-134a units in terms of performance, cost, weight and dimensions. The new concept thus offers a complete solution to the environmental problems associated with motorcar air conditioning, and eliminates all uncertainty with respect to possible unforeseen effects from new refrigerant compounds. Further advantages of the natural fluid CO₂ as a refrigerant are: No need for recycling or recovery, low cost of fluid, excellent availability, well-known properties, and more compact machinery and components.

Introduction

Simple logic would indicate that substances which are present naturally in the biosphere, and for which the effects are long established, must be generally preferred as refrigerants. A list of such fluids will, for instance, include air, water, nitrogen, the noble gases, hydrocarbons, ammonia, and last but not least, carbon dioxide.

The design of a system must be adapted to the refrigerant used and may be quite different for each fluid and application. One important aspect is, of course, the energy efficiency. According to the second law, the theoretical efficiency depends exclusively on the thermodynamic process which is realized, and is independent of the properties of the working fluid. Rather than trying to develop a chemical compound to satisfy the requirements of a particular cycle, e.g. the Evans-Perkins process, we should adapt the cycle to the properties of the substance which we want to use. In this way it is readily possible to obtain better performance with several of the environmentally neutral refrigerants than with present systems.

The new automobile air conditioning (A/C) system described in the following has been developed along these lines, using CO₂ as the refrigerant. Since the large and growing number of automobile A/C systems represent a dominating source of refrigerant emissions to the atmosphere, the choice of refrigerant fluid is of particular importance.

Although the investigations so far have been focused mainly on automobile A/C, CO₂ may be effectively used as a refrigerant in a number of other applications as well. More details on the technology and results are reported in [1-5].

Technology: Trans-Critical Vapour Compression

The critical temperature of carbon dioxide is 31.1°C (88°F), at a pressure of 73.8 bar (1070 psi). Owing to the high ambient temperatures encountered in automobile A/C, the CO₂ system will operate in a "transcritical" cycle most of the time, i.e. with heat rejection above the critical temperature and supercritical high-side pressure. The low-side conditions remain subcritical, however. At 0°C (32°F) evaporating temperature, the saturation pressure of CO₂ is 34.8 bar (505 psi).

When the high side is supercritical, no saturation condition exists, and the pressure is more or less independent of the temperature. Adjustment of the high-side pressure affects both the capacity and the compressor work, and thereby also the coefficient of performance (COP). In order to maintain a maximum COP, the pressure should be varied in accordance with the operating conditions, e.g. heat rejection temperature. As the cooling-air inlet temperature varies, for instance from 25°C to 40°C, the pressure should be adjusted from about 80 bar to about 100 bar.

A special flow circuit enabling efficient operation and simple high-side pressure control has been devised, Figure 1. The thermodynamic cycle is demonstrated for varying pressures and capacities in the pressure-enthalpy diagram. In this circuit, the high-side pressure is regulated by varying the throttling valve position.

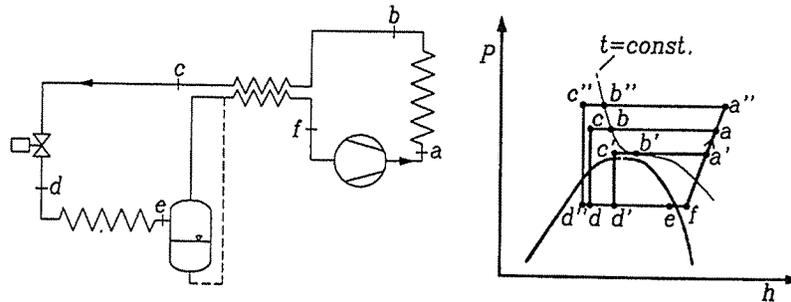


Figure 1 Trans-critical system flow circuit and thermodynamic cycle in the pressure/enthalpy diagram

In order to regulate the high-side pressure, the momentary refrigerant charge in this part of the circuit is varied. This is obtained by adjusting the throttling valve opening, thereby transferring charge to or from the receiver. A reduction of the valve opening temporarily reduces the refrigerant flow to the receiver. Since the compressor inlet flow remains virtually constant, the high side charge and pressure is increased. In Figure 1 this is illustrated as a change from cycle a-b-c-d-e-f to cycle a''-b''-c''-d''-e-f. The refrigerant temperature at the cooler outlet (b) remains more or less constant, slightly above the cooling-air inlet temperature. Conversely, an increase of the valve opening will act to reduce the high side charge and pressure, as illustrated

by cycle a'-b'-c'-d'-e-f.

The throttling valve acts in a very different way compared to the conventional system and offers an unique possibility of continuous high-side pressure control. A small liquid flow is bled from the receiver (dashed line) for the double purpose of providing an overfeed of the evaporator and returning oil to the compressor. The liquid overfeed improves the heat transfer and prevents the evaporator from starving when the throttling valve is regulated to increase the high-side pressure.

The receiver serves to supply or absorb liquid for high side pressure regulation and ensures that sufficient refrigerant is available at all time, regardless of operating conditions. Furthermore, it protects the compressor from liquid slugs, and provides sufficient volume to avoid excessive pressure when the system is inoperative at high ambient temperature. The internal heat exchanger assures evaporation of the excess refrigerant liquid and improves the COP of the system. At extreme ambient temperatures, the internal heat exchanger also prevents the refrigerating capacity from disappearing.

Application: Vehicle Air Conditioning

The described trans-critical (MAC-2000) system is mainly intended for vehicle air conditioning applications, as a third-generation replacement technology for HFC-134a. The concept may also be applied in heat pumps with large temperature glide, e.g. in water heaters or for district heating purposes. With modified or different cycle concepts, CO₂ vapour compression technology will also be highly competitive in many other heat pump, air-conditioning or refrigeration applications, for instance as outlined in [4] and [5].

A laboratory prototype of the mobile A/C concept has been developed, built and tested at the Norwegian Institute of Technology. A complete standard CFC-12 mobile air conditioning system from a 1990 European passenger car served as a reference, both in terms of design, capacity and efficiency. The evaporator and the 'condenser' of the CO₂ prototype system were built within the same dimensional limits as the CFC-12 units, and the 3-cylinder wobble-plate CO₂ compressor is of a relevant design and size for automobile A/C. The internal heat exchanger of the CO₂ system replaces the liquid and suction lines of the conventional circuit.

Figure 2 shows the components of the standard system to the left, and the CO₂ prototype to the right. The compressor (without clutch) and the filter receiver of the CFC-12 system are located between the evaporator (rear) and condenser (front). Relevant refrigerant lines are also included.

In the CO₂ system, the U-shaped line between the 'condenser' and the evaporator is the counterflow internal heat exchanger, and the black unit close to the evaporator is the receiver. This pressure vessel was deliberately made larger than necessary and with flanges to provide easy access to the liquid/oil return system. A more typical receiver size is indicated by the white vessel placed in a vertical position in front of the lab. prototype receiver.

Benefits: Efficiency, Environment, Compactness, Cost, Safety

Environment: CO₂ has zero ODP, and zero effective GWP (global warming potential), since sufficient amounts of CO₂ can be recovered from waste gas. As a natural constituent of the biosphere, carbon dioxide will not give any unexpected long-term effects on health or environment.

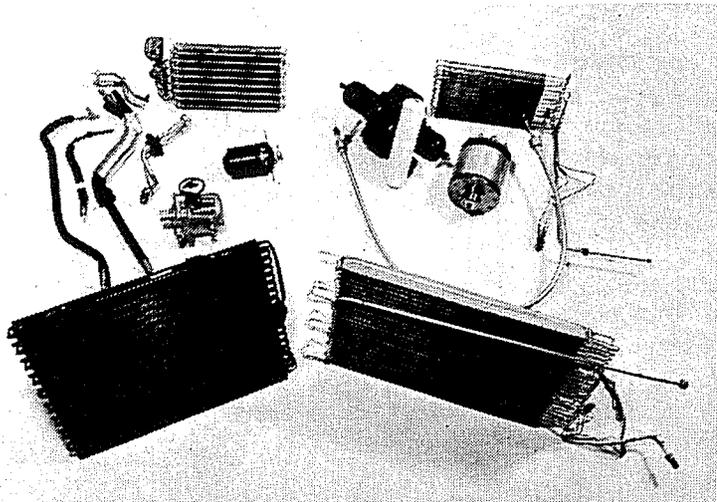


Figure 2 Components of the reference CFC-12 mobile A/C system (left) and the CO₂ laboratory prototype (right)

Personal Safety: CO₂ is not combustible (fire-extinguishing agent!) and non-toxic. Maximum short- and long-term exposure limits are comparable to or better than those of the "freons" and their replacements. In a fire, CO₂ will not develop the toxic or irritating decomposition products typical of the CFC/HFC compounds.

Equipment based on carbon dioxide will, of course, be designed and operated with the same safety requirements as present-day systems, e.g. with a high-pressure switch disengaging the compressor clutch, high- and low-side pressure relief devices, and minimum burst pressure of the components 2.5-3 times higher than the pressure relief device settings.

Owing to the reduced refrigerant-side volume of all components and lines in the CO₂ system, the possible energy release (pressure multiplied by volume) in the very unlikely case of a rupture will be moderate. A carbon dioxide system, which has a refrigerant-side volume of less than 2 liter, will represent a lower potential energy release than a typical CO₂ fire extinguisher.

Cost: Carbon dioxide is truly inexpensive, with a price on a mass basis that is two orders of magnitude lower than for HFC-134a. Owing to the lower liquid density and smaller system volume, the refrigerant charge will be lower with CO₂, further increasing the cost difference. Recycling or recovery of the refrigerant will not be necessary when using CO₂, neither for environmental nor for economic reasons. This will reduce costs and simplify work immensely during the whole lifecycle of the system.

Availability: In contrast to the new fluorocarbon alternatives, CO₂ is already available in abundant quantity in all parts of the world, and production capacity or distribution logistics need not be developed. Several million tonnes of CO₂ is already used each year in soft drinks, beer, fire extinguishing equipment, drinking water treatment, welding equipment, metallurgical industry etc.

Documentation and Data: All properties and characteristics of carbon dioxide are well known and thoroughly documented. Further toxicity testing is obviously not required. CO₂ is thermally stable and behaves inert, thus eliminating material problems or chemical reactions in the refrigerating system.

Weight and space requirements: The relatively high working pressure is an important advantage of CO₂. For a given capacity, the required compressor volume is in roughly inverse proportion to the suction pressure. The size of the CO₂ machine and the tubes are therefore reduced dramatically, compared to conventional systems. In fact, the necessary compressor displacement is reduced by 85% compared to R-134a. Although a design pressure in the order

of 100-150 bar is much higher than used in conventional systems today, it is by no means extreme in other technical equipment, and will not cause any particular design problems. The increased energy density of this high pressure fluid gives considerable advantages through reduced dimensions and weight, two factors of special importance in automobile systems.

Energy Efficiency: By adaptation of the thermodynamic cycle and the circuit to CO₂ and the application, a very competitive efficiency can be obtained [1-3]. Figure 3 shows the measured coefficient of performance (COP) of the standard CFC-12 mobile A/C system and the CO₂ laboratory prototype, at varying ambient (condenser/cooler inlet) air temperature. The test conditions simulate full capacity operation in two typical modes, 'idling' and 'driving'. Both systems have a refrigerating capacity of about 4.5 kW at 43°C.

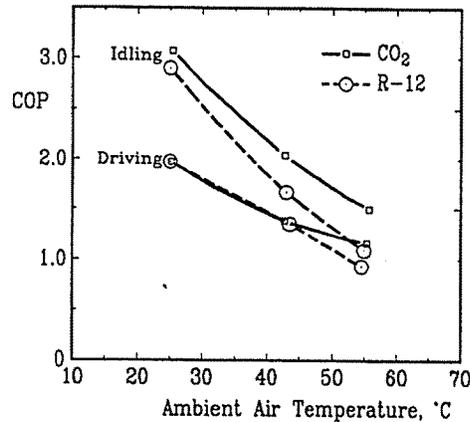


Figure 3 Recorded coefficient of performance (COP) for the CO₂ laboratory prototype system and the standard CFC-12 unit, at two typical modes of operation and varying condenser air face velocity. The passenger compartment (evaporator air inlet) temperature is maintained at 30°C, and the ventilation air fan is operated at full capacity

A general conclusion from Figure 3 is that the COP of the carbon dioxide system is as good as, or even slightly better than, that of the standard CFC-12 system. There are several important factors which contribute to the good practical performance of CO₂: Efficient compression due to the low pressure ratio, favourable heat transfer characteristics, and a close approach to the ambient air temperature at the CO₂ cooler outlet. In addition, the internal heat exchange contributes to improved COP.

Tests conducted with HFC-134a systems indicate that the COP will be about the same as with CFC-12.

Technical Issues: Further Prototype Development and Testing

Before the CO₂ system can be commercialized, further development and testing of prototype systems is required. Some of the major tasks and technical challenges in this phase are:

Compressor: Development of a compact, efficient, reliable and lightweight compressor. Factors like high operating pressure (max 150 bar), small displacement (20-25 cm³), low pressure ratio and large pressure differential are in favour of a reciprocating compressor concept for the CO₂ system, although other types may also be considered. A compressor with relatively long stroke and small cylinder diameters has the advantage of limiting the forces on the drive

system and offers the best possibility of avoiding internal leakage. Owing to the relatively low molecular mass and high pressure of CO₂, piston velocities and gas flow velocities e.g. in valves can be higher than for the heavier CFC/HFC compounds. Limited space (small cylinder diameters) and potentially high impact velocities are challenges related to conventional valve designs in CO₂ compressors. Mechanically operated valves of the sliding/rotating type may offer advantages, in particular since pressure ratio variations and therefore losses by over/under-compression will be small. A good shaft seal design with minimum leakage and high reliability is also needed.

Both theoretical and practical investigations have confirmed that oil return is not a problem in the MAC-2000 system. The liquid bleed system from the low-side receiver assures that the oil discharged from the compressor is safely metered back. The design of the system with high flow velocities and absence of "pockets" effectively eliminates any possibility of oil return problems. Ordinary mineral oil may be used, eliminating the need for expensive and specially developed lubricants. Possible oil degradation due to higher compressor discharge temperature will have to be investigated.

Heat Exchangers: Development of efficient, compact and lightweight heat exchanger units, i.e. evaporator, gas cooler and internal heat exchanger. In general, the higher pressures are in favour of an increased number of small-diameter tubes or flow-channels, resulting in a large air-side surface, lightweight construction, high-pressure capability, reduced inside volume and reduced air-side pressure drop. The reduced refrigerant-side surface is compensated for by the 2-4 times higher heat transfer coefficients with CO₂ than with CFC/HFC. Minimum burst pressure requirements will be in the range of 300-350 bar for the CO₂ evaporator and 400-450 bar for the gas cooler, corresponding to between 2.5 and 3 times the maximum operating pressure, i.e. pressure relief device setting.

The internal heat exchanger can either be based on a concentric counterflow tube concept or a compact heat exchanger unit e.g. of a plate/fin type.

A unique feature of the CO₂ system is that the ambient cooling air flow can be dramatically reduced in counterflow heat exchange, as a consequence of the gliding heat rejection temperature. The cooler can be provided with an efficient centrifugal fan, eliminating the problems of poor A/C system performance during idling or low speed driving. The much reduced face area requirements of this counterflow concept opens for improved aerodynamic car front design and more flexibility in the cooler location. By providing the CO₂ cooler with its own small air flow system, the heat load on the radiator can also be eliminated.

Control system: Development of a reasonably priced and efficient control system for capacity regulation and high-side pressure control. This task also includes the determination and development of a high-side pressure control strategy, also considering the interaction between pressure control and capacity control. Furthermore, this task comprises development of hardware, i.e. expansion device, control system hardware, sensors and actuators.

Other issues: Development of connection elements and joints for the high-pressure refrigerant line system, including static sealing elements and coupling concepts. Clarification of issues like noise, vibration, overall safety characteristics, reliability, dynamic response etc. will also have to be included in the further development program.

Economics: Equivalent to Present Systems

Since a final design of MAC-2000 systems has not yet been established, it is not possible to establish a firm estimate of production cost. Nevertheless, an estimate has been made, based on the main components of the laboratory prototype, with some suggested design modifications. Differences in production cost have been estimated as percentage figures based on design,

materials and/or other factors that affect the cost, with the CFC-12 reference system as a basis. For the two major heat exchangers, variable production costs have also been estimated. Certain assumptions regarding distribution of the total production cost between the main components were made in order to come up with a total figure.

A general conclusion from this investigation is that the CO₂ system can be produced at a cost that is comparable to or lower than that of present systems. This conclusion is supported by the fact that the new concept is still a quite simple vapour compression system, and that the number of components and their complexity and size are more or less the same as in existing circuits.

Status and Outlook

As already shown, a first laboratory prototype of the MAC-2000 automobile A/C system has been developed, built and tested. Since this system was finished in 1990, the compressor and cooler has been slightly modified, and extensive performance measurements have been conducted. Furthermore, a number of supporting practical and theoretical investigations have been made, and computer-based design/simulation and analysis tools for components and complete circuits have been developed. As a part of this work, a high-accuracy library of thermodynamic and transport data for CO₂ has been established.

The next stage will be further prototype development and testing within the car industry, before the final system/component design and production facilities can be established.

The conclusion that the CO₂-based concept is highly competitive is supported by the fact that the first laboratory prototype obtained equal and even somewhat higher efficiency than a state-of-the-art CFC-12 system, which is based on a technology that has been refined for decades. Considering all the potential improvement possibilities in the new system, its future looks bright.

Conclusion

- 1) There is a general belief that the only viable replacement refrigerant for automobile air conditioning is the new fluorocarbon substance HFC-134a. A transition to this new fluid will result in emissions of several hundred thousand tonnes of a new and unfamiliar chemical to the atmosphere each year, involving both known negative consequences and potential risks of serious unknown environmental effects
- 2) By development and practical testing of a laboratory prototype, it has been documented that the natural fluid carbon dioxide is a viable refrigerant for automobile air conditioning. This solution completely solves all present and future environmental problems associated with such systems, and eliminates all uncertainty with respect to possible unforeseen effects.
- 3) Use of CO₂ as a refrigerant gives a number of additional economic and practical advantages in the present situation. Examples of such advantages are: Absence of recycling or recovery needs, low cost of fluid, excellent availability, well-known properties, and compactness of machinery and components.
- 4) Through proper adaptation of the thermodynamic cycle and the machinery, the use of carbon

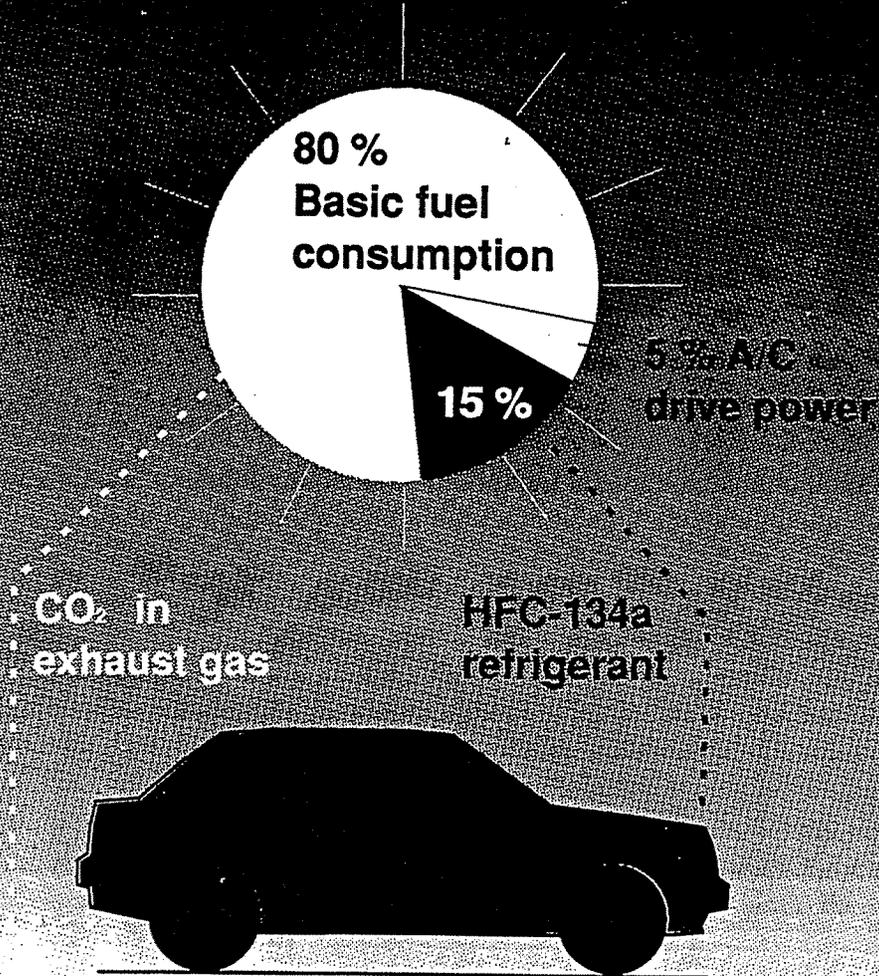
dioxide as refrigerant may offer a key to the solution of environmental problems in many areas of refrigeration technology.

References

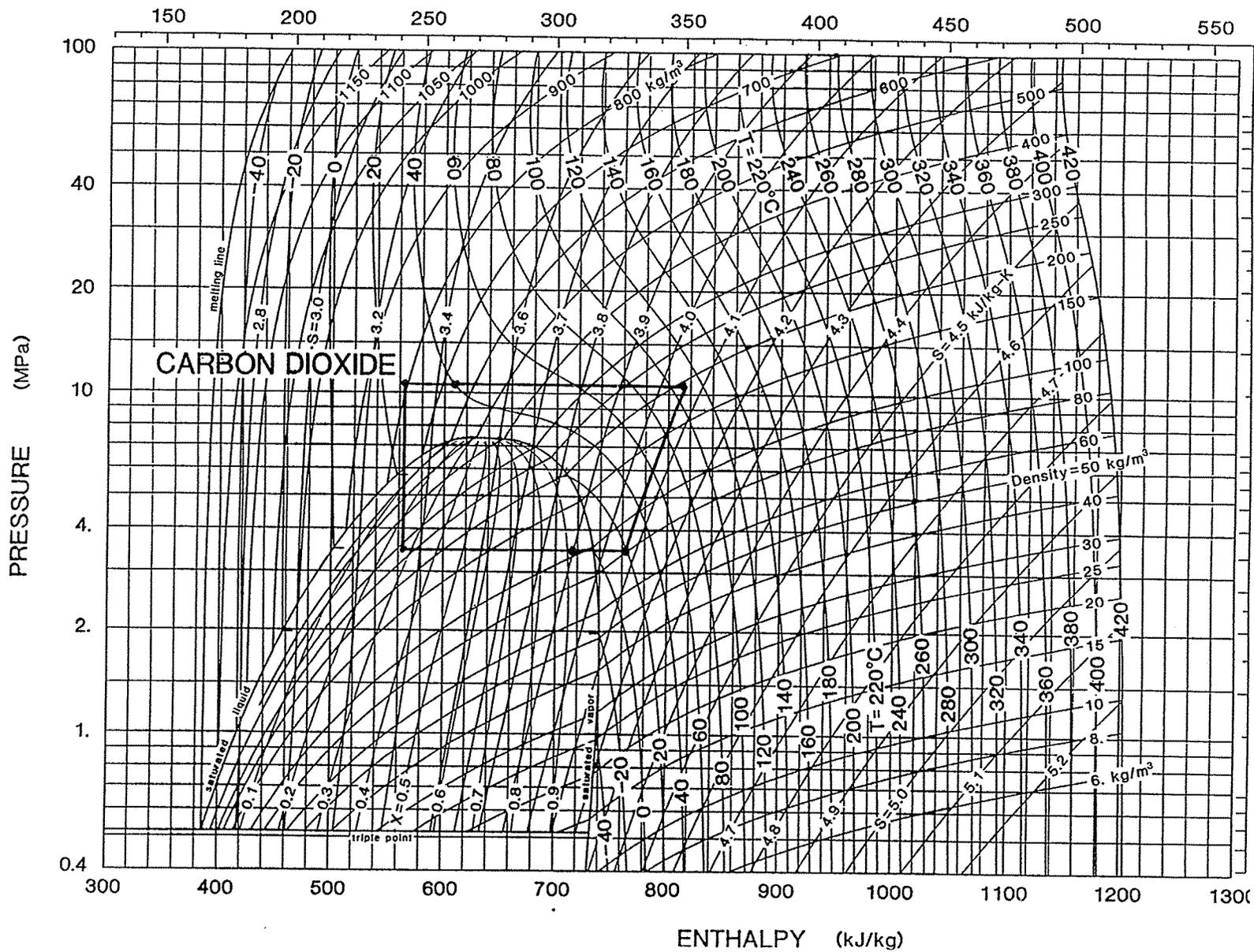
1. **Petterson, J. and Lorentzen, G.** A New, Efficient and Environmentally Benign System for Automobile Air Conditioning, SAE Paper 931129 Presented at the 1993 Vehicle Thermal Management Systems Conference, Columbus, Ohio, March 1993.
2. **Lorentzen, G. and Petterson, J.** A New, Efficient and Environmentally Benign System for Car Air-Conditioning, Int.J.Refrig 1993 Vol 16 No 1 pp 4-12.
3. **Petterson, J. and Lorentzen, G.** Eine neue, effiziente und umweltfreundliche Pkw-Klimaanlage mit CO₂ als Kältemittel, Luft- und Kältetechnik No 3 1993.
4. **Lorentzen, G.** Application of "Natural" Refrigerants: New System Concepts For The Use of CO₂, IIF/IIR Meeting, Ghent, May 1993
5. **Lorentzen, G.** Revival of CO₂ as a Refrigerant. To be presented at the meeting "Refrigerants Beyond the Crisis: Practical Solutions" Institute of Refrigeration, Joint one day conference with Institution of Mechanical Engineers, London, November 4, 1993.



CONTRIBUTIONS TO GW IMPACT FROM CAR WITH HFC-134a AIR CONDITIONING



Assumptions: 40 MPG (0.60 l/10 km), 160.000km
gCO₂/mile = 8855/MPG, 3 kg HFC-134a, GWP=1200



CHARACTERISTICS OF REFRIGERANTS

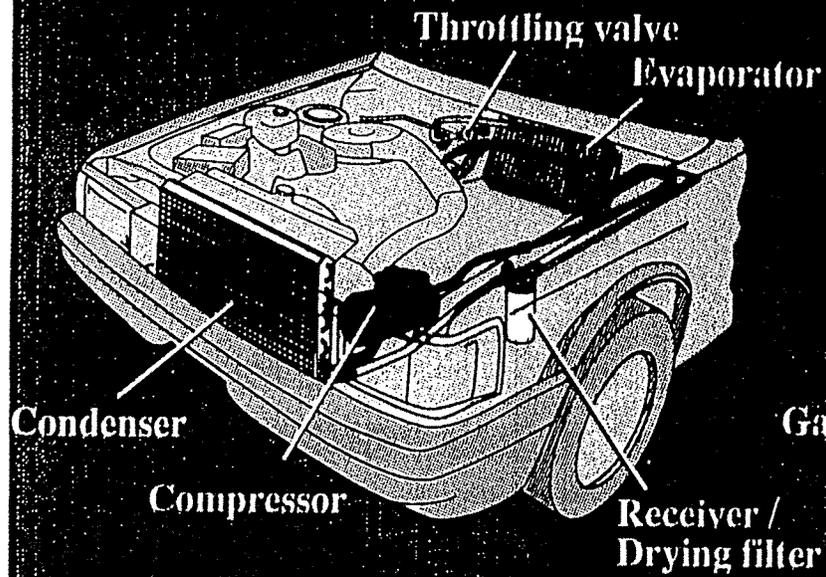
| | CFC-12 | HFC-134a | CO ₂ |
|---|--------|----------|-----------------|
| Natural Substance? | No | No | Yes |
| GWP 100 years | 7100 | 1200 | 1(0) |
| 20 years | 7100 | 3100 | 1(0) |
| ODP | 1 | 0 | 0 |
| TLV, ppm _v | 1000 | 1000 | 5000 |
| Flammable / explosive? | No | No(Yes) | No |
| Toxic / irritating decomposition products | Yes | Yes | No |
| Corrosive? | No | No | No |
| Approx. relative price | 1 | 3-5 | <0.1 |

- CO₂ is already available in large quantities (no producer-monopoly)
- Recycling/recovery is not necessary
- CO₂ is well documented, and all properties are known
- Exclusive and expensive lubricants are not required
- CO₂ has good heat transfer properties
- High working pressure gives compact system and reduced sensitivity to pressure drops

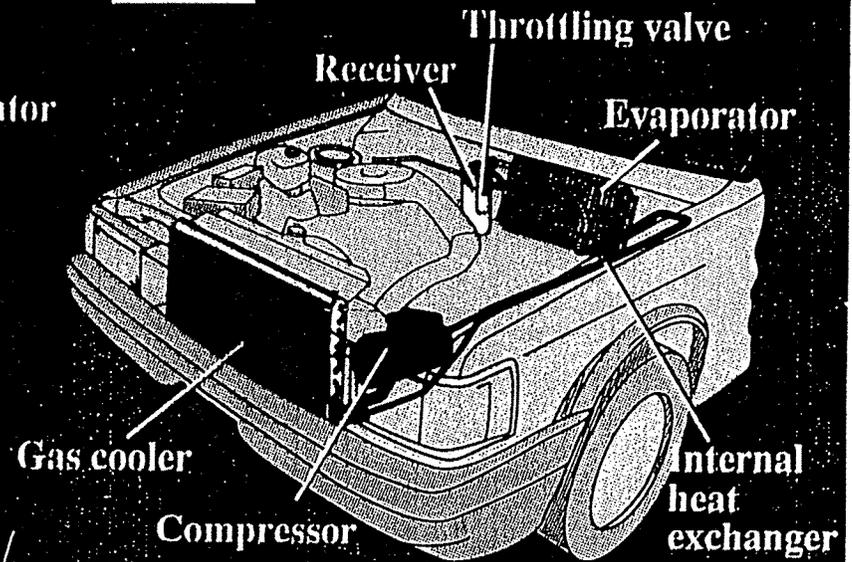


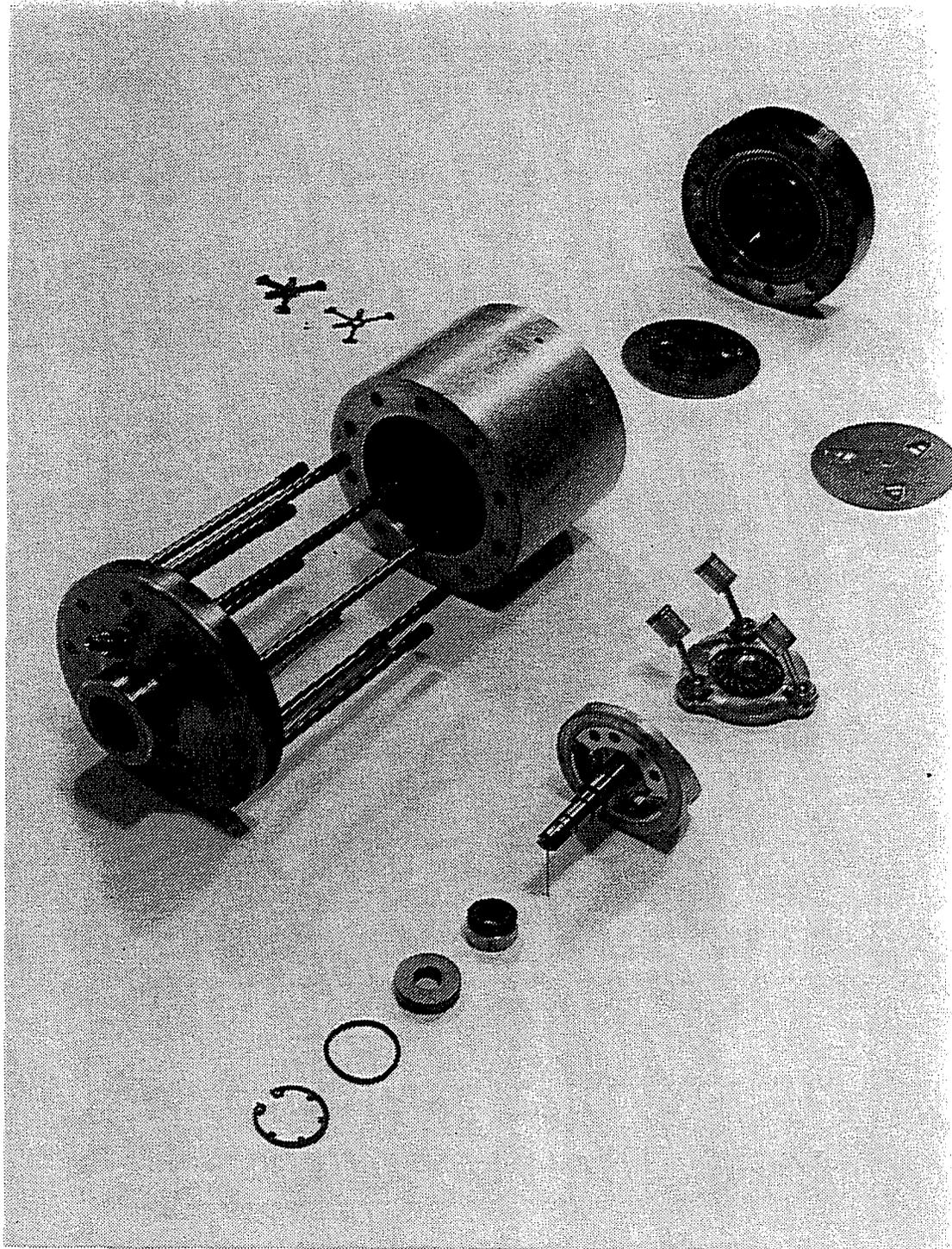
A/C SYSTEM IN CAR

R-12 / 134a

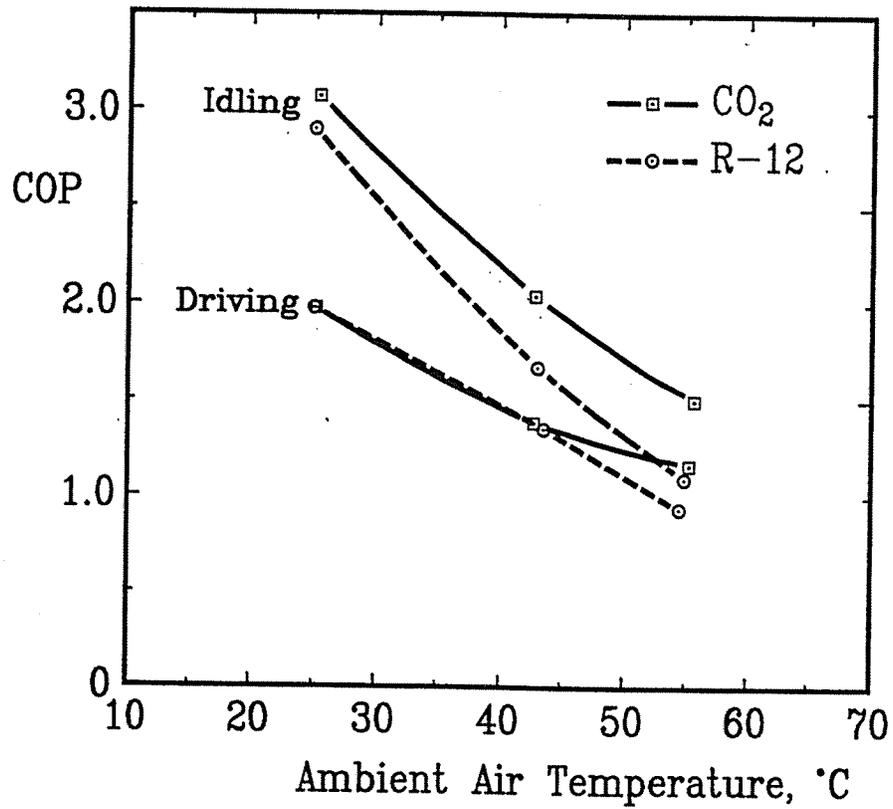


CO₂

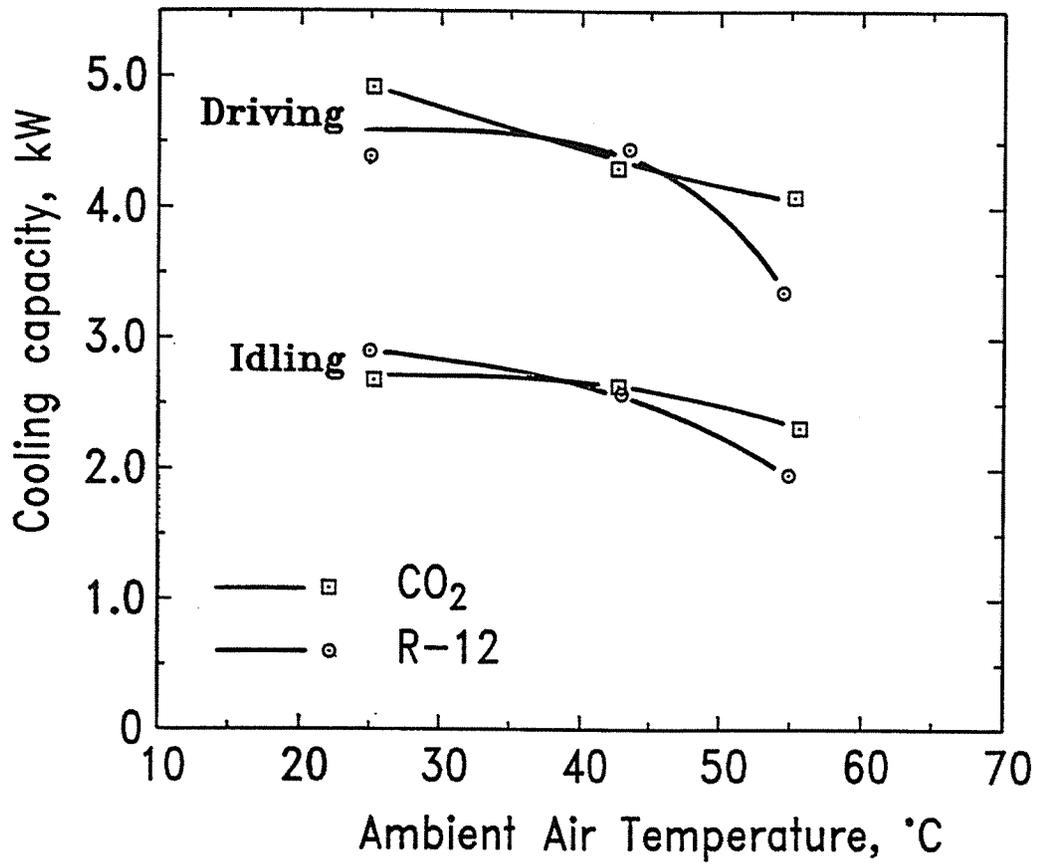




LAB. PROTOTYPE COMPRESSOR (CO₂)
26 ccm



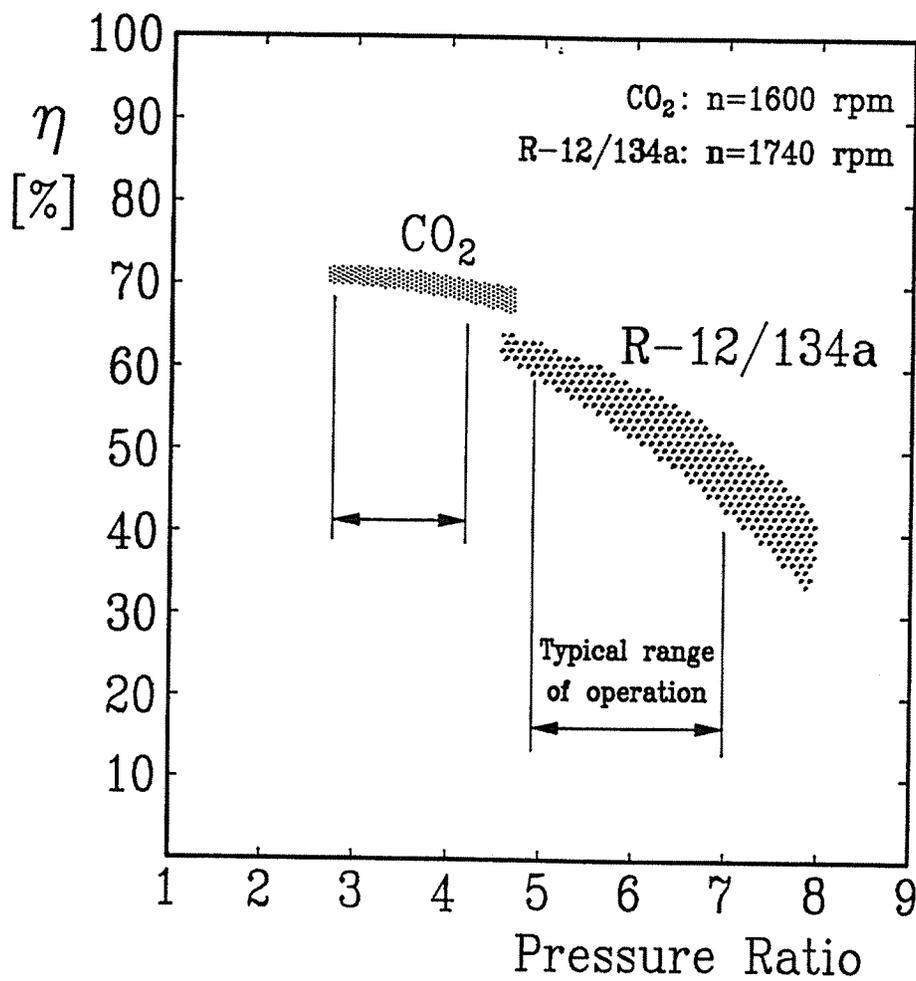
| | n, rpm | | u, m/s |
|---------|--------|-----------------|--------|
| | R-12 | CO ₂ | |
| Idling | 700 | 640 | 1.0 |
| Driving | 1740 | 1600 | 2.5 |

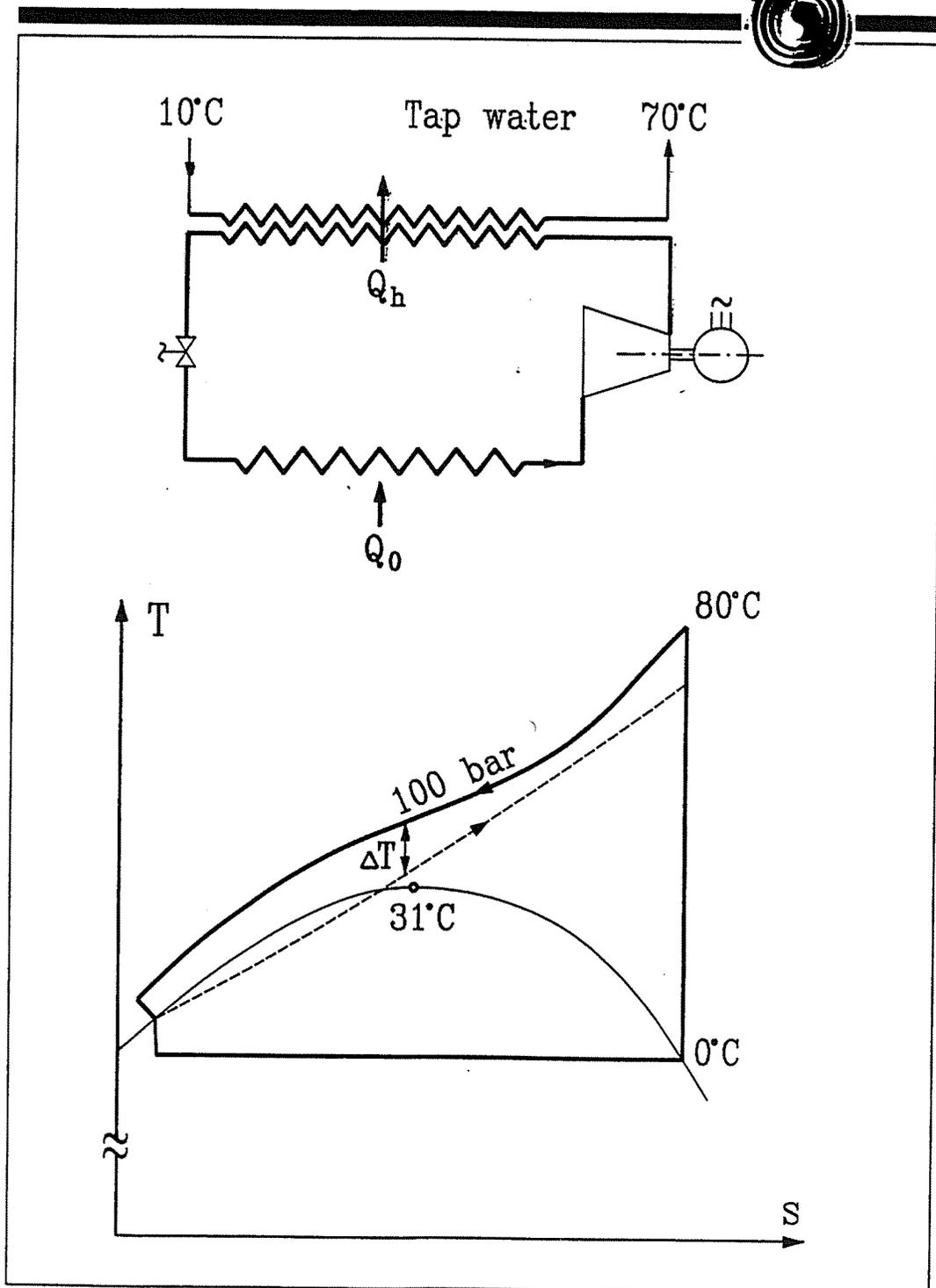




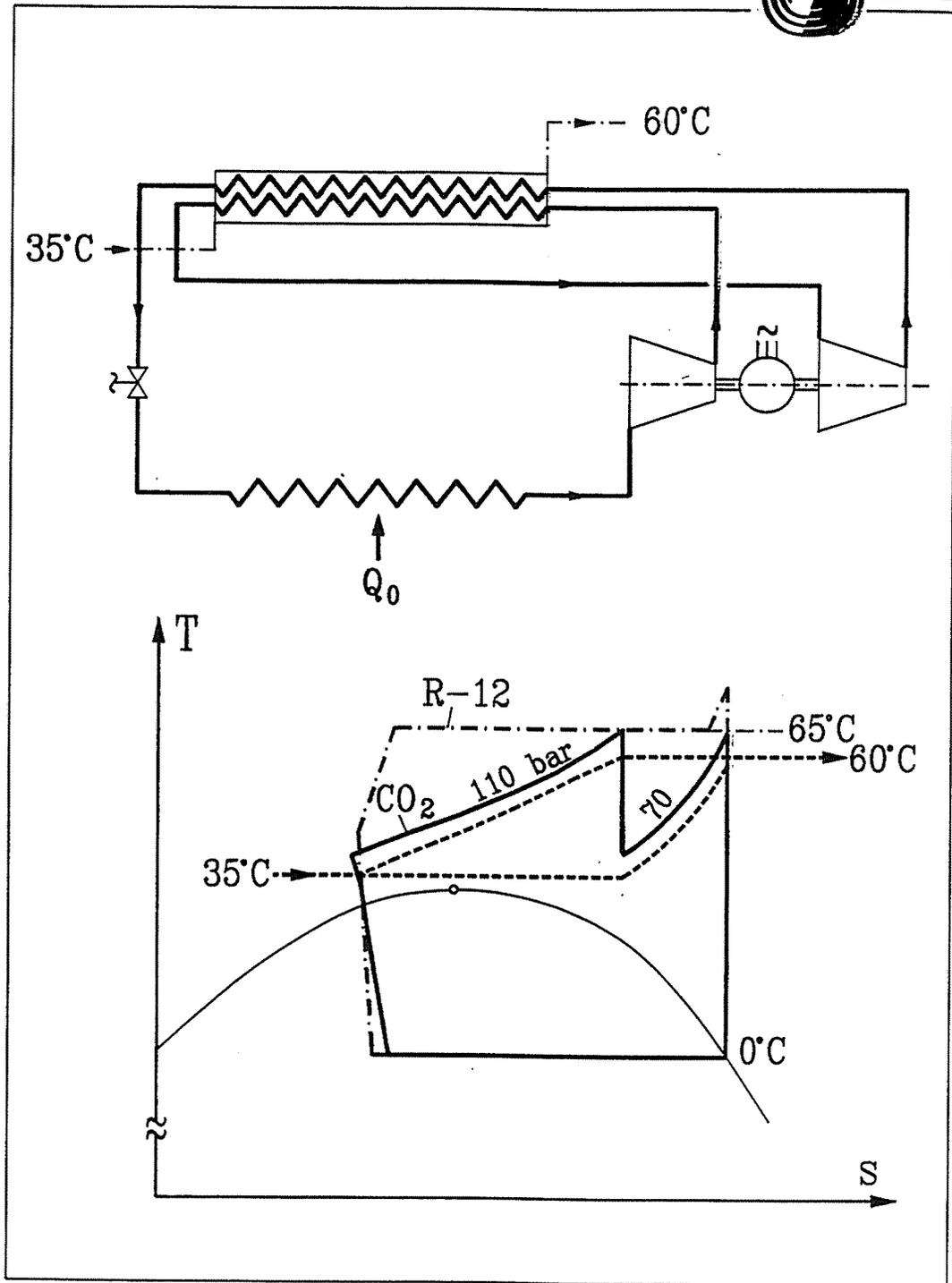
COMPRESSOR PERFORMANCE

Isentropic Efficiency

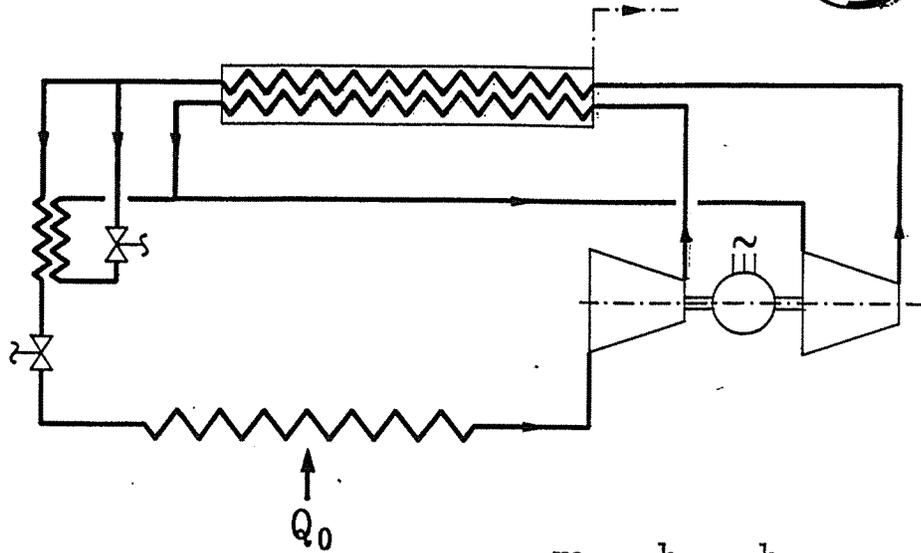




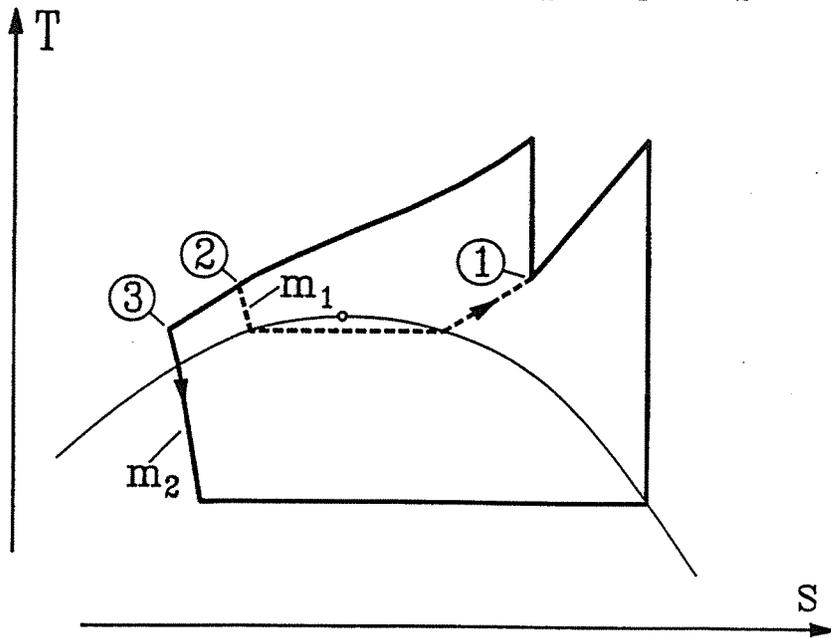
FROM LORENTZEN

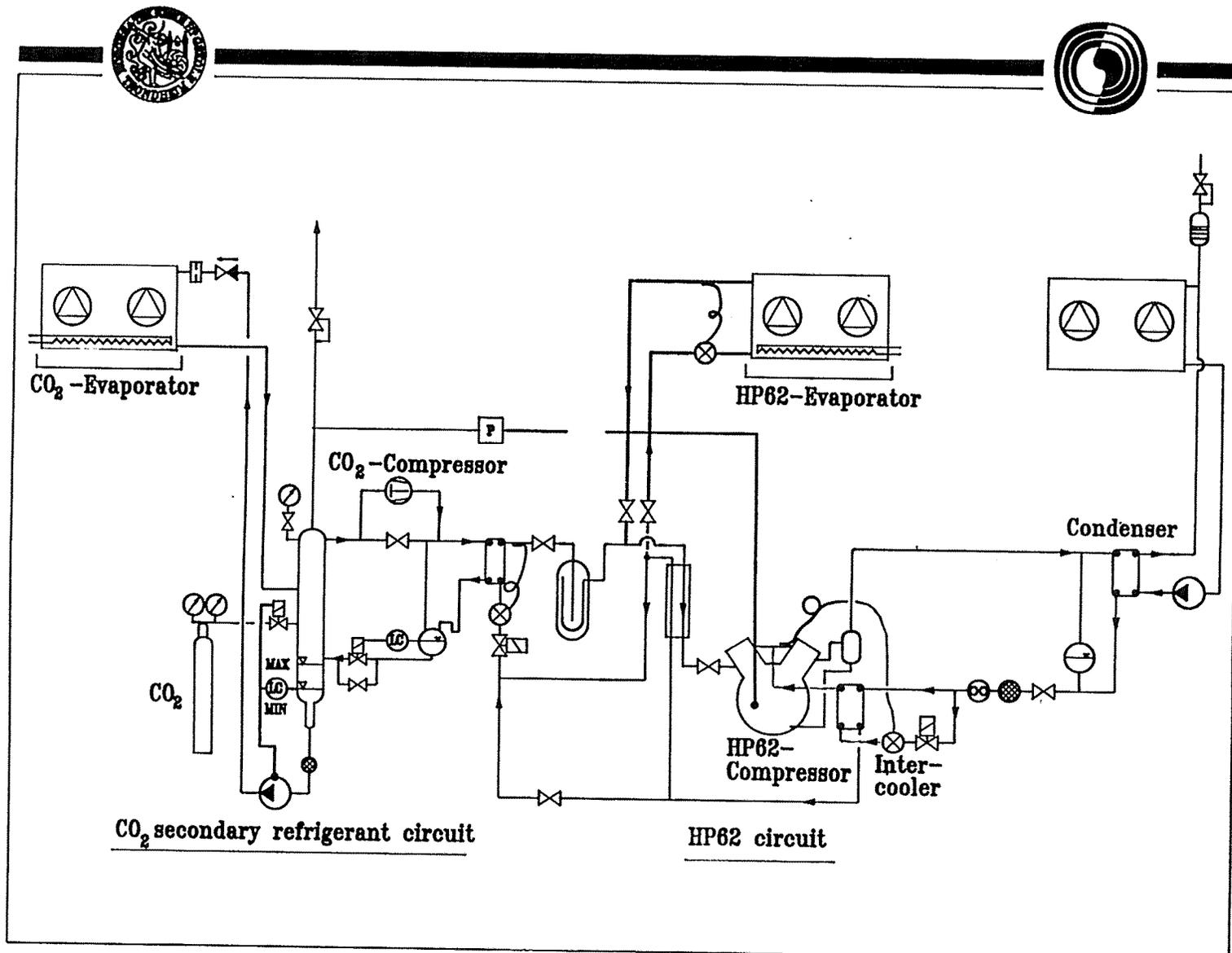


SINTEF Refrigeration Engineering



$$\frac{m_1}{m_2} = \frac{h_2 - h_3}{h_1 - h_2} \sim 0.06$$







MARKET OBSTACLES

- Investments made in replacement refrigerants, e.g. R-134a
- Investments needed to develop alternatives based on CO₂
- Perceived safety problems (high pressure)
- Perceived higher weight/volume requirements

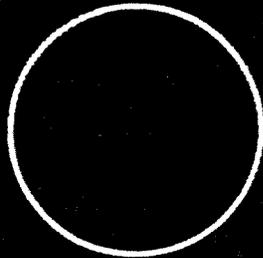
TECHNICAL "OBSTACLES"/ CHALLENGES

- Higher pressure rating and new design required for all components
- New control system required (high-side pressure)
- Factors like lubrication, noise, reliability must be clarified
- New cycle concepts are needed

WORKING PRESSURES AND DIMENSIONS

Condenser/gas cooler tubes with similar stress:

R-134a



Pressure : 20 bar
Inner diameter : 8mm
Wall thickness : 0.8mm
Weight : 100%

CO₂



Pressure : 110 bar
Inner diameter : 2.5mm
Wall thickness : 1.1mm
Weight : 56%

Compressor cylinders, equal cooling capacity and stroke:

R-134a

Pressure: 20 bar
Inner diameter: 100%



Vol.:
100%

Force:100%

CO₂

Pressure: 110 bar
Inner diameter: 40%

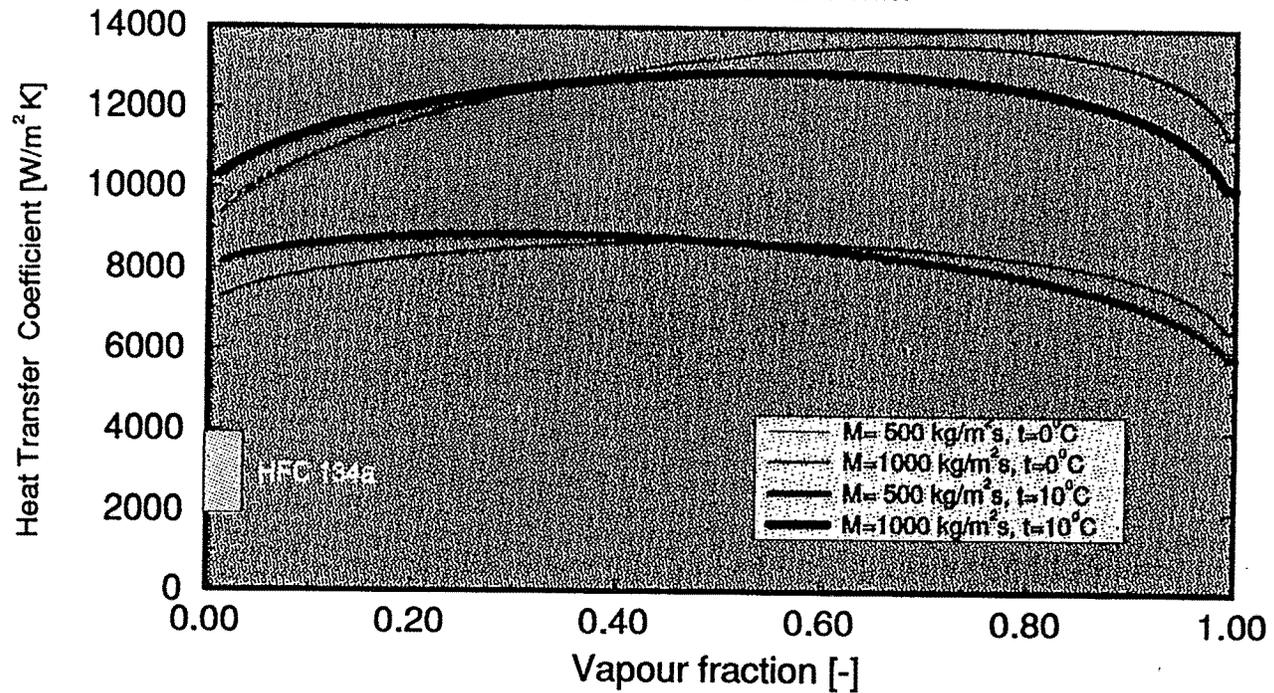


Vol.:
15%

Force:83%

Calculated local CO₂-HTC for the evaporator

Tube diameter: 2.0 mm

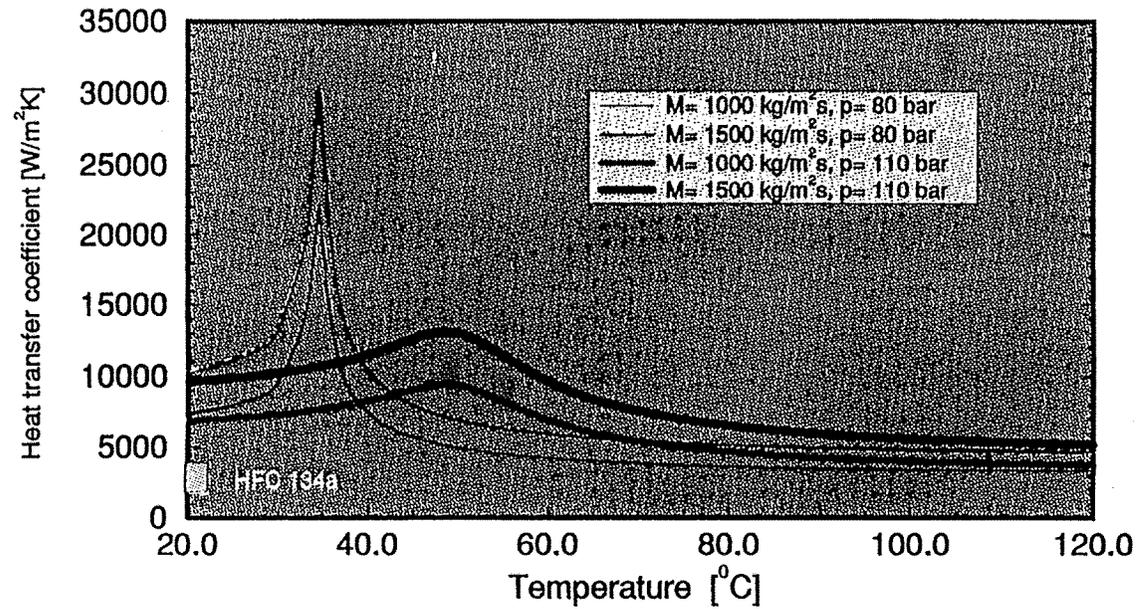


Correlation used: Gungor (HTFS)



Calculated local HTC for the CO₂ gas cooler

Tube diameter : 2.0 mm



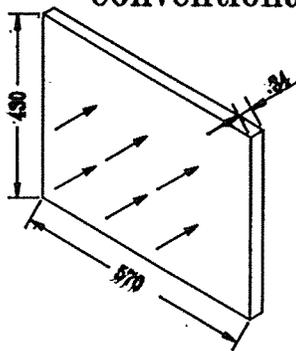
Correlation used: HTFS - supercritical heat transfer

SINTEF Refrigeration Engineering 1993



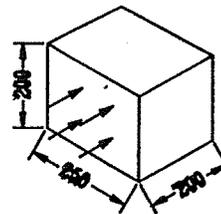
GAS COOLER DESIGN CONCEPTS

Conventional

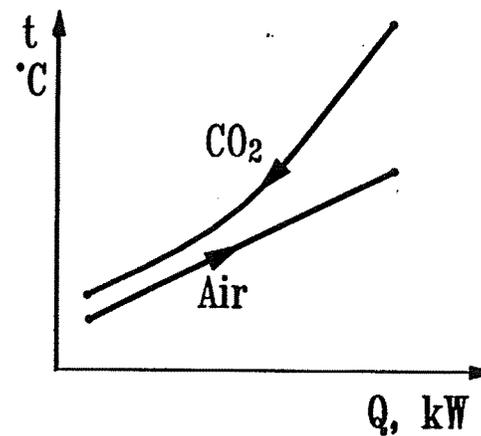
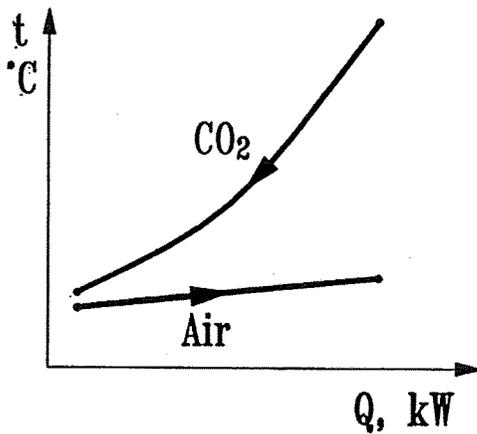


$V = 100\%$
 $\dot{v}_{\text{air}} = 100\%$
 $A = 100\%$
 $m = 100\%$

Counterflow



$V = 120\%$
 $\dot{v}_{\text{air}} = 20\%$
 $A = 114\%$
 $m = 110\%$



APPLICATION OF "NATURAL" REFRIGERANTS

New System Concepts For The Use of CO₂

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THE REFRIGERANT SITUATION

A good half century ago the "freons" were introduced with a massive advertising campaign. The main arguments put forward in their favour were complete safety and harmlessness to the environment. Both of these claims have been proved wrong. Many accidents have occurred due to suffocation in the heavy gas, without warning, in below threshold spaces. Today the CFC's are being banned world wide as a result of their alleged effect on the ozone layer. At the Copenhagen meeting recently it was decided that the HCFC's must be controlled too.

This is by no means a unique experience. Similar predicaments have occurred by release to the environment of many other new chemicals. The extensive use of ever new compounds is one of the big problems of our time. In this situation it does not seem very sensible to replace the CFC/HCFC's with a new family of related halo-carbons, equally foreign to nature, to be used in quantities of hundred thousand's of tons every year.

In principle it must be a much better solution to use naturally occurring substances as refrigerants, compounds already circulating in quantity in the biosphere and which we know are harmless. Examples can be water, air, carbon dioxide, ammonia, hydrocarbons, nitrogen or the noble gases. Some of them are already in the focus for extended use in the future, in particular air, ammonia and propane. In the following it will be shown how the "old" refrigerant CO₂, which has been completely abandoned during the last 40 years, can be used to advantage in new and properly designed systems.

COMPARISON OF REFRIGERANTS

Let it be said again: The absolutely ideal refrigerant in every respect does not exist. All available compounds have their weak sides, which must be taken into account in the design and operation of the system. The halocarbons for instance have, in addition to the environmental effects, relatively large flow resistance losses and poor heat transfer, associated to their high molar mass. Other substances can be combustible or poisonous, like ammonia, and require special safety precautions. This is not technically difficult, but more an economic question, and restricts the use in certain applications.

The alternative refrigerants also differ greatly with regard to pressure and volume requirement, the relative influence of water, oil and impurities, the effect on the common machine building materials, leak detection, availability and price. The art of choosing the best compound for a given application consists in minimizing the effect of all these properties on the overall cost, reliability of operation and efficiency.

The power consumption for a given system concept is of crucial importance and deserves some discussion.

POWER REQUIREMENT

The efficiency or COP of any reversible (loss free) process, working between given temperature limits, is exactly the same and completely independent of the properties of the working medium used. This follows directly from the 2. law of thermodynamics. The thermal properties of the refrigerants influence the power consumption only through their effect on the thermodynamic losses.

Much misteaching has been heard concerning the "efficiency or COP of different refrigerants". A host of publications in recent years compare different substances when they are used in the traditional reference process, the Evans-Perkins (E-P) process from 1834, Fig. 1A. This is encumbered by two irreversible elements, the superheat peak which is lost in heat exchange in the condenser, and the throttling loss which is supplied as heat to the evaporator. Both losses are shown hatched in the figure. They are affected differently by the refrigerants specific heat capacity properties, and this more or less cancels out, so that only a marginal difference shows up in the efficiency comparison. This is often much overestimated in importance, and many people are actually given to believe that a refrigerant really "has an efficiency".

In a real machine a number of additional irreversibilities occur, which depend on the refrigerant properties and may be far more important than those included in the E-P process. They are also heavily influenced by plant design. Figs. 1B and C give a schematic survey in the temperature-entropy chart for refrigeration and heat pump, respectively, with the individual losses indicated by the squares $\Delta s \cdot T_0$. The loss energy which is released as heat at the evaporation temperature, also represents a loss of refrigeration capacity. The part of the loss area between this level and the ambient T_0 , can be interpreted as the work which is theoretically required to compensate for this. In the case of the heat pump this effect is small, since the evaporation temperature is normally close to ambient.

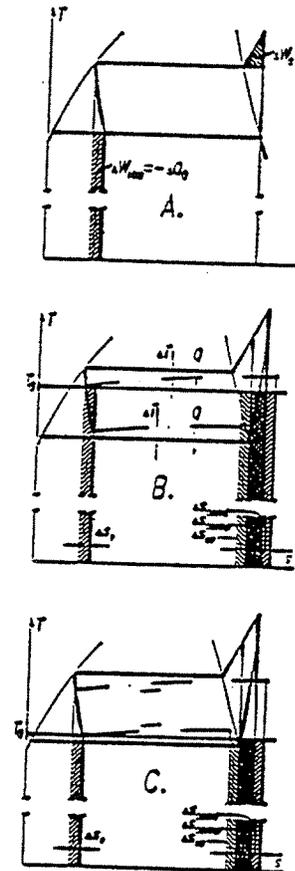


Fig. 1 - Temperature - entropy diagrams showing A: irreversibility losses in the normal reference (EP) process. B: real cycle losses ($T_0 \cdot \Delta s$) in a refrigeration machine and C: in a heat pump.

The main losses in a common single stage system are the following:

- Compressor loss, $\Delta s_{\text{comp}} \cdot T_0$, depending of the absolute pressure level, the pressure ratio for a given temperature lift, the adiabatic exponent and other thermal properties

of the working medium, and diverse design parameters.

- Condenser loss $\Delta s_{\text{cond}} \cdot T_o$, depending of the fit to the actual temperature boundary of the application and the heat transfer properties of the medium.
- Throttling loss $\Delta s_t \cdot T_o$, depending of the ratio of the specific heat capacity of the liquid and the evaporation enthalpy, cp/r .
- Evaporator loss $\Delta s_{\text{ev}} \cdot T_o$, again a function of temperature fit and heat transfer properties.

In addition the flow resistance losses in the circuit depend of the refrigerant properties and in particular its molar mass, deciding the amount which has to be pumped for a given capacity.

All the individual losses, including those integrated in the theoretical E-P process, can be influenced by the design of the system; type and design of compressor, dimensioning of heat exchangers and piping, adjustment to temperature boundaries, choice of expansion aggregate etc. In principle any thermodynamic loss may be reduced as much as desired by increased expenditure in technical resources; optimization is an economic question. The evaluation of the suitability of a refrigerant is only possible in relation to the system in which it is going to be used. A compound which does not show up well by the conventional comparison on the basis of an E-P process, may actually give superior performance in a suitably designed plant.

DESIREABLE PRESSURE LEVEL

The work exchanged in any thermodynamic machine, be it a heat engine, a water turbine, a refrigeration plant or what ever, is a direct function of the product $P \cdot V$, the pressure and volume changes of the working medium, or more exactly the area of the process in the P-V chart, $\oint P \cdot dV = -\oint V dP$. A high pressure means small dimensions and, within reasonable limits, low first cost. In modern energy systems where the working pressure can be chosen freely, it has increased steadily over the years in direct consequence of technical development. Such is the case for instance with cold gas machines (ex. Philips, ~100 bar) and in the oil hydraulics field, where pressures in the range 100-400 bar are common today. Refrigeration and heat pump systems are generally composed of piping units and displacement machinery of a similar nature, and a corresponding pressure level would be desirable for optimal economy.

A parallel development has not been possible in refrigeration and heat pump technology due to the desire to operate well below the critical point, in order to avoid excessive overheating - and throttling losses in the E-P process. For nearly all currently used refrigerants, including all the halocarbons, the critical pressure is in the range 30-50 bar. The exceptions are water vapour (221 bar), ammonia (113 bar) and carbon dioxide (71 bar). Standard compressors on the market therefore have a maximum pressure rating in the order of 25 bar. Recently an ammonia machine for 40 bar pressure was introduced for the use in heat pumps with temperature up to 80°C [1]. But in general refrigeration engineers use pressures, which were common in other fields of power machinery 100 years ago.

In order to operate at rational pressures from an engineering viewpoint, it is necessary to use a supercritical or transcritical process, with the exception of water vapour or possibly ammonia refrigerant systems. Supercritical systems are well established for the so-called "cold gas machines", which are best suited for applications with high temperature lift.

Continued efforts to adapt them for the normal range of refrigeration usage have not been successful so far. Trans critical cycles have been avoided except for gas liquefaction, due to their poor efficiency when they are evaluated on the basis of the E-P process.

The following will demonstrate how it is possible to design such systems with very competitive performance characteristics.

CO₂, A NEAR IDEAL REFRIGERANT

Carbon dioxide was a commonly used refrigerant from the late 1800's and well into our century. Due to its complete harmlessness it was the generally preferred choice for usage on board ships, while ammonia was more common in stationary applications. By the advent of the "Freon's" and R-12 in the first place, CO₂ was rapidly abandoned, and it has nearly been forgotten in the course of the last 40-50 years. The main reasons for this development was certainly the rapid loss of capacity at high cooling water temperatures in the tropics, and not less the failure of the manufacturers to follow modern trends in compressor design towards more compact and price effective high speed types. Time is now ripe for a re-assessment of this refrigerant for application with present day technology.

Some important properties for the comparison of CO₂ with currently used refrigerants can be found in Table I. CO₂ is naturally present everywhere in our environment. The air contains about 0,35 promille of it, in total nearly 300 billion tons for the whole atmosphere, and several hundred billion tons per year circulate in the living biosphere. No complicated and time consuming research is needed to ascertain its complete harmlessness.

Somebody may possibly object that CO₂ is also a greenhouse gas, and this is of course correct, although its effect is minute compared to that of the halocarbons. But in reality gas will be used which is already available in unlimited quantity from other activities. What we do is just to postpone its release. This is in principle good for the environment, like planting a tree to bind carbon for a period of time.

With regard to personal safety, CO₂ is at least as good as the best of halocarbons. It is non-toxic and incombustible, of course. By release from the liquid form about half will evaporate while the remainder becomes solid in the form of snow and can be removed with broom and dustpan, or just left to sublimate. Most people are already familiar with the handling of "dry ice". In the case of accidental loss of a large quantity, a good ventilation system is required in order to eliminate any risk of suffocation, in particular in spaces below ground level.

It is some time asserted that the high pressure of CO₂ could constitute a special danger in the case of accidental rupture. Actually this is not so since the volume is so small. In the same way as the product P•V is approximately the same for all systems with the same capacity, the same holds for the explosion energy, regardless of the refrigerant used.

CO₂ also has a number of further advantages:

- pressure close to the economically optimal level
- greatly reduced compression ratio compared to conventional refrigerants
- complete compatibility to normal lubricants and common machine construction materials
- easy availability everywhere, independent of any supply monopoly
- simple operation and service, no "recycling" required, very low price

Table 1 Characteristics and properties of some refrigerants

| Refrigerant | CFC-12 | HCFC-22 | HFC-134a | NH ₃ | CO ₂ |
|---|---------|---------------------|---------------------|-----------------|---------------------|
| Natural substance? | No | No | No | Yes | Yes |
| ODP | 1.0 | 0.05 ⁽¹⁾ | 0 | 0 | 0 |
| GWP ⁽²⁾ , 100 years 20 years | 7100 | 1500 | 1200 | - | 1(0) ⁽³⁾ |
| | 7300 | 4100 | 3200 | - | 1(0) |
| TLV _{3h} (ppm) | 1000 | 1000 | 1000 ⁽⁴⁾ | 25 | 5000 |
| IDLH ⁽⁵⁾ (ppm) | 50.000 | - | - | 500 | 50.000 |
| Amount per room vol. ⁽⁶⁾ , (vol% / kg/m ³) | 4.0/0.2 | 4.2/0.15 | - | - | 5.5/0.1 |
| Flammable or explosive? | No | No ⁽⁷⁾ | No ⁽⁷⁾ | Yes | No |
| Toxic/irritating decomposition products? | Yes | Yes | Yes | No | No |
| Approx. relative price | 1 | 1 | 3-5 | 0.2 | 0.1 |
| Molar mass | 120.92 | 86.48 | 102.03 | 17.03 | 44.01 |
| Volumic ⁽⁸⁾ refr. capacity at 0°C (kJ/m ³) | 2740 | 4344 | 2860 | 4360 | 22600 |

(1) Somewhat higher values have been suggested by recent studies. (2) Global warming potential in relation to CO₂, with 20 and 100 years integration time (IPCC 1990, 1992). (3) Abundant amounts of CO₂ is recovered from waste gas. Thus, the effective GWP of commercial carbon dioxide, for instance used as refrigerant, is 0. (4) Suggested by ICI etc. (5) Maximum level from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects [17]. (6) Maximum refrigerant charge in relation to refrigerated room volume, as suggested in ANSI/ASHRAE 15-1989: Safety Code for Mechanical Refrigeration. (7) Although considered to be non-flammable, both R-22 and R-134a are combustible in certain mixtures with air at elevated pressures, but ignition may be difficult. (8) Enthalpy of evaporation divided by saturated vapour volume.

The effective application of this medium depends on the development of suitable methods to achieve a competitively low power consumption in operation near and even above the critical point. The following paragraphs will give examples of how this can be done.

A COOLING SYSTEM FOR MOTORCAR AIR CONDITIONING

More than 20 million new cars are equipped with an air cooling system every year, and the number is increasing. Until now these units have been working with CFC-12 refrigerant exclusively, and the yearly loss to be atmosphere has been estimated at 120-150.000 tons, much more than for any other field of refrigeration application. Presently a rapid conversion to R-134a has been initiated, and this will solve part of the problem. But an important influence on the greenhouse effect remains, increasing the total contribution of an average future motorcar by an average 15-20 per cent, and the need for a more environmentally benign solution remains [2].

At Institutt for kuldteknikk, NTH/SINTEF, we have for some years worked on the development of a motorcar air conditioning unit using CO₂ refrigerant, presenting a complete solution to the environmental problem. The system and its performance characteristics are

more completely described in a recent publication [3] and will probably also be the subject of another paper at this conference [6]. I will therefore limit myself to a brief description of the principals:

A schematic diagram of the new system and its working principle in the P-h chart are shown in Fig. 2. It is also demonstrated how the refrigeration output and power consumption can be changed by varying the discharge pressure of the compressor, and this should normally be regulated to give a COP near its maximum. When needed the capacity can be increased above its normal value by a further increase of pressure at the cost of a somewhat higher power consumption. This is an important advantage, for instance in starting from a overheated condition of the passenger compartment. The cooling time is shortened, the size of the system can be smaller than otherwise required, and the total energy expenditure is actually decreased.

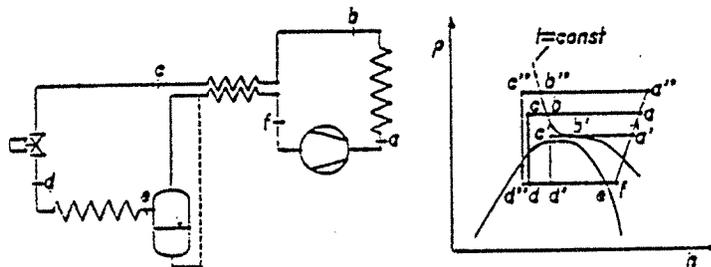


Fig. 2 - Flow circuit and P-h diagram for the trans-critical cycle [4]

The low side liquid separator/receiver in combination with the internal heat exchanger is essential to the proper functioning of the system and has a multi-various purpose:

- to permit a certain excess amount of liquid supply to the evaporator in order to simplify the control system and enhance heat transfer
- to withdraw or deliver extra charge of refrigerant for the regulation of the high side pressure by means of the throttling valve
- to hold a sufficient amount of liquid to cover the needs under all possible working conditions and compensate for unavoidable losses by leakage over a reasonable time
- to meter a suitable amount of lubricant to the compressor by means of a capillary tube or throttling valve to the suction line.
- to provide a sufficient gas volume to avoid excessive pressure build-up when the plant is idle at very high ambient temperature.

Extensive testing of prototype equipment in the laboratory has shown that the new system works well under all conditions which can be expected in practical usage. The energy performance is as good or even better than for the systems presently used, as demonstrated by the exergy flow charts in Fig. 3 [3]. The good result is much due to the excellent performance of the compressor, when operating with a very high mean pressure in combination with a very moderate compression ratio. The efficient heat transfer in the evaporator also contributes to the result.

LARGE HEAT PUMPS

Another example relates to a very different application; space heating by means of large heat pumps.

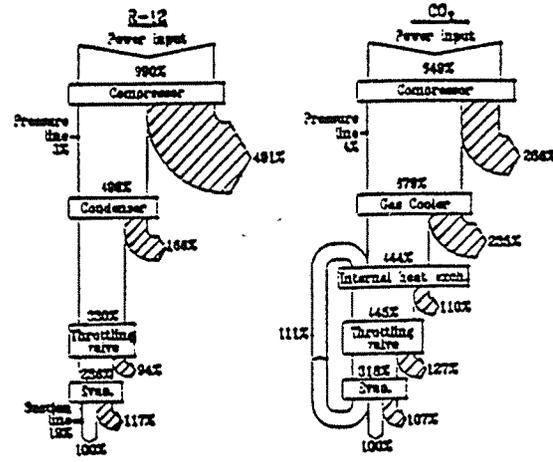


Fig. 3 - Exergy flow in the standard R-12 system (left) and the CO₂ prototype (right) at ambient temperature 43°C and 30°C in the passenger compartment, driving conditions.

Most heat pumps extract low temperature heat from the immense reservoir of the environment (air, water, rock) and a process with constant temperature evaporation is therefore quite suitable for the purpose. They give off the thermal energy at a higher temperature to a finite stream of air or water with limited heat capacity, resulting in a more or less gliding temperature. The amount of temperature change can range from a few degrees in a small direct condensation air heater, 15-20 K for normal "split units", up to 30-40 K in large district heating networks and even more in some industrial applications and direct tap water heating. This causes a very considerable excess power requirement in the normal type of cycle with condensation and heat rejection at essentially constant temperature, Fig. 4A. What one should really have, is a cycle with gliding temperature output as indicated schematically in Fig. 4B.

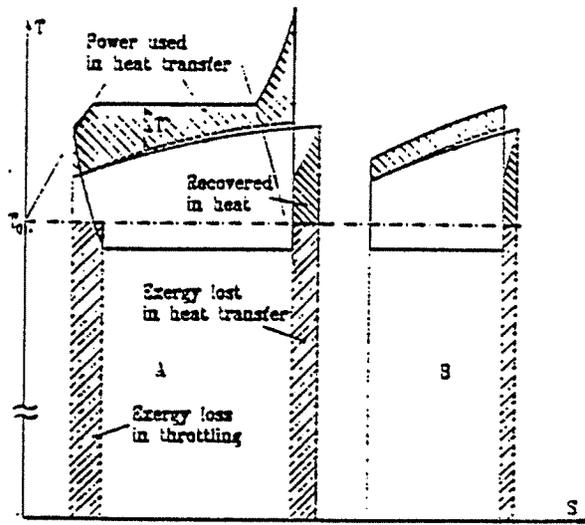


Fig. 4 - Exergy loss in heat rejection from a heat pump to a stream of fluid with finite capacity. A: Conventional E-P process. B: Gliding temperature ("Rhombic") process.

Such a process can be approached by a trans-critical cycle, using CO₂ as a working medium, Fig. 5. In order to get a satisfactory fit to the near logarithmic temperature curve of the heat absorbing medium (water), the discharge pressure should be well above critical, in the order of 90-100 bar or higher. This means that when the evaporation temperature is for instance 0°C, the discharge temperature in single stage compression with dry saturated suction will be about 70-80°C. This temperature can be adjusted in a certain range, up or down, by varying the discharge pressure and suction gas state as illustrated schematically in Fig. 5B, using a conventional suction gas heat exchanger or, eventually, some liquid injection. The flexibility in the direction of a temperature reduction is rather limited, however. Lowering

the pressure too much will deteriorate the temperature curve fit in heat exchange, while wet suction rapidly leads to poor compressor performance. The single stage system shown is therefore most suitable when the required temperature glide is higher than 40-50 K, depending on the heat source temperature. In such cases it may easily reduce the specific power consumption by up to 40 per cent compared to the conventional process, improving the COP correspondingly.

For most applications we need heat pumps with a smaller temperature glide. This problem is readily solved by a system of staged compression, to give a discharge temperature close to the desired level. Fig. 6 gives an example of a two stage arrangement, suitable for a modern low temperature district heating application with a heating range for instance 35-60°C. The temperature-entropy chart compares the transcritical CO₂-process with a conventional R-12 system for the same capacity and temperature requirement. The power saving achieved by the better temperature fit in heat transfer is a good 20 per cent, but much of this is lost again in the throttling from a relatively high temperature. On the other hand the compressor efficiency will be much better for the CO₂ alternative as a result of the greatly reduced compression ratio. All told the CO₂ system will be considerably superior to the conventional one with regard to energy performance.

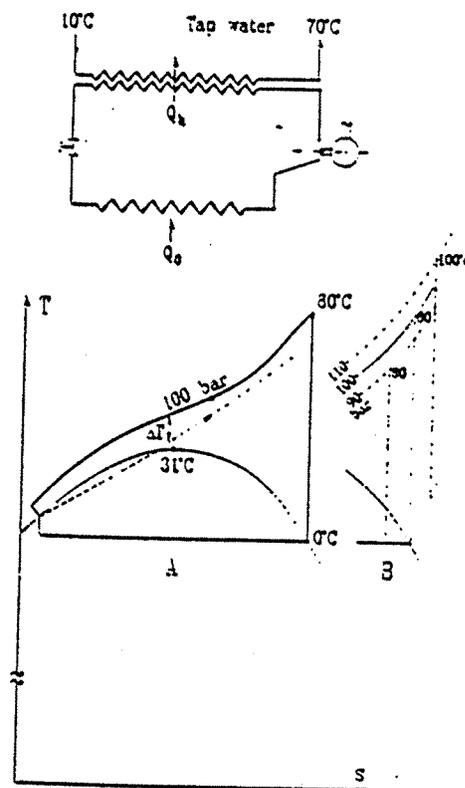


Fig. 5 - Temperature - entropy chart for a trans-critical heat pump producing hot water.

It may be objected that a two stage system is a complication and means added cost. The difference in this respect is very modest, however. Two stage centrifugal compressors is normal in district heating plants anyway, and the splitting of the high side heat exchanger in two parallel circuits is actually a minor adjustment. The modifications will be paid for many times over by reduction in the physical dimensions alone, not to mention the important saving in power. Very important is also elimination of the heavy leakage of CFC or HCFC to the atmosphere, often associated with large district heating heat pumps.

As pointed out above, the relatively high throttling loss for CO₂ detracts considerably from the advantage of this refrigerant in a simple system as shown. This can be amended by a number of well known methods [5]. One solution is a normal two flow throttling and subcooling as shown schematically in Fig. 7. It is also expedient to recover the expansion energy directly, since the properties of CO₂ makes this feasible.

With a conventional refrigerant like R-12 most of the theoretical expansion work comes from the flash gas and the P-v diagram becomes very thin, with a low mean pressure, Fig. 8. For CO₂ the situation is quite different, with most of the work in the liquid phase, a high mean pressure and small volume requirement. An expansion aggregate becomes a cost effective element in a large installation, which may take the form as shown schematically in Fig. 9.

Such a system with a temperature glide in the order of 25-30K has the capability of increasing the COP by at least 20-25 per cent in comparison to conventional installations. Operating under conditions deviating from the ideal temperature match the efficiency will suffer, but will still be superior over a fairly wide range.

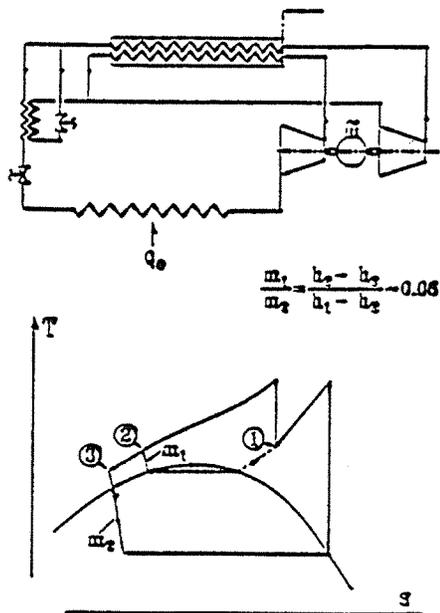


Fig. 7 - Two flow throttling and subcooling.

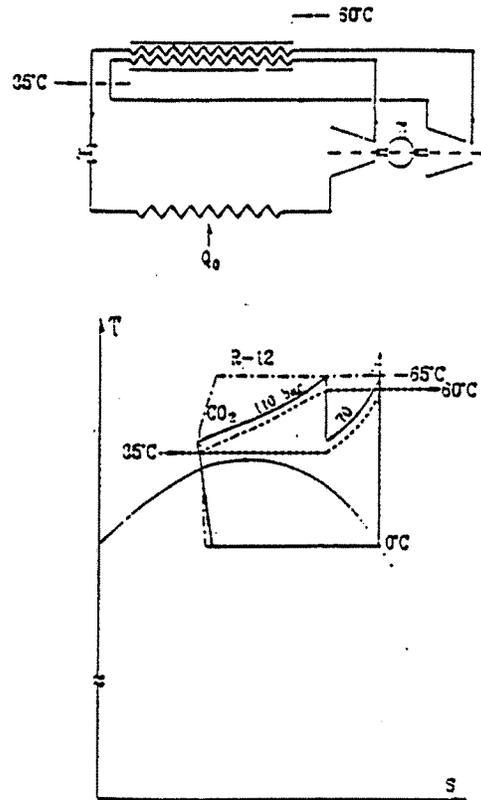


Fig. 6 - Schematic flow diagram and T-s chart for a two stage CO₂ heat pump with 25K temperature glide for district heating. A conventional R-12 process for the same service is plotted for comparison. Ancillary equipment needed for pressure regulation etc. is omitted.

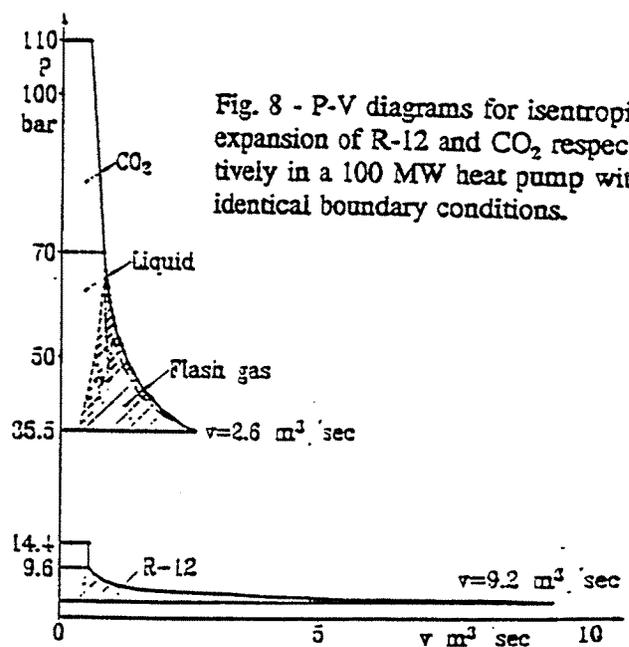


Fig. 8 - P-V diagrams for isentropic expansion of R-12 and CO₂ respectively in a 100 MW heat pump with identical boundary conditions.

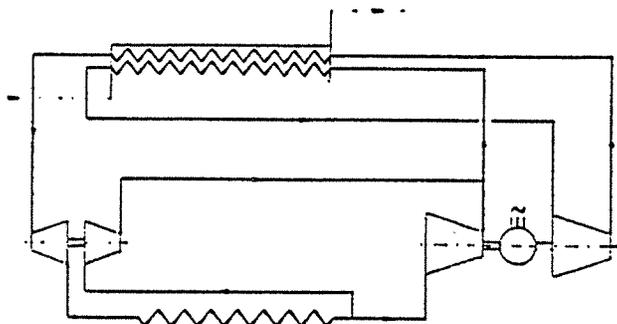


Fig. 9 - Schematic flow diagram for a two stage CO₂ heat pump with expander unit for a typical temperature glide 20-30K (district heating).

CONCLUSION

Simple logic would indicate that the sensible way to solve the CFC/HCFC predicament is to use substances which are already present in the natural ambience and for which circulation systems have been long established. One alternative is carbon dioxide, which is absolutely ideal from a safety and environmental point of view. It is also inexpensive and readily available everywhere. Its relatively high pressure and moderate molar mass give important advantages in volume and cost of the system when the equipment is properly designed.

The drawback of CO₂ is that it requires modification of the thermodynamic cycle in order to achieve a satisfactory energy efficiency. By way of example it is shown how this can be done in automotive cooling and for typical large heat pumps.

Making use of the special properties of CO₂ in transcritical operation it is possible to achieve a nearly ideal fit to the gliding temperature, which is required in such applications as for instance large district heating schemes. The high pressure differential and relatively small flash gas volume open the possibility of efficient recovery of the expansion exergy in a compact expander. By taking advantage of these qualities it is possible to design large heat pumps with the following merits:

- Completely safe and environmentally compatible refrigerant
- Superior performance, about 20 per cent higher COP than conventional CFC systems
- Compact and cost effective components

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RESUMÉ

APPLICATION DES FLUIDES FRIGORIGÈNES NATURELS Des Systèmes Nouvelles pour l'utilisation de CO₂

De point de vue protection de l'environnement il est désirable d'appliquer des frigorigènes "naturels", déjà présents dans la biosphère. Dioxide de carbone CO₂ est un tel combinaison chimique, presque idéal quand it est utilisé dans une cycle donnant un COP competitive. Des exemples montrent comment ca peut être réalisé en pratique.

Mots clefs: Frigorigènes, Dioxide de carbone, Thermodynamique, Cycles thermodynamiques.

CFC- and FHC-free refrigerators by FORON Hausgeraete Co. - A breakthrough in household refrigeration

by A.Meyer, FORON, chief of testing laboratory cooling

1. History of using different refrigerants

- 1870 using of ammonia (NH_3)
- 1920 using of sulphur dioxide (SO_2) or methylchloride (CH_3Cl)
- 1930 development of CFC (chlorinated fluorcarbone) in the United States
- 1950 wide using of CFC in Germany
- 1970 dominant use of CFC worldwide; regarding CFC-overall consumption see Fig.1; small refrigeration devices are responsible only for 5-6% of this consumption
- 1968 first signs that the ozone layer of the earth is being destroyed
- 1970 permanent widening of the "ozone hole"
- 1986 discovery that chluride are responsible for the destroying of the ozone layer
- 1987 (16.September) Signing of the Montreal Protocol by 43 states fixing that the use of CFC will be reduced by 50% until 1998
- 1993 agreement at the Kopenhagen conference that due to the ongoing destruction of the ozone layer the CFC-production will be ceaseds completely by 1996

2. Criteria dor choosing alternative refrigerants

The foreseeable ban on the production and consequently the use of CFC as so far widely used refrigerant forced the science community and the industry to search for alternatives.

Preconditions in choosing were:

- It could be only refrigerants allowed for use by legislation, in Germany according to the standards DIN 8962 G 1-3. (see Table 1)
- The substitutes must comply with the legislative standards set in Par.1 of the Montreal Protocol.
- The energy efficiency should be equal or better compared with the predecessor, which means
 - * same proportion concerning q_{av} / l_{ad} see Table 2
 - * same or better proportion concerning p/p_0 (see Fig. 2)
 - * low adiabatic exponent
 - * chemical stability with conventional materials
 - * good mixturebility with simple oils
 - * as far as possible resulting in the same cooling load of the compressor to avoid serious changes.

Besides ammonia, sulphur dioxine and carbon dioxine, known refrigerants are derivates of hydrocarbons as seen in Fig. 3. To compare them and to judge on the impacts of various derivates of different hydrocarbons as foaming agents and/or re-

frigerants, the main components are marked with different colors: red - chloro, yellow - fluoro, green - carbono and blue - hydro.

To comply with the above mention CFC-ban, the refrigeration industry in fact unanimously orientated on the fluorinated hydrocarbone (FHC) R 134a, neglecting that it is accelerating the "greenhouse effect" as another important global environmental danger.

3. Energy efficiency of hydrocarbons

To decide the future strategy of FORON in using alternatives for CFC numerous testings were made on compressors and refrigerators.

The results of the testings of refrigerants can be seen from Fig. 4.

The main results are as follows:

- The refrigerating capacity $t_0 \leq -15^\circ\text{C}$ of R 134a is smaller than that of R 12 or R 290/600a (propane/isobutane).
- The energetical disadvantages of 134a are obvious.
- R 12 and R 290/600a have the same refrigerating capacity in the whole t_0 -range.
- The testings showed clear energetical advantages of R 290/600a at $t_0 \geq -35^\circ\text{C}$ compared with R 12 and R 134a.
- By using R 290/600a it is possible to lower the temperature of the compressor and its motor in the whole range of using.
- R 290/600a have a good mixturebility with mineral oils.

All these results let to the conclusion that as far as energy efficiency of the refrigerant and the compressor is concerned, hydrocarbones (here propane/isobutane) will be a better alternative to CFC 12 than the FHC 134a preferred by others.

4. Energy efficiency regarding refrigerators

The results of the subsequent extensive tests of an refrigerator using 3 different refrigerants are seen in Table 3:

- Though when using CFC 12 or FHC 134a no changes (except the oil) at the refrigeration device were necessary, minor details had to be changed before using hydrocarbones.
- The main steps in lowering the energy consumption are shown in Fig. 5 (dkk 0111/92):
 - + 40% compared to CFC 12 by drop-in of pure propane.
 - + 22% compared to CFC 12 by drop-in of R 290/600a
 - 0 after the first changes of the evaporator
 - 10% after the next changes of the evaporator.

By that it was proved that the energetic advantages of hydrocarbons as an alternative refrigerant could be successfully transferred to the household refrigerator as a whole.

5. Insulation

After the agreement on the future CFC ban most of the producers were searching for substitutes of CFC 11 for insulation foaming to. The history here was as follows:

- 1988 reducing the CFC 11 portion by 50%
- 1992 allowing of R 142b/22
allowing of R 141b
- 1993 allowing of R 134a
allowing of cyclo-pentane

The difference to the refrigerant problem is here a variety of solutions, especially the use of R 134a or cyclo-pentane. As far as FORON is concerned, we are so far using pentan/hydro- and hydro-foamed polystyrol as shown in Fig. 6. The reason for this are the obvious advantages of polystyrol concerning recycling compared with foamed PUR. To compensate the known disadvantages in the insulation capability of polystyrol compared with PUR, the insulation was made 10 mm thicker than before. Further works to minimize the heat gain are under way.

6. Security technique

The above mentioned results of the development works concerning the cooling unit and the insulation led to the decision of preparing a whole range of completely CFC/FHC-free refrigerators for serial mass production. These refrigerators had to comply with the same strict security standards as other household refrigeration appliances. To satisfy these high standards even when using inflammable hydrocarbons, additional measures were taken to avoid possible dangers in the case of an unlikely uncontrolled disposal during the lifetime use:

- Because of the minimized portion of the refrigerant (24 g-R 290/600a instead of 75 g CFC 12) an inflammable mixture can not occur outside the refrigerator.
- To eliminate the highly theoretical danger that an inflammable mixture could occur inside the refrigerator the following additional changes were made:
 - * using of a newly developed hermetically sealed lightning
 - * transfer of the temperature control and the light switch from the inside to the outside.

After these changes were made, the safety of the fridge was confirmed by the TÜV (Technical Monitoring Association) Bavaria/Saxonia and the TÜV Product Service Hannover as independent experts, including the awarding of the "GS (Proved Security)" mark.

7. Conclusion

Considering the foreseeable CFC-ban according to the Montreal Protocol, began the surge for alternative substances as refrigerant and foaming agent worldwide. Though many companies preferred the FHC 134a, despite the fact that it is accelerating the "greenhouse effect", FORON choosed the path of using hydrocarbons as an environment saving alternative.

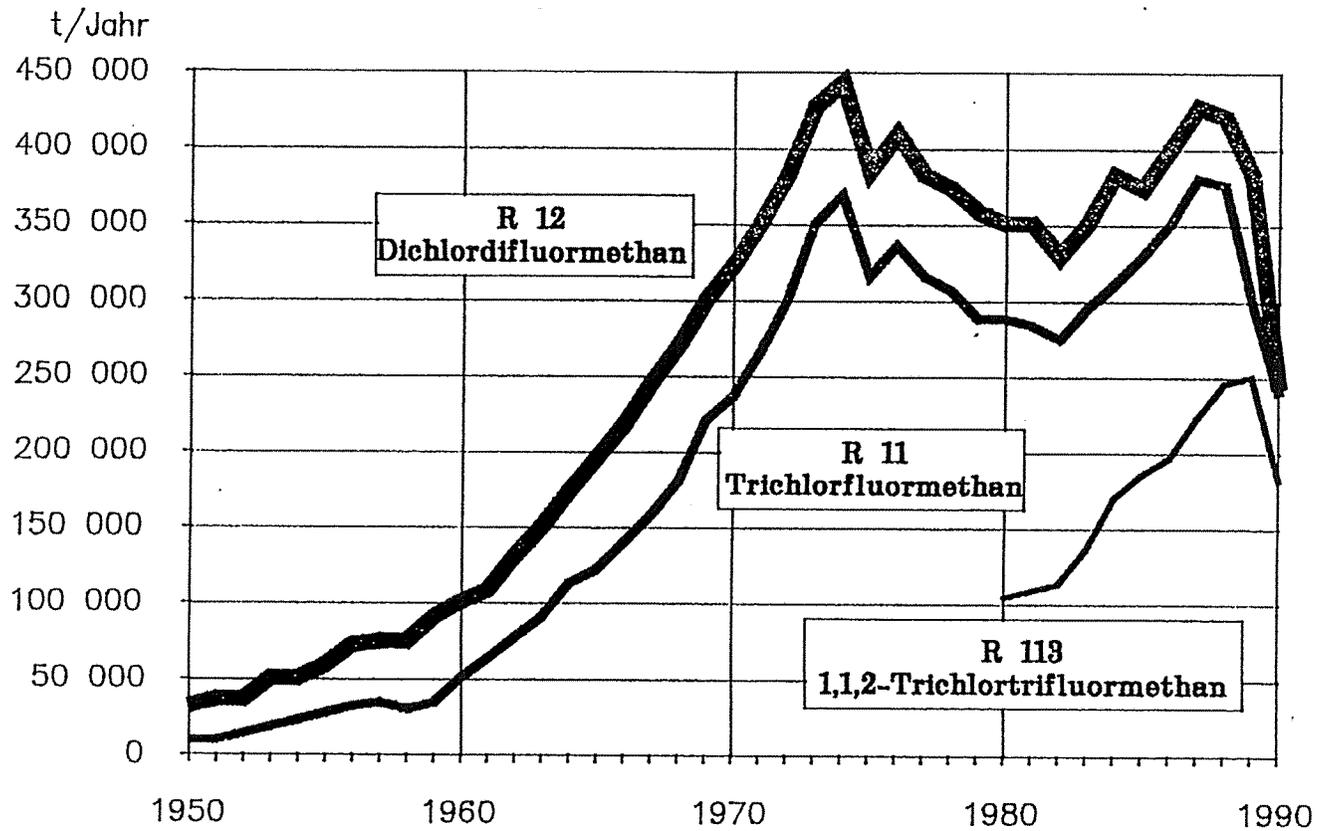
The results of extensive tests over many years proved, that these natural gases have obvious energetical advantages, that their using in the mass production process is rather uncomplicated and that the security problems concerning inflammable gases could be successfully solved. Since the starting of serial production in mid-March over 60.000 completely CFC/FHC-free refrigerators were produced and sold mainly in Germany. Further development works on the improvement of the technology are under way (see Table 5 GT 200 DC/KT 200 RC).

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figure 1

world-production CFC



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figure 3

Die Einordnung des Kälte- und Treibmittels vom Öko-Kühlschrank KT 1370 RC im Stammbaum der Fluor- u. Chlorerivate der Kohlenwasserstoffe (Methan bis Hexan)

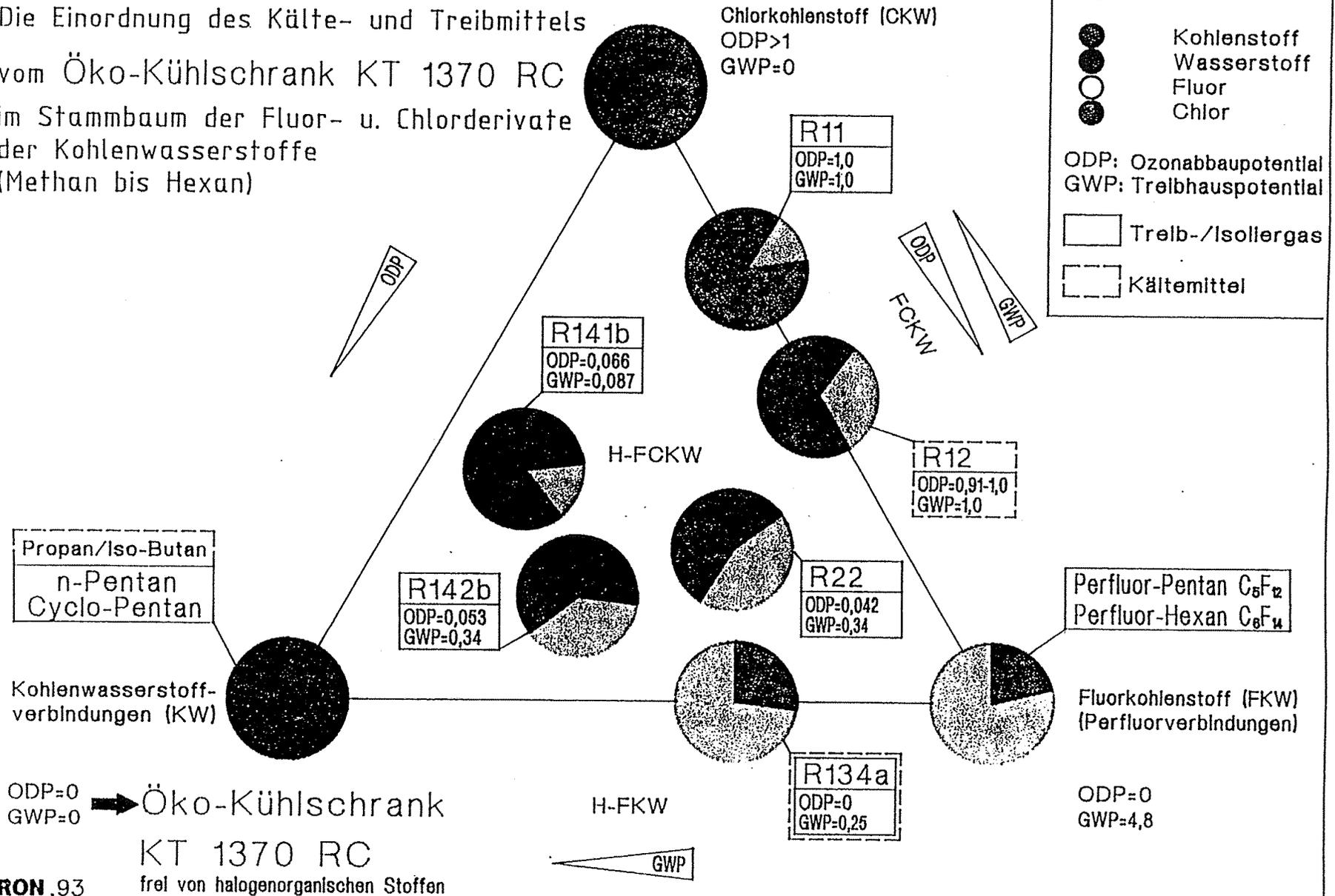


figure 4

hermetic compressor parameters

- KV 0,63 with R 290/R600a , 50/50
- - - KV 0,63 with R 12
- KV 0,63 with R 134a

conditions : $t_f = 55\text{ }^\circ\text{C}$
 $t_g = t_{g1} = t_{f1} = 32\text{ }^\circ\text{C}$
 220 V, 60 Hz
 statically ventilated
 $\Delta h = h_{g1} - h_{f1}$

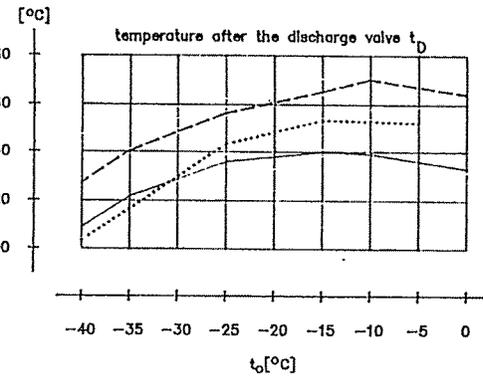
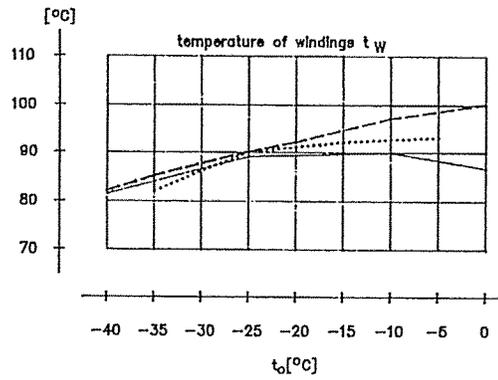
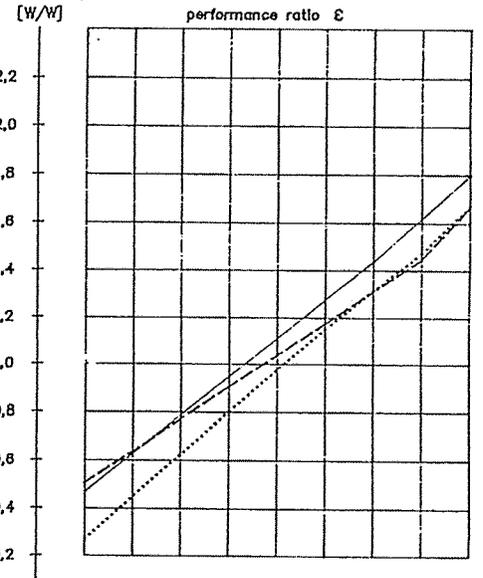
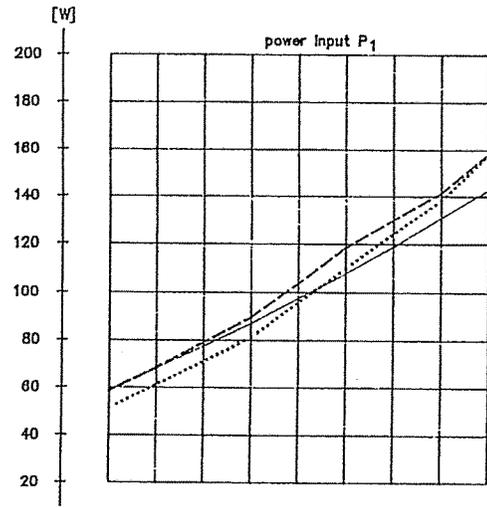
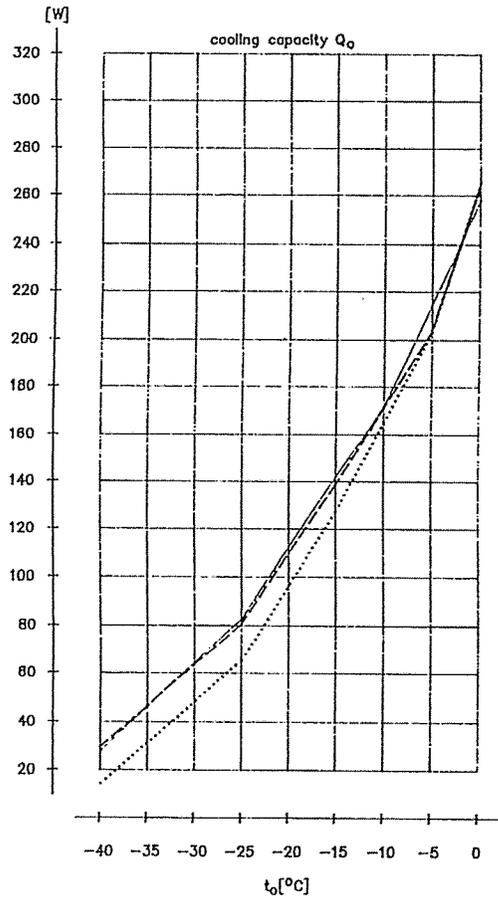
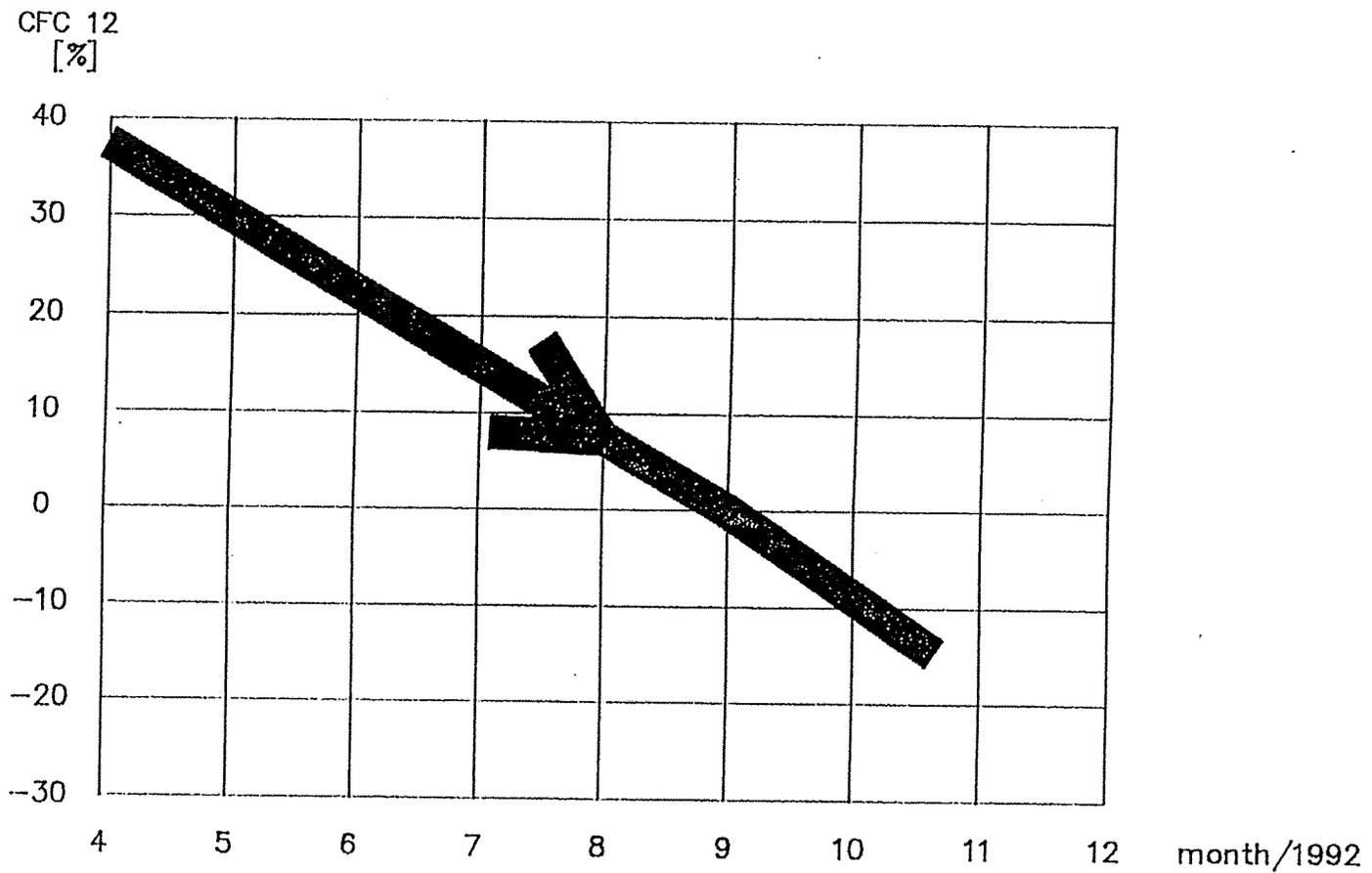


figure 5

Reduce energy consumption by use of Propan/Isobutan in relation to CFC 12



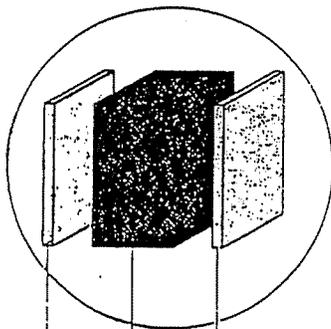
Clean Cooler

figure 6

- kein FCKW
- kein FKW
- recycelbar

Verbundlose Wandkonstruktion

→ einfache Demontage



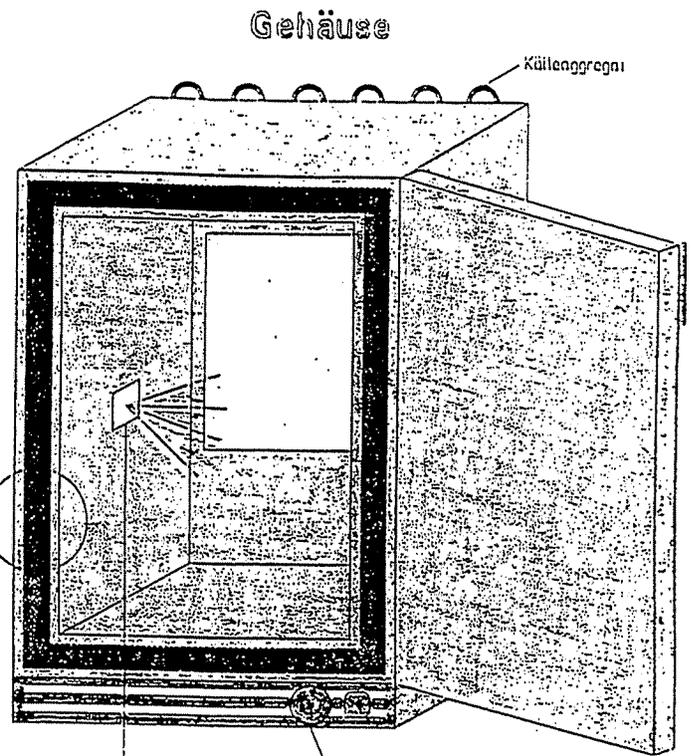
Stahlblech

Wärmedämmung

Innenverkleidung

recycelbare
Thermoplaste

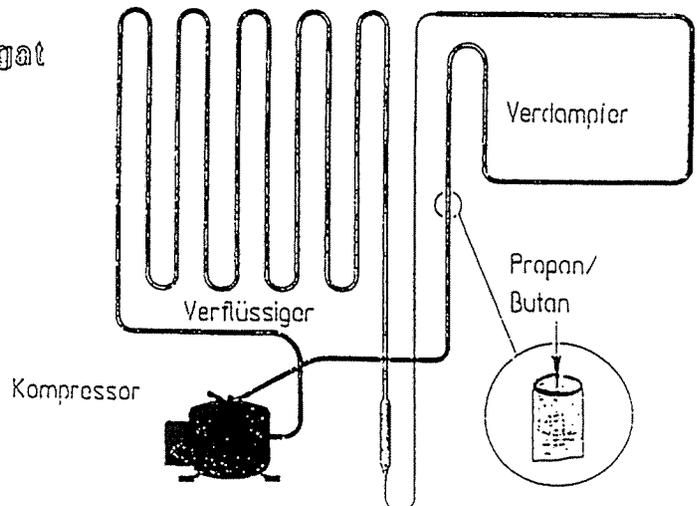
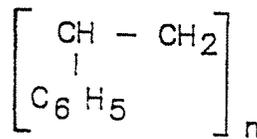
Hermelisch gekapselte
Beleuchtung



Temperaturregler und
Lichtschalter außerhalb

Kälteaggregat

EPS



FORON , 93

Table 1 classification of refrigerants

| Gruppe | Kältemittel Nummer | Benennung | Formel | Gruppe | Kältemittel Nummer | Benennung | Formel | Gruppe | Kältemittel Nummer | Benennung | Formel |
|--------|--------------------|--------------------------------|---|--------|--------------------|--------------------|--|--------|--------------------|---------------------------|---|
| L | R | | | L | R | | | L | R | | |
| 1 | 718 | Wasser | H ₂ O | 2 | 717 | Ammoniak | NH ₃ | 3 | 1270 | Propylen | C ₃ H ₆ |
| 1 | 744 | Kohlendioxyd | CO ₂ | 2 | 152a | Difluorethan | CHF ₂ CH ₃ | 3 | 50 | Methan | CH ₄ |
| 1 | 134a | Tetrafluorethan | CF ₃ CH ₂ F | 2 | 32 | Bifluormethan | CH ₂ CH ₃ | 3 | | Bi-(difluor-methyl)-ether | CHF ₂ OCHF ₂ |
| 1 | 123 | Dichlortrifluor-ethan | C ₂ HCl ₂ F ₃ | 2 | 611 | Methylformat | C ₂ H ₄ O ₂ | 3 | 170 | Ethan | CH ₃ CH |
| 1 | 123a | Dichlortrifluor-ethan | | 2 | 764 | Schwefeldioxyd | SO ₂ | 3 | 280 | Propan | CH ₃ CH ₂ CH ₃ |
| 1 | 124 | Chlortetrafluor-ethan | CHClFCF ₃ | 2 | 142b | Chlordifluor-ethan | CClF ₂ CH ₃ | 3 | 600 | n-Butan | CH ₃ CH ₂ CH ₂ CH ₃ |
| 1 | 22 | Chlordifluor-methan | CHClF ₂ | 2 | 30 | Methylenchlorid | CH ₂ Cl ₂ | 3 | 600a | Isobutan | CH ₃ CH ₂ CH ₂ CH ₃ |
| 1 | 132b | Dichlordifluor-ethan | CH ₂ ClCClF ₂ | 2 | 40 | Methylchlorid | CH ₃ Cl | 3 | 1150 | Ethylen | CH ₂ =CH ₂ |
| 1 | 125 | Pentafluorethan | CF ₃ CHF ₂ | 2 | 160 | Ethylchlorid | CH ₃ CH ₂ Cl | 3 | 134 | Tetrafluor-ethan | CHF ₂ CHF ₂ |
| 1 | 501 | R 12 (20 %) + R 22 (75 %) | CCl ₂ F ₂ CHClF ₂ | 2 | 1130 | Dichlorethylen | CHCl=CHCl | | | | |
| 1 | 113 | Trichlortri-fluorethan | CCl ₂ FCClF ₂ | 2 | 141b | Dichlorfluor-ethan | CCl ₂ FCH ₃ | | | | |
| 1 | 500 | R 12 (73.6 %) + R 115 (26.2 %) | CCl ₂ F ₂ CH ₂ CHF ₂ | 2 | 143a | Trifluorethan | CF ₃ CH ₃ | | | | |
| 1 | 502 | R22 (48.8 %) R115 (51.2 %) | CHClF ₂ CClF ₂ CF | 2 | | Dimethylether | CH ₃ OCH ₃ | | | | |
| 1 | 11 | Trichlorfluor-methan | CCl ₃ F | | | | | | | | |
| 1 | 1281 | Bromchlorid-fluormethan | CBrClF ₂ | | | | | | | | |
| 1 | 1381 | Bromtrifluor-methan | CBrF ₃ | | | | | | | | |
| 1 | 12 | Dichlordifluor-methan | CCl ₂ F ₂ | | | | | | | | |
| 1 | 114 | Dichlortetra-fluorethan | CClF ₂ CClF ₂ | | | | | | | | |
| 1 | 115 | Chlorpenta-fluorethan | CClF ₂ CF ₃ | | | | | | | | |
| 1 | 503 | R 13 (59.9 %) + R 23 (40.1 %) | CClF ₃ + CHF ₃ | | | | | | | | |
| 1 | 13 | Chlortrifluor-methan | CClF ₃ | | | | | | | | |
| 1 | 23 | Trifluormethan | CHF ₃ | | | | | | | | |
| 1 | C318 | Octofluorcyclo-hutan | C ₄ F ₈ | | | | | | | | |

table 2

comparison between different refrigerants

| comparison between | | | | $\epsilon_{th} = q_o / l_{ad} [-] / [%]$ | | | | | | $q_o / v_{g1} [kJ/m^3] / [%]$ | | | | | |
|----------------------------|----------|-------|----------|--|--------|-------|--------|--------------|---------|-------------------------------|--------|-------|--------|--------------|---------|
| conditions [$^{\circ}C$] | | | | R 12 | R 134a | R 290 | R 600a | R 290/R 600a | | R 12 | R 134a | R 290 | R 600a | R 290/R 600a | |
| t_o | t_{oh} | t_f | t_{f1} | | | | | 0,5/0,5 | 0,7/0,3 | | | | | 0,5/0,5 | 0,7/0,3 |
| -10 | 32 | 40 | 40 | 4,27 100 | 99 | 96 | 104 | 104 | 101 | 1469,9 100 | 99 | 139 | 55 | 95 | 111 |
| -10 | 32 | 55 | 55 | 3,18 100 | 92 | 88 | 98 | 98 | 94 | 1299 100 | 97 | 134 | 54 | 94 | 109 |
| -25 | 32 | 40 | 40 | 2,95 100 | 99 | 96 | 105 | 104 | 102 | 822,3 100 | 93 | 143 | 52 | 95 | 112 |
| -25 | 32 | 55 | 55 | 2,2 100 | 97 | 93 | 104 | 103 | 99 | 727,7 100 | 91 | 155 | 51 | 94 | 110 |

Table 3

Results of energy consumption with different refrigerants at the example of the refrigerator KT 135 R with the compressor KH 0,52 N 05-2

| Refrigerant | ambient temperature | | | | | | | | |
|--|---------------------|----------------|----------------|------|----------------|------|------|----------------|------|
| | 32°C | | | 25°C | | | 16°C | | |
| | RT | t _i | P _i | RT | t _i | E | RT | t _i | E |
| R 12 (75g) | | | | | | | | | |
| R 134a (68g) | 100 | +0,5 | 74 | 65 | +5 | 1,26 | 40 | +5 | 0,77 |
| R 290 (30g) | | | | | | | | | |
| R290/ R 600a ¹ (18g) | | | | | | | | | |
| R 290/ R 600a ² (24g) | | | | | | | | | |

¹ first change of the refrigerator plant

² second change of the refrigerator plant

RT: run time in %

t_i: average temperature of inside in °C

P_i: performance input in W

E: energy consumption in kWh/24h

Table 5

| type of appliances | GA 070 D | GS 110 D | GS 150 D | KT 145 L | GA 0700 DC | GS 1100 DC | GS 1500 DC | KT 1450 LC |
|---|-------------|----------|----------|----------|---------------------|------------|------------|------------|
| | Freezer | | | | Cooler | Freezer | | |
| climate class | SN | | | | SN | | | |
| rated netto voltage in dm ³ | 61 | 91 | 119 | 135 | 61 | 91 | 119 | 135 |
| 3-star compartment in dm ³ | - | - | - | 19 | - | - | - | 19 |
| dimensions | | | | | | | | |
| high in cm | 65 | 85 | 105 | 85 | 65 | 85 | 105 | 85 |
| width in cm | 55 | | | | 55 | | | |
| depth in cm | 60 | | | | 60 | | | |
| rated voltage in V | 220 ... 240 | | | | 220 ... 240 | | | |
| energy consumption in kWh/24 h | 0.80 | 0.90 | 1.05 | 0.85 | 0.75 | 0.85 | 1.0 | 0.80 |
| sp. energy consumption in kWh/24 h | 1.31 | 0.99 | 0.88 | 0.63 | 1.23 | 0.93 | 0.84 | 0.59 |
| differenz sp. energy consumption in % | - | - | - | - | -7 | -6 | -5 | -6 |
| Freezing capacity | 10 | 12 | 12 | - | 10 | 12 | 12 | - |
| refrigerant | CFC 12 | | | | R 290/600 a 0.5/0.5 | | | |
| mass of refrigerant in g | 65 | 80 | 95 | 110 | 24 | 26 | 28 | 24 |
| start of production | 1989 | | | | 1993 | | | |

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Table: Household refrigerators, CFC - HC

| type of appliances | KT 135 R | KT 132 E | KS 185 R | KS 186 K | KT 1370 RC | KT 1320 EC | KS 1850 RC | KS 1860 KC |
|---|----------|-------------|----------|----------|-------------|-------------|------------|------------|
| Climate class | SN | N | SN | N | SN | N | SN | SN |
| rated storage volume in dm ³ | 127 | 130 | 175 | 172 | 127 | 130 | 175 | 172 |
| ice-compartment in dm ³ | - | 8 | - | - | - | 8 | - | - |
| linear dimensions | | | | | | | | |
| Height | 85 | 85 | 107 | 107 | 85 | 85 | 107 | 107 |
| Width | 55 | 55 | 55 | 55 | 55 | 55 | 55 | 55 |
| Depth | 60 | 60 | 60 | 60 | 60 | 60 | 60 | 60 |
| rated voltage range in V | | 220 bis 240 | | | | 220 bis 240 | | |
| energy consumption | | | | | | | | |
| in kWh/24 h | 0,7 | 0,65 | 0,80 | 0,75 | 0,63 | 0,65 | 0,74 | 0,72 |
| in kWh/24 h / 100 Liter SV | 0,55 | 0,50 | 0,46 | 0,44 | 0,50 | 0,50 | 0,42 | 0,42 |
| refrigerant | R 12 | R 12 | R 12 | R 12 | R 290/600 a | | 0,5/0,5 | |
| mass of refrigerant in g | 75 | 50 | 80 | 80 | 24 | | | |
| start of the production with HC | | | | | 03/93 | 05/93 | 06/93 | 06/93 |

**The Conversion of German Household-Appliance Refrigeration
Industry from CFC's to Hydrocarbons and Fluorocarbons in 1993**

**Helmut Lotz
Bosch-Siemens Hausgeräte GmbH**

industry from CFC's to hydrocarbons and fluorohydrocarbons in 1993

Helmut Lotz, BOSCH-SIEMENS HAUSGERÄTE GmbH, Germany

1. Technology description

1.1. Refrigerant

On a mass production scale the only substitute for refrigerants usable at the present time is the fluorohydrocarbon R 134 a. Secured experience is available from several years of trial use under extreme conditions. R 134 a is available on the market in sufficient quantity and purity and so are the ester oils necessary for compressor lubrication.

The refrigerant has as well known no depletion effect on the ozone layer and directly contributes a multiple less to the global warming than the CFC 12 to replace. The result being a visibly diminished TEWI greenhouse effect, which reflects the global atmosphere pollution including the direct greenhouse effect produced by the worst-case total emission of refrigerant and insulation blowing agent without recycling and the indirect greenhouse effect as emission of CO₂ in fossil fuel power stations, resulting of the energy consumption of an appliance. As an example the phase-in-step to the CFC-free technology in August 1993 reveals for the fleet-emission of BOSCH-SIEMENS refrigerators/freezers a TEWI-reduction by 40 %.

The use of hydrocarbons as refrigerant will further reduce the overall pollution provided the energy consumption of the appliance will not rise beyond the energy consumption achieved with the use of R 134 a by more than a percentage that offsets the nil-direct TEWI-contribution of hydrocarbons. Actually a deterioration by a few percent already defeats the advantages gained in respect of the direct greenhouse effect. By that the use of hydrocarbons allowed up til now only to lower TEWI compared to the use of R 134 a in some product groupes - refrigerators without evaporator compartement in general and some small refrigerators with evaporator compartement. Here most manufacturers use isobutane, whilst one manufacturer uses with equal success a mixture of propane and isobutane at varying mixing ratios.

Most manufacturers aim at extending the use of hydrocarbons to the remainder of refrigeration appliances. But actually potential leakages to the appliance interior or into narrow external vents which may occur are seen as a risk with respect to flammability by most german refrigeration appliance manufacturers. This concerns predominantly refrigerators and freezers with internally exposed evaporators, build-in appliances and the globally widely spread nofrost-appliances. Design-modifications and basic construction-changes are prepared actually to at least solve a high share of these safety-problems.

1.2 Insulation

The dominant step-out of CFC's with respect to nullifying ozone-depletion and reducing TEWI is and was the change-over of the insulation. A convincing solution was found with the use of pentane as insulating and blowing gas for the PU-foams without using the bypass with H-CFC's. Two manufacturers (BOSCH-SIEMENS and LIEBHERR) directly went this step out, two manufacturers (AEG and BAUKNECHT) use for a short time the bypass using HFC 134 a and one manufacturer (FORON) actually predominantly using polystyrene directly will change-over to PU-pentane in 1994.

Compared with the PU-CFC 11 insulations the initial heat-conductivity of PU-pentane foams suffer from a some 10 % higher figure which with respect to the operating life time of an appliance quickly will be more than counterbalanced by the fact, that the ageing of PU-pentane foams is remarkably reduced. That means that nearly no diffusion occurs which by the way avoids any safety problems during operation, also influenced by the fact that PU-insulations foamed with pentane have no other flammability characteristics than PU foamed with CFC 11.

Safety precautions to be complied with under production-technology aspects are feasible and are practised by the way in other usages like slab-foaming plants too.

2. Application

2.1 Refrigerant

As described under 1.1 german producers mostly will use R 134 a with increasing percentage of isobutane, one producer will use a propane/isobutane (R 290/600 a)-blend completely and one company sees the middle of 1994 as a possible deadline for the reshuffling of its appliance programme to hydrocarbons.

2.2 Insulation

As described under 1.2 in 1994 nearly all products from german manufacturers will be insulated by PU-pentane foam, some products additionally containing vacuum-insulating panels VIP.

3. Benefits

The ozone-depletion will be nullified. The greenhouse impact as described under 1.1 will be reduced remarkably - enlarging the example mentioned under 1.1 a TEWI-reduction by roughly 40 % can be concluded.

4. Technical Issues

4.1 Refrigerant

R 134 a: Technical problems which were solved occurred with lubrication (eventually using ester oils) and leak-detection (eventually using mass-spectrometry).

HC's: Safety-problems dealing with flammability still exist with most appliances, see 1.1. Compressor-Lubricating oils are mostly mineral oils. Service-repair must be changed (i.g. no use of open (soldering) flames). Leak-detection using mass-spectrometry.

4.2 Insulation

Insulating gas R 134 a: high-pressure foaming, solved by avoiding increase about saturating concentration.

Insulating gas Pentane: Safety precautions in production to avoid flammable concentrations or to explode-protect devices had to be provided.

5. Economics

Cost-influencing are the higher prices for components, before all the compressors, and refrigerant R 134 a resp. the ester-oil. In addition costs for explosive-protection connected with pentane-foaming and the whole investment connected with the change-over from CFC's to ozone depleting-free refrigerant, from design-invest to assembling lines and quality-control must be taken into account. Roughly a price-increase between 5 and 10 % could be appraised, appliances with HC-refrigerants being at the lower end.

6. Technology Outlook

As described in the preceding clauses with refrigerants a transitional period is expected with a start using mostly R 134 a and a more or less slow shift towards HC's.

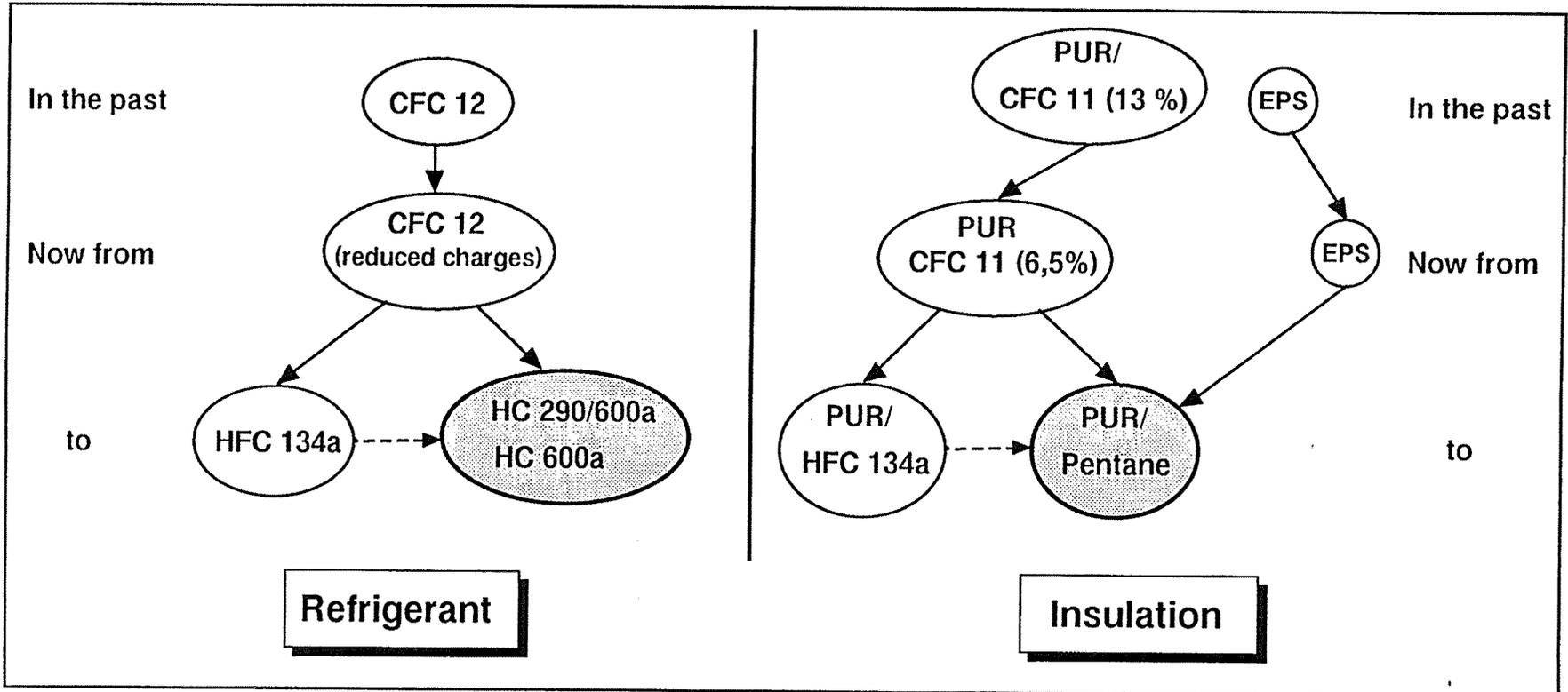
On behalf of the insulation a full market-penetration with PU-pentane-insulations can be expected 1994/1995.

BSHG/ZTV-Prof. Dr. Lotz/tz
15.09.1993

ORNL/DOE/AFEAS-Workshop Wiesbaden 29.9.1993
 NIK- and next generation Technologies for Insulation and Refrigeration Applications

THE CONVERSION OF GERMAN HOUSEHOLD-APPLIANCE REFRIGERATION INDUSTRY
 FROM CFC's TO HYDROCARBONS AND FLUOROHYDROCARBONS IN 1993
 Helmut Lotz, BOSCH-SIEMENS Hausgeräte GmbH, Germany

Current state of Development



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Requirements and properties of PU blowing agents

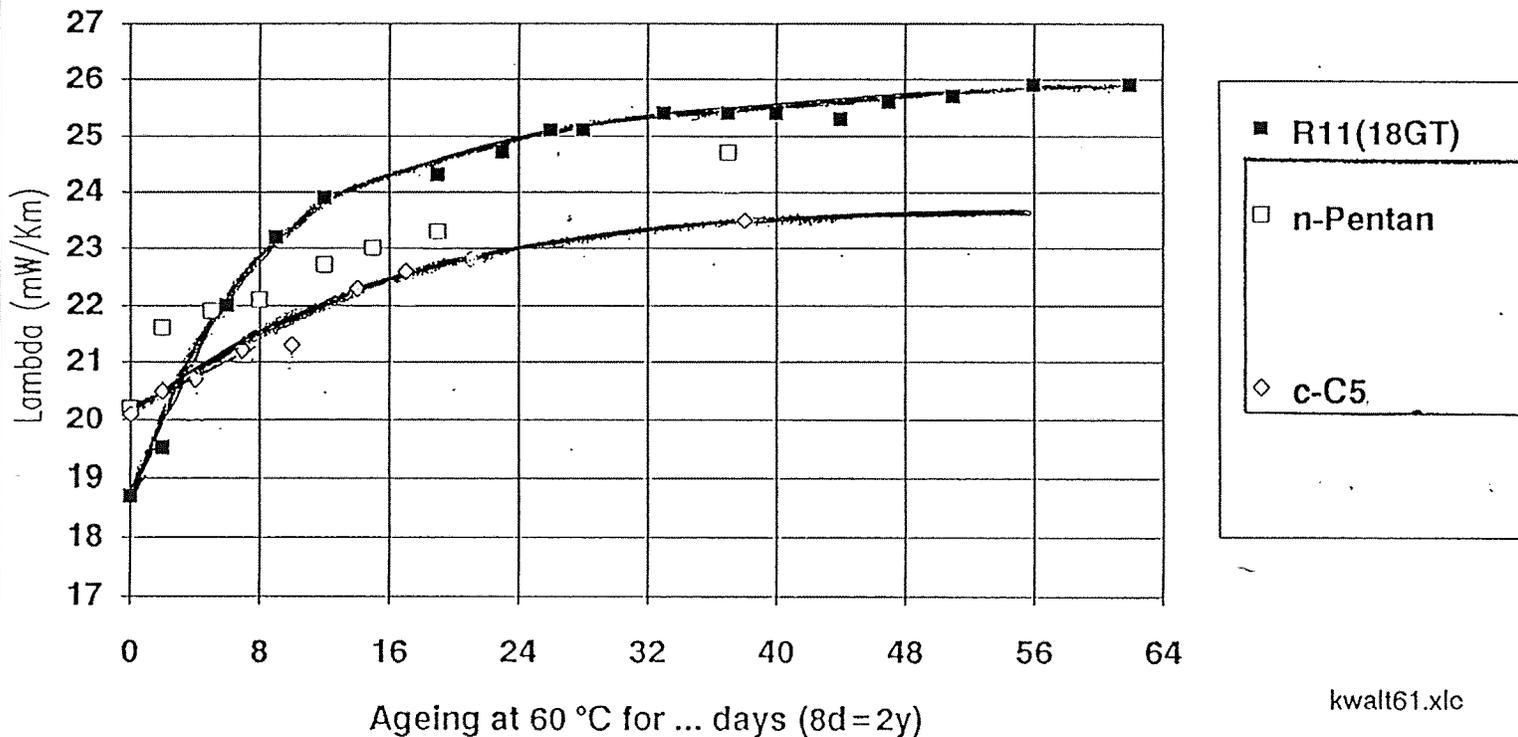
| Requirements | CFC 11 | Pentane |
|-------------------------------|--------|-----------|
| - low ODP | - | + |
| - low GWP | - | + |
| - low thermal conductivity | + | (+) |
| - boiling point <50°C/122°F | + | + |
| - low diffusion in PU-matrix | + | + |
| - low toxicity | + | + |
| - availability, price | + | + |
| - solubility in polyols | + | + |
| - no chem. attack to plastics | (+) | (+) |
| - not flammable | + | - |
| requirements | met + | not met - |

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Ageing-efficiency of thermal conductivity for different insulations

Thermal Conductivity of PUR Foams



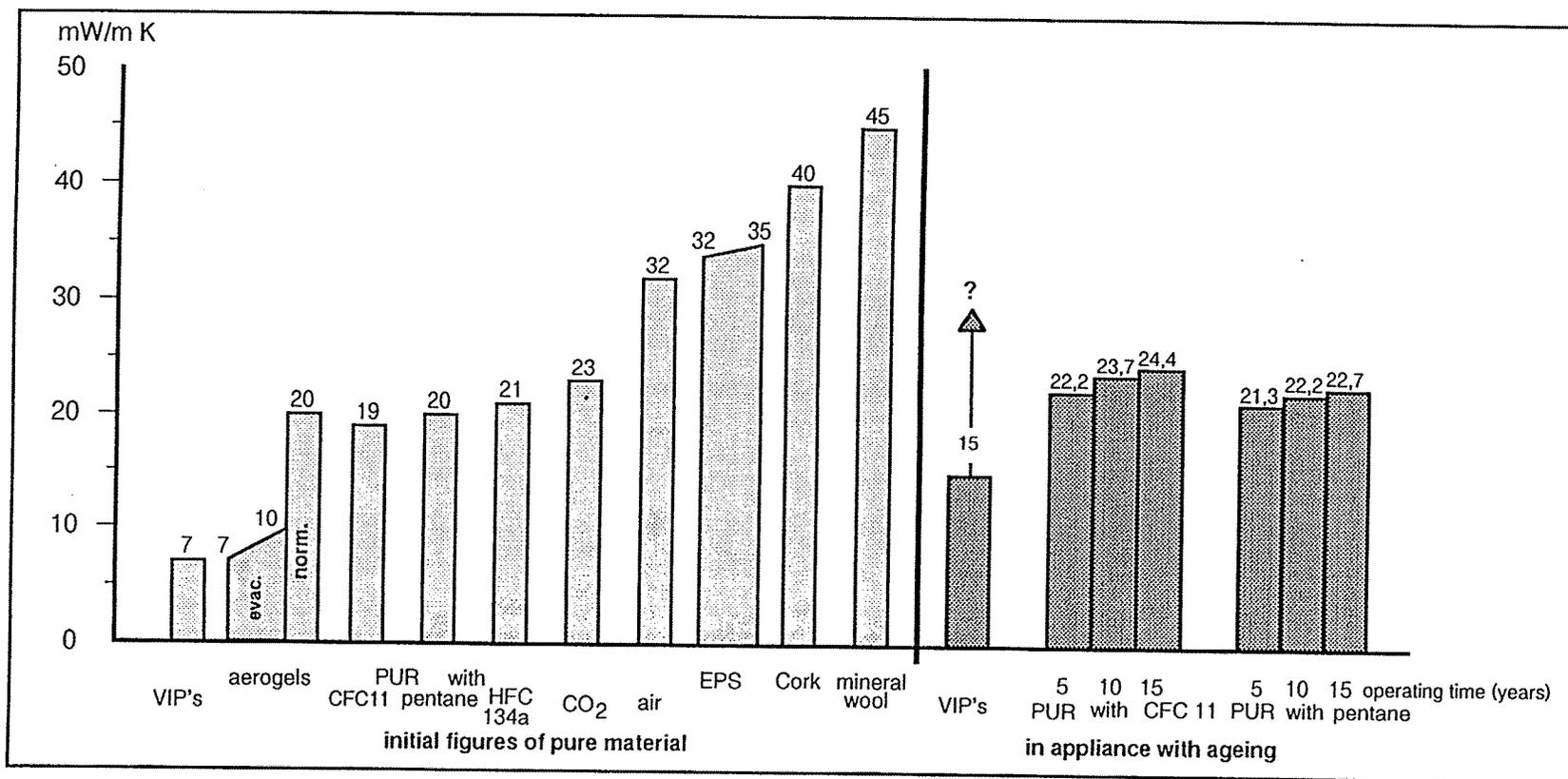
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 Helmut Lotz, BOSCH-SIEMENS Hausgeräte GmbH, Germany

Thermal conductivity of different insulating-materials

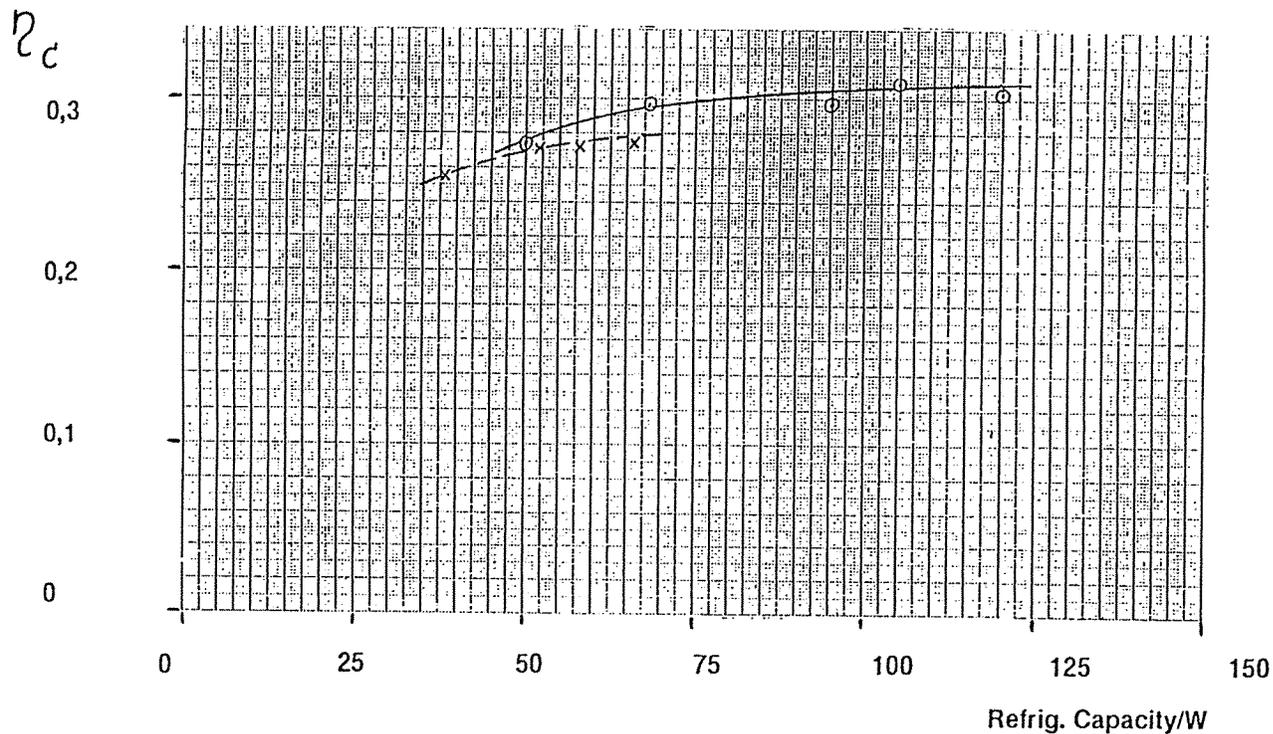


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ORNL/DOE/AFEAS-Workshop Wiesbaden 29.9.1993
 NIK- and next generation Technologies for Insulation and Refrigeration Applications

THE CONVERSION OF GERMAN HOUSEHOLD-APPLIANCE REFRIGERATION INDUSTRY
 FROM CFC's TO HYDROCARBONS AND FLUOROHYDROCARBONS IN 1993
 Helmut Lotz, BOSCH-SIEMENS Hausgeräte GmbH, Germany

Carnot Efficiencies of existing Refr.-Compressors



Theoretically calculated η_c (%)

| t_c | t_o | R 12 | 134a | 600a |
|-------|-------|------|------|------|
| 35 | -5 | 47,2 | 50,8 | 42,2 |
| | -25 | 42,6 | 40,0 | 36,8 |
| 55 | -5 | 37,4 | 37,4 | 34,9 |
| | -25 | 33,5 | 31,1 | 28,1 |

---x HC 600a
 —o— HFC 134a

BSHG/ZTV-Prof.Dr.Lotz
 24.09.1993

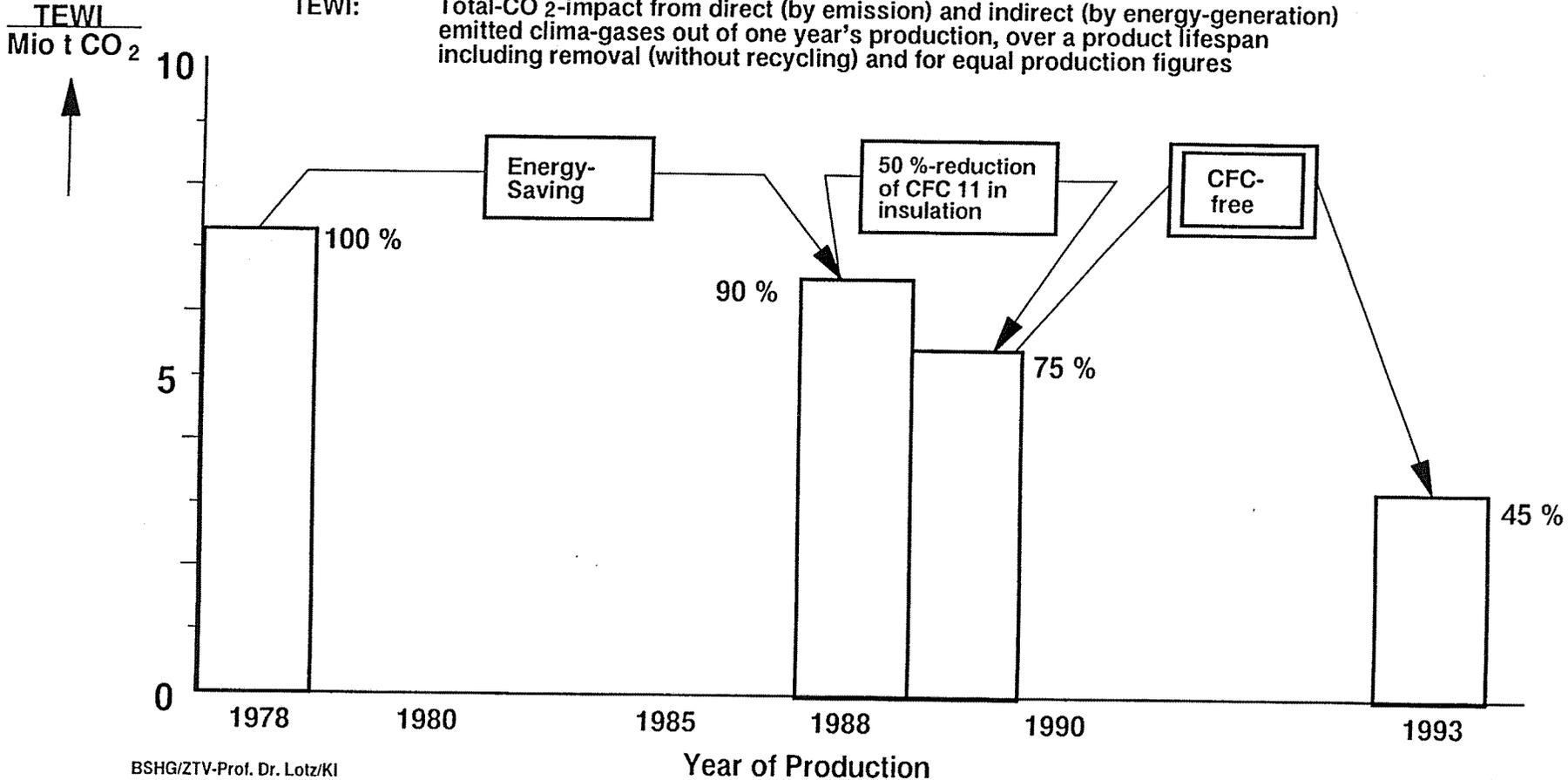
Carnot/DHW

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TEWI-impact from BSHG-produced german refrigerators and freezers

TEWI: Total-CO₂-impact from direct (by emission) and indirect (by energy-generation) emitted clima-gases out of one year's production, over a product lifespan including removal (without recycling) and for equal production figures



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Qualitative Assessment of MARKET PENETRATION

| | SHORT TIME FRAME | TREND |
|--------------------|--|--|
| REFRIGERANT | > 90% HFC 134a Rest HC-Blend 290/600a HC 600a | Further decline of HFC 134a |
| INSULATION | PUR-Foam with share of > 50% pentane ~ 100% pentane end of 1994 Small amount of VIP's | R + D-activities towards: - vacuum insulation - aerogels |

Flammable Refrigerants in Household Refrigerators

Heinz Jürgensen
AEG Hausgeräte AG, Kassel

Introduction

Flammable refrigerants have been in the discussion for the phase out of CFC from the beginning. R 152a was one of the candidates, but propane and other hydrocarbons (HC) seemed to work too. The main discussion point was the flammability risc. On the basis of some risc studies in 1988 to 1990 the home appliance manufacturers decided not to take R 152a or other flammables, in USA, Western and Eastern Germany.

In october 1990 the discussion was startet on a new by the *Hygieneinstitut der Stadt Dortmund* together with the BUND (Bund für Umwelt- und Naturschutz). They proposed à simple drop in change over from CFC 12 to a mixture of HCs with a lower energy consumption as a result too. In january 1991 there was a meeting at the institute with a discussion of the chance for these working fluids. A mixture of up to four substances, propane, butane, isobutane and cyclopropane was preferred by the people working there.

The decision was made to test the mixture in a one temperature refrigerator at a neutral institute in a standard test because no measurements were made until that day. If there should be an improvement in energy consumption, the fluids would have a chance even if they are flammable. Dortmund proposed up to 30% less energy consumption although theoretical calculations of AEG and BSHG for the pure fluids did not show any advantage greater than 5%.

Theoretical analysis

AEG decided to start a test programme in the beginning af 1991. The working fluids were chosen to be R12 and R134a as reference and R152a, propane (R290), cyclopropane (RC270), normal butane (R600), isobutane (R600a) and some mixtures of HCs for drop in tests.

Theoretical calculations were made for the pure fluids and several mixtures of the four HCs for the following points, which cover the typical working conditions in home appliances.

Table 1: Operating conditions

| | | | | |
|-----------------|------|------|-----|----|
| evaporation at | -10 | -25 | -30 | °C |
| condensing at | + 40 | + 55 | | °C |
| suction line at | + 32 | | | °C |

The calculations were made with suction line heat exchange, which is very important for R134a, but the like for the HCs, not so much for R12 and R152a.

If the calculations are made without heat exchange, the energy efficiencies are about 10% less than R12 for the HCs and R134a. If the heat exchange is taken into account, the differences in energy efficiency between R12, R134a, R152a and the HCs are around 1% to 2%, which is the accuracy of thermodynamic data. Only the normal and isobutane were calculated to be about 5% better at these operating conditions (see figure 1). The data for the volumetric capacity was calculated too (see figure 2) and there are big differences. This results in the need of other compressor sizes for the pure fluids. Normal butane needs a 3 times bigger, isobutane a 2 times bigger and propane a 35% smaller swept volume compared to R12. R134a and R152a need only about 10% bigger volumes.

With a computer program we calculated the possible drop in mixtures for the use of the R12 compressor. We searched for a mixture with the same suction and discharge pressures and the same volumetric capacity like R12 at comparable heat exchanger temperatures. The best matching mixture with the smallest temperature glide, still around 6 K, was a propane isobutane mix at 60/40% of weight. The addition of other components, cyclopropane or normal butane did not show positive effects.

Results

For the test we choose a 250 litres one temperature refrigerator, because the comparison is easy with this type, the effect of temperature glide of mixtures is small and because of the medium sized compressor.

The measurements were made corresponding to DIN/ISO at 25 °C room and +5°C compartment temperature. For the pure fluids we adopted the compressor size, chosen out of a R12 range, R134a and R152a working with a R134a compressor (see table 2). Propane got a bigger motor size and cyclopropane and the mixtures were tested with the standard R12 type with 5 cm³, having a rated capacity around 100 W at ASHRAE conditions with R12. The mixture was adopted to the compressor for drop in. The charge was optimized for every fluid and different capillary sizes were tested.

Table 2: Compressors for the working fluids

| fluid | swept volume in cm ³ | remark |
|---------------|------------------------------------|------------------------------|
| R 12 | 5 | series type |
| propane | 4 | motor like 5 cm ³ |
| cyclopropane | 5 | R12 series type |
| isobutane | 8 | 50 Hz and 60 Hz |
| normal butane | 8 and 11 | R12 motor too big |
| R 134a | 5 | R134a type, ester oil |
| R 152a | 5 | R134a type |

In the tests with the mixture propane isobutane 60/40% the pressure values were found to be significant higher than R12 values. This is an effect of the

suction line accumulator placed in the evaporator, where a part of the mixture, with higher percentage of the isobutane is separated. We had to charge 50/50% to get a working percentage near 60/40% in this appliance. This is different depending on the appliance, but also dependent of the mixture components and charge level. So an optimisation of an appliance is more difficult with a mixture and the energy consumption is more dependent of the charge accuracy than with pure fluids.

The measured energy consumption is shown in figure 3 in terms of percent more than R12. We made the standard test with two appliances in parallel and some additional test with other interesting models. In these tests no HCs reached the energy efficiency of R 12. The best HCs were isobutane with a 5% and the propane isobutane 50/50% mixture with 6% efficiency penalty. The R134a and R152a values were better, with +4% and -1% in consumption, another 170 l refrigerator showed -7% for R134a. The isobutane results showed a cooling capacity not high enough for higher ambient temperatures (32 °C), so a new test was made running the compressor with 60 Hz which means a nearly 20% higher capacity. This test showed the same standard energy consumption like with 50 Hz, but now an acceptable cooling capacity.

The 50/50% propane isobutane mixture was tested in a 160 l refrigerator with a 18 l freezer compartment. The consumption was 31% higher than R134a in the basic test because of the temperature glide. The +5°C compartment reached the nominated value at higher running time percentages, because the evaporator part is at the end of the refrigerant flow, this means at the highest evaporation temperature. A compensation of this effect by using a bigger evaporator part there is not possible because there is no space left in this model, which is of a very much used size.

The 40% higher energy consumption level is the result of the cabinet tested in the neutral test institute and charged with a mixture in cooperation with the people in Dortmund.

Conclusions

In these tests it was not possible to reach the energy efficiency of R12 and R134a with HCs, neither with pure fluids nor mixtures. Because of the theoretical analysis it seems to be possible to reach these levels, at least in simple one temperature refrigerators. The mixture propane isobutane is a possible candidate for these appliances with some modifications on R12 compressors. For small cooling capacities isobutane seems to be a good candidate, but with some design changes on compressors. For bigger capacities may be propane will give good results too. But no fluid or mixture except the exotic chemical cyclopropane is able to work in the complete R12 capacity and refrigerator and freezer range. R134a or R152a are comparable to R12.

The use of flammable HCs in the whole range would need some years of work, with very little effect as a result. On many appliances we would have to change electrical parts and evaporators and so on because of fire risc. The theoretical analysis shows little or no improvement in energy efficiency by using HCs. If we take a look on TEWI balances for refrigerators and see, the GWP of

the refrigerant is about 1% or 2% compared to the energy consumption, there is no reason not to start with R134a, it is a very big step forward in phasing out CFC. There is no ODP and a strongly reduced GWP and there are compressors available. The next steps to be taken should, TEWI in mind, be steps to reduce energy consumption.

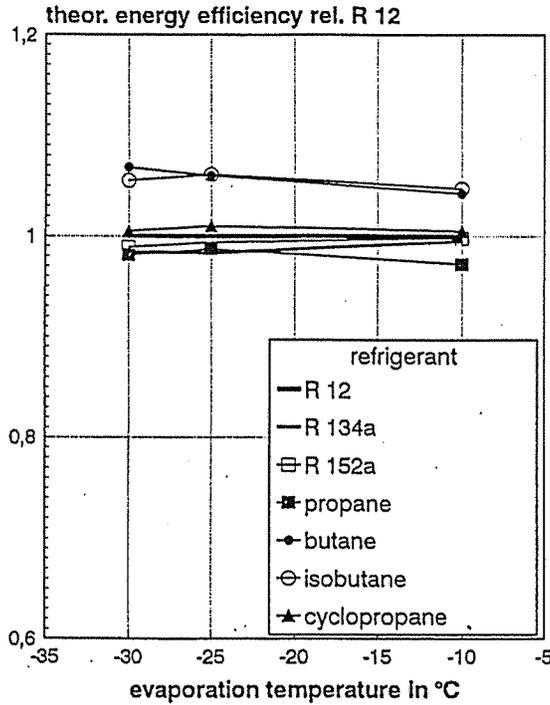


figure 1: energy efficiency of refrigerants

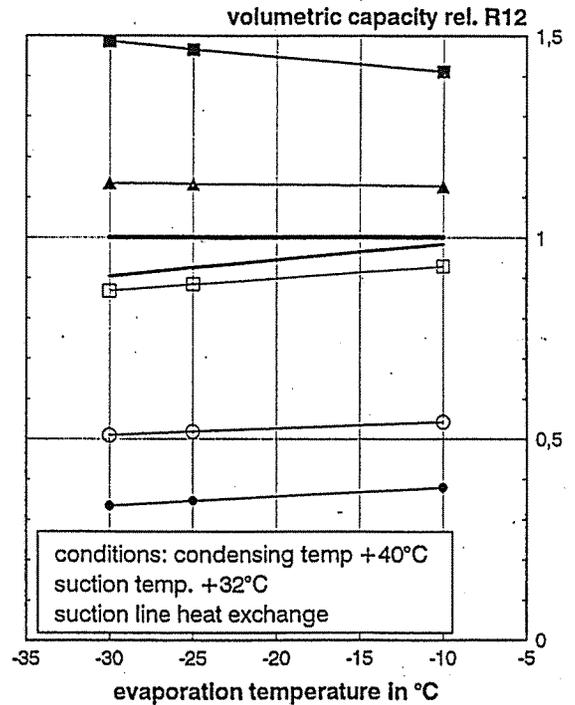


figure 2: volumetric capacity of refrigerants

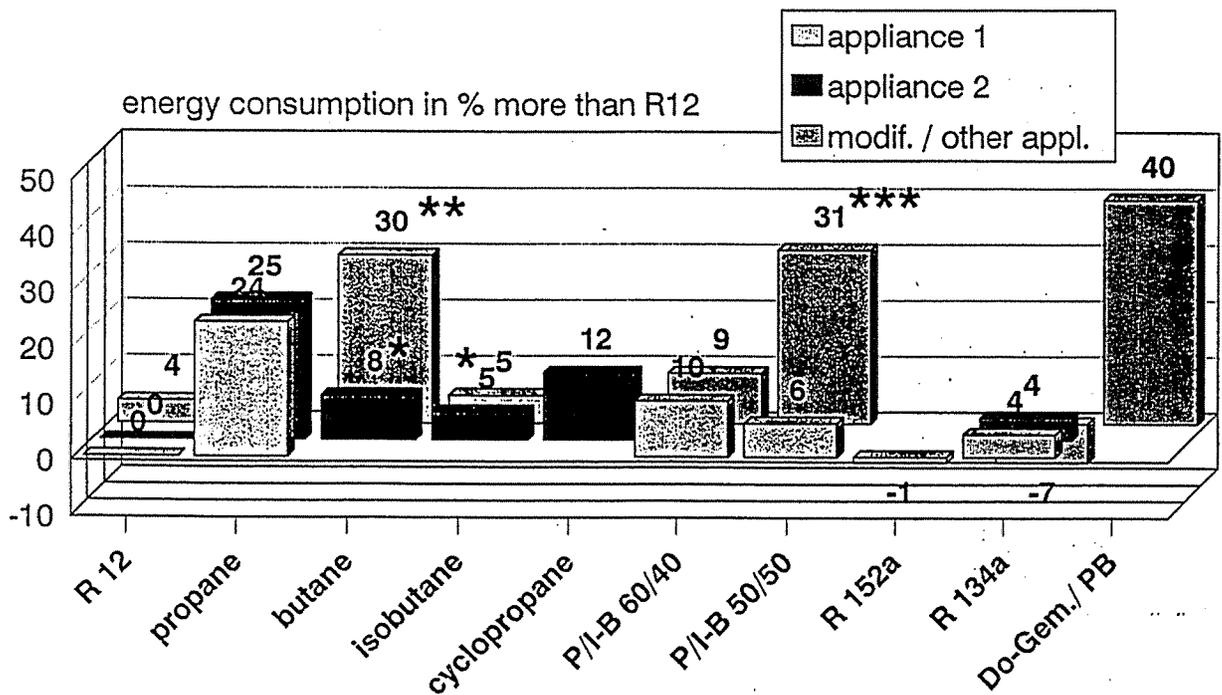


figure 3: energy consumption with different refrigerants

*) cooling capacity too low **) compressor motor too big ***) ***-appliance 1630E

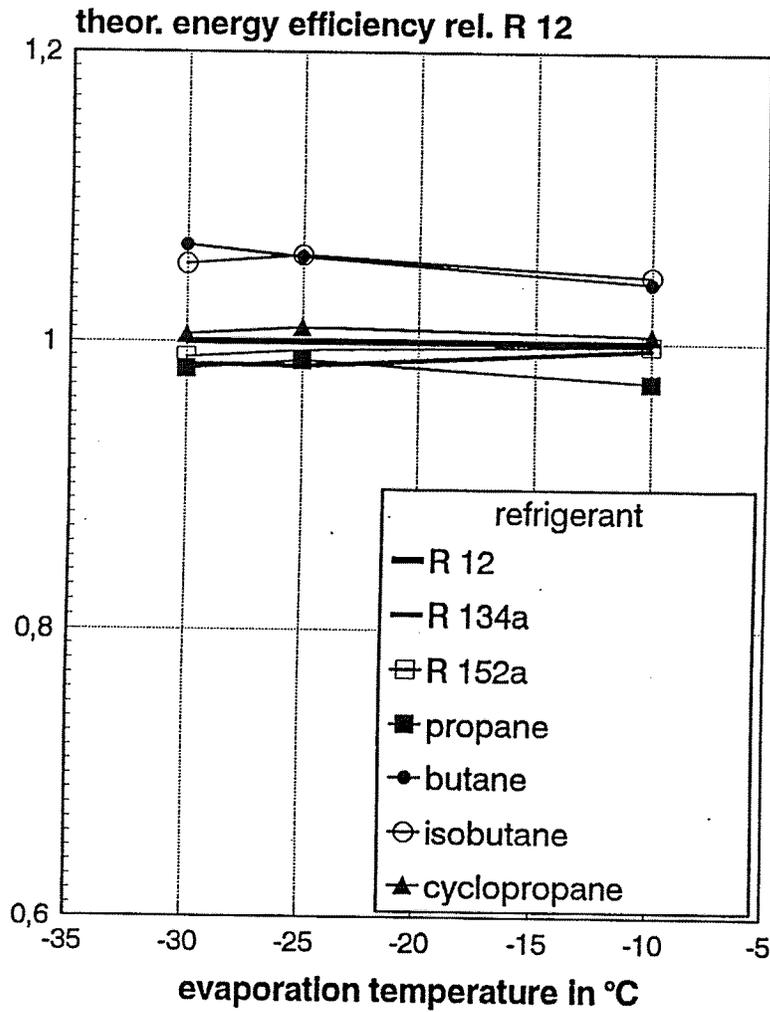


figure 1: energy efficiency of refrigerants

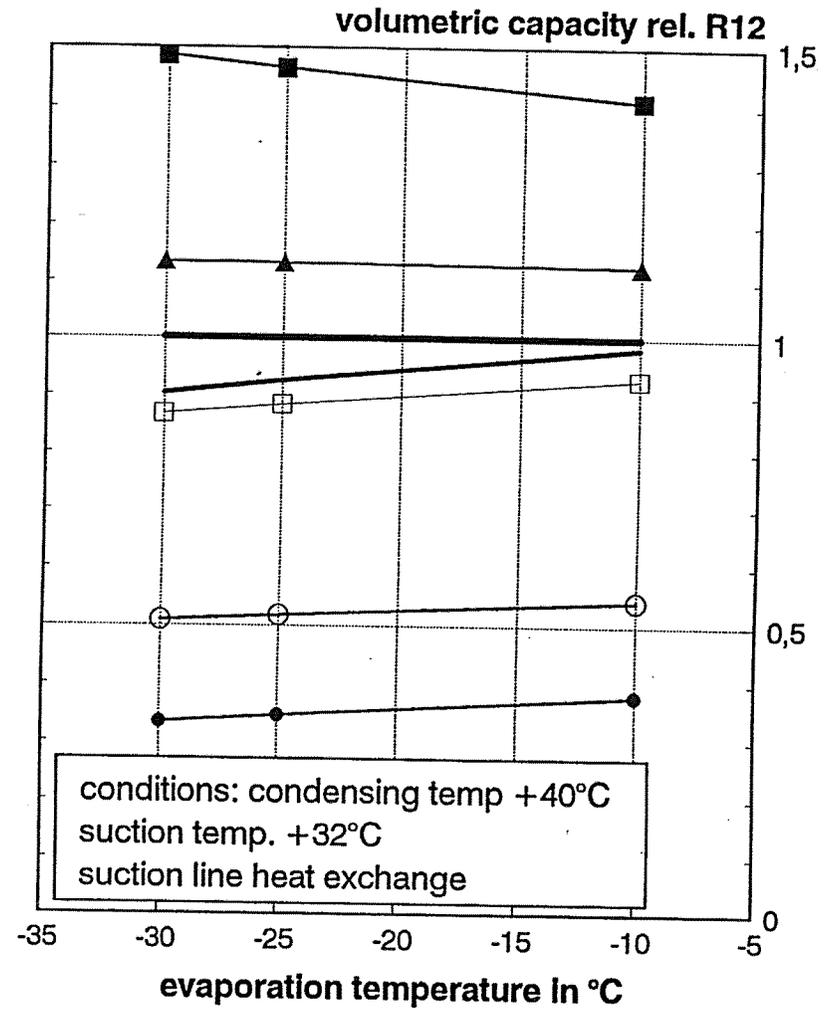


figure 2: volumetric capacity of refrigerants

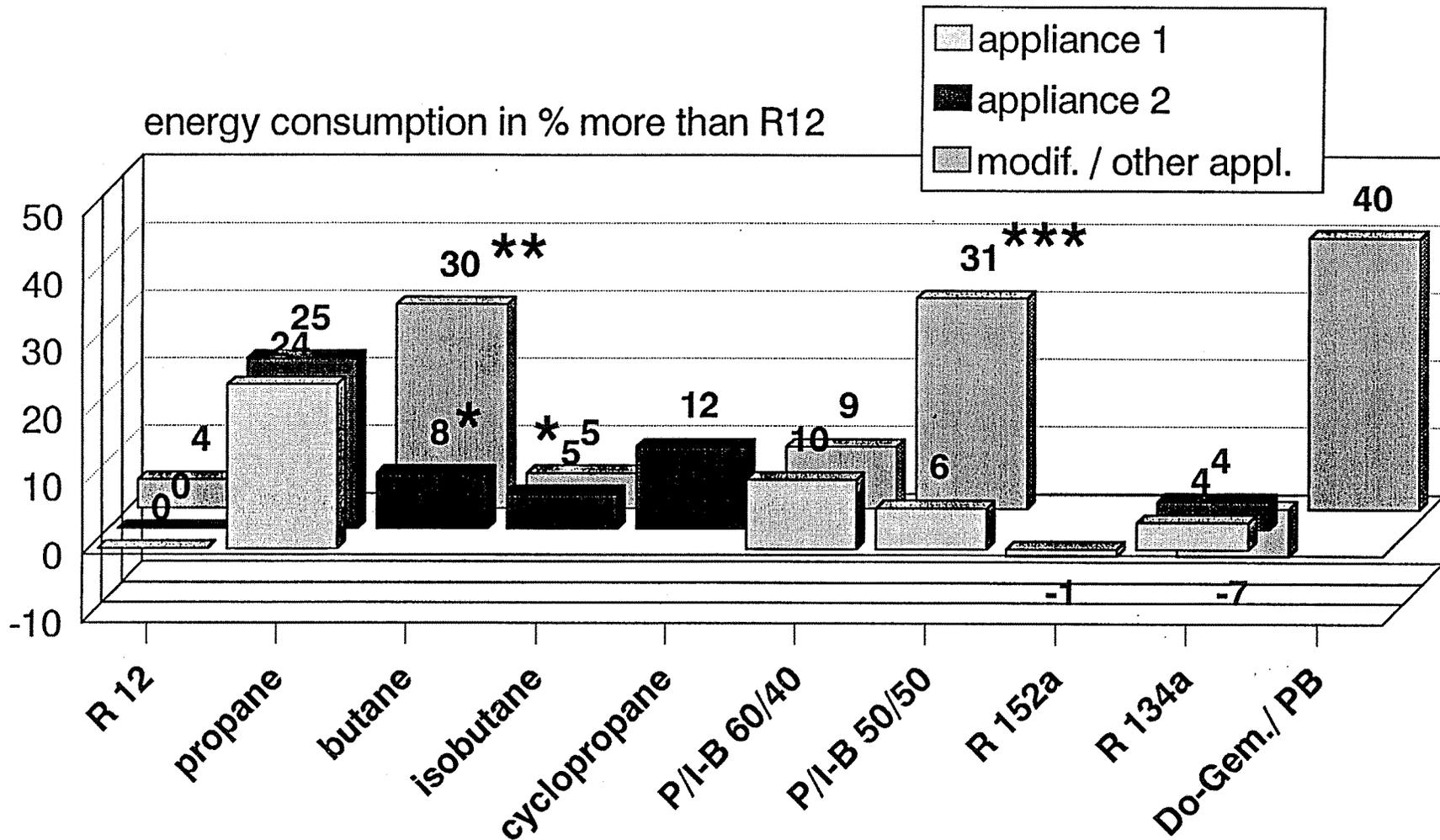


figure 3: energy consumption with different refrigerants

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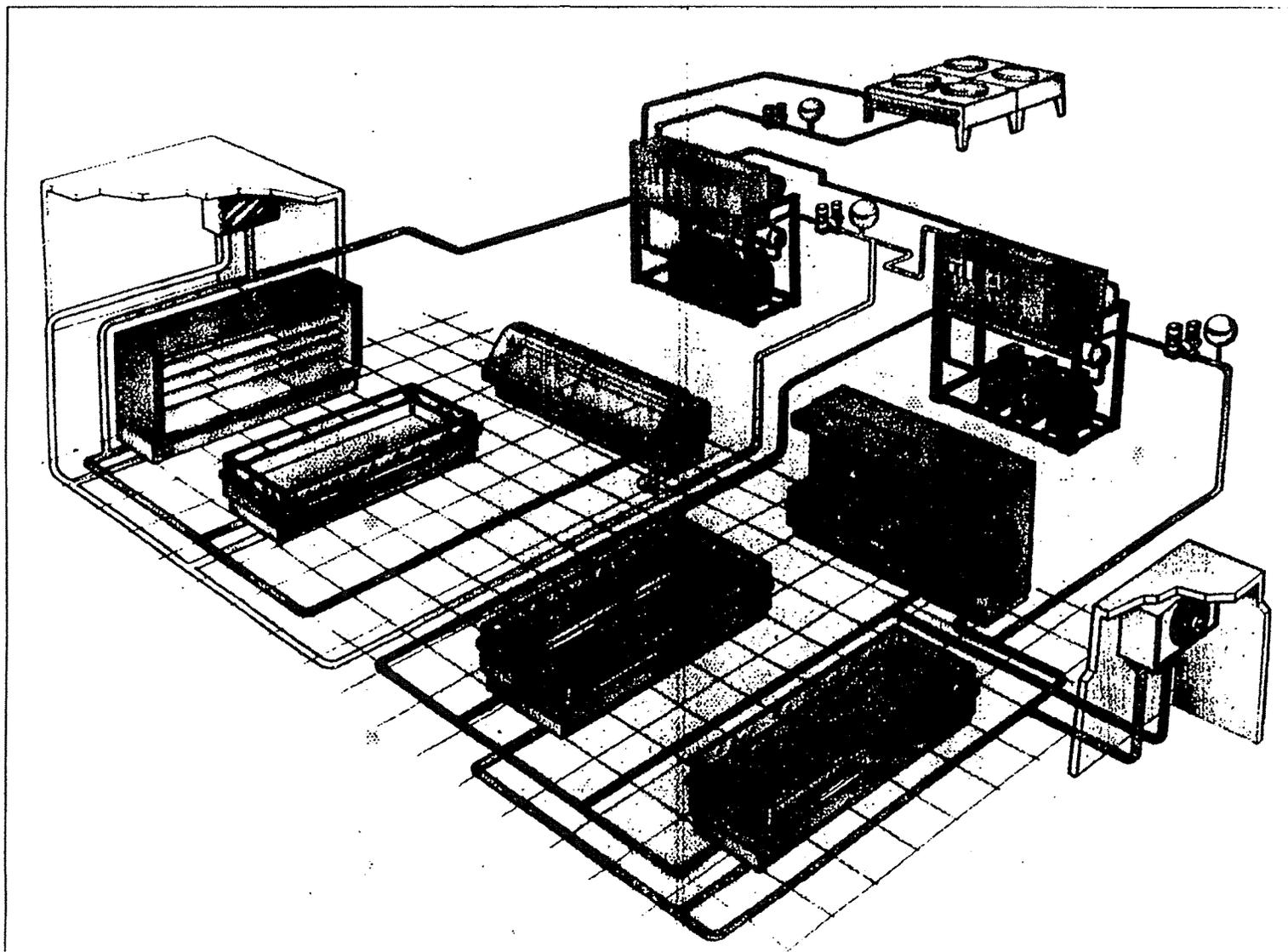
**Air Cycle Air Conditioning and the Use of Ammonia in
Supermarket Refrigeration Systems**

Ulrich Hesse
Universität Hannover
Institut für Kältetechnik
und Angewandte Wärmetechnik

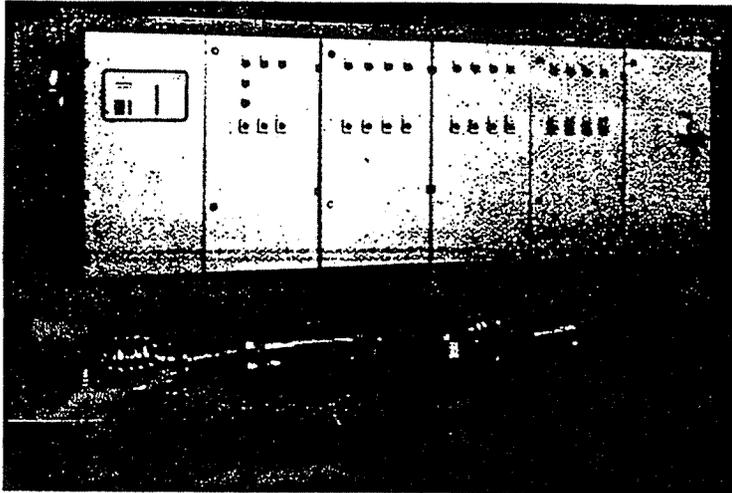
NH₃ in Commercial Refrigerators

- No Problem for Companies active in industrial NH₃ - Business to build "Standard Solutions" (brine systems)
- Stal Elektrolux
- Linde

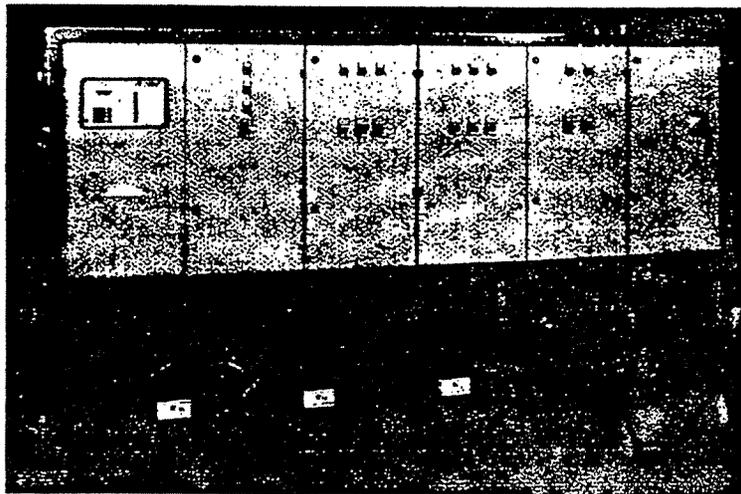
Bild 3: Kälte­trä­ger­kreisläuf­e im Normal- und Tief­kühl­be­reich (System 3)



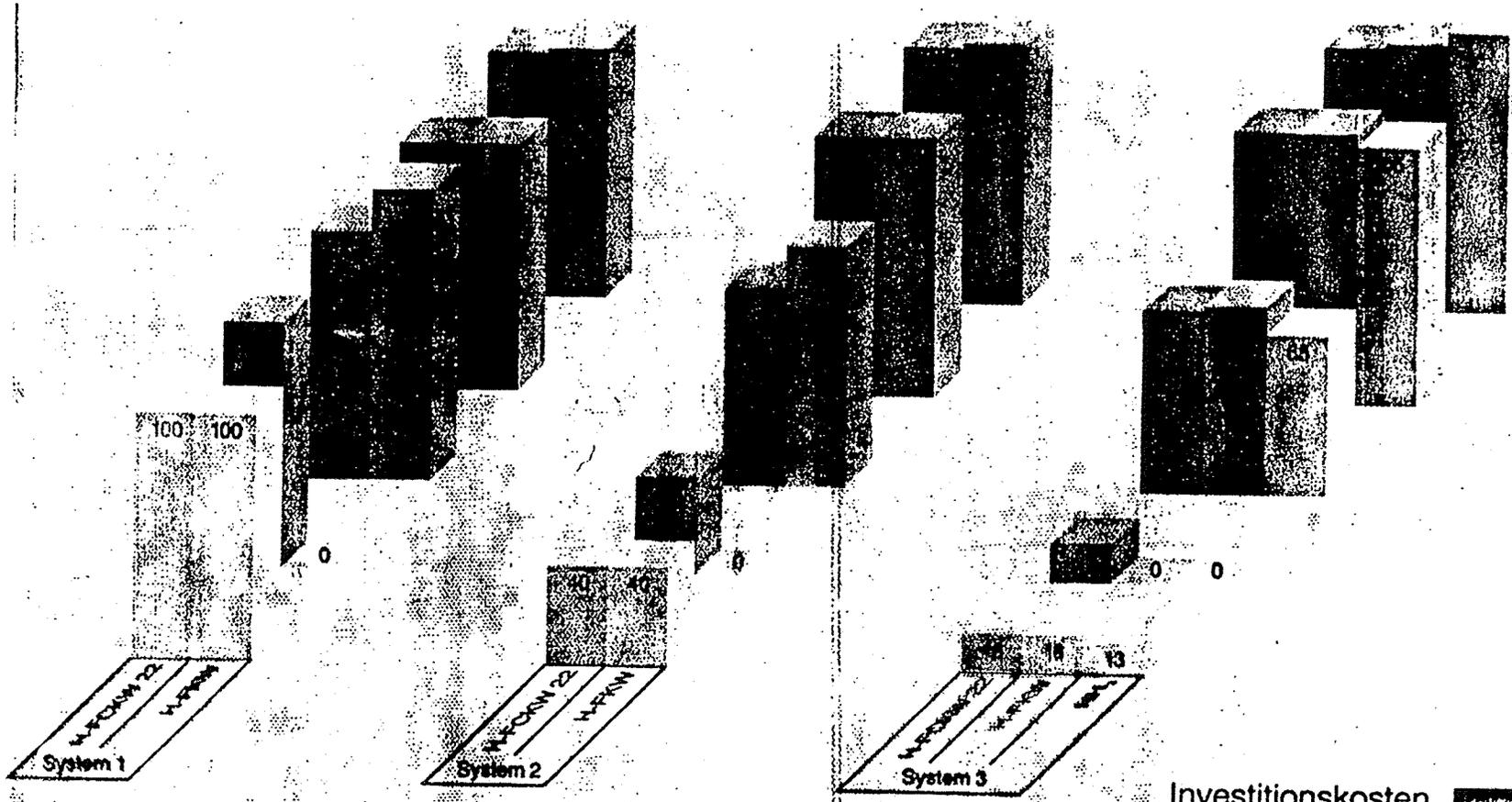
Linde Kältetechnik: Kälteanlagen mit Kälte­träger­kreisläufen für Lebensmittelmärkte



Ammoniak (NH₃) -Flüssigkeitskühlsatz



H-FKW-Flüssigkeitskühlsatz



| System | 1 | 2 | 3 |
|---------------|-------------------|-------------------|--------------|
| Normalkühlung | Direktverdampfung | Kälte­träger | Kälte­träger |
| Tiefkühlung | Direktverdampfung | Direktverdampfung | Kälte­träger |

- Investitionskosten
- Energieverbrauch
- Treibhauseffekt direkt
- indirekt
- Ozonschichtschädigung
- Kältemittelfüllmenge

Edeka kühlt mit Ammoniak

14.09.93

FCKW-freie Kälteanlage: Pilotprojekt in Hildesheim vergangene Woche eröffnet

ra. Frankfurt, 9. September. Ende vergangener Woche eröffnete in Hildesheim ein umstrukturierter Edeka 2000 der Edeka Minden-Hannover GmbH. Die Investitionen in der Umbauphase betragen rund 5,5 Mio. DM. Besondere Attraktion: Die Installation einer FCKW- und H-FCKW-freien Kälteanlage. Kostenpunkt: 300 000 DM.

Die Edekaner verstehen ihr Projekt als „Initialzündung, das auf gar keinen Fall eine Solitäranlage bleiben soll“, so Hans Moog, Geschäftsführer bei der Edeka Minden-Hannover. Zusammen mit den beiden Unternehmen ABB Stal Astra GmbH, Hamburg, und Electrolux Sümak, Hildesheim, wurde das neue Technologie-Konzept für den „in die Jahre gekommenen E-Super 2000“ entwickelt, wie es in einer Pressemitteilung der Mindener heißt.

ABB Stal Astra, Anbieter von Kältetechnischen Anlagen, ist ein Tochterunternehmen des Asea Brown Boveri-Konzerns, Zürich, beschäftigt in Deutschland rund 250 Mitarbeiter und setzt 110 Mio. DM um. Für die Kühlung von Supermärkten sei man erstmals tätig geworden. Electrolux Sümak, der Hersteller von Kältemöbeln, beschäftigt in Deutschland rund 300 Mitarbeiter und gehört zu einem schwedischen Mutterkonzern.

Das Projekt in Hildesheim ist die erste Kooperation der drei Beteiligten. Eingerechnet wurden 30 Meter Bedienungs- und Selbstbedienungsregale, 37 Meter Wandkühlregale, 4 Meter Obst- und Gemüseregale und 26 Meter Tiefkühlinseln.

Die Kälteanlage von ABB Stal Astra arbeitet mit Ammoniak (NH₃). Sie besteht aus zwei sogenannten ND-Kolbenverdichtern sowie zwei HD-Kolbenverdichtern. ND- und HD-Kreislauf sind voneinander getrennt und arbeiten nach einem „Kaskadensystem“. Eine „Compact-Unit“ ist der einzige Teil der Anlage, in dem das Kälte-

mittel Ammoniak enthalten ist. Diese ist in einem nach außen belüfteten Maschinenraum untergebracht, ebenso wie alle nötigen Sicherheitseinrichtungen. Die Anlage enthält 50 kg Ammoniak.

Die abzuführende Wärme der verschiedenen Kühlstellen, Kühlmöbel und Kühlräume wird über drei sogenannte Solesysteme zunächst der „Compact-Unit“ und anschließend dem Trockenluftkühler zugeführt, wo sie an die Außenluft abgegeben wird.

Die Temperaturen der verschiedenen Kühlstellen sowie die Betriebszustände der „Compact-Unit“ werden durch eine elektronische Schalt- und Regelanlage überwacht. Die Daten werden per Fernübertragungsanlage in eine Überwachungszentrale übermittelt.

Neu an dem System sind die „lebensmittelverträglichen“ Kühlsole, heißt es aus dem Hause ABB. Dabei handelt es sich um eine Zubereitung aus registrierten Altstoffen, die biologisch abbaubar sind.

Die Kühlmöbel für den Normal- und Tiefkühlbetrieb wurden speziell für den Solebetrieb entwickelt, teilt Thomas Jacobsen, Marketingleiter bei Electrolux Sümak, mit. Der Korpus und das Design der Möbel sei zwar identisch mit „normalen Kühlmöbeln“, die innere Technik dagegen völlig anders. Das heißt konkret, daß Art und Größe des Verdampfers sowie die innere Verrohrung der Organe in den Möbeln den Bedürfnissen des „Solebetriebes“ angepaßt seien.

Die Rohre bestehen aus Kupfer, denn in dem Möbel selbst fließt kein Ammoniak, sondern nur im Maschinenraum in der Kaltezentrale. „Im Laden“, erklärt Jacobsen, „fließt nur die biologisch abbaubare Sole (Salzlösung) in den Möbeln.“ Die gesamte Kälteanlage ist nach der UVV 20 erstellt. Sie steht unter Kontrolle des Technischen Überwachungsvereins (TUV), durch den auch eine Erstabnahme vor Ort

durchgeführt wurde.

In der Praxis gilt Ammoniak zwar als Alternative zu FCKW, wird aber wegen seiner Giftigkeit kritisiert, erläutert Edgar Buth, Fachgebietsleiter für alternative Kältemittel bei Du Pont de Nemours, Bad Homburg. Er merkt an, daß alle Anlagen, die mit Ammoniak gefüllt sind, komplett aus Edelstahl gebaut und sehr strikt gewartet werden müssen. Neben der Ozon-Unschädlichkeit weist Ammoniak im Gegensatz zu allen H-FCKW-Kältemitteln kein Treibhauspotential auf. Dieses bei Industriekälteanlagen schon immer gebräuchliche und bewährte Kältemittel wird für Lebensmittelmärkte nur zusammen mit einem Kälteträgerkreislauf empfohlen. Bislang wurden hauptsächlich die riesigen Zentrallager der Handelsfilialisten mit Ammoniak gekühlt „und zwar direkt, ohne Sole“, vermerkt Jürgen Böttger, technischer Leiter bei ABB Stal Astra.

Hans Moog von der Edeka Minden-Hannover geht davon aus, daß mit der Pilotanlage annähernde Energieleistungen wie mit einer herkömmlichen R 22-Verbundanlage erbracht werden können. Weil der Hildesheimer Markt als Pilotprojekt gilt, habe man die Vorichtsmaßnahmen übertrieben genau erfüllt und beobachte den Betrieb mit „Argusaugen“. Nach drei bis vier Monaten erwartet man erste Ergebnisse. Dann stellt sich heraus, ob durch die neue Kälteanlage eine Mehrbelastung auf die Marktbetreiber zukommen wird. Moog wertet die Pilotanlage als einen „Schritt in die richtige Richtung“.

Neben der Edeka Minden-Hannover machen diverse Handelsfilialisten derzeit Versuche mit FCKW-freier Kühlung. Konkretes passierte bislang jedoch kaum, beobachtet Edgar Buth von Du Pont de Nemours. Er kritisiert, daß „noch 99 Prozent aller Märkte ihre Kälteanlagen mit FCKW betreiben“.

Bäro will in SB-Warenhäusern präsent sein

Lichttechnik-Unternehmen diversifiziert in viele Branchen / Von Herbert Pistor

Leichlingen, 9. September. Die lebensmittelechte Ausleuchtung der Warenpräsentation ist Thema für jeden, der im Handel sein Geld verdient. Das jedenfalls ist die Meinung der Bäro KG, Leichlingen, eines der innovativen Unternehmen der Lichttechnik

überboten, ihre Innovationen auch auf Messen aufwendig zu präsentieren, bemüht sich Bäro um Understatement. Wie sonst war zu erklären, daß sich die Leichlinger seit unzähligen Jahren in der Lichttechnik

z.B. den Lebensmittelbereich, technische Innovationen auf hohem Niveau und der Ausbau eines Direktvertriebes, der von einem wissenschaftlichen Beratungsteam unterstützt wird, um den Kunden mit dem Namen Bäro

NH_3

Areas of R + D:

- secondary reference
 - "standard" brines
 - additives
 - phase change - CO_2
- safety
- dry expansion HX
- solutable oils
- reduced charge
- hermetic compressors

Versuchsanlage

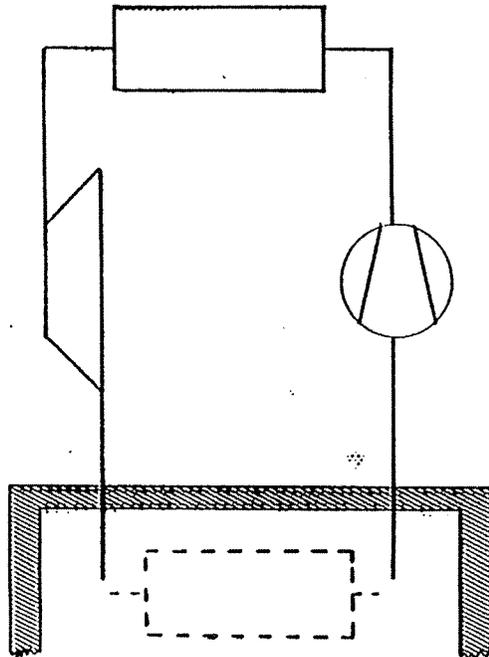
- Kälte­träger mit Phasenwechsel
 - CO₂:
 - nicht brennbar
 - nicht toxisch
 - ODP = 0
 - GWP = 1
 - natürliches Kältemittel
 - hoher Druck -> Lösemittel
- Komponenten
 - Kompakt-Kälteanlage
 - konv. Verkaufskühlmöbel
 - Indirekter Kreislauf
 - Kälte­träger: CO₂
- Funktionstest
 - erfolgreich
 - Einsparpotential
 - geringe Temperaturdifferenzen



Kö,9/93-04

Cycle Modifications

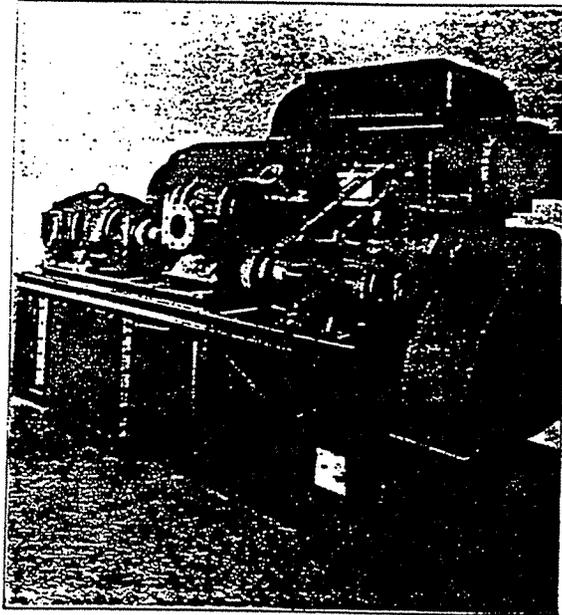
A)



Open To Room :

- Fast Response
- No Fan Required
- Omission of One HX
- High Compression Temperature

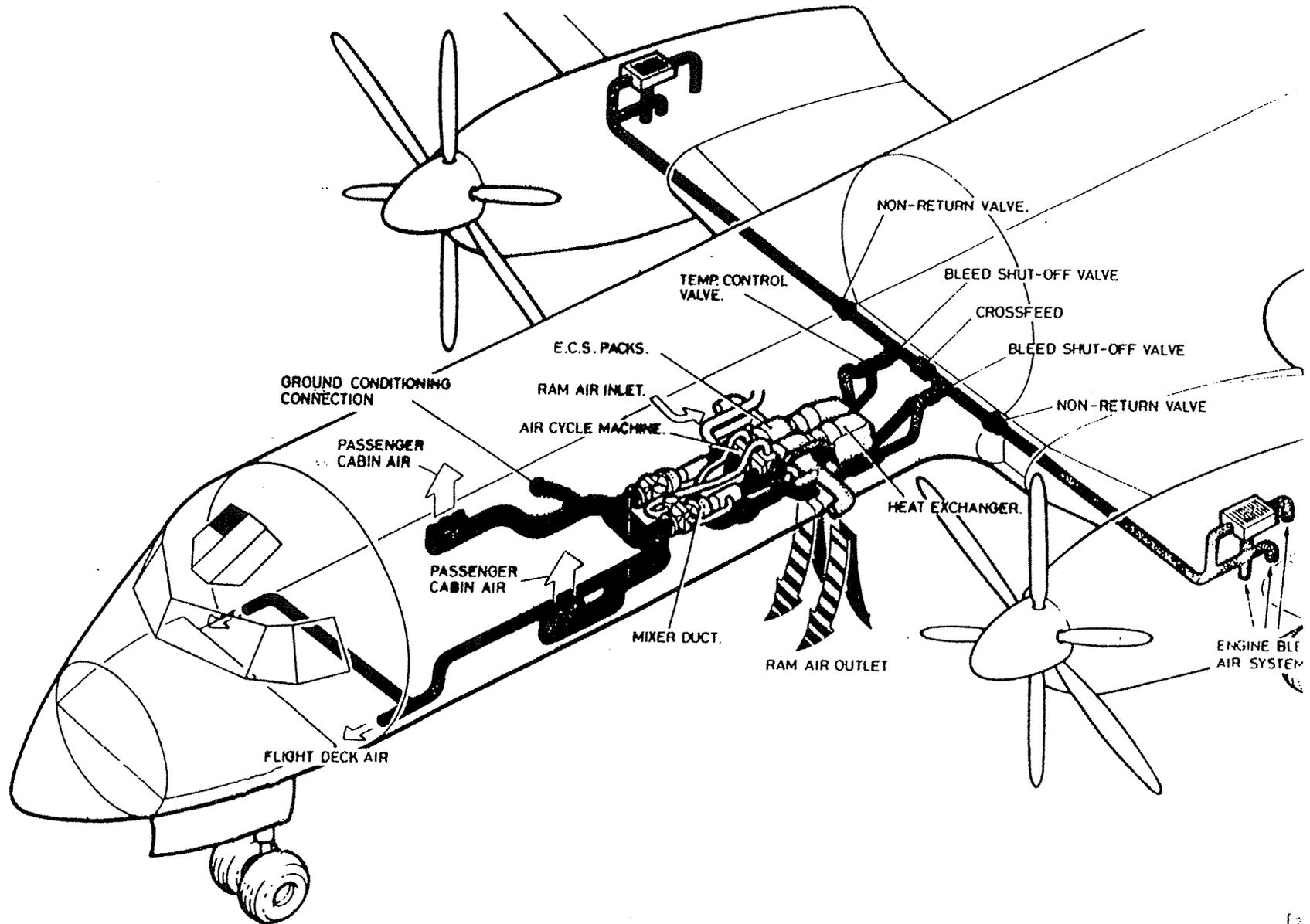
Wärmepumpe im Züricher Kongreßhaus (1939)



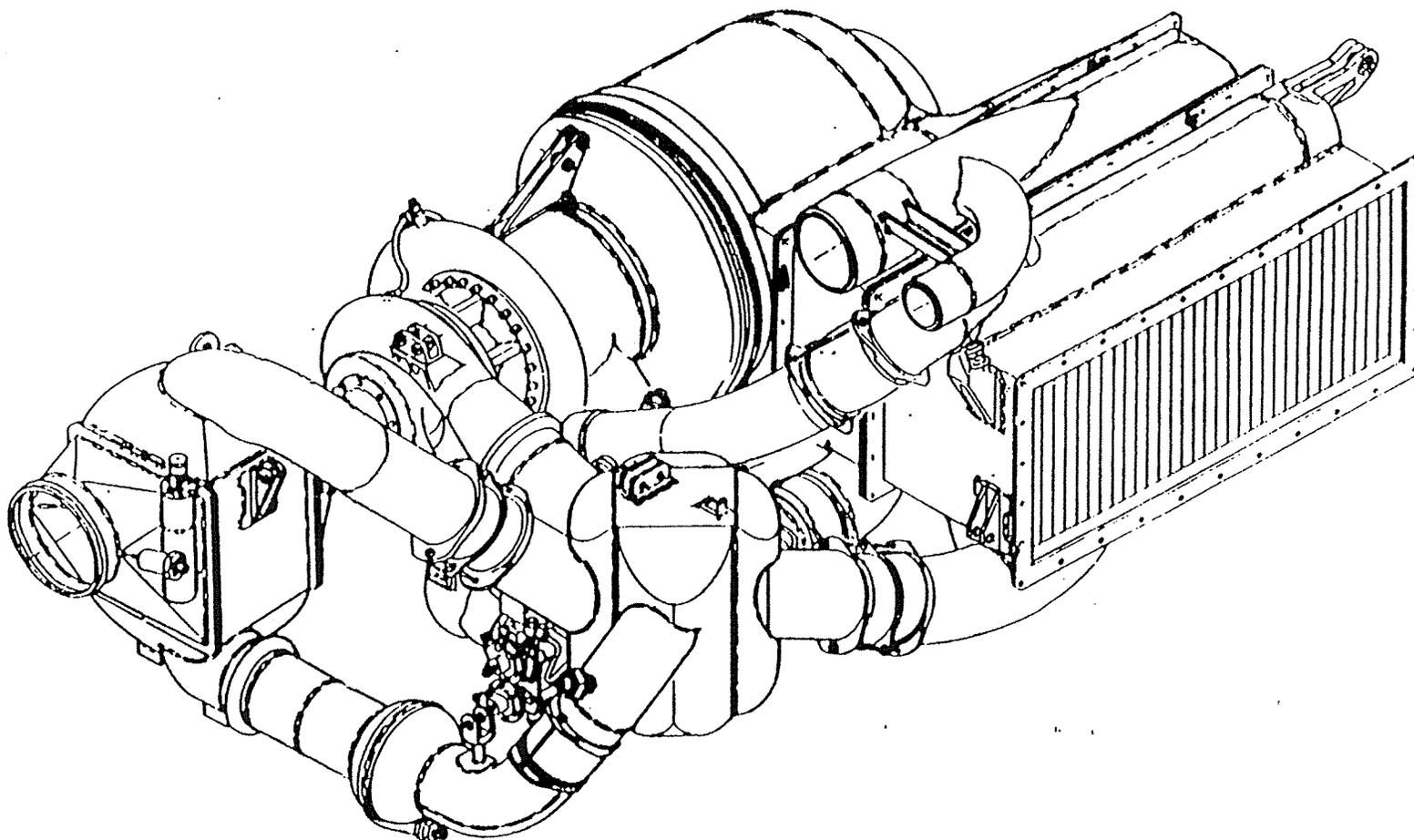
Heizleistung = 58 kW (c.o.p.= 2,41)
Kälteleistung = 31 kW (c.o.p.= 1,31)

Eine weitere Anlage wurde 1940 am Bodensee für die Abwärmenutzung einer Papierfabrik erstellt.

Heizleistung = 128 kW (c.o.p.= 2,55)



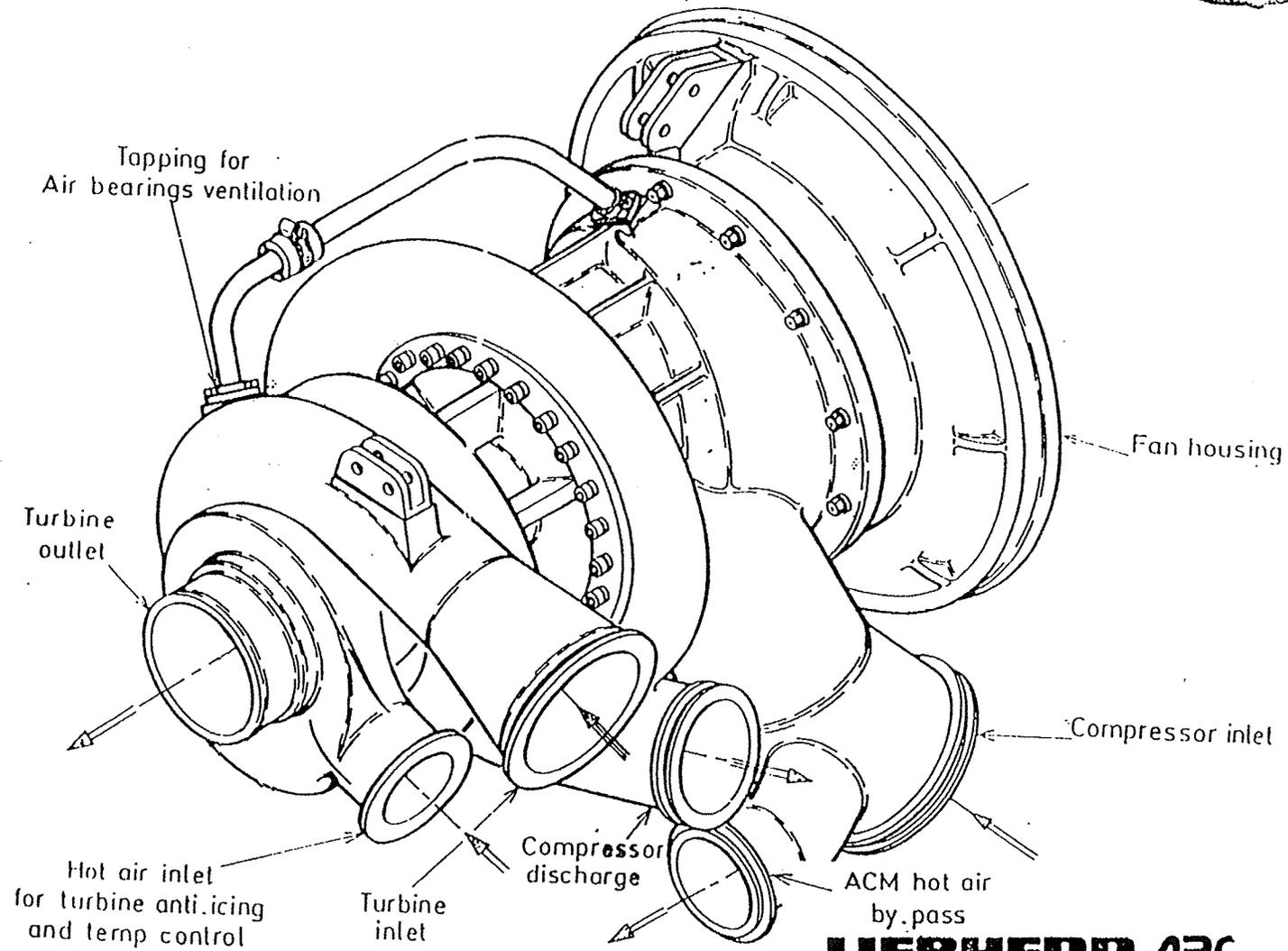
KÜHLAGGREGAT



308

LIEBHERR АБГ
ЛІБХЕР

3 RAD MASCHINE

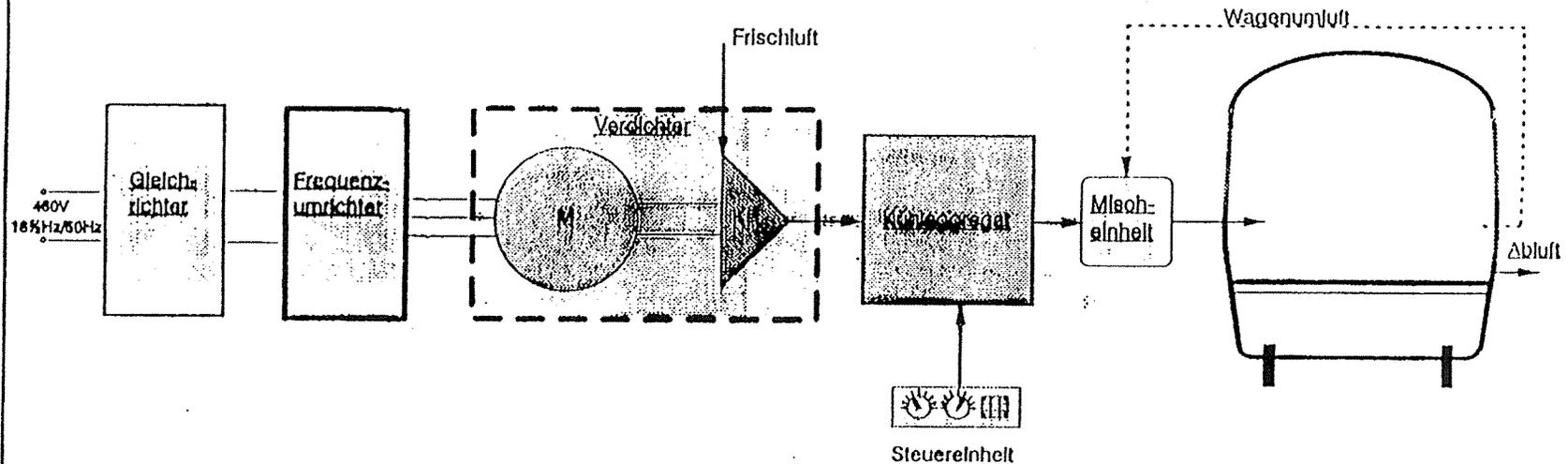


309

LIEBHERR AG
SEMCA

Luftgestütztes Klimatisierungssystem für I C E

Blockschema:



Liebherr - Erfahrung

- Systemführung Airbus A 320
- Systemführung Airbus A 330/340
- weitere Partizipationen

A. Why using the "Air Cycle" Principle?

| Topic | "Vapor Cycle" - System | "Air Cycle" - System |
|-------------------------|--|---|
| Environmental pollution | <p>Refrigerants:</p> <p>CFC's (R12, R22, etc.)</p> <ul style="list-style-type: none"> - ozone depletion - greenhouse effect - legal restriction 1996 (USA, Europe, etc.) <p>"Alternative" Refrigerants:</p> <p>HFC (R134a)</p> <ul style="list-style-type: none"> - greenhouse effect - assumed restriction 2000 - hygroscopic | <p>Refrigerant:</p> <p>Ambient Air</p> <ul style="list-style-type: none"> - no fluid with influence to environment - low CO₂ - emission - equivalent (see table) - "state of the art" - technology in aeronautical applications |

Continue of A.

| | | |
|--|-------------------------------------|--|
| <p>➤ Weight per wagon e.g. for 30 KW cooling performance (including air distribution system)</p> | <p>- 100% - approx. 2800 kg</p> | <p>- 50% - approx. 1600 kg</p> |
| <p>➤ Installation volume</p> | <p>-100%</p> | <p>- 80% - fixation of all subcomponents in one frame - complete installation in upperfloor area possible - Air conditioning pack = 1 "module"</p> |

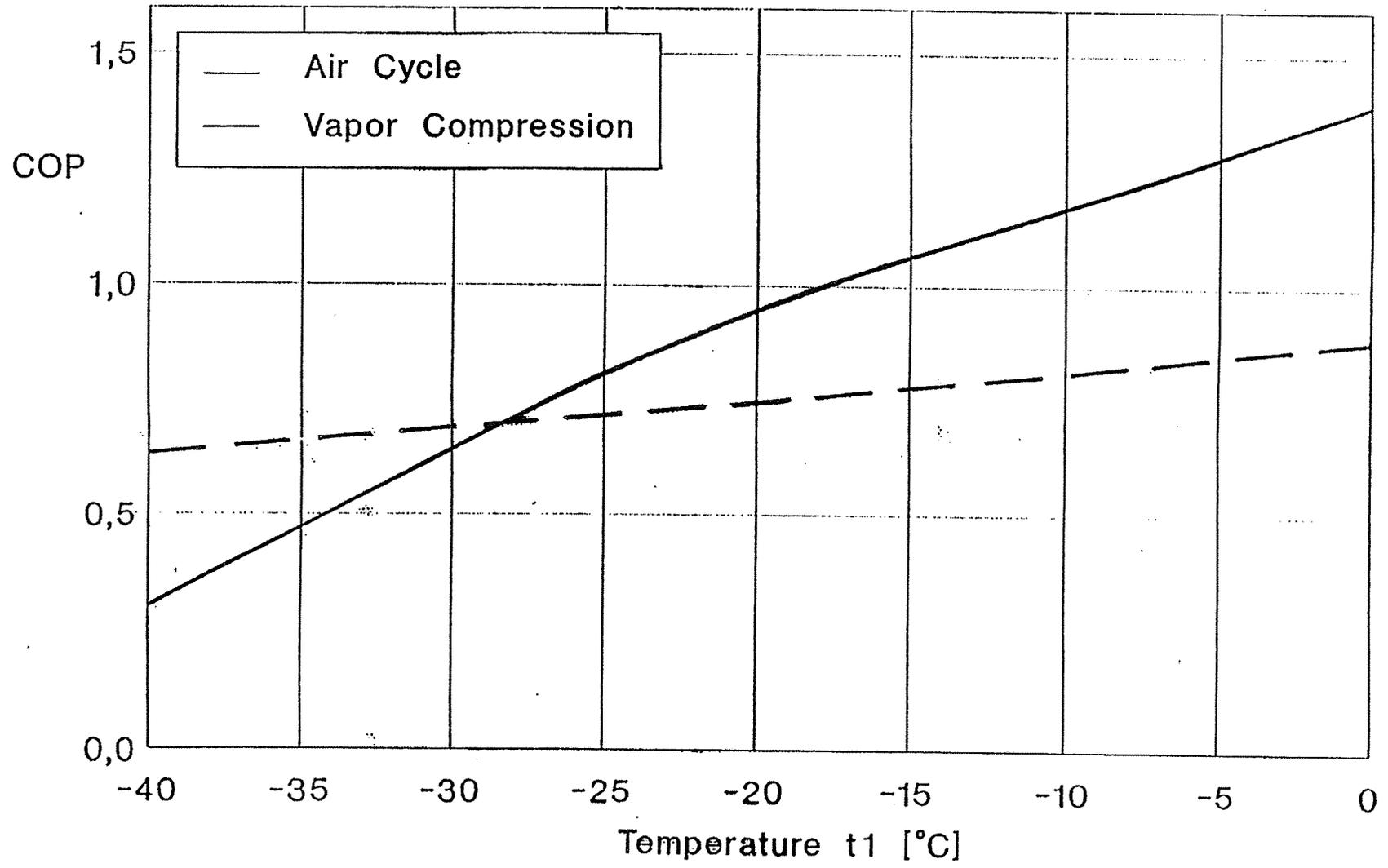
Air Cycle Air Conditioning Systems

22.12.92

Influence on Environment of different Air Conditioning Systems

Consideration for a 80 passenger - car

| Premises | Vapour Cycle - System CFC's (R 12, R 22, etc.) | Vapour Cycle - System HFC's (R 134a) | Air Cycle - System |
|---|---|---|--------------------|
| Indirect CO2 emission due to ECS energy input | 52.800 kg / a | 52.800 kg / a | 57.200 kg / a |
| Average energy consumption per year | 24 kW | 24 kW | 26 kW |
| Max. required electrical power | 38 kW | 36 kW | 45 kW |
| Operation per year | 4400 h | 4400 h | 4400 h |
| Conversionfactor of electr. power plant [emitted kg CO2 / generated kWh] | 0,5 | 0,5 | 0,5 |
| Indirect CO2 emission due to ECS weight influence | 165.000 kg / a | 143.000 kg / a | 88.000 kg / a |
| Total ECS weight | 3000 kg | 2600 kg | 1600 kg |
| Specific tractional power [kW/kg train mass] | 0,025 | 0,025 | 0,025 |
| Direct CO2 - equivalent emission due to refrigerant leakage | 6.390 kg / a | 2.240 kg / a | 0 kg / a |
| Greenhouse potential relative to CO2 | 7100 | 3200 | 1 |
| Freon filling | 20 kg | 20 kg | - |
| Quote of leakage per year | 2,50% | 2,50% | - |
| Quote of recycling at repair | 90,00% | 95,00% | - |
| Intervall of maintenance [years] | 5,00 | 5,00 | - |
| Total CO2 - equivalent emission per year | 224.190 kg / a | 198.040 kg / a | 145.200 kg / a |
| Comparison of CO2 - equivalent emission | 100% | 100% | 73% |
| Comparison of ozone depletion potential | 100% | 0% | 0% |





4. Technical Issues

(Technical Results and Problems to be Solved)

- Automatic Oil Return and Use of Ammonia Insoluble Refrigeration Oils (Quasi-Continuous Oil Return)
- Thermosyphon Refrigeration Circuit in Evaporator/ Liquid Separator Circuit (Layout Guidelines with Respect to Actual Local Arrangement of System Components)
- Application of the Safety Rules VGB 20 (Germany) to the Safety Conception for the Place of Installation (in Case of Breakdown)
- Inclusion of Refrigerant-Cooled Oil Cooler in Plant Conceptions with Air-Cooled Condenser or Evaporative Condenser



5. Economics

(What Are the Anticipated First Costs of the System? How Were These Calculated? What Are They Like in Comparison with Existing Systems That Perform the Same Function?)

- Comparison of Market Prices R134a-/Ammonia System

- Ammonia System More Expensive by 10...15%, Although the 134a-Compressor for the Same Refrigerating Capacity (e.g. 500 kW) Must be Made by 83 % Larger, and the Heat Exchangers Must be Made more than Twice as Large

Reason: - Ammonia Technology (= Steel Welding Technology) for Chillers Still Comparatively New

- R134a-Technology (= Copper Brazing Technology) Already Wide-Spread Due 10 CFC Chillers

- Additional Expenditure for Ammonia (Use of Ammonia Insoluble Oils)
 - Use of Open Compressors
 - Oil Fine Separation
 - High Pressure Float

Comparison of All Costs per Year

| Ammonia | R134a | |
|-----------|-----------|---|
| 20.000,- | 18.500,- | - Capital Costs (12,5% Depreciation as Fixed Costs) |
| 114.000,- | 128.500,- | - Energy Costs |
| 35.500,- | 36.500,- | - Cooling Water Costs |
| 3.200,- | 4.150,- | - Service/Maintenance Costs |

for a Refrigerating Plant of 500 kW

Conclusion

Starting From an Operating Time of More Than 475 h per Year the Ammonia Chiller Represents the More Efficient Solution.



6. Technology Outlook

(What Is the Development Status of Technology? Timetable for Commercialization, Qualitative Assessment of Market Penetration)

Development Status: Marketable Since 03/93

Commercialization: 03/93 Bosch-Einspritzpumpenfabrik
Stuttgart

Status 09/93: 3 Constructional Series of Ammonia Chillers with
11 Different Refrigerating Capacities From 100 up
to 2300 kW with Screw Compressors

Market Penetration: Comprehensive

Sales Outlets: Sales Partner System for Germany and Switzerland

References: Orders Received for 150 Chillers

Applications: - Water Chilling for Different Purposes up to
10.5 MW (Air Conditioning of Fair Halls at
Hannover Fair)
- Brine Cooling for Different Purposes up to
Approx. 2000 kW

NATURES REFRIGERANT - PROPANE

By

James R W, and Missenden J F

School of Engineering Systems and Design
South Bank University, London, UK.

ABSTRACT

The advantages of using propane for refrigeration systems are examined; these relate to energy efficiency, compressor lubrication, availability, costs, environmental factors and safety. It is concluded that propane is an attractive and environmentally-friendly refrigerant for small systems.

August 1993

NATURES REFRIGERANT - PROPANE

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1. Introduction

Almost all single component substances which could be used as refrigerants have been tried at some time. However the introduction of CFC's in the 1930's slowed experimentation. In seeking alternative environmentally-friendly refrigerants, attention was directed towards the foundation family of compounds, the alkanes or straight-chain saturated hydrocarbons. These have only two reactive characteristics, combustion and halogenation, otherwise they are very stable. They also form a homologous series which allows a member of the series to be found which approximates to any desired range of properties. The most convenient hydrocarbon for use in small refrigerators is propane; its salient characteristics have been examined^{1,2,3}. Some of these are summarised in Table 1.

This paper re-examines some of the issues including energy efficiency, compressor lubrication, safety, availability and costs.

| Refrig. name | Safety Group Note a | Evap. press. bar | Press. ratio | COP | COP Note b | Vol.flow for 100kW m ³ /s | Comp. dischg °C |
|--------------|---------------------|------------------|--------------|------|------------|--------------------------------------|-----------------|
| R12 | 6 | 1.83 | 4.07 | 4.72 | 2.53 | 0.0782 | 38 |
| R22 | 5a | 2.95 | 4.04 | 4.69 | 2.52 | 0.0480 | 55 |
| R290 | 5b | 2.91 | 3.77 | 4.55 | 2.35 | 0.055 | 36 |
| R134a | None | 1.64 | 4.68 | 4.62 | 2.38 | 0.082 | 35 |

Note a : Underwriters Laboratories Classification of comparative hazard to life of gases and vapours.

Note b : For condensing temperature of 55°C.

Table 1. System comparison with various refrigerants. Isentropic compression of saturated vapour is assumed. Evaporating and condensing temperatures: -15°C and 30°C respectively.

2. Related Work

The performance and refrigerant cost of two systems used for refrigerated transport were analysed for propane of varying degrees of purity and for R12 by Bodrin et al ⁴, both systems were designed for use with R12. They achieved increased capacity and similar COPs by using propane, the influence of propane purity was found to be

should be reduced. An alternative is to use a mixture of R290, R600 and R600a which is marketed in the UK for aerosol propellants and would have characteristics close to those of R12. Some manufacturers are known to be considering propane/ butane mixtures for domestic refrigerators and one such system is being marketed.

11. Conclusion

Experiments have shown that, even without design changes or system optimisation, a refrigerator in which propane has been substituted for R12 is capable of similar performance with a lower charge. The explosion risks are small and the fire risks are similar but significant in terms of smoke and lubricant burning.

Propane presents an attractive alternative to current CFC's in small systems such as the domestic refrigerator, given correct technical application for operational and safety factors. Energy consumption could be improved with optimisation. In the case of the very large Third World requirements propane is well suited because of its wide and multiple sourcing and low cost.

12. References

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cyanides and choking smoke. By contrast propane burns with a minimum of toxic products. It should also be noted that most fire injuries are due to smoke inhalation, not to burns or explosions.

If a flammable mixture were to be released and ignited locally before mixing with the bulk of the room air a local flash fire of short duration would result. This would not in itself be damaging unless the flame finds readily combustible material in its path, this could be avoided at installation. A residential sprinkler fitted into the kitchen or a fire detector would be very effective against this extremely unlikely event and against the very many more probable kitchen fire situations.

Manufacturers may be reluctant to introduce flammable refrigerants. Aerosol manufacturing facilities must now be sited away from built up areas, otherwise the amount of hydrocarbon stored must be limited. Their factories must be equipped with ventilation, gas and fire detection facilities, sprinkler systems and fail-safe valves. An aerosol filling station must be housed in explosion tolerant buildings with special grounded electrical equipment. Refrigerator manufacturers already store and use flammable gases such as acetylene often with few precautions. The additional storage and distribution of hydrocarbons is small by industrial standards, often much smaller than the factory's space heating plant.

9. Standards

The regulations and standards on the application of flammable refrigerants results from the use of methyl chloride. When this refrigerant was popular a typical domestic refrigerator would require approximately 1.5 kg of refrigerant. The systems had open belt driven compressors with copper connecting tubes which readily became work hardened, so pipe fractures and loss of refrigerant were common. Today's domestic refrigerators hold the refrigerant in a sealed system with a charge in the region of 100 g. It should also be noted that methyl chloride is both toxic and flammable whereas propane is simply flammable.

The British Standard BS 4434 1989^e classified propane as a group 3 refrigerant which has flammable and explosive characteristics. This standard prohibits the use of group 3 refrigerants in domestic occupancy; however, it allows the use of this group of refrigerants in commercial occupancy providing the refrigerant charge does not exceed 2.5 kg. In fact some of the absorption refrigerators use natural gas as a power source and they are recognised by the British Standard. Although there are risks in using flammable refrigerants in domestic refrigerators, the advantages of these refrigerants are manifest. It is believed that the British Standard should take the latest scientific and engineering facts into account and review BS 4434. It is proposed that group 3 refrigerant should be allowed to be used in domestic appliances providing the maximum refrigerant charge does not exceed 200 g.

10. Design Changes

The required compressor swept volume for R12 is about 30% larger than that required for R290; improved motor cooling and lower compressor discharge temperatures will allow some liberties to be taken but this

annual production of propane is 3.3 billion tonnes mostly for combustion but with unquantifiable leakage to atmosphere. R12 production for the domestic market was about 10 million tonnes which by comparison is small. In addition the propane refrigerators will require less refrigerant. The ozone depletion potential of propane is zero. These effects are summarised by Hansen et al⁵.

7. Costs

The cost of propane depends on the required purity. The performance and refrigerant cost of two systems used for refrigerated transport were analysed for propane of varying degrees of purity and for R12 by Boldrin et al⁴, both systems were designed for use with R12. They achieved increased capacity and similar COPs by using propane, the influence of propane purity was found to be small. They concluded that using widely available LPG reduced the refrigerant costs to 2% of that of R134a. An investigation by Wong showed similar cost savings, but for a domestic refrigerator with a small charge refrigerant cost is less important.

8. Safety

One way of assessing the risk associated with using propane as a refrigerant is to consider what quantity of propane would need to be released in order to create a combustible mixture with air in a small kitchen. A very small kitchen would have a volume of 20 m³. At the lower inflammable limit (2.3% propane) this would require the release of 0.65 kg of propane. Typically a domestic refrigerator would contain only 40 g, of propane; an order of magnitude below the ignition point. In addition a large proportion of this propane will not be released by the compressor oil.

The three main issues were addressed:

1. Leakage into an enclosure and ignition.
2. Leakage in the vicinity of a flame such as a pilot light on a boiler or cooker.
3. The risks in the event of a fire.

The first of these is relatively easy to overcome, the evaporator may be placed between the insulation and the inner cabinet skin. This is already done by some manufacturers for other reasons. Alternatively both light switch and thermostat may be placed outside the refrigerated enclosure. In any event the consequences are not catastrophic.

The second problem was considered by Missenden et al⁶. Flammable gas risks already exist to greater and acceptable extents in kitchens. The user should be requested (as at present) not to place the refrigerator next to the cooker or boiler, just as in the case of flammable aerosol propellants sprayed on the person.

The third point was the subject of the fire test. The products of combustion from propane are much less dangerous than those of R12 leaking in the vicinity of a flame where intensely toxic products such as carbonyl chloride (COCl₂) are produced. The toxic fumes from the cabinet and its insulation are a much greater hazard and include

facing the cameras, the propane charge unit to the left. The cage was suspended over a small amount of loose kindling (dry box wood), this allowed a small fire to be started without excessive heat and flame intruding into the visual test of refrigerator combustion. The fire was ignited underneath the units, the prevailing wind causing the left cabinet (propane) to ignite first. Subsequent events were recorded by video camera (VHS), and the tape is available for inspection.

Ignition was observed first of the light polystyrene panels at the rear used to separate cabinet and condenser together with PVC electrical sheathing. Presently the liner and insulation took fire with the emission of copious thick black smoke which continued to be evident until the end of the test over 30 minutes later. After about five minutes, the propane unit charge escaped over a c20s period when the aluminium evaporator failed. The propane did not noticeably add to the conflagration nor escape catastrophically.

The R12 unit, sheltered somewhat because of the prevailing wind, behaved in a similar manner except that the gas escape was more pronounced with a horizontal jet of deflected flame. This comprised the pyrolised R12 and hot gases, a particularly poisonous mixture.

Intense smoke from both machines obscured much of the rest of the test, except that the boiling of the compressor lubricant and burning of the resulting vapour produced a sustained long flame (about 0.3 m) which persisted to the end of the test. Finally both units were extinguished leaving only steel parts intact.

The influence of charge was not significant in regard to type or flammability. Catastrophic failure did not occur but the unit containing a greater mass of charge (R12) showed a correspondingly stronger discharge effect. Propane was not seen to add materially to the intensity of the fire.

The lubricant was a flammable oil in relatively large quantity and boiled in the system producing a torch-like flame. This materially contributed to the severity of the fire and would cause particular hazard in a house fire.

By far the most significant observed effect was the smoke emission. The quantity and length of time of emission of such large volumes of toxic gases must cause immediate concern over the use of the insulating materials in unprotected domestic situations.

5. Compressor lubricant

A recent paper by Fannin³ indicated that refrigeration systems using propane as the refrigerant can be lubricated with lubricants based on poly-alkylene glycols. This was confirmed by the propane tests just reported, the lubricant inside the system being unchanged.

6. Atmospheric Effects

The influence of propane on the greenhouse effect appears to be insignificant compared to R12. It is most likely to have a similar effect to methane; less than 0.15% of the effect of R12. The world

4.3 Combustion test

A connection was made to the evaporator which allowed the refrigerant to enter the cabinet and an internal ignition device was constructed to produce a high energy spark. Tests were conducted with the ignition being energised immediately after the propane was allowed to leak into the enclosure, and after a settling time of 15 minutes. The resulting ignition was only partly explosive; a modest report accompanied the door opening and a small short lived flame was observed inside the cabinet and recorded by video. The intensity of the flame was not sufficient to scorch the plastic liner even after numerous tests. The explosion was somewhat more robust after a longer mixing time had been allowed but again part of the gas had stratified at the bottom of the cabinet, to burn off quickly after the ignition. The mechanism of ignition was thus demonstrated to be the explosion by chain reaction of that fraction of the gas which lay within explosive limits followed by combustion from the perimeter of the rich gas mixture, inwards.

The flame intensity was of too short a duration to cause surface pyrolysis. As an illustration of the limited strength of the explosion, in one case a small piece of adhesive tape inadvertently applied held the door closed against the expanding gases. These vented partly through the rear push-out panel of insulation (arguably the best route for their egress) and partly through the flexible door gasket.

4.4 Motor protection

If a domestic refrigerator with R12 is switched off and on again after a short period, it is unlikely to start. The motor will trip as a result of the action of the over-current protection until the pressures approach the balance point and the motor is able to deliver the required starting torque. It was observed that after a brief stop the propane refrigerator would trip cyclically for a longer period than the R12 refrigerator before starting; ideally if propane is used in a machine designed for R12 the over-current protection should allow the compressor to trip out for longer periods. However parallel refrigerators working with propane without this modification have proved satisfactory.

4.5 Fire test

A fire test was conducted to examine the relative behaviour of refrigerators using R12 and R290. No such tests had been reported previously, nor performed at the Fire Services College test facility.

Two identical standard refrigerators of 5 ft³ (142 l) capacity were used for this investigation, both originally operated with R12 refrigerant. The refrigerant in one was replaced by propane. The final sealing of charge was identical to the R12 unit. The test rig was the fire simulation facility of the Fire Services College. This consisted of a concrete room with solid floor, ceiling and two opposite walls. The third wall had a large window, the fourth a double door width aperture through which the test was visually observed and recorded.

The two refrigerators, both having hot compressors from normal running, were mounted in an open steel cage with the condensers

The higher propane pressure ratio resulted from the compressor having too large a swept volume. This increased the required condenser capacity, resulting in a higher temperature difference and condenser pressure. It is also possible that the capillary tube may require tuning for propane. The reduction in energy requirements resulting from the improved heat transfer with propane were not achieved; the higher pressure ratio of the propane unit had evidently offset the benefits. This shows that design optimisation on the whole refrigeration system is required, although many existing systems have components sufficiently near optima to allow drop-in replacement if necessary.

4.2 Refrigerant quantity

Several refrigerators similar in size and design to the one on which the energy consumption tests were conducted have been charged with propane, all have required less than 40 g. By ratio of liquid densities the propane charge should have been about 31 g, the difference is considered to be the influence of the compressor shell and its oil.

A 5 ft³ (142 l) domestic refrigerator was used to carry out tests to determine the refrigerant charge and the quantity which could escape in the event of an evaporator leak. A pipe was connected to the bottom of the evaporator which could be used to release the refrigerant either to atmosphere at the back of the refrigerator or to the refrigerated enclosure.

After an initial charge of propane was inserted the system was evacuated and the vacuum was held for 2 hours. From a vacuum condition a charge of 22.4 g of propane was inserted into the system which was sufficient to restore normal operation. The system was switched off for 5 minutes in order to allow the refrigerant to migrate to the evaporator.

The refrigerant was first exhausted to atmosphere. The system then was re-charged to the same evaporator pressure and condensing temperature (55°C). The mass of propane charged into the system was measured and found to be 11.9 g.

A period of normal operation was then followed by an off cycle of 5 minutes, the refrigerant was again allowed to leak to atmosphere. The volume that escaped was measured by a displacement method and its mass was calculated; this method gave 13.4 g after 14 minutes, 13.7 g after 30 minutes and 13.8 g after 105 minutes. The system then was re-charged and found to require 13.6 g of propane to achieve normal operation, this confirmed the measurements taken by the displacement method.

The test was repeated with a similar system from another manufacturer. The compressor was replaced with a unit which had never been used with CFCs. The initial charge of propane was 39 g, recharging after evacuating for 2 hrs required 28 g and re-charging after the refrigerant was exhausted to atmosphere required 19 g. This indicated that 11 g of propane was still in the oil after evacuating for 2 hrs and a further 9 g was in the pipes at atmospheric pressure.

modification was made to the compressor which in the event proved to be adequately rated for these tests.

To determine the quantity of refrigerant required and the quantity which escapes if a leak occurs two similar refrigerators were evacuated and charged with propane. One of these units was fitted with a tube which allowed the refrigerant to escape into the cabinet together with an ignition device for combustion tests.

To assess the risk when refrigerators are caught in a house fire two identical refrigerators, one charged with R12 and the other with propane were incinerated in a controlled, video recorded test at the Fire Services College, UK.

4.1 Energy consumption test

As the refrigerators were from a mass production assembly line, the performance deviation between these units could have been substantial. Hence, the refrigerators, designated A and B, were monitored with their original R12 charges for two weeks before the experiments with propane commenced. The refrigerators were located side by side centrally in a large laboratory known to behave in an isothermal manner having stagnant air movement, so that any disturbance was applied to both units. It was established that there was no significant difference in performance between these units, i.e. > 1% in power input.

The refrigerant inside unit A was removed and the system was evacuated. Propane was then inserted into the system through a filter-drier. This procedure was repeated once after 24 hours of normal operation. The refrigerators were then placed as before in the laboratory and a similar comparative test was carried out over a period of 45 days. During this time, the two units remained undisturbed to ensure comparative results. The recorded data has been published⁷.

The test showed initially that Unit A was consuming more energy than Unit B. However, after 17 days, the energy consumption of Unit A became lower than that of Unit B. Although the data show a general trend of behaviour, the differences are small, with the advantage to the propane unit. The two units were then placed on public display in London for six weeks, where the ongoing performance readings were available for public inspection.

The condensing and evaporating temperatures of the refrigeration systems were recorded to show the system operation conditions. The data and the corresponding calculation results are shown in Table 4.

| | R12 | Propane |
|------------------------------|-------|---------|
| Condensing temperature (°C) | 40.0 | 42.0 |
| Condensing pressure (bar) | 9.6 | 17.8 |
| Evaporating temperature (°C) | -20.0 | -20.0 |
| Evaporating pressure (bar) | 1.51 | 2.50 |
| Pressure Ratio | 6.35 | 7.12 |

Table 4 Test measurement and results.

| Refrigerant | Suction Sup. (K) | COP | Relative COP | Refrigerant | Suction Sup. (K) | COP | Relative COP |
|-------------|------------------|------|--------------|-------------|------------------|------|--------------|
| R290 | 0 | 4.55 | 1.0 | R22 | 0 | 4.69 | 1.0 |
| | 10 | 4.65 | 1.022 | | 10 | 4.64 | 0.989 |
| | 20 | 4.88 | 1.073 | | 20 | 4.60 | 0.981 |
| R134a | 0 | 4.62 | 1.0 | R12 | 0 | 4.72 | 1.0 |
| | 10 | 4.64 | 1.004 | | 10 | 4.71 | 1.0 |
| | 20 | 4.68 | 1.013 | | 20 | 4.72 | 1.0 |

Table 2 Effect of useful superheat on COP, evaporating and condensing temperatures assumed are -15°C and 30°C respectively.

| Refrigerant | Suction Sup. (K) | COP | Relative COP | Refrigerant | Suction Sup. (K) | COP | Relative COP |
|-------------|------------------|------|--------------|-------------|------------------|-------|--------------|
| R290 | 0 | 2.35 | 1.0 | R22 | 0 | 2.52 | 1.0 |
| | 10 | 2.44 | 1.038 | | 10 | 2.517 | 0.999 |
| | 20 | 2.57 | 1.094 | | 20 | 2.516 | 0.998 |
| | 30 | 2.63 | 1.120 | | 30 | 2.525 | 1.002 |
| R134a | 0 | 2.38 | 1.0 | R12 | 0 | 2.53 | 1.0 |
| | 10 | 2.44 | 1.025 | | 10 | 2.56 | 1.010 |
| | 20 | 2.51 | 1.053 | | 20 | 2.60 | 1.026 |
| | 30 | 2.57 | 1.078 | | 30 | 2.63 | 1.041 |

Table 3 Effect of useful superheat on COP, evaporating and condensing temperatures assumed are -15°C and 55°C respectively.

The relative COP is the ratio of isentropic COP with useful suction superheat to its value with saturated suction vapour; a value in excess of unity indicates an increase in COP which results from useful suction superheat. It is seen that for R12 and R22 there is little difference but R290 and R134a systems will benefit from suction/ liquid line heat transfer. Both refrigerants are therefore suitable for systems utilising capillary tubes as expansion devices.

Extensive theoretical comparisons of CFC, HFC and HC refrigerants undertaken at the Norwegian Institute of Technology also indicate that hydrocarbons are an efficient replacement to R12 and R502.

4. Experimentation

Two new domestic refrigerators designed to operate with R12 were used by Wong² to compare the energy consumption with R12 and with R290. The long term power consumption was measured with a kWh meter and thermocouples were used to measure the air temperature and surface temperatures of the evaporator and condenser. A 25 W heater was placed inside the compartment of each unit and switched on for 30 minutes in each hour to simulate cyclical loading. Table 1 shows that the calculated compressor swept volume required for the propane system was 29.7% less than that for the R12 system. However, no

small. They concluded that using widely available LPG reduced the refrigerant cost to 2% of that of R134a.

Researchers have used propane in refrigerant mixtures. Camporese et al⁵ investigated R290/R134a mixtures for domestic refrigerators and concluded that a 20-80% mixture gave a better performance than R12, the author also suggested that this mixture should be considered as a R502 substitute.

Pearson⁶ developed a non-flammable replacement for R502 containing R22, R218 and 6% R290. For economic reasons the quantity of R218 was minimised, two mixtures were investigated and were denoted R69S and R69L containing 20 and 39% of R218 respectively. The propane added improved oil/refrigerant miscibility. The mixtures give good energy efficiency and were shown to be drop-in replacements for many applications. The refrigerant in a deepfreeze designed for R502 was changed to R69s at the South Bank University, this has since maintained an air temperature of -40°C for two years. The system behaviour closely matches that achieved with R502. Manufacturers are now including propane in some refrigerant mixtures.

3. Calculated Results

The heat transfer coefficients for these refrigerants were calculated using the Dittus-Boelter equation for vapour at -15°C and with an assumed velocity of 10 m/s, being warmed in a 8.0 mm tube:

| Refrigerant | R12 | R22 | R290 | R134a |
|--------------------------|-----|-----|------|-------|
| HTC (W/m ² K) | 174 | 217 | 280 | 183 |

Measured heat transfer coefficients are higher as a result of liquid droplets being entrained in the superheated vapour at the evaporator exit and the influence of oil and direction changes. The comparison shows that for R12 the heat transfer coefficient is lower than with the other refrigerants; the superheated region of DX evaporators will therefore be large. In this respect propane is particularly advantageous. For the same degree of useful superheat the dry region of the evaporator will be smaller, this gives a higher overall heat transfer coefficient for the evaporator. In the evaporator's two phase region the heat transfer coefficients are much higher, changes in their value have little effect on evaporator performance owing to the poor heat transfer coefficient on the air side. A similar analysis shows that propane also improves the cooling of the motor inside suction gas cooled hermetic compressors.

Most small refrigeration systems utilise a capillary tube as an expansion device, this small bore tube is attached to the suction pipe. The device is therefore equivalent to an expansion valve and suction/ liquid line heat exchanger. It is therefore informative to consider the influence of useful suction superheat on the COP. This is shown in Table 2 for refrigerants condensing at 30°C and evaporating at -15°C and Table 3 for refrigerants condensing at 55°C and evaporating at -15°C.

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