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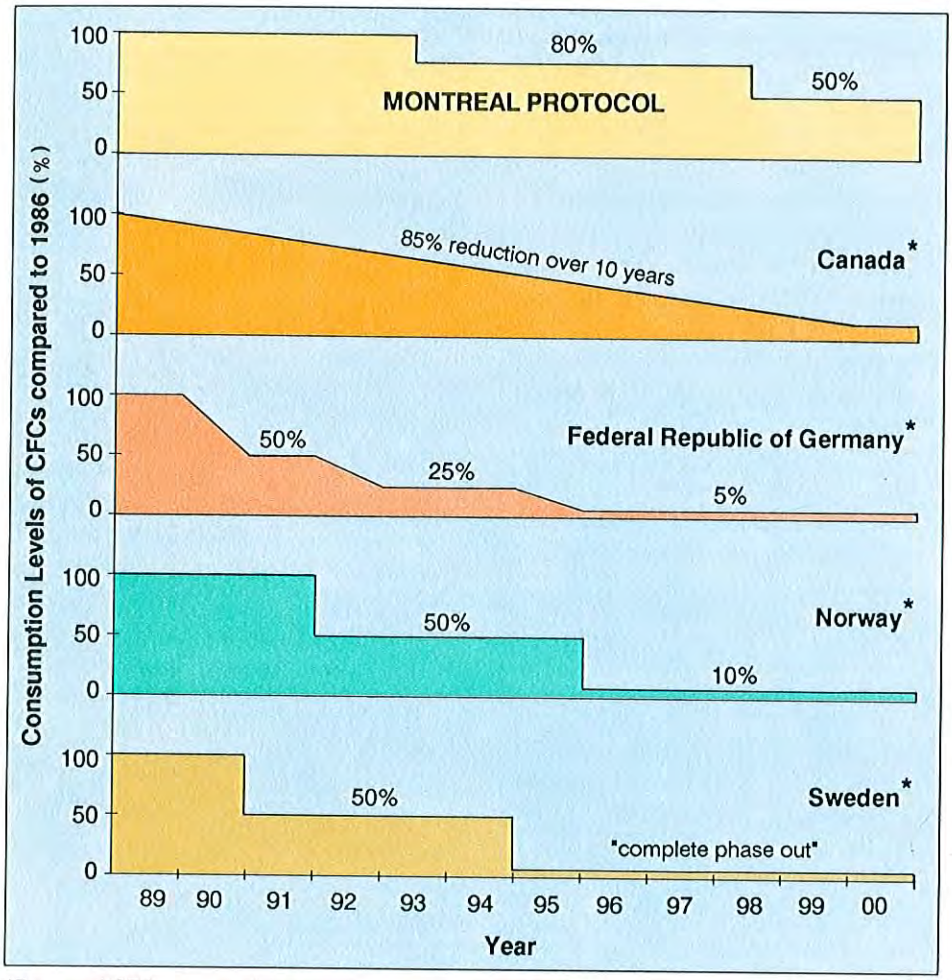

*Proposed CFC consumption reduction plans compared to the Montreal Protocol[1,2,3]

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This issue: Heat pumps and the environment

Editorial*

The CFC issue has become the topic of discussion in the heat pump, refrigeration, and air conditioning communities. The role played by CFCs in ozone depletion and in the greenhouse effect is of increasing concern to the public. As shown in the figure above some countries are already planning or have implemented more stringent cuts than those required by the Montreal Protocol. The recent Helsinki ozone conference and the member countries of the European Community have called for a revision of the Montreal Protocol aimed at phasing out CFC production and use by the end of the century.

Along with the common aim of most industrialized countries to reduce CFC consumption to levels as low as possible, there are many questions which need to be answered for and by the politicians; the CFC producers; and the heat pump, refrigeration, and air conditioning industries before definite decisions can be made. Some of these questions are:

-- What are the flammability, material compatibility, toxicity, environmental impact, and thermodynamic characteristics of the new alternative refrigerants?

- What role will the refrigerants HCFC-22 and ammonia play in the future?
- How will the limited supplies of CFCs be distributed in the future? Will there be adequate amounts of CFCs available for the remaining lifetime of existing installations? Will taxes be placed on CFCs to limit their consumption?
- What is the impact of heat pumps on ozone depletion and the greenhouse effect? Accounting for the fact that most heat pumps currently use CFC or HCFC refrigerants, will the net impact of heat pump use be positive (reduction of CO_2 emissions) or negative (emission of CFC refrigerants) upon the environment?
- How can developing countries build up their HVAC industries without the use of CFCs?

To answer some of the questions mentioned above several international and national R&D programs have been initiated. For instance:

- In the "Program on Alternative Fluorocarbon Toxicity Testing" (PAFT1), 14 of the world's largest CFC producers have joined together for a five to seven year period, beginning 1987, to investigate the toxicity of HFC-134a and HCFC-123. In PAFT2 eight manufacturers are investigating HCFC142b for a similar time period beginning in 1988. Eight million US dollars are being invested in this program.
- In the "Alternative Fluorocarbon Environmental Acceptability Study," financed by a number of CFC manufacturers, an independent group of scientists is investigating the environmental impacts of the potential alternative substances HCFC-22, 123, 124, 141b, 142b and HFC-125, 134a, 152a.
- The DKV (Deutscher Kälte und Klimatechnischer Verein) is coordinating the R&D activities of German industry and research institutions in a program called "Solving the CFC-ozone problem in refrigeration technology." The program is sponsored by the German federal ministry of research and technology (BMFT).
- ASHRAE is funding a program for research and evaluation of the properties of HCFC-123 and HFC-134a. Duration of the project is five years and the funding level is 400000 US dollars, 220000 from the US government.
- The International Energy Agency, through the Implementing Agreement on Advanced Heat Pumps, is considering a number of new projects (annexes) dealing with the CFC issue as recommended at its CFC Seminar in Rome, Italy in May 1988.

The articles in this Newsletter also address some of the above questions. The first four articles give an overview and update of the current CFC situation, the status of substitutes, and the activities being undertaken in the refrigeration industry. An alternative working fluid for use in compression cycle heat pumps is discussed in an article by Bärnthaler. Articles by Narodoslawsky and Macriss discuss working fluids appropriate for absorption heat pumps.

Articles by Gilbert, Ritter, Takemoto, and Lorentzen address the environmental benefits of heat pump use in terms of CO_2 reduction and energy savings. An article by Alefeld presents an analysis method for identifying areas where efficiency improvements can be made in absorption cycles.

We hope this Newsletter will be an informative reference and guide to our readers for determining future trends. We also believe that the current environmental discussions are a positive factor for more widespread use of heat pump technology in the future. In the meantime the heat pump community must not only react to political decisions but must provide decision makers in government with accurate information on the environmental benefits of heat pump use.

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1. Erster Zwischenbericht der Enquete-Kommission des Deutchen Bundestages, Vorsorge zum Schutz der Erdatmosphäre, 2.11.88.
2. The NEWS, March 6, 1989.
3. Montreal Protocol on Substances that Deplete the Ozone Layer, Final Act 1987, United Nations Environmental Programme.

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L.J.M. Kuijpers*

The CFC Issue; International Actions

In the last one-and-a-half year period, the CFC issue has resulted in the initiation of many international investigations. The main target of these investigations is to set-up an inventory of the different uses of CFCs and of the technologically feasible alternatives. Two kinds of investigations get special attention in this article: (1) An International Institute of Refrigeration (IIR) study into the possibilities for a reduction of CFC emissions in refrigeration; and (2) a UNEP investigation into the options which exist in order to seriously restrict CFC emissions. (The author is chairman of the UNEP refrigeration expert panel.) A number of preliminary results of the IIR investigation are presented. Furthermore the set-up of the UNEP study is described. The latter study is of utmost importance due to the fact that, from this study, recommendations are derived for a reassessment of the Montreal Protocol in 1990. This article also contains a summary of recent developments in chemical substitutes for the conventional, environmentally non-acceptable CFCs.

Introduction

In 1987 a clear change occurred in the way the so-called "ozone-CFC issue" is discussed. The refrigeration world, in these discussions, considered itself as one of the most important CFC users taking into account the importance of the cold food chain. At that moment, 1987, the first results of the 1986 ozone measurements were published and preparations were made for establishing the Montreal Protocol, under which name it now has evoked ubiquitous discussion.

This attitude could clearly be observed during the IIR congress in Vienna in August 1987. Here a CFC working group was established in order to cope with the consequences of the issue. The necessity of an inventory of the problem even became more apparent at the moment the 50% "Montreal Protocol" saving was decided upon. At that moment the decision was of a purely political nature and did not make any subdivision in the usage of CFCs for various applications.

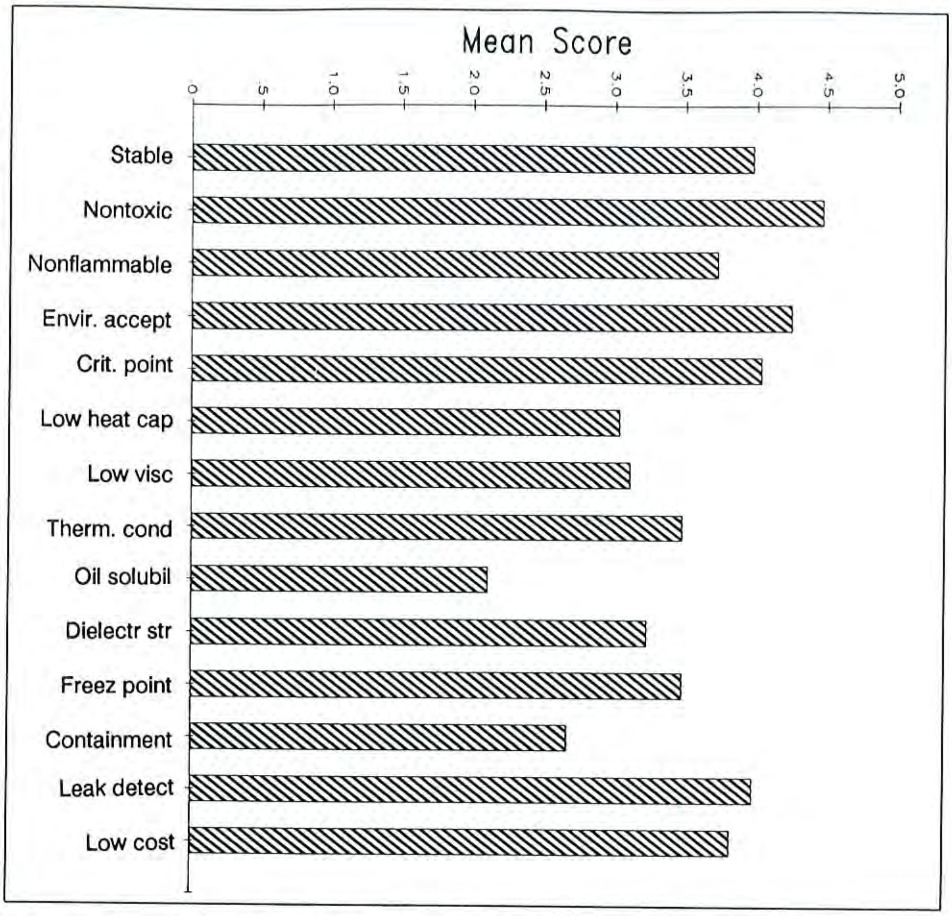

Figure 1. Scores of the different properties a refrigerant should have (IIR investigation)

For the refrigeration and heat pump world, being split up into numerous specific application areas, a big problem arose. There was no real knowledge about the amount of CFCs used in the vapor compression cycle, neither about the short-term saving possibilities. Furthermore, since 1977 only one realistic substitute for CFC-12 had been discussed, i.e., HFC-134a. At that moment it became urgent to determine whether this was the real alternative or if there existed other ideas for alternatives to be obtained from refrigeration experts. Thorough, time consuming studies would not yield results which would fit within the time schedule of the international developments. Therefore the IIR decided upon a questionnaire enquiry among its members which would make it possible to come to a fast inventory.

In the course of 1988, the United Nations Environmental Programme, UNEP, urged the world to gather information for an update of the Montreal Protocol in 1990. This reassessment should be based upon newest knowledge on ozone science, effects, and technological measures. During an orientation conference at The Hague, NL - on an invitation of the Dutch Environmental Minister, Mr. Nijpels - it was decided to install a number of so-called Review Panels, which should highlight further possibilities for saving and the necessity for this. Also here it could be concluded that an important task would be to investigate the lack of data for CFC usage in various application sectors. As a main target for the UNEP technology study it was considered necessary to gather data, to describe all possible options for saving and to give the time scale involved. In this way technological knowledge could form the realistic basis to build upon decisions to be made by politicians. This UNEP study is in full progress at the moment, April 1989.

In the meantime the discussions on the ozone layer are being governed by purely political points of view. Various conferences are used to clearly demonstrate the willingness to solve "the problem." This, for example, especially holds for the "Saving the Ozone Layer" conference in London, UK, 5-7 March 1989. Numerous delegations did give statements here which contained the message that one would go much further than the savings envisaged in the Montreal Protocol. At the same time the Protocol got more support; 31 countries stated they will consider ratification and will therefore be parties in a further update of the Protocol in 1990.

Developments in the CFC issue have substantially accelerated. Only a fast reporting on necessary but also realistic saving possibilities can direct further political actions. This certainly holds for the refrigeration and heat pump world where there is a strong dependence on refrigerants and where a switch over to alternative processes is extremely difficult. This is in contrast to areas where CFCs are used as intermediary substances in production processes only (foams, solvents, etc.).

IIR-questionnaire study

Shortly after the IIR-congress in Vienna a working group was established to carry out an investigation of the emissions in the refrigeration/heat pump sectors; and to study the possibilities of existing and future substitutes. Some members concentrated on the "refriger-

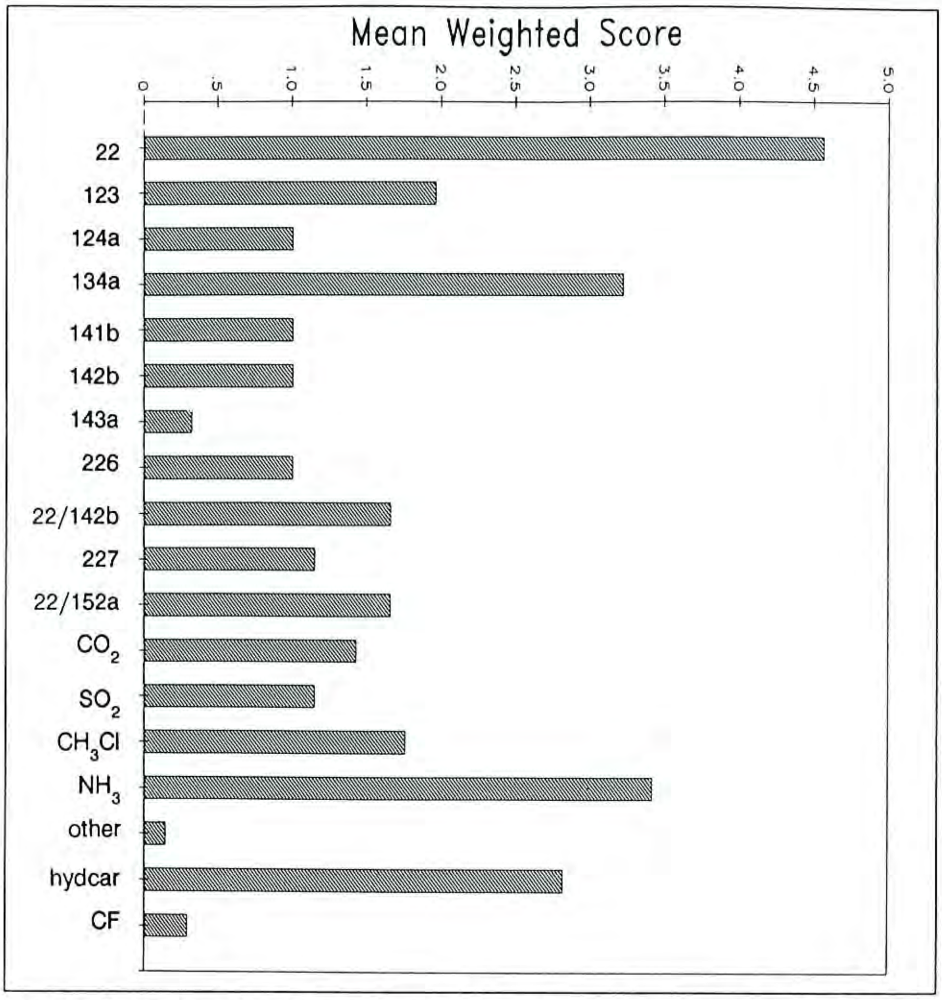

Figure 2. Scores concerning the realistic chance for application a number of CFC substitutes are assumed to have (IIR investigation)

ant"-side (the IIR B1-commission); others with the different application areas (domestic and commercial refrigeration, heat pumps, automotive air conditioning, etc., subjects for the IIR-B2/E1/E2 commissions).

For both areas questionnaire forms were designed. The refrigerant part concentrated on the questions of feasibility of old, present-day and future substitutes; at the same time on the question which supplementary research should be performed here. The refrigerant application equipment part concentrated on the emissions, the reasons why these occurred and the possibilities for reclaim and recycling; at the same time an opinion was asked for about the chances of certain substitutes. Preliminary results are discussed below.

Refrigerants

In contrast with the questionnaire for the application/equipment side which was meant for developers, producers and users of refrigeration equipment, the investigation concerning refrigerants was meant for those persons having expertise in refrigerant research.

It was asked how important the criteria were judged which are normally applied to refrigerants and whether there would exist certain substitute candidates provided certain requirements were less important. Furthermore it was asked whether one had experience in the application of formerly applied refrigerants and whether the use of H(C)FC-123, 124, 134a was considered a realistic one. A number of questions dealt with the use of the refrigerant HCFC-22. There was also an enquiry implemented to determine which research had been and which should be performed; here also information was gained about the time scale which was assumed realistic in the development of new refrigerants. Partially these topics covered the same area as did the IEA questionnaires sent out in the beginning of 1988 to various research institutes. The results of this latter questionnaire are discussed in an article in the IEA Heat Pump Newsletter published in June of 1988.

Most of the reactions expressed experience in the investigation of the refrigerant CFC-12. Concerning refrigerant properties, non-toxicity and environmental acceptability are considered most important. The importance of other properties can be taken from Figure 2. Although differences are marginal, it is astonishing that "easy leak detection" and "low cost" get a higher score than "nonflammability." Furthermore it deserves attention that oil solubility gets a very low score, whilst this aspect needs attention in many refrigeration/heat pump applications.

As to candidate refrigerants, substances which could be applied at once are considered to be HCFC-22, ammonia, nonazeotropes and - in case flammability is accepted - hydrocarbons. For future application few candidates are mentioned and only HFC-134a gets an important role to fulfill. Mean scores are further presented in Figure 3. Methylchloride, nevertheless, gets the same score as, for example, the non-azeotropic mixtures HCFC-22/142b and HCFC-22/152a. On the other hand, it is stated that no further investigations on methylchloride should be performed. It should be underlined that no reaction indicates possibilities for the refrigerants H(C)FC-124, 125, 143, 143a, etc. Especially experienced people in this area emphasize the research into hydrocarbon applications; also the possibility of using ethers - especially dimethylether - is mentioned. Further study into all possibilities of non- and "near"-azeotropes is considered to be urgently required, before one of the new pure new substitute fluids will be defined as best. A period of four and a half years is assumed to be necessary before reliable data will have become available. This period fits in the time scale for toxicity investigations (order of magnitude five years). These data studies are not required anymore for HCFC-22 and ammonia, the two substances which are being considered as the front runners among the substitutes.

Applications

A major part of the questionnaire which concentrated on the application and the emission of CFCs was in a "multiple choice" format. Information about the size of the installation, the operating conditions and the type of compressor was requested. The major part also dealt with the emission of refrigerant, either via leakage, or via maintenance or component breakdowns; at the same time the connection to certain components was investigated. Finally a number of questions were asked as to the possibilities of different refrigerants, the experience obtained in this field and the time which was assumed necessary in order to change to a substitute refrigerant on a large scale. At the same time information was asked about effects which could prohibit this change.

Without dealing with the different types of installations in an extensive way, some examples from the outcome of the questionnaire study are given below. The numbers attached to the different effects denote the mean score given (scale 1-least important to 5-most important).

Heat pumps

In heat pump installations using open compressors:

1. Maintenance (3.55),
2. Component breakdowns (3.36), and
3. Sneaking leakage (2.27)

are declared to be the main causes for emissions, where breakdowns and leakage usually occur in compressors and pipework. In order to reduce the emissions, which are estimated to be in the order of 40% (including recycling) the following possibilities exist:

1. Better education (3.50)
2. Higher quality (3.50)
3. Better routines (2.71)
4. New designs (2.29)

Surprisingly most of these can be realized without changing to a newly designed installation. Much more can be realized by introducing higher quality into all current steps and actions. Figure 4 presents a histogram of the aforementioned causes (mean scores).

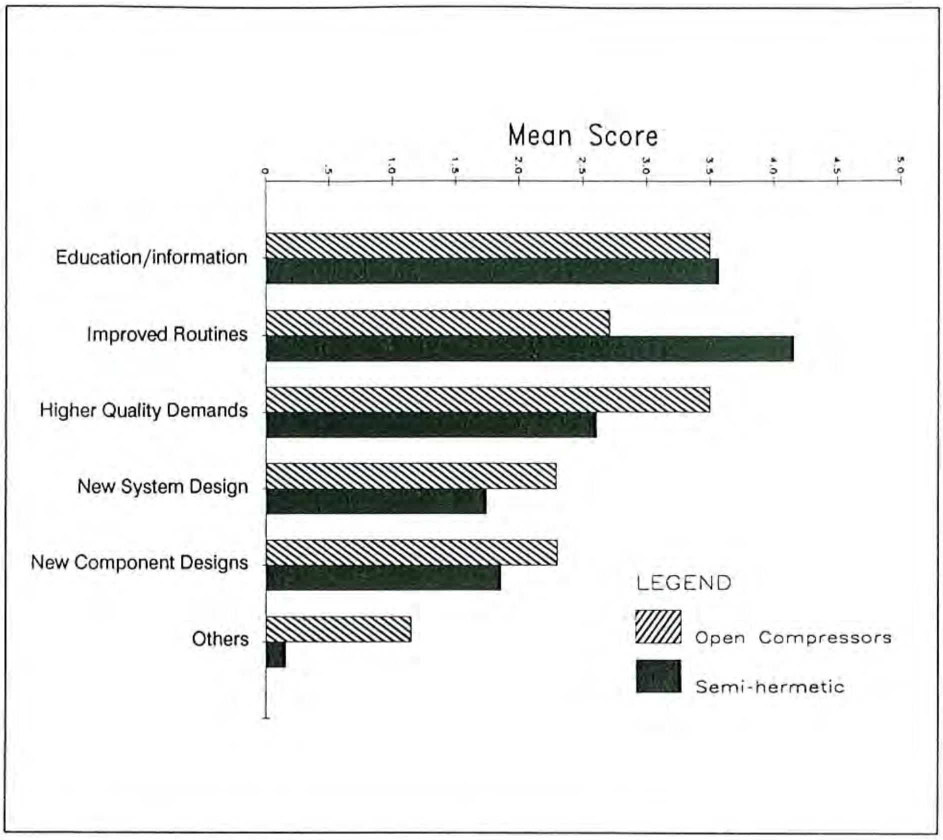

Figure 3. Scores attributed to effects which are assumed to reduce the CFC emissions in heat pumps (IIR investigation; black columns refer to semi hermetic, cross-hatched to open compressors). In contrast to "higher quality," which is leading in the case of open compressors, "improved routines" form the most important factor in semi-hermetic compressor installations.

In case of semi-hermetic compressors, similar remarks are made, where, however, servicing routines get a lower score. Here new designs are also seen as less important. Where HCFC-22 and ammonia are considered as the most important candidates for open compressor installations, HFC-134a can be added in the range of substitutes for semi-hermetic equipment.

Commercial equipment

Here the most important reasons for CFC-emissions are:

1. Component breakdowns (46% of the yearly loss)
2. Leakage and leakage tests (36%)
3. Servicing (19%)

The most important reasons for breakdowns are:

1. Bad operation
2. Lack of expertise
3. Improper control operation

A large number of answers consider recycling of the refrigerant as possible and necessary. The price of the refrigerant could play an important role here. Averaged it is stated that a reduction of CFC-emissions by 46% is possible using relatively simple means.

Automotive air-conditioning

The emissions of CFC-12, the refrigerant which is normally used in automotive air-conditioning, is due to:

1. Maintenance (50%)
2. Leakage (35%)
3. Component breakdown (10%)
4. Miscellaneous (3%)

If during maintenance the reclaim and recycling of the refrigerant is applied, a reduction of the emissions between 30 and 50% should be possible. This is also dependent upon how far servicing can be carried out by official automotive dealers/garages. Emission reductions are possible through:

1. Better education/training
2. Improved routines
3. Higher quality norms
4. New designs

Subsector	First author
0. Coordination/chairman	Kuijpers, Philips Research, Netherlands
1. Domestic Refrigeration	Hallett, WCI, USA
2. Commercial/Retail Refr.	Kruse, DKV President, FR Germany
3. Transport Refrigeration	Heap, SRCRA, UK
4. Industrial Refrigeration	Haukas, Uni Trondheim, Netherlands
5. Cold Storage/Processing	Lindborg, Frigoscandia, Sweden
6. Heat Pumps	Frivik, Uni Frondheim, Netherlands
co-authors:	Berntsson, Chalmers Gothenborg, Sweden
	Benstead, Electr.Res. Capenhurst, UK
	Schneeberger, Nat. Electr. Board, Austria
7. Comfort Air Conditioning	Hayes, Trane Co, USA
8. Automotive Air Conditioning	Baker, GM/Harrison, USA
9. Refrigerant Handling	Taylor, Recor. Systems, USA
10. Refrigerant Data	McLinden, Nat. Inst. St. Tech., USA
co-authors:	Angelino, Politecnico Milano, Italy
	Ishikawa, Tokyo Res.Inst., Japan
	Narodoslawsky, Graz University, Austria
	Agarwal, Delhi Inst. Refrigeration, India
	Bhaduri, IIT Powai, Bombay, India

Table 1. Subsectors of the expert panel group for refrigeration, air-conditioning and heat pumps, and the first authors for each of these. As an example, co-authors are given for subsectors 6 and 10.

In the automotive air conditioning field HFC-134a is seen as the most promising substitute. HCFC-22 and non-azeotropic nonflammable mixtures might be other substitute candidates. The price of the refrigerant is not seen as prohibitive, instead nontoxicity and nonflammability are considered important requirements.

Domestic equipment

The number of responses in this refrigeration area has been very low. On the other hand, most of the questions in the questionnaire are of a different importance for domestic equipment. Servicing and effects due to servicing are less applicable here. Although the share of the small equipment in the total CFC usage is low (less than a 5% share in refrigeration, less than 1% in the total CFC consumption) there are two ways for a further reduction of CFC emissions:

1. Reclaim/recycling after use
2. Application of environmentally acceptable substitutes.

Domestic appliances are also characterized by a certain CFC usage in the polyurethane insulation (4-5 times the amount applied in the refrigeration cycle). The application of substitutes with a lower energetic efficiency - both in the insulation and in the cycle - will have a double effect on the total consumption. Certainly also on the design of appliances which is often restricted by a large number of temperature boundary conditions. The efficiency aspect deserves special attention here.

Final remarks on the IIR investigation

The most important conclusion of the IIR-investigation is that substantial reductions should be possible by better implementation of procedures and by providing better education and information of servicing personnel. Savings in the CFC consumption in the order of 30-50% should certainly be possible. The figure is slightly dependent on the application sector considered.

From the questionnaire investigation a number of R&D recommendations can be derived :

1. R&D into the properties of H(C)FC refrigerants
2. R&D into properties and applications of hydrocarbons
3. Studies into nonazeotropic mixtures
4. R&D into better sealing methods
5. Investigations into possibilities for better piping connections.

Furthermore action has to be undertaken on a number of levels:

a. Emission reductions via improvement of the "state-of-the-art", including codes for good practice. This can only be done by involving the national refrigeration institutes.
b. Establishing the importance of the thermodynamic efficiency.
c. Further study into the best substitute solution for domestic equipment which is under the highest "public pressure" and most affected by considerations on energy consumption.
d. Investigations into the influences of the price level of CFCs and substitute refrigerants.

UNEP study

As mentioned previously, four UNEP review panels were established in October 1988 and given the task of summarizing the present day status of science (ozone layer, technology measures, and effects - biological and economic). The aim of this effort is that the so called "Contracting Parties," the parties involved in the Montreal protocol, will be provided with a "total" report in due time. Only in this way can the reassessment procedure be carried out thoroughly and appropriate decisions be taken at the London UNEP Conference in March 1990. These decisions will go into force in October 1990. One of the most important Review Panels is the one which should summarize the present status of technology and options for conservation of CFCs. This Technology Review Panel consists of five expert groups each covering the important CFC application areas.

Application Area	Chairman Expert Group
1. Refrigeration, AC, heat pumps	Kuijpers, Philips Research, NL
2. Foams	Lupinacci, EPA Washington, USA
3. Solvents	Andersen, EPA Washington, USA
4. Miscellaneous	Kökerits, Env. Sweden, Sweden
5. Halons	Taylor, Taylor Inc., Canada
Coordination UNEP	Buxton, Env. Canada

Each application area will conceive a so-called "Options Report" in which the different options for savings in CFC emissions are summarized. Based on this information the chairmen of the different expert groups will write a comprehensive report, the so-called "Report of the Technology Review Panel." In this report a translation will be found from options to concrete advice concerning saving percentages. This report will in turn form part of the "total" report (ozone science, technology, effects) which will be presented to the Contracting Parties.

Fully Halogenated CFCs	Formula	Boiling Point (°C)	Substitute Refrigerants H(C)FCs	Formula	Boiling Point (°C)
			141b	CCl_2FCH_3	32
11	CCl_3F	24	123/123a	$C_2HCl_2F_3$	27
114	$CClF_2CClDF_2$	4	142b	$CClF_2CH_3$	-9
			124	$CHClFCF_3$	-12
			134	CHF_2CHF_2	-20
			152a	CHF_2CH_3	-25
12	CCl_2F_2	-30	134a	CF_3CH_2F	-27
115	CCF_2CF_3	-39	22	$CHClF_2$	-41
			143a	CF_3CH_3	-48
			125	CF_3CHF_2	-48
			32	CH_2F_2	-52
13	$CClF_3$	-81	23	CHF_3	-82

Table 2. Fully halogenated CFC refrigerants and the - ethane/methane derived - possible environmentally more acceptable substitutes (McLinden[2])

The whole reporting must be completed by July 1989. Taking into account that the experts for the expert panel were asked for cooperation in December 1988/January 1989, this means that the set-up of the "Options Report" must be done within three months, from February 1989 to April 1989, a very short period.

In the composition of the expert panels important topics are the broad "geopolitical" spread of the experts and the industrial background of the majority of the experts. As an example, the refrigeration expert panel consists of 45 members, which is a very high number in this procedure (see also Table 1).

In the area of refrigeration, air-conditioning and heat pumps, nine subsectors have been defined. One of the experts has been nominated first author of a paper - which forms part of the "Options Report" - which is being reviewed by a small number of co-authors (3 to 4). Next a tenth subsector has been defined which summarized all knowledge available in the field of conventional refrigerants and new substitutes, all knowledge and data to be expected within the short term, and which presents recommendations for further refrigerant data evaluation.

Some first impressions from this UNEP study can already be presented here. The international chemical manufacturer organization, CMA, has published a CFC consumption for refrigeration of roughly 250,000 tons in 1987 in the western world only. A first inventory from the different subsectors yields a much lower number which can only be explained by:

-- much more is emitted during production than assumed (first filling of installations);
-- much more is used in servicing the equipment than assumed;
-- the above given subsectors do not cover all kinds of equipment.

It points to a problem which is present for all CFC application areas and certainly for refrigeration, air-conditioning and heat pumps. It makes it extremely difficult to derive a maximum saving percentage for refrigeration as a whole. In part, the aforementioned difficulty is also due to the fact that nobody can present a global picture.

Generally a short term 40-50% saving is expected (good practice, better education/information, and reclaim/recycling of refrigerant). In a number of refrigeration, AC, and heat pump installations refrigerants can be applied which are non-Protocol controlled substances. In this way the use of HFCF-22 and non-azeotropic mixtures based on HCFC-22, of hydrocarbons and, certainly, of ammonia will sharply increase. It means that, within a period of two to three years, and certainly if HFC-134a will become available thereafter, 60 to 70% less CFCs will be emitted. On the other hand, existing installations will need CFCs 11 and 12 for servicing. This implies that the last 30 to 40% will gradually decrease in the next 10 to 15 years, down to a negligible level.

The greatest consumer of CFC-12 in refrigeration is automotive air conditioning (almost 50% of the total use of all controlled CFCs in refrigeration, air conditioning and heat pumps). On one hand it is caused by the enormous amount of cars which are AC equipped (240 million in the whole world); on the other hand by the procedures applied in servicing and recharging. It is of utmost importance that this "part" of the refrigeration industry switches as soon as possible to more environmentally acceptable refrigerants, such as HFC-134a. The automotive industry already clearly expressed their willingness and their ability to do so.

A number of other subsectors is not convinced of the qualities/benefits of HFC-134a at all. They raise problems such as energetic efficiency, "copper-aluminum" plating, the behavior of polyethylene glycols, the necessary lubricant. Generally they prefer HCFC-22, nonazeotropic refrigerants and nonflammable refrigerants, by the application of which large energetic savings are assumed to be possible as well.

Refrigerants and refrigerant data

There are indications that, in the future, there will be a larger number of refrigerants commercially available than there has been in the past. Although, also in former years different CFCs were used in the different application areas (CFCs 11 and 12, CFC-500 (HFC-152a) and CFC-502, HCFC-22 and CFC-114).

Table 2 presents some of the possible substitute refrigerants. At the moment four of these environmentally acceptable CFC substitutes are commercially available. HFC-23 and HFC-152a can be found in azeotropic mixtures (CFC-503 and CFC-500). HCFC-142b is used in many non-refrigeration applications. Both HFC-152a and HCFC-142b are used as precursors in the chemical industry for the production of fluorinated polymers. Finally there exists the well-known HCFC-22 which is generally available and which is already applied on a large scale. Especially this holds for the United States where it can be found in all normal air-conditioning apparatus.

Refrigeration all over the world is asking for guarantees for the future use of HCFC-22. In a first instance, the atmospheric science has derived an Ozone Depletion Potential which is comfortably low (0.05). However, in a second instance there exists always some uncertainty in the atmospheric science, furthermore the production of HCFC-22 will very strongly increase in the future and thus chlorine load of the stratosphere is partially due to HCFC-22 usage. The Environmental Protection Agency has performed investigations here.[5] It can clearly be observed that part of the chlorine load is due to emissions of methylchloroform (ODP value 0.10-0.15) which is used in cleaning processes; equal to HCFC-22 methylchloroform can be considered as an HCFC. This illustrates the difficulty which will exist in case HCFC-22 should be definitely excluded from the Protocol or in which way attention should be paid to all HCFC substitutes in the Protocol. For example, it might be that a production ceiling for all HCFCs is agreed upon - expressed in ODP value - which is obligatory for all application sectors. Anyhow, refrigeration applications should not worry too much about HCFC-22 usage, certainly not if HCFC-22 is handled in the future in the same way one should handle the controlled substances at present. Needless to say the application of HCFC-22 always has an uncertainty attached to it.

Taking into account the above, the industry is clearly searching for alternatives for HCFC-22. For example, HFC-32 has the highest heat of vaporization and excellent heat transfer characteristics; it has also been produced in former years. However, HFC-32 is flammable which might be prohibitive for certain applications. The same flammability characteristic is valid for HFC-143a which can be a byproduct in the production of HCFC-142b. A byproduct in the manufacturing process of HCFC-123 is HFC-125, a substance which is nonflammable and has been declared as the final replacement for HCFC-22 by the chemical industry several times. However, it should be noted that, for most of these alternatives, toxicity values are not known, neither can they be expected within the short term, if at all.

The only realistic substitute for CFC-12 is HFC-134a. Development of this substance was initiated due to the fact that HFC-134a seemed to have "drop-in" characteristics for CFC-12. The automotive air conditioning industry played a large role in its selection in the late seventies. At present HFC-134a is not considered as a drop-in substitute anymore. Various refrigeration subsectors do not see HFC-134a as a realistic replacement due to an expected 8 to 10% lower thermodynamic efficiency.

A study made by Hodgett[3] forecasts that HFC-134 will be a much better candidate than HFC-134a from an efficiency point of view. Furthermore, HFC-143 should have much better characteristics compared to HFC-134a for heat pump applications. These statements, however, are only based on estimates of thermodynamic properties. Further data are not known concerning HFC-134 and HFC-143 and this certainly holds for possible toxicity values.

A number of studies, among which one is in the area of domestic equipment,[4] concludes that, from an energetic point of view, HFC-152a has to be preferred over HFC-134a. Also HFC-152a is not a direct "drop-in" substitute for CFC-12 and changes in components will have to be made. However, HFC-152a is flammable and its application is considered impossible by most manufacturers due to safety problems. One should put the question whether this remark is an appropriate one, certainly in the case of small domestic equipment (refrigerant contents 100-200 g). That the flammability aspect would lead to large changes in logistics in the manufacturing process is certain; it is questionable whether it has to be decided upon in this stage of the "CFC issue" development. Anyhow, the remark should be made here that discussions on flammability are not always based on purely technical arguments (question of education, etc.) and these will keep their difficult character.

It will be clear that one of the consequences of the "CFC Issue," the conversion from CFCs to substitutes, should lead to the selection of the best possible refrigerants. This implicitly yields a divergence in the availability of substances for the different subsectors. This divergence can even be enlarged by the definition of nonazeotropic mixtures for certain applications such as HCFC-22/142b and 22/152a. A good example was given by the Dupont firm at the ASHRAE Conference in Chicago, January 1989, where the so-called "blend" HCFC-22/124/152a was presented. This "blend" should have the "drop-in" characteristics (no oil problems, etc.) for CFC-12 equipment and should have a 3% better efficiency in normal refrigeration applications. However, the ODP value of this "blend" is 0.03 and in principle the same arguments hold here as in case of HCFC-22, which were given above. On the other hand, compared to HFC-134a applications a 10% energetic efficiency difference is apparent. With some simple assumptions on the power level of the equipment that can be operated using one ton of the "blend" and on the CO_2 production in power plants the following question can be formulated.[6] Should the emission of one ton of ODP material, that leads to a more favorable energetic picture compared to HFC-134a, be preferred over the emission of more than a half million tons of CO_2? Refrigeration, AC and heat pump applications were already stated to be partly causing the greenhouse effect, via the emission of CFCs. Via other relationships, which are of energetic nature, refrigeration contributes to the discussion on necessary CFC savings in a different and very interesting way. Maybe this can be avoided by giving a special status to each CFC consuming sector; this, however, remains an open question.

Conclusions

Concerning the use of refrigerants, controlled substances or CFCs, developments were taking place in an accelerated way during the last year. Refrigeration, AC, and heat pump applications form an area which is directly influenced by these developments. It is the only area which needs the refrigerant in order to realize the refrigeration process and which is therefore limited by extra boundary conditions. Nevertheless, this area can also contribute substantially in the reduction of the environmentally harmful CFC emissions; and this also at short notice.

The main result of the IIR questionnaire investigation has been that, in the normal refrigeration installations, substantial savings can be realized at very short notice, i.e., in the order of 30 to 50%. Important short term substitutes are HCFC-22 and ammonia. Consequences for the CFC world consumption in a certain time scale are difficult to estimate.

The UNEP technology study, which fits into a larger framework, will try to summarize and quantify all possible options for savings. From these data a guide will be formulated for the necessary and possible CFC savings in the coming ten years. The UNEP refrigeration report will contain extra information on future refrigerants which makes clear that there is still much divergence in the consideration of all possibilities. However, there are numerous options, which will have to be investigated by the refrigeration, AC and heat pump industry. The final result should be that the best possible refrigerant is used in each of the different application areas.

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S. Fischer*

CFCs Dominate Agenda at Chicago ASHRAE Meeting

Five seminars were held at the American Society of Heating, Refrigeration, and Air-Conditioning Engineers (ASHRAE) convention in Chicago concerning chlorofluorocarbons (CFCs) . The speakers presented information on the Montreal Protocol to limit the production of CFCs, chemical properties of alternative refrigerants and blowing agents for foam insulation, and the use of CFC substitutes in equipment and insulation. This article summarizes the material presented in those five seminars.*

(*This paper has adopted the nomenclature promoted by DuPont to identify fluorocarbons containing chlorine by CFC, those with hydrogen and chlorine by HCFC, and those with hydrogen but no chlorine by HFC. Under this terminology refrigerants R-11, R-12, and R-22 are designated by CFC-11, CFC-12, and HCFC-22.)

Introduction

The winter meeting of the American Society of Heating, Refrigeration, and Air-Conditioning Engineers (ASHRAE) was held in Chicago, Illinois from January 29 to February 1, 1989. The members of this society will be profoundly affected by the terms of the Montreal Protocol which restricts future production of refrigerants 11, 12, 113, 114, and 115 (and Halons 1211 and 1301). The countries that have ratified this treaty have agreed to reduce their production of chlorofluorocarbons to the amounts produced in 1986 (a 20-25% reduction from 1988 levels in the U.S.) beginning on July 1, 1989, and then to cut to 80% of the 1986 levels in 1993 and to just 50% of the 1986 levels in 1998. (Currently proposed legislation in the U.S. would impose a complete cessation of production by 2000.)

The interest in alternative or substitute chemicals has intensified among the ASHRAE members as these production cutbacks become more imminent. There were five different seminars at the Chicago meeting devoted exclusively to the subject of CFC alternatives. The presentations can be grouped into three general categories: chemical properties of ozone-safe alternative refrigerants and blowing agents, the performance of equipment and insulations using these alternative chemicals, and the U.S. Environmental Protection Agency (EPA) regulations and proposed rulemaking and industry responses to those regulations.

Properties of ozone safe alternatives

The refrigeration and building insulation industries are facing two problems in adapting to EPA regulations. They must survive in the short term, during the next three to five years, using increasingly scarce supplies of CFC-11 and CFC-12 until environmentally acceptable alternative chemicals become commercially available. In the long term they have to design their equip-

	HCFC-123	HCFC-141b
initial k-factor	- (3-10%)	- (3-10%)
aged k-factor	?,*	?,*
foam flammability	?,*	?,*
toxicity of combustion products	?	?
closed cell content	NC	NC
foam corrosivity	NC,?,*	NC,?,*
water vapor transmission	NC	NC
foam adhesion properties	?	?

+	better than CFC-11 blown foam
?	not much data
-	worse than CFC-11 blown foam
*	very important question
NC	no change

Table 1. Properties of foam insulation using alternative blowing agents presented by Ian Shankland.

ment to use these new compounds while maintaining or improving thermal efficiency. Ian Shankland of Allied-Signal presented a series of charts rating the relative properties of HCFC-123 and HCFC-141b compared to CFC-11 as foam blowing agents (Table 1). Joseph Sutej of Mobay identified six possible problems in using either HCFC-123 or HCFC-141b as the blowing agent for foam insulation in appliance cabinets: the viscosity of the chemicals, cabinet filling, foam friability (ease of crumbling), dimensional stability, k-factor drift, and the removal of exothermic heat in the foaming process (the blowing agent serves as a heat sink and poorer performance will increase demold time and slow down production). Neither HCFC-123 nor HCFC-141b will be available as foam blowing agents in the short term, though, and about the only viable substitute is to replace some of the CFC-11 with CO_2. This alternative faces the same six problems mentioned earlier, except they are likely to be exacerbated.

Four presenters spoke directly to the thermophysical and thermodynamic properties of HFC-134a, HCFC-123, and HCFC-141b. Paul Reed of DuPont and Mark McLinden of the U.S. National Institute of Standards and Technology (NIST) summarized progress to date on measuring the liquid and gas viscosities for these materials, their heat capacity, thermal conductivity, vapor-liquid equilibrium, critical point, vapor pressure-volume-temperature relationships, the density, vapor pressure, specific heat, enthalpy, entropy, and speed of sound. Both DuPont and NIST are working to get this information into a publishable form and McLinden expects to have this completed by the Vancouver ASHRAE meeting in June. NIST is planning on further testing of HCFC-141b and mixtures of HCFC-22/HFC-152a and HCFC-22/HCFC-142b for refrigerator/freezers and HFC-32/HFC-125 for low temperature applications. They also intend to investigate the use of HFC-134a/HFC-152a, HFC-134a/HFC-134, and HFC-134/HFC-152a in ternary blends. Keshav Sanvordenker of Tecumseh Compressors spoke about the materials compatibility of HFC-134a in refrigeration systems and Ward Wells of DuPont talked about applications testing.

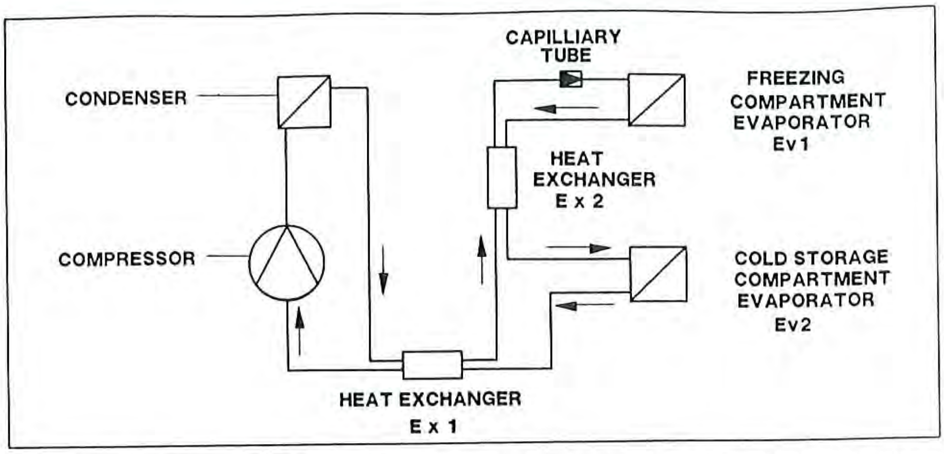

Figure 1. Schematic drawing of refrigerant circuit of a dual evaporator refrigerator/freezer using a blend of HCFC-22 and HCFC-142b as presented by H. Kruse

Equipment/insulation performance with alternatives

Amana has been working rigorously with Mobay to reduce their use of CFCs in refrigerators. Ruth Dodd reported that Amana has made 25-30% reductions of CFC-11 at the mix-head of production line equipment with very little change in the thermal properties of the foam. They have also reduced the CFC-12 charge in a refrigerator/freezer from 240 g to 130 g (8.5 oz to 4.6 oz) by using smaller diameter tubes in the heat exchangers. The charge may be cut even further by eliminating the accumulator and reducing the condenser subcooling.

Duncan Malcolm of Tecumseh spoke about the importance of refrigerant properties on compressor design. A good design is a compromise between cost, sound attenuation, and energy efficiency. He described the impacts of changing refrigerants on the valves, piston, muffler, and motor of a hermetic reciprocating compressor.

Professor H. Kruse of the University of Hannover in West Germany gave a European perspective on the impact of the Montreal Protocol on refrigerators and freezers. He addressed four subjects: recycling of CFCs, partial replacement of CFCs to reduce usage, the long-term development of ozone-safe refrigerants, and the use of non-azeotropic refrigerant mixtures in refrigerators. The recovery rate of CFC-11 from recycled foam insulation from appliances is likely to be low, but in Kruse's view the recovery of CFC-12 from the refrigeration system is not insignificant. He also believes that use of CFC-11 and CFC-12 in new units can be reduced by partial replacement of CFC-11 with CO_2 in the foam insulation, by using HCFC-500 or a blend of CFC-12 and dimethyl ether (DME) as the refrigerant, and by reducing the refrigerant charge.

Kruse reported that many European manufacturers will be able to reach a 50% reduction in CFC use almost immediately which will allow them time to find the most energy efficient, environmentally acceptable alternatives for future products. They do not like the idea of substituting HCFC-22 for CFC-12 and are looking at HFC-152a, although it has problems with flammability, and HFC-134a, which has shown lower efficiencies than CFC-12 and has problems with mineral oil based lubricants. Kruse also presented results from tests he performed with a refrigerator using a non-azeotropic mixture of HCFC-22/HCFC-142b. The refrigerator had been modified to use a dual evaporator with special high to low side heat exchangers as shown in Figure 1. This design showed at least as good efficiency as a refrigerator with CFC-12 under steady-state testing and performed better in a pull-down test.

Ed Vineyard, of Oak Ridge National Laboratory (ORNL) in the United States, presented results of testing he has done of alternative working fluids in a refrigerator/freezer. His test equipment is shown in Figure 2. Vineyard performed the standard 32°C (90°F) closed door test on an unmodified, commercially available 510 dm^3 (18 ft^3) refrigerator. In each test the refrigerant charge was determined to give the best

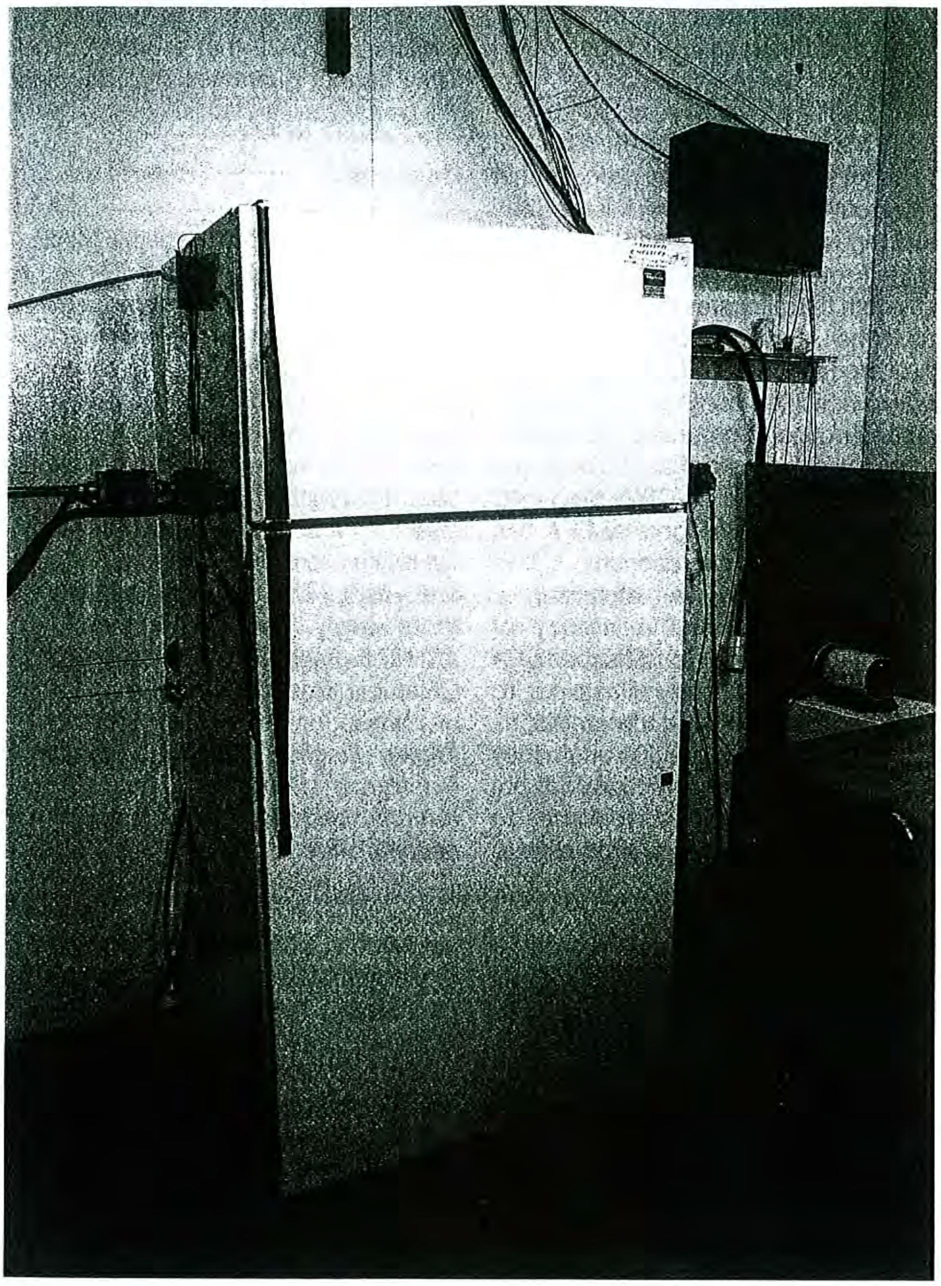

Figure 2. Refrigerator/freezer used at ORNL for evaluating alternative refrigerants

energy efficiency at 32°C (90°F). Of the refrigerants tested to date, CFC-12/DME and HCFC-500 showed a decrease in energy-use, HFC-134a with a polyglycol oil showed an 8% increase in energy-use, and mixtures of HCFC-22/HFC-142b and HCFC-22/HCFC-124 showed 7.4-8.6% increases. These results are shown in Table 2. A proprietary mixture of three refrigerants that was supplied by one of the major chemical manufacturers showed a decrease in energy use. ORNL plans to do additional testing with HFC-134a/HFC-152a, HFC-134, HCFC-22/HFC-134a, HCFC-22/HFC-152a, and HFC-134a with different oils.

U.S. government regulations and industry reactions

Five speakers addressed the subject of government regulations and industry and trade group responses to government action. David Bateman of DuPont spoke about the current and projected availability of CFC alternatives, Kevin Fay talked on behalf of the Alliance for Responsible CFC Policy, Kent Anderson addressed what ASHRAE is doing, Jean Lupinacci spoke for EPA, and Dick Denny appealed to EPA on behalf of the Air-Conditioning and Refrigeration Institute (ARI) not to regulate HCFC-22.

Kevin Fay's presentation covered several topics of interest to the HVACR industry. First he addressed the status of the Montreal Protocol; 46 countries had signed the agreement as of the end of 1988 and it had been ratified by 31 countries (including all of the major producer nations). Technical committees have been set up to review the scientific and economic data on ozone depletion and they will incorporate their recommendations into a draft document by October 1989. These proposed revisions to the Montreal Protocol are to be voted on in April 1990, and would enter into effect in October 1990. The most likely outcome of this process will either be an agreement that no new equipment will be produced using CFCs after 1998 or that there will be a 98% phase-out of CFCs after 1998 except for what is necessary to maintain existing equipment.

Fay warned the CFC users that they must be alert to attempts at unilateral action by the U.S. Congress and by individual state legislatures. The production or use of CFCs could be affected by clean air and acid rain bills before Congress or by proposed environmental users' fees. It is particularly important to direct useful information to state legislators considering laws affecting CFCs in order to inform them of the possible impacts of their actions.

Refrigerant	Oil	Charge (oz)	 (gm)	Energy Use (kWh/day)	Increase (%)	Decrease (%)
12	Suniso 3GS	6.0	170	2.43	-	-
134a	LB-165	5.5	155	2.62	7.8	-
134a	LB-525	5.5	155	3.53	45.3	-
22/142b (60/40)	Suniso 3GS	5.4	153	2.64	8.6	-
22/142b (60/40)	Zerol 150	5.4	153	2.64	8.6	-
12/DME (86/14)	Suniso 3GS	4.8	136	2.27	-	6.6
12/DME (90/10)	Suniso 3GS	4.8	136	2.34	-	3.7
500	Suniso 3GS	5.3	150	2.29	-	5.8

Table 2. Refrigerator/freezer daily energy use relative to CFC-12.

There were 12 different state laws passed in 1988, including a law in Rhode Island which bans the purchase of all products produced with CFCs. This law has not been enforced.

ASHRAE itself has a formal position and policy on CFCs and stratospheric ozone. Kent Anderson reported that ASHRAE supports the Montreal Protocol and recognizes the great importance of the continued use of CFCs in existing equipment. ASHRAE will be developing guidelines for minimizing emissions of CFCs that are based on the European code and will look at existing industry standards to see if they need to be modified for substitute refrigerants. ASHRAE has already acted on behalf of the HVACR industry by submitting comments to the EPA on proposed regulations. ASHRAE is also participating in the reassesment of scientific data mentioned earlier through the Refrigeration Technology Assessment. ASHRAE is supporting two CFC research projects at NIST, evaluating two proposed projects, and has referred nine others to committees.

Jean Lupinacci of EPA spoke briefly about the current status of the Montreal Protocol and the revision process that is currently underway. EPA issued the final regulation implementing the terms of the Protocol in August of 1988 using a system that allocates production quotas to the U.S. manufacturers based on their production of CFCs in 1986. EPA is also soliciting comments on an advanced notice of proposed rulemaking concerning the use of auctions or users' fees to allocate the CFCs produced between users. The goal of EPA has been to protect stratospheric ozone while at the same time maintaining or improving the thermal efficiency of equipment using CFCs. Thus far EPA has relied on voluntary measures to encourage users to reduce emissions or recycle refrigerants, although they will resort to regulatory actions if it becomes necessary. EPA continues to view HCFC-22 as a viable alternative to CFCs, but they would discourage new uses of HCFC-22 that are not critical. They cannot guarantee that HCFC-22 will be available indefinitely.

Conclusion

ASHRAE is preparing a special publication on CFCs that will be published in the spring of 1989. Many of the seminar papers presented in Chicago will be included as well as a selection of earlier papers from ASHRAE publications and the International Journal of Refrigeration. There was a keen interest in Chicago for anything related to the Montreal Protocol and CFCs and this interest is likely to continue for the next several years. There will undoubtedly be more lively sessions at the next ASHRAE meeting in Vancouver, British Columbia, Canada in June.

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H. Kruse*

Latest Developments and Future Trends in the Field of CFC Substitutes

Introduction

The Montreal Protocol, signed on September 14, 1987, on the basis of the Vienna Convention adopted by the UNO, has already in part been called into question by more recent developments.

In some countries, further political action for more stringent rules was demanded; at the same time, developments in the market led to an unexpected drive in the use of substitutes. Moreover, recent knowledge about the effects of CFCs on the ozone layer prompted some signatory states of the Montreal Protocol to change their attitude, while further information on suitable substitutes threw new light on future possibilities. For this reason, one has to consider first of all the latest state of restrictions on CFCs.

Latest state of restrictions

Taking as a starting point the Protocol, which came into force on January 1, 1989, the most recent developments in restrictions on CFCs are as follows.

Current state of implementation of the Montreal Protocol

The Montreal Protocol was to take effect on January 1, 1989, the date of the ratification of the Protocol by 11 or more states representing at least two thirds of the world's CFC production in 1986. It calls for the freezing of CFC consumption at 1986 levels beginning January 1, 1989, with a further reduction of 80% by July 1, 1993, and 50% by July 1, 1998. Beginning 1990, the Protocol will be reviewed annually.[1]

As stated in a communication of the US Environmental Protection Agency, 25 countries, representing at least two thirds of the world's consumers of CFCs, had ratified the Montreal Protocol by December 16, 1988. On December 31, 1988, it had been ratified by 29 states. Therefore the protocol came into force on January 1, 1989.

It should be pointed out that the Federal German Bundestag ratified the Montreal Protocol on October 13, 1988; however, ratification can only be by all the countries of the European Community. On the occasion of the ratification, the federal minister for the environment drew attention to the fact of the Montreal Protocol being an inadequate convention; consequently, he aims to conclude international agreements to reduce the use of CFCs world-wide, as quickly as possible, by 85 or 90%.[2]

Severer restrictions

Some of the dynamic developments towards severer restrictions that set in shortly after the signing of the Montreal Protocol were:

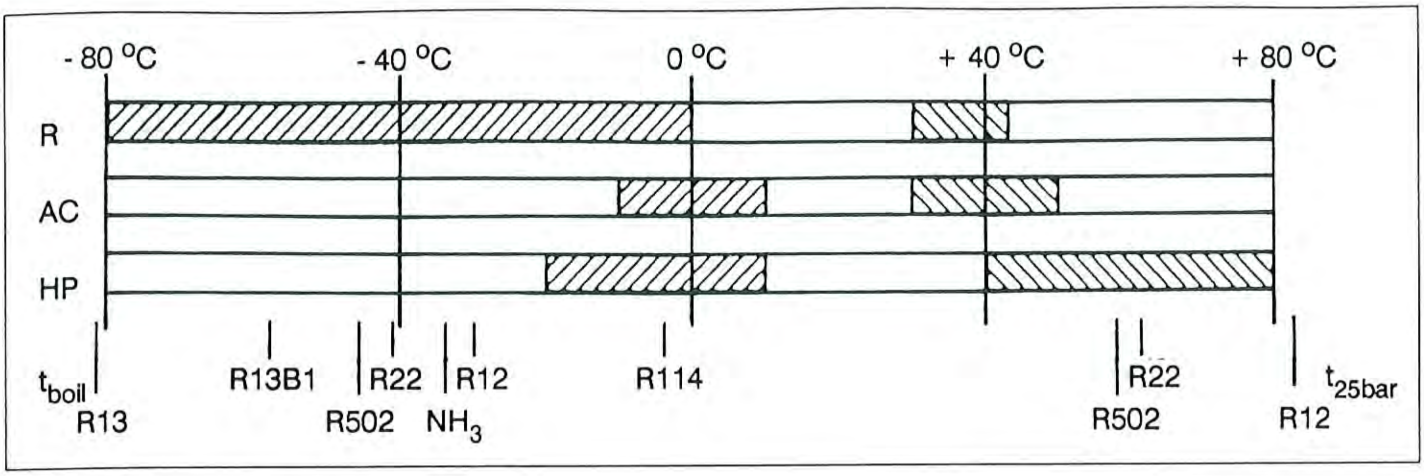


Figure 1. Refrigerant application ranges

1. The United States, through its Environmental Protection Agency, issued a statement on September 26, 1988, requesting that all countries ratify the Montreal Protocol and aim at a complete ban of ozone-depleting CFCs.[3] Two facts are at the background of this surprising declaration. First, the Ozone Trends Panel has established an unmistakable connection between ozone depletion and chlorine content in the stratosphere. Secondly, a reduction in ozone of 1.7 to 3.1% has been established already over North America. Accordingly, CFC manufacturers like Dupont, Dow Chemicals, and Hoechst, have decided on the phase-out of CFC production. These dynamic developments have aggravated the situation in the refrigeration engineering sector, all the more since other sectors using CFCs have substantially cut down on CFCs already.

2. The environment ministers of the Scandinavian countries decided already in autumn last year on a complete ban of fully halogenated CFCs beginning 1995, with a scheduled cut to 25% by 1991. The Austrian minister for the environment, too, has warned that fully halogenated refrigerants are to be completely prohibited by 1999. The Netherlands and the Federal Republic of Germany, as already mentioned, have called for severer restrictions than laid down in the Montreal Protocol, but both countries are bound by community law and cannot act independently in this regard. Therefore the federal minister for the environment has declared in the Bundestag on October 13, 1988, that the German federal government will make special efforts to agree on more stringent rules at the community level. This proposal was unanimously accepted by the German Bundestag on March 9, 1989.

3. A Memorandum of the Environmental Council recommends a reduction by 85%, while the Enquete-Commission of the German Parliament proposes 95% by 1999, with intermediate reductions of 20% by 1992 and of 50% by 1995.

Additional influences

In the Netherlands, consumer organizations have called on the public to refrain for the time being from purchasing commodities containing CFCs (for instance refrigerators and freezers). In Great Britain, supermarket chains have started installing R22 freezers instead of units using R502, and are emphasizing this in their advertising. In the Federal Republic of Germany, the Max Planck Institute of Aeronomics in Lindau has carried through measurements on the stratosphere establishing larger quantities of R22 in the higher layers than suggested previously by life-time calculations for the refrigerant.[4] These publications by Fabian were the object of numerous discussions last year and were again dealt with at the World Ozone Congress in Göttingen in August 1988. Without any objections being raised to the values measured, it was their interpretation for the future that was intensely discussed.[5]

Although the UNEP symposium at The Hague confirmed the RODP value of 0.05 for R22 and disregarded Fabian's statements as important for the entire ozone shield of radiation there are still official concerns regarding R22 especially in Germany because of open questions of toxicity and of the greenhouse effect of R22.

Alternative refrigerants

Analyzing the spheres of application of refrigeration, air conditioning and heat pump engineering for their temperature ranges and different refrigerants, one realizes that fully halogenated refrigerants, as well as the azeotropic refrigerant mixture R502, are dominant in large sectors (Figure 1).[6] The large quantities of these CFCs consumed in the USA and other industrialized countries shows that alternative refrigerants must be provided for the following refrigerants: R11, R12, R13, R114, R502 (an azeotropic mixture of R22 and R115) and, possibly, R22, if this refrigerant is included in further discussions.

Search for alternatives

Last year was marked by an intensive search for alternatives, with publications presented especially by the Technical University of Graz on substitutes for working fluids in heat pumps,[7] while a large-scale search for substitutes was carried through by the NBS.[8]

Study of the Technical University of Graz

The Technical University of Graz conducted a comprehensive search for substitutes to be used in heat pumps for the temperature range of 60°C to 120°C. A database with 940 compounds was used. Three substances proved essentially appropriate for use as substitutes for R114: ethyl chloride C_2H_5Cl, ethyl bromide C_2H_5Br, and propylene chloride C_3H_7Cl. All three substances are flammable. Figure 2 shows the normal boiling point of these compounds.

NBS study

The National Bureau of Standards of the USA has carried through a data base study for the conventional field of refrigeration engineering on the basis of 860 important industrial chemicals. This search for alternative refrigerants employed the following criteria: Substitutes should be nonpolluting, stable, non-poisonous, non-flammable, and should be compatible with other materials, especially oils and plastics. Moreover, they should satisfy the demands for low energy consumption and low cost. As a result of this study, 51 suitable chemicals were pointed out, 15 of which were hydrocarbons, 5 oxygen compounds, 5 nitrogen compounds, 3 sulphur compounds, and 4 other chemicals. All of these 32 compounds are flammable or poisonous or both. The remaining 19 compounds are exclusively chlorofluorocarbons, with some being flammable or poisonous or both and others not. Since the fully halogenated chlorofluorocarbons are subject to the Montreal Protocol, alternative refrigerants can be found only in the group of partially halogenated chlorofluorocarbons.

Employing as further search criteria flammability, respectively chlorine content, and posing the question of which of these substances are non-flammable and free of chlorine, only four substances are left which are suitable as substitutes for the conventional, fully halogenated refrigerants. These are R134, R134a, R125, and R23 (Figure 3). Assuming the chlorine content of these alternative compounds to be relatively uncritical if they contain hydrogen and are largely degraded in the troposphere before reaching the stratosphere, a further essential criterion for their use as refrigerants is toxicity. Evaluating the individual substances additionally for their - more or less pronounced - toxicity, the NBS study on chlorofluorocarbons showed the following: in the well-known triangle representation at the corners of which molecules contain only hydrogen or chlorine or fluorine besides carbon, areas are assigned to flammable and to toxic substances, as well as to fully halogenated CFCs. Employing strictly the criteria of flammability and toxicity in the search for possible substitutes, only the compounds in the white areas are left over (see Figure 2 on page 23).

Considering these triangle arrangements for the methane and ethane families (Figure 4), the following status is observed:

Currently, compounds R23, R22, R152a and R142b are commercially available and might possibly be considered as short-term alternatives. R134a, R123, and R141b are under development and are presently undergoing toxicity testing. They could be used industrially within five years, at the earliest. These might be considered as medium-term substitutes. The remaining six substances from the NBS data base study - R32, R123, R124, R125, R134 and R143a - might constitute long-term solutions in case of a negative turn in the development of some short-term alternatives as, for instance, R22, and medium-term substitutes such as R134a.

Present alternatives

Considering the substances now available commercially, that is R22, R23, R152a and R142b, these might constitute alternative refrigerants for immediate use, as shown in the table in Figure 5. Their atmospheric lifetime is short owing to their hydrogen atoms, and as far as they contain no chlorine atom, their ozone-depleting potential would be zero, which is particularly desirable.

Fully Halogenated NBP (°C)		Alternatives NBP (°C)	
		R141b	32
R11	24	R123/a	27
R114	4	R142b	-9
		R124	-12
		R134	-20
		R152a	-25
		R134a	-27
R12	-30	R22	-41
R115	-39	R143a	-48
		R125	-48
		R32	-52
R13	-81	R23	-82

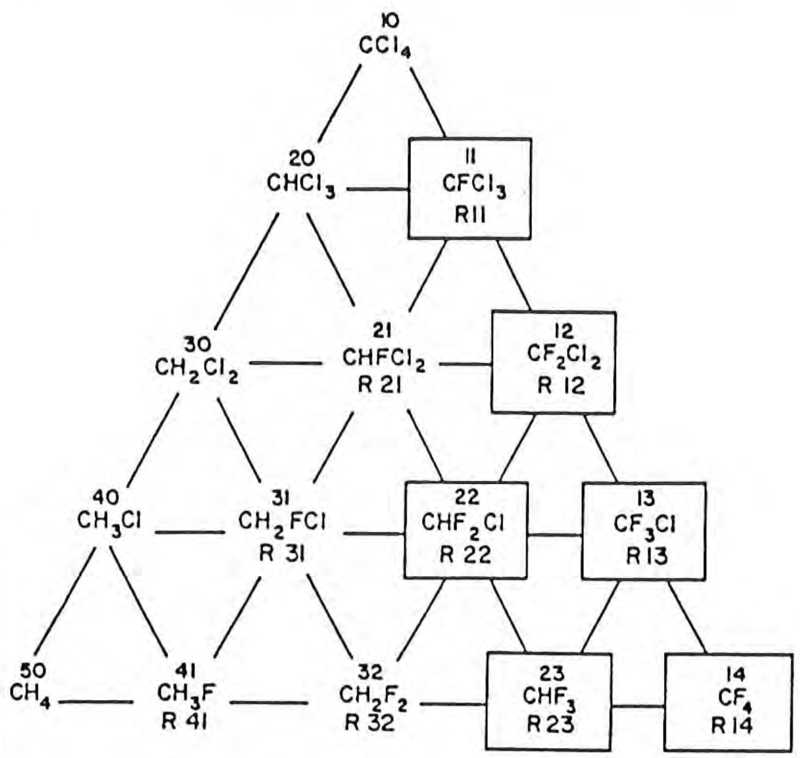
Figure 2. Normal boiling point of alternative compounds identified in Graz study

Of the four substances mentioned, only R23 and R152a contain no chlorine atom; but R152a is flammable. Of the two refrigerants that do contain chlorine - R22 and R142b, both of which have a low ozone-depleting potential - the latter, again, is flammable; however, the flammability is considered low.

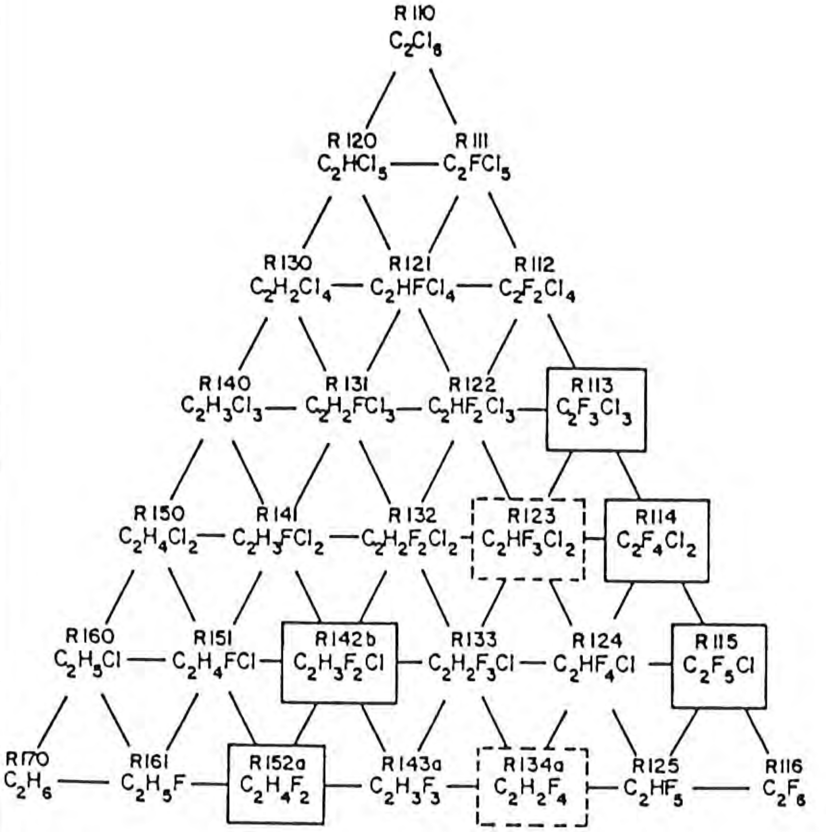
Using these four refrigerants as immediate substitutes for fully halogenated refrigerants, R23 could directly replace R13 in lower temperature plants as its boiling point is similar to R13. R152a would be a suitable alternative for R12, but its flammability must be considered. In systems with a completely closed cooling cycle - for instance, household refrigerators and freezers - R152a might be used. R22 could replace both R502 and R12, but in either case the need to change the system configuration must be pointed out; this will be referred to later. R142b might become a substitute for R114, but again, this refrigerant is flammable, if only slightly. As this list of currently available substances shows, only R23 is an actual equivalent in re-

		Non-flammable?	
		No	Yes
Chlorine free?	No	R141b R142b	R123/a R124 R22
	Yes	R152a R143a R32	R134 R134a R125 R23

Figure 3. Substitutes for conventional refrigerants identified by the NBS study



CFC derivatives of methane (CH_4). □, On the market



CFC derivatives of ethane (C_2H_6). □, On the market; ⬚, under development

Figure 4. CFC derivatives of methane and ethane

placing R13. Its boiling point is in the same range, it is neither flammable nor fully halogenated, and since it contains no chlorine, its ozone-depleting potential is zero, making it an ideal substitute. In the case of the other three substances, compromises are inevitable if they are to be used as substitutes for the fully halogenated refrigerants mentioned: on the one hand, concerning flammability, on the other, concerning pressure and temperature levels.

Considering, beyond these pure substances, mixtures of said compounds, the list of available alternatives to replace fully halogenated refrigerants is increased substantially. Refrigerants can be mixed to obtain properties that are tailor made, concerning especially the ozone-depleting potential, boiling curve characteristics, favorable thermodynamic properties, flammability, compatibility with other materials, oil solubility characteristics, energy aspects, and cost aspects.

Forming compounded refrigerants from a mixture of several substances requires a basic distinction between azeotropic and nonazeotropic refrigerant mixtures. Azeotropic refrigerant mixtures are those that behave like pure substances, a very desirable characteristic particularly in view of replacing a refrigerant by a mixture. At a particular concentration, the boiling curve and the dew curve meet; as a typical feature, the azeotropic boiling temperature is always lower than the boiling temperature of the two pure components.

Azeotropic refrigerant mixtures are classified as series 500 (see Figure 6).

As shown, these currently known azeotropic refrigerant mixtures are essentially made up of fully and partially halogenated substances. Consequently, drastic cuts in ozone-depleting potential are not to be expected from these mixtures; however, they are convenient alternatives for the short-term to achieve a slight decrease in ozone-depleting potential. This holds true in particular of R500 as a substitute for R12, yielding a 26% reduction of the ozone-depleting potential. However, this substitute requires also a slight adaptation of the size of the compressor, since its boiling temperature is not exactly in the range of R12. In this connection, the azeotropic mixture of R12 with dimethylether should be mentioned. Its boiling temperature is roughly in the same range as that of R12; so it can be directly substituted in plants using R12. Dimethylether, the second refrigerant to have been widely used following ethylether, already in the last century, is flammable. Mixed with R12 in the composition shown in Figure 6 it is non-flammable, making it a direct substitute for R12. The cut in ozone-depleting potential will be moderate, but as a slightly smaller amount of filling may be required in comparison with R12, a slightly higher cut in ozone-depleting potential is entirely possible. Investigations as to the substitution of this mixture for R12 are currently under way.[9]

Refrigerant	RODP	t_{boil}	Replacement for	
HFC R23	0	-82°C	R13	---
HFC R152a	0	-25°C	R12	flammable
HCFC R22	0.05*	-41°C	R502 R12	---
HCFC R142b	0.05*	-9°C	R114	flammable
		*or higher	Wubbles: Fabian:	$RODP_{R22}$ = 0.05 $RODP_{R22}$ 0.25
1. low atmospheric lifetime 2. no RODP if possible		= > H-atoms = > no Cl-atoms if possible		

Figure 5. Alternative CFC refrigerants

Generally speaking, however, azeotropic refrigerant mixtures like those known at present cannot reduce the ozone-depleting potential considerably and are merely a very short-term, transitory solution.

Among the short-term solutions, nonazeotropic mixtures have better prospects than azeotropic refrigerant mixtures, as the range of substances to choose from is much wider: refrigerant mixtures, in general, are not azeotropic, they are exceptionally so. As the properties of nonazeotropic refrigerant mixtures range somewhere between those of the pure substances, they can be optimized as substitutes for fully halogenated CFCs. This concerns, in particular, the boiling range, which is between those of the pure components, and the adaptation of the boiling point by the choice of suitable components. Flammability can also be lowered by mixing flammable with non-flammable substances. Furthermore, a special property of nonazeotropic mixtures - their phase change capability at continuous temperature change - can be exploited to save energy. After intensive work conducted in previous years at the University of Hannover, Mulroy, Kauffeld, McLinden and Didion[10] at the NBS, Washington, verified experimentally a 32% energy savings for a heat pump using a nonazeotropic refrigerant. To exploit this capability, the temperature variation during phase change by both condensation and evaporation must correspond roughly to the temperature variation of the heat source or heat sink. This is the case in two positions of the boiling diagram: when the mixture is rich in component A or rich in component B. The highest temperature variations obtained are nearly in the center of the "boiling lens." How far the "boiling lens" opens depends on the difference between the normal boiling points of the two refrigerants in the mixture. For instance, as shown in Figure 7, the "lens" formed by the boiling point curves for the components R22 and R152a is much narrower than the one formed by R22 and R142b. The latter mixture is more suited to make energetic improvements if the temperatures at phase change are adapted to the external media. This might be the case in refrigerators, where the refrigerating and the freezer section must have different temperatures.

If with nonazeotropic refrigerant mixtures the boiling temperature extends over a small range only, then these so-called near-azeotropes can more easily substitute pure fluids. This may be the case with small differences in the boiling points of the components especially with ternary mixtures which often show not real but near azeotropic behavior As these refrigerants change their temperature only minimally during phase change, they are more suited than other substitutes to replace fully halogenated refrigerants without specia modification of the plant configuration So, one could conceive, for instance, of a mixture of the refrigerants R22 and R152a having boiling characteristics corresponding to R12. But if a large portion of R152a is present, this mixture is still flammable. By adding another refrigerant, for example R124, as the recently issued DuPont patent provides, a near azeotrope results which is claimed as a drop-in substitute for R12 if R124 will be available.

Summing up, it may be said that nonazeotropic refrigerant mixtures of substances currently available extend considerably the scope for finding substitutes for fully halogenated chlorofluorocarbons.[11]

Medium-term substitutes

As already mentioned, development work on R134a to replace R12, and on R123 and R141b to replace R11 is un-

Refrigerant	Composition			Boiling Temperature	RODP
R500	74%	CFC 12 + 26%	HFC 152a	-33.5°C	0.74
R501	75%	HCFC 22 + 25%	CFC 12	-41.5°C	0.29
R502	49%	HCFC 22 + 51%	CFC 115	-45.5°C	0.33
R503	40%	HCFC 23 + 60%	CFC 13	-87.9°C	0.60*
R504	48%	HFC 32 + 52%	CFC 115	-57.2°C	0.31
R505	78%	CFC 12 + 22%	HCFC 31	-29.0°C	0.79*
R506	55%	HCFC 31 + 45%	CFC 114	-12.4°C	0.48*
	87%	CFC 12 + 13%	DME	-30°C	0.87

* RODP estimated

Figure 6. Azeotropic refrigerant mixtures

der way. Such development work involves such things as a several year study of toxicity, the development of production processes, and the study of their use as refrigerants in plants.

Conceivable substitutes for R114 are, beyond those already mentioned, short-term alternative refrigerant R142b - a flammable compound - the three compounds known from the Graz study: ethyl chloride, ethyl bromide, and propylene chloride. But since they are also flammable and contain chlorine and in part the even more dangerous bromine, application-technological studies regarding these compounds as substitutes for R114 are necessary but not known at present. Therefore, until long-term substitutes are available, the slightly flammable compound, possibly in a mixture with R134a or R123 to make it non-flammable, seems to be a better choice as an R114 substitute.

For R502, no medium-term substitute is in development. The same holds true of R22, if its use were to be challenged.

Long-term perspective

Should critical questions arise as to the acceptance of the short- and medium-term substitutes, such as the energy efficiency of R134a or its toxicity, or the ozone relevance of the partially halogenated chlorofluorocarbons (for instance R22 and R142b) then the other substances mentioned in the data base study of the NBS would have to be examined for their suitability. These substances are mainly produced to a small extent together with the compounds mentioned above, or originate from the respective manufacturing processes. Thus, the substitute for R11 currently being developed, R123, contains a small portion of its isomer R123a, while the two refrigerants R124 and R125 are by-products of the manufacture of R123 and could be obtained in this process. These are planned to be marketed in the long term as substitutes for R114 and R502, respectively. Refrigerant R143a is a by-product of R142b now being produced commercially and could equally be obtained from this process. By contrast, special manufacturing processes would have to be adopted for the two refrigerants R134

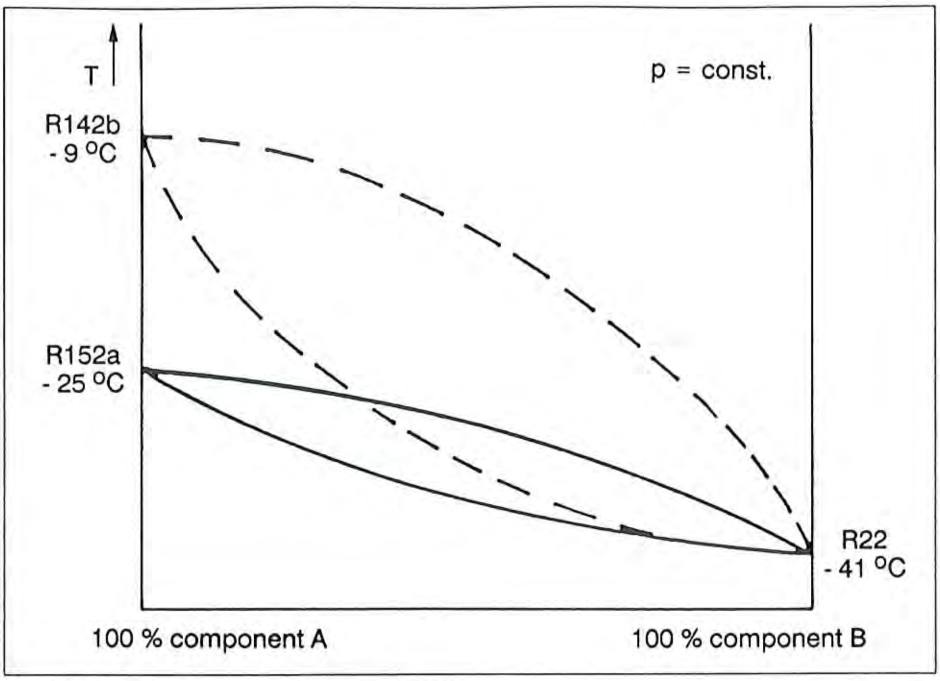


Figure 7. Nonazeotropic refrigerant mixtures

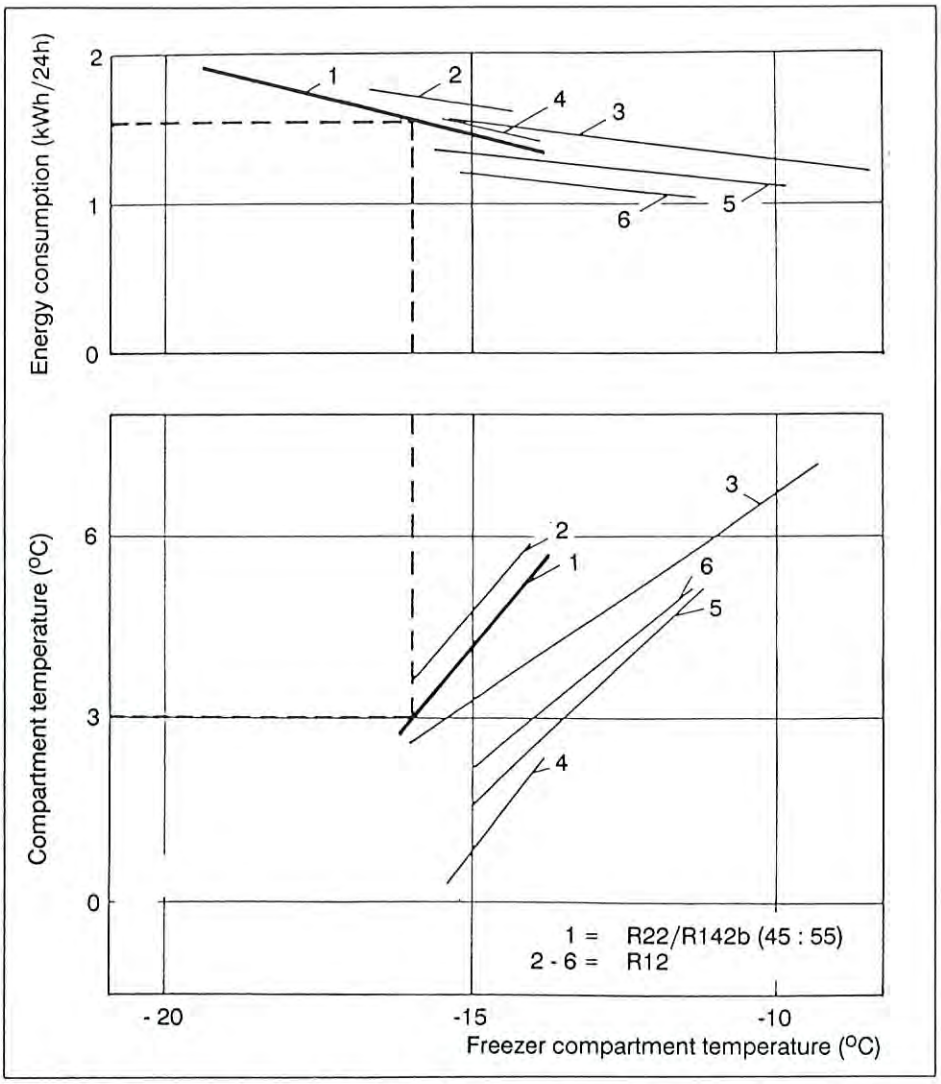


Figure 8. Comparison of the mixture R22/R142b with R12 in refrigerators currently available

Substance	COP	P_{COND}/ P_{EVAP}	q_v (kJ m^{-3})	P_{COND} (bar)	$T_{COMP,OUT}$ (°C)	Heat exchanger area (m^2MW^{-1})	
						Evap[a]	Cond[b]
Ethyl bromide	4.63	4.36	1821	8.8	139	303.4	98.4
Propyl chloride	4.60	4.57	1602	7.1	184	167.4	--
Ethyl chloride	4.39	3.82	3467	17.4	138	13.9	64.4
R114	3.37	3.59	2830	20.5	122	3.2	--
R114B2	4.27	4.36	1182	6.5	122	501.2	--
R21	4.36	3.79	3891	19.5	144	17.8	95.6

[a] Heat source: water T_{in} = 65°C: T_{out} = 62°C
[b] Heat sink: water T_{in} = 85°C: T_{out} = 118°C

Figure 9. Performance for 60-120°C

and R32; the former has properties similar to R134a, while R32, in particular, seems to possess excellent thermodynamic properties and could be a substitute for R502.

Finally, the possibility should be pointed out of employing the vapor compression (resorption) cycle in combination with the two commercial refrigerants R22 and R23, to lower the pressure curve of these refrigerants.

Evaluation of the substitutes

Pressure and temperature curve

If, as mentioned, R12 and R502 are to be replaced by refrigerant R22, effects on plant configuration because of the vapor pressure curve and other properties are inevitable. Especially, the pressure characteristics of refrigerant R22 compared to R12 shows the need for changes in plant design. The same holds true, of course, of the size of the compressors because of the volumetric capacity of R22. Replacing R502 by R22 would call for a multi-stage design in commercial refrigerating plants because of the higher discharge temperature of compressed R22.

Energy and volume (utilization)

Replacing R502 by R22 and using the multi-stage plant concept also yields energetic advantages. This is because R22 is energetically a more advantageous refrigerant, R22 compressors have a higher efficiency, and multi-stage plants are energetically more advantageous. A comparison between the use of R22 in commercial refrigerating plants and R502 shows that the R22 plant has a cooling efficiency of 0.79 compared to 0.59 for the R502 plant. Obviously, substantial energetic improvements are feasible by changing the plant design together with the refrigerant.

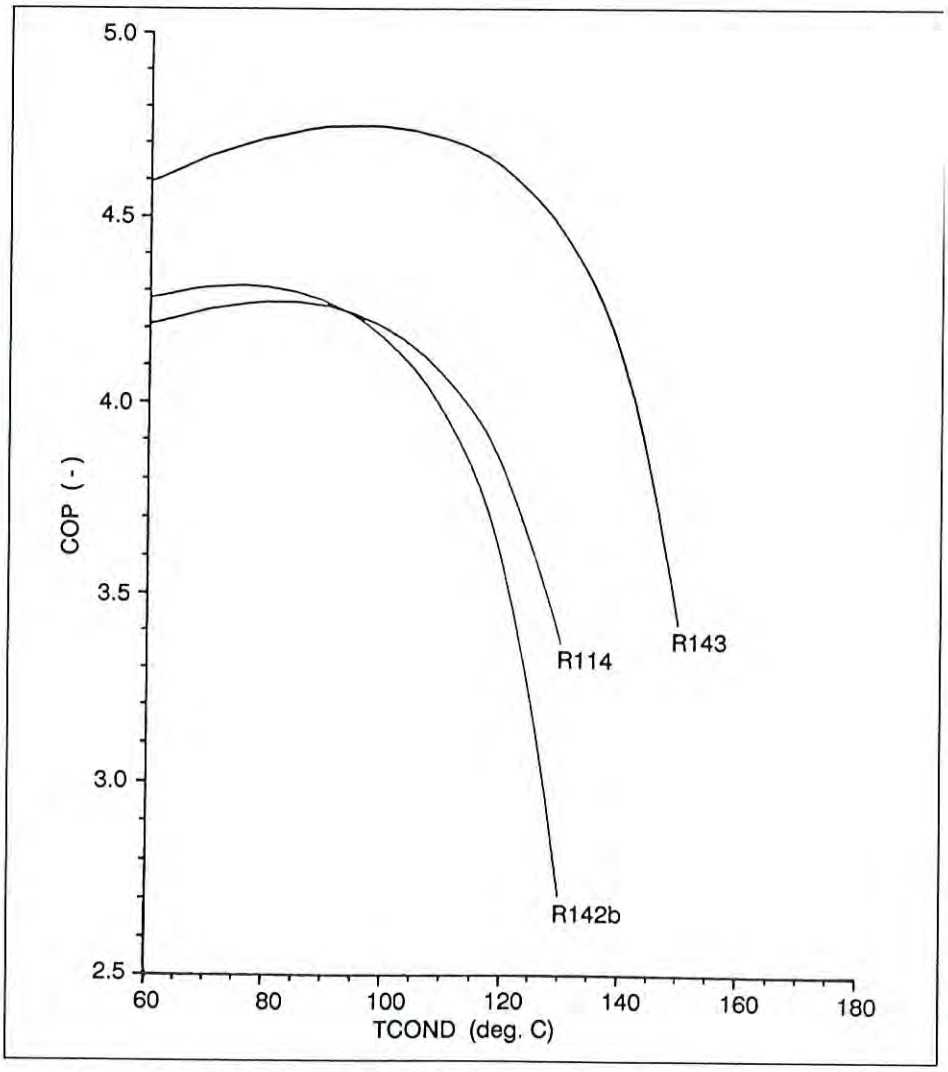


Figure 10. Possible replacements for R114 (COP vs T_{COND}, T_{COND}-T_{EVAP}=60K)

Replacing R12 by one of the above mentioned alternative refrigerants wi also have energetic and/or volumetri effects. Investigations in this respec were made by Hodgett (UK), who carried through calculations in comparison with R12 to establish the performance coefficient and volumetric refrigeration capacity of refrigerants R152a R134a, and R134.[12] These calculation revealed energetic disadvantages fo refrigerant R134a, and advantages fo the refrigerants R152a and R134 a compared to R12. Less favorable i terms of volumetric effects are, at lo condensation temperatures, refrigeran R134, and at high condensation temperatures (above 90°C), refrigeran R134a which is therefore not to be rate too high as a heat-pump refrigerant.

Measurements by the Sharp Compan in Japan permitted a comparison of th

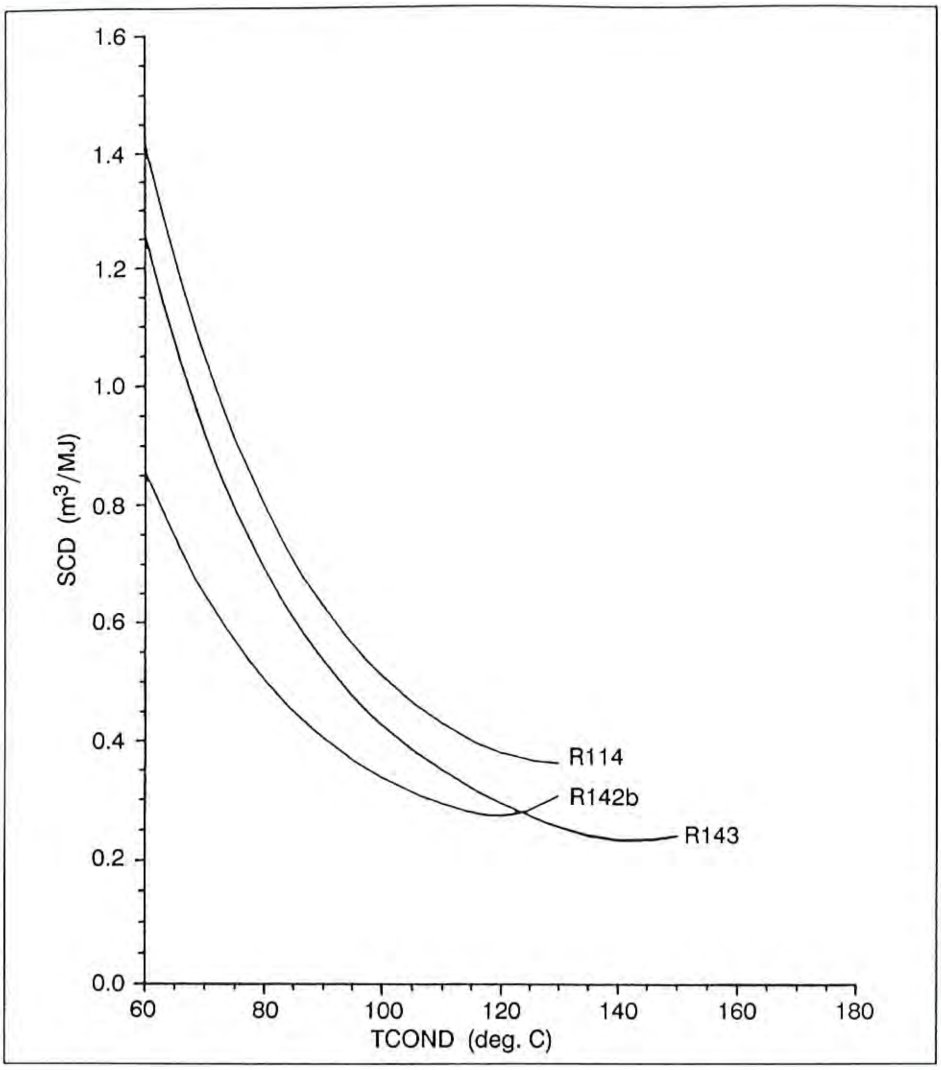


Figure 11. Possible replacements for R114 (compressor displacement vs T_{COND}, T_{COND}-T_{EVAP}=60K)

two refrigerants R12 and R134a, both as regards calorimetric measurements from compressors of household refrigerators and refrigerator measurements.[13] Given equal conditions, the test indicated a nearly 10% increase in energy consumption for refrigerant R134a.

Measurements at the Fisher and Paykel Company, New Zealand, compared the use of refrigerant R12 with the mixture of R22 and R142b in a refrigerator having a low-temperature compartment.[13] This measurement (Figure 8) generally indicates that energy consumption conditions were in the range of various similar models of the same type using R12. It seems, then, to be also a mixture fit to replace R12 in a drop-in situation without disadvantages.

In the event that R114 were to be replaced by the substitutes indicated, that is R142b, ethyl chloride, ethyl bromide, or propylene chloride, only forecasts on the energy and volume utilization of the last-mentioned ones can be made on the basis of the theoretical values shown from the Graz University study (Figure 9). Ethyl chloride, above all, would appear more favorable both as to coefficient of performance and volumetric refrigerating capacity.

Hodgett in Britain also made a comparison between refrigerant R114 and the other substitutes. These were the already-mentioned short-term alternative R142b and the long-term potential substitute R143. Theoretical calculations pointed to the following (see Figure 10): Refrigerant R142b may be a fair substitute for R114, especially in the temperature range up to condensation temperatures of 120°C. But the long-term alternative refrigerant, R143, has a substantially higher coefficient of performance than refrigerant R114. Both substitutes are superior to R114 also in regards to required compressor displacement as illustrated in Figure 11.

Problem areas

Important problems are particularly those arising in the actual shift to substitutes. Considering first of all the substitutes for R12, problems presented by R152a are its flammability and interactions with oil, which must be considered in plant design. In combination with refrigerant R22, R152a is flammable up to a portion of about 68%, beyond that it is non-flammable. In other words, this mixture is generally always flammable in the interesting mixing range where it is apt to replace refrigerant R12.

The mixture of refrigerants R22 and R142b is a different matter: it is non-flammable as long as it contains a minimum of about 34% of R22. This makes it a non-flammable substitute for R12, but its interactions with oil must again be considered. Further, it has a larger boiling range, although this may provide scope for energetic improvements. Looking at R134a as a substitute, mention must be made of its higher energy consumption as well as its known unfavorable oil behavior. Toxicity is still unclarified; in addition, given the timetable for developing this compound, speedier replacement of fully halogenated compounds than scheduled by the Montreal Protocol may lead to supply shortages. In this connection it may be pointed out that leading chemical manufacturers are making great efforts in order to market this compound as soon as possible. But ICI, in a press release of September 1988, said they were expecting to need another five years or so.[14] DuPont, too, made a statement to the effect that full-scale production will start in 1993.[15] Therefore, a short-term alternative may be necessary in the meantime.

Concerning substitutes for refrigerant R114, besides the long-term substitute R124, only flammable substances are currently being discussed, such as refrigerant R142b, whose oil behavior would have to be more closely examined, as well as the compounds ethyl chloride, ethyl bromide, and propylene chloride. These last three are also flammable. On the application-technical properties of these, no information is available.

Conclusion

Potential substitutes in the different spheres of use for the long-term are as shown in Figure 12.

The following are essential questions remaining in replacing fully halogenated chlorofluorocarbons:

For 134a: Will this refrigerant generally meet with acceptance in view of its toxicity, oil behavior and energy consumption, and will it be available early enough in sufficient quantities permitting thorough technical investigations to be carried out before marketing?

For R22: Is the use of refrigerant R22 likely to be continued over a longer period of time, or will it possibly be included in the year-to-year revision of the Montreal Protocol beginning 1990?

The answers to these questions will determine whether short-term or medium-term substitutes will be used instead of the fully halogenated refrigerants. Should they contain uncertainties, then the flammable compounds or refrigerant mixtures may further be considered as substitutes for fully halogenated chlorofluorocarbons, possibly with positive side effects such as energy savings. The mixture of R23 and R152a, two components which are commercially available, could serve as a substitute for R502 in the commercial sector.

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Sector	Alternative refrigerant		
	First choice	Second choice	Others
Household refrigeration	R134a? (energy efficiency)	R152a	R22/R152a, R22/R142b
Commercial refrigeration	R22	R134a	R152a, R22/R152a, R22/R142b, R23/R152a
Industrial refrigeration	NH_3	R22	
Heat pumps	R134a? (energy efficiency)	R124, R142b	C_2H_5Cl?, C_2H_5Br? C_3H_5Cl?, C_3H_7Cl?

Figure 12. Potential long-term substitutes

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Alternative Refrigerants for Vapor Compression Refrigeration/Air Conditioning Applications

Alternative refrigerant compounds are being evaluated as part of a nonazeotropic refrigerant program at Oak Ridge National Laboratory (ORNL). Wherever possible, coefficient of performance and refrigerating or heating capacity values for these compounds are being calculated with cycle models and are experimentally measured in an instrumented test loop. Comparisons of modeled and measured performance are given for several potentially useful alternative refrigerants. Efforts to develop these data are hindered by a lack of physical property and material compatibility information.

Introduction

Recent scientific expeditions to measure stratospheric ozone and odd chlorine concentrations have confirmed Molina and Rowland's 1974 hypothesis concerning the catalytic destruction of stratospheric ozone by chlorine.[1] Industrialized nations of the world community have responded with a plan to limit and eventually to decrease production of chemical compounds responsible for this global atmospheric perturbation.[2] Most of the chemicals regulated by agreement are used as refrigerant fluids in vapor-compression cycles to provide refrigeration or space conditioning. New, environmentally safe refrigerants will have to be identified, tested, and manufactured to replace those which are to be regulated.

Since its initial signing in 1987, provisions of the Montreal Protocol, which will limit the amount of chlorine or bromine containing, fully halogenated, alkylhalides (CFCs) produced by the leading industrialized nations, have been extensively reviewed in the literature.[3,4] (NOTE: For the purposes of this article, "CFC" is used to indicate the fully halogenated compounds containing chlorine, fluorine, and carbon atoms. "HCFC" is used for the compounds in which one or more of the chlorine atoms have been replaced by a hydrogen atom, and "HFC" is used for compounds containing hydrogen, fluorine, and carbon.)

The coincidental emergence of this protocol with results from the second National Ozone Expedition (NOZEII) have virtually assured the eventual phaseout of all long-lived chlorinated compounds that can diffuse to the upper atmosphere and be photolytically cleaved by ultraviolet radiation to provide free chlorine atoms.

Vacillations in the predicted extent of ozone depletion have caused the CFC issue to run hot and cold since 1974, but scientific facts are now falling into place and virtually no one is disputing the link between CFC emissions and diminished stratospheric ozone. Naturally, the ultimate threat results from additional cancer related deaths, cataract eye injuries, and possible damage to the human immune system resulting from higher levels of biologically active radiation filtering down through the outer atmosphere. Both E. I. duPont de Nemours and Co. and Allied Chemical Corp., the two major U.S. manufacturers of CFC's, have pledged to cease production of R12 and R11 when adequate substitutes are available.

The two leading candidates to replace R12 and R11 as refrigeration fluids are R134a and R123, respectively. Both of these were identified as potential replacements soon after the possible problem with fully halogenated R12 and R11 was initially suggested.

In addition to the two restricted refrigerants already mentioned, strict production controls are also specified for halogenated alkanes with the designations R113 ((1,1,2-trichloro-1,2,2-trifluoroethane), R114 (1,2-dichlorotetrafluoroethane), R115 (chloropentafluoroethane), Halon 1301 (bromotrifluoromethane), Halon 1211 (bromochlorodifluoromethane), and Halon 2402 (1,2-dibromotetrafluoroethane). Most R113 is used in critical solvent cleaning applications for computers and printed circuit boards. R114 is used as a high temperature refrigerant and, to a lesser extent, as a blowing agent. R115 is one of the components in R502, an azeotrope which is used primarily in frozen food and supermarket display cabinets. The halons are used almost exclusively as fire and explosion extinguishants and are not discussed in this article.

Research and laboratory investigations needed to establish R123 and R134a as replacements for R11 and R12 are proceeding well. Accurate thermodynamic and thermophysical property data have been reported in the literature. Long-term, inhalation toxicity testing and the construction/start-up of commercial plants appear to be the two major hurdles remaining before these alternatives are commercially available. Much less activity has been directed at finding replacements for the other regulated refrigerants and azeotropes that contain these refrigerants.

As part of a larger program at ORNL to investigate the energy-saving aspects of nonazeotropic refrigerant mixtures (NARMs), over 200 potential refrigerants were evaluated as possible components for a NARM to be used in a residential heat pump.[5] The materials selected from this screening are candidates for other refrigeration or air conditioning applications.

Data base

An extensive listing of compounds (available from the Heat Pump Center) that have normal boiling points between -268.94 and 65 °C was compiled from the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) Handbook, *The Matheson Gas Book*, chemical handbooks, tables, and vendor contacts.[6-8] Most structural isomers which can be obtained by substituting chlorine, fluorine, and hydrogen on methane, ethane, and propane skeletons are included. Normal boiling points were given for most of the listed compounds. Some critical properties had to be approximated for compounds with desirable boiling points and heat capacities in order to estimate COP and capacity.

A chart was constructed from this listing of refrigerants (Figure 1) which separated these compounds on the basis of their normal boiling point (NBP) and the availability of thermodynamic and thermophysical property information. Level 1 in this figure corresponds with readily available, accurate physical property data; whereas, Level 4 indicates not much beyond the normal boiling point could be found. Other compound characteristics such as flammability, toxicity, chemical stability, and refrigerant performance are indicated by the shading or cross hatching used in the boxes. Two observations suggested by this display are that most of the Level 1 compounds have some safety or environmental liability now that long atmospheric lifetimes are a disadvantage and that insufficient property information exists for several good refrigerant prospects. It is also interesting to note that very few compounds have all the desirable characteristics of an ideal refrigerant.

Authors have suggested that the demanding requirements placed on refrigerants severely limit the number of compounds suitable for working fluids.[9] This is certainly true for the family of alkylhalides. It is possible, however, that new, attractive substitutes might be identified from other classes of compounds.[10] Using mixtures of known or new refrigerants is another possibility that is largely unexplored.

Refrigerant mixtures offer an approach to the development of substitutes for restricted, pure-compound refrigerants. Examples such as the R22/R142b and R22/R152a/R124 mixtures have been proposed as substitutes for R12. With nonazeotropic refrigerant blends, undesirable characteristics of one component, such as flammability, can be overcome by prudent selection of the other constituents. Ternary and quaternary systems extend the range of possibilities considerably.[11]

Selection criteria

Some physical and chemical properties must be used to select compounds for further consideration as alternative refrigerants. We choose to distinguish between "hard criteria," which were inflexible enough to eliminate compounds from further consideration and "soft criteria," which were judged as desirable but not essential characteris-

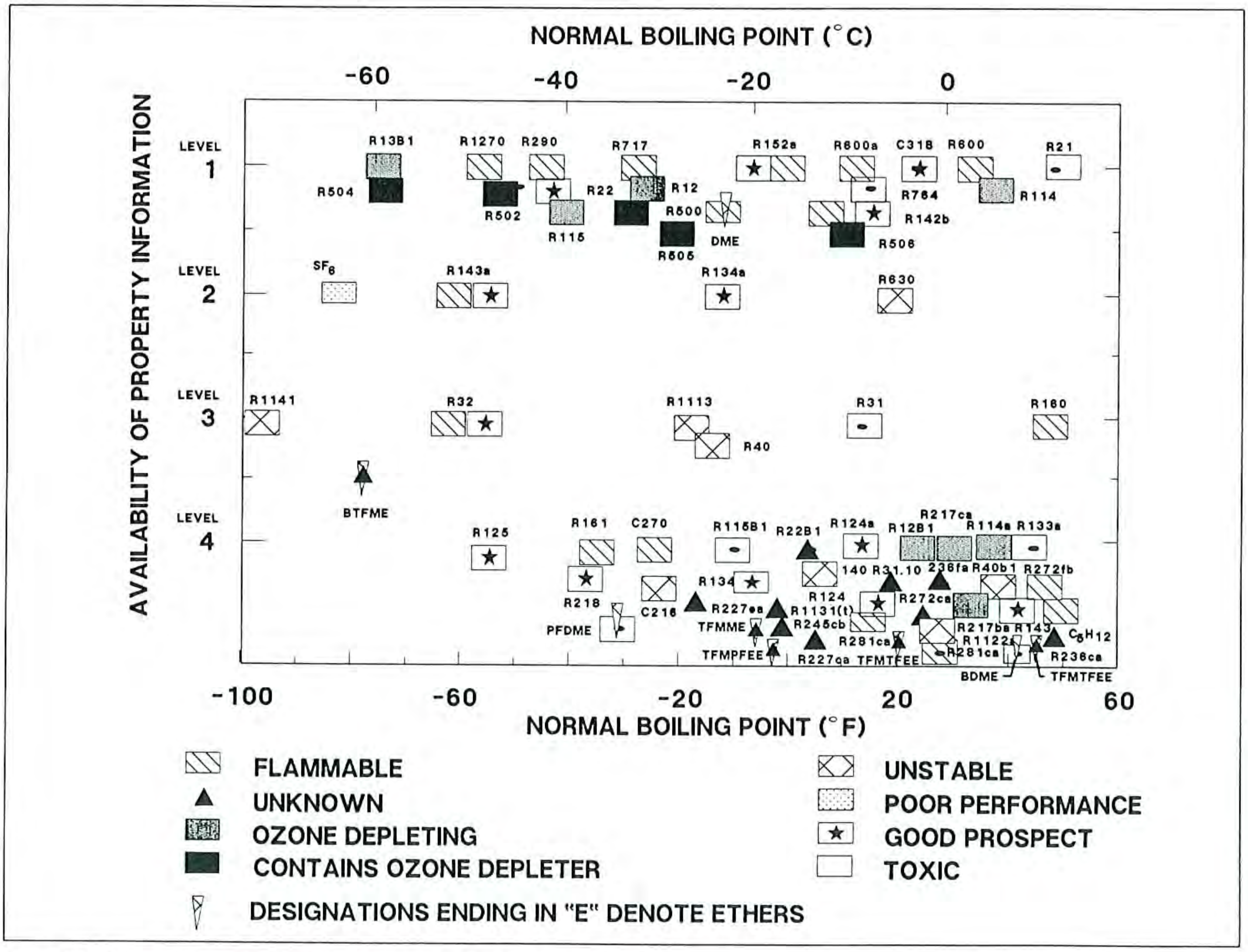

Figure 1. Refrigerant alternative chart (boiling points vs. property information)

tics. The following hard criteria were applied before a compound was considered as an ozone-safe refrigerant. The material could not have any known acute toxicity, it had to be chemically stable in the presence of oils and metals commonly used in refrigeration equipment, and it had to have an ozone depletion potential (ODP) less than 0.05 (i.e., the ODP of R22). Naturally, some judgment is required in applying these criteria.

Properties such as flammability, commercial availability, and oil solubility were considered soft criteria. Flammable refrigerants can be blended with other compounds to form nonflammable mixtures that can function as alternatives. Commercial availability was equated with market demand. Presumably, a market would develop for an attractive CFC alternative. R134a was not commercially available before it became a serious candidate to replace R12, and efforts are now underway to produce it on a commercial scale. Similarly, the poor solubility of R134a in the refrigeration oils normally used is apparently not an insurmountable problem in its commercialization.

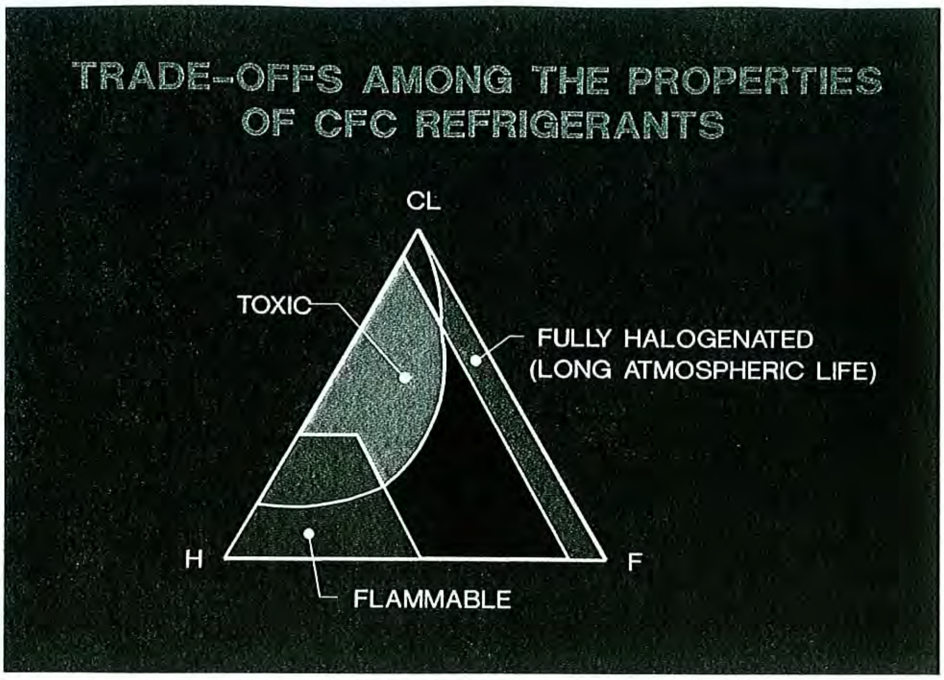

Figure 2. Trade-offs among the properties of CFC refrigerants

An excellent method to gauge the atmospheric lifetime, toxicity, and flammability of saturated alkylhalides was suggested by McLinden and is shown in Figure 2.[9] In this figure, fully halogenated compounds (blue section) have long atmospheric lifetimes which can

CFC REFRIGERANTS					CFC ALTERNATIVES				
NAME	FORMULA	NBP (°C)	ODP[a]	GP[b]	NAME	FORMULA	NBP (°C)	ODP[a]	GP[b]
R113	$CFCl_2CF_2Cl$	48	0.8	0.3 - 0.8					
R11	CCl_3F	24	1.0	0.32	R141b	CCl_2FCH_3	32	0.1	0.05
					R123/123a	$C_2HCl_2F_3$	27	0.02	0.1
R114	$CClF_2CClF_2$	4	0.8	0.5 - 1.5	R143	CHF_2CH_2F	5	0	—
					C318	$CF_2CF_2CF_2CF_2$	-6	0	—
					R142b	$CClF_2CH_3$	-9	0.06	< 0.2
					R124	$CHClFCF_3$	-12	0.02	< 0.1
					R134	CHF_2CHF_2	-20	0	< 0.1
R12	CCl_2F_2	-30	1.0	1.0	R152a	CHF_2CH_3	-25	0	< 0.1
R500	CCl_2F_2/CHF_2CH_3	-33	< 1.0	< 1.0	R134a	CF_3CH_2F	-27	0	< 0.1
					R218	$CF_3CF_2CF_3$	-37	0	—
R115	CCl_2F_3CF	-39	0.4	1 - 3	R22	$CHClF_2$	-41	0.05	0.07
R502	$CHClF_2/CClF_2CF_3$	-45	< 0.4	1 - 3	R143a	CF_3CH_3	-48	0	< 0.3
					R125	CF_3CHF_2	-48	0	< 0.2
					R32	CH_2F_2	-52	0	—
					R23	CHF_3	-82	0	—

a. OZONE DEPLETION POTENTIAL RELATIVE TO R11 = 1.0,
DATA FROM UNEP MEETING, THE HAGUE, 17-18 OCTOBER 1988

b. GREENHOUSE POTENTIAL RELATIVE TO R12 = 1.0,
DATA FROM DuPONT, FLUOROCARBON/OZONE UPDATE, MARCH 1987

Table 1. CFC refrigerants and alternatives

	REFRIGERANT		SUCTION GAS TEMPERATURE (°C)	EVAPO-RATING PRESSURE (bar)	CONDENS-ING PRESSURE (bar)	COMPRES-SION RATIO	NET REFRIGER-ATING EFFECT (kJ/kg)	REFRIG-ERANT CIRCULATED (g/s)	SPECIFIC VOLUME OF VAPOR (dM³/Kg)	COMPRES-SOR DISPLACE-MENT (dM³/s)	POWER (W)
	No.	NAME									
		-7 °C EVAPORATING, 27 °C CONDENSING									
■	32	DIFLUOROMETHANE	-7	6.58	18.09	2.8	284.5	12.4	57.4	0.71	522
■	125	PENTAFLUOROETHANE	-7	5.34	14.14	2.6	98.4	35.8	29.3	1.06	559
■	143a	1,1,1-TRIFLUOROETHANE	-7	4.95	13.66	2.8	161.9	21.7	46.2	1.01	529
	290	PROPANE	-7	3.78	9.71	2.6	300.3	11.7	118.6	1.39	
	22	CHLORODIFLUOROMETHANE	-7	3.93	10.77	2.7	170.5	20.6	58.7	1.21	515
	717	AMMONIA	-7	3.28	10.41	3.2	1130.0	3.1	369.0	1.15	500
	500	(AZEOTROPE)	-7	2.86	7.97	2.8	149.1	23.6	70.5	1.66	507
	12	DICHLORODIFLUOROMETHANE	-7	2.43	6.73	2.8	123.3	28.5	68.6	1.96	507
■	134a	1,1,1,2-TETRAFLUOROETHANE	-7	2.28	6.97	3.1	160.0	21.9	88.0	1.93	515
■	152a	1,1-DIFLUOROETHANE	-7	2.07	6.22	3.0	262.8	13.4	150.5	2.02	492
	40	METHYL CHLORIDE	-7	1.99	5.87	3.0	359.4	9.8	206.6	2.02	492
■	124	2-CHLORO-1,1,2,2-TETRAFLUOROETHANE	-7	1.29	3.98	3.1	122.8	28.6	117.4	3.36	544
	600a	ISOBUTANE	-7	1.24	3.67	3.0	278.0	12.6	292.2	3.70	
	764	SULFUR DIOXIDE	-7	1.17	4.06	3.5	336.1	10.4	280.3	2.93	
■	142b	1-CHLORO-1,1-DIFLUOROETHANE	-7	1.14	3.54	3.1	180.0	19.5	184.2	3.60	492
■	C318	PERFLUOROCYCLOBUTANE	-7	0.98	3.25	3.3	85.6	41.0	106.1	4.36	679

■ ESTIMATED FROM AVAILABLE REFRIGERANT PROPERTY INFORMATION

Table 2. Comparable refrigerant performance per 3.5kW

lead to ozone depletion or contribute to greenhouse warming. As a general characteristic, highly chlorinated compounds that would be present in the yellow area of the figure tend to be physiologically toxic. Finally, when the ratio of hydrogen atoms to halogen atoms on a molecule becomes one or greater, the compounds are likely to be flammable.

Table 1 lists the potentially useful alternative refrigerants which were chosen using the previously described selection criteria and the "rule of thumb" approach suggested by Figure 2. Relative ODP's and greenhouse potentials (GP's) are listed if they are known. Refrigerants with normal boiling points greater than 5°C are not extensively discussed in later sections of this report, because we are primarily interested in fluids whose performance brackets R22 and R12. Several flammable compounds are included to provide a more continuous array of normal boiling points.

Estimated performance

To a first approximation, normal boiling points and molecular weights provide a reasonable estimate of refrigerant fluid performance.[12] Besides normal boiling points, several other methods have been suggested for estimating the relative performance efficiency and refrigeration capacity of vapor compression fluids.[13,14] The similarity of these various approaches is that a minimal amount of physical property data can be used to get estimated fluid performance data.

The most versatile and useful representation of fluid performance is an equation of state which accurately predicts P-V-T relationships of fluids under saturated and superheated conditions. A complete set of FORTRAN refrigerant property subroutines have been developed based on the Carnahan Starling DeSantis (CSD) equation of state.[15] An advantage of the CSD refrigerant property routines is that they have been written to accommodate binary refrigerant mixtures, therefore they are extremely useful for NARM work.

Accurate saturated vapor pressure and corresponding liquid and vapor density data can be conveniently used to calculate CSD equation of state coefficients and to fit new compounds into a form compatible with the useful subroutines. These are the most commonly available and generally most reliable property data that can be found in the literature. At ORNL, we have been able to calculate equation-of-state coefficients for about 20 potentially useful refrigeration fluids and to perform ideal refrigeration cycle calculations for evaluation of their potential usefulness as refrigeration fluids. Reasonably accurate property information must be used for these calculations, because first and second derivatives of the P-V-T data are used to determine thermodynamic properties and heat capacities.

Modeled/experimental performance

Using these refrigerant property subroutines and an ideal cycle model, COP and capacity data were predicted for most of the selected alternative compounds (Table 2). Minus seven degree (-7°C) evaporating temperatures and 27°C condensing temperatures were assumed to calculate these data. These conditions correspond to 20°F evaporating and 80°F condensing tem-

	COMMERCIAL REFRIGERANTS	RESEARCH CHEMICALS
MOISTURE	< 10 ppm	10 - 200 ppm
BOILING POINT RANGE	0.3°C (0.5°F)	1-2 °C (2-3 °F)
CHLORIDE ION CONTENT (ACIDITY- CORROSIVITY)	NONE DETECTABLE	APPROX. 100 ppm
MAXIMUM HIGH BOILING RESIDUE	< 0.01 vol %	....
PERCENT REFRIGERANT	99.+ (wt %)	(97-99 wt %)

Table 3. Commercial refrigerants vs. research chemicals

peratures in the inch/pound (IP) engineering unit system.

An attempt was made to obtain small samples of compounds where model calculations indicated good COP and capacity so that predicted performance could be confirmed experimentally. Many of these compounds are not available commercially and are very expensive to obtain from specialty chemical supply houses. In small lots, prices can range from hundreds to thousands of dollars per kilogram. In addition, the purity level specifications generally accepted for commercial refrigerants are not practical for small batches from laboratories specializing in custom synthesis (Table 3). These impurities tend to be acidic and corrosive, so samples usually are not suitable for material compatibility or toxicity testing.

The main problem associated with modeling and testing uncommon refrigerants is the lack of physical, thermodynamic, and thermophysical property data. Without this information, it is impossible to model the performance of these fluids using routines based on an equation of state. It also precludes any experimental testing because saturated, superheated, and subcooled states cannot be accurately predicted. Experimentally measured values of COP and capacity for several fluids identified as potentially useful refrigerants were determined in an instrumented heat pump breadboard[16] operating at established rating conditions. This determination permitted a comparison between modeled and experimentally measured data which are given in Table 4. We are generally pleased with the agreement shown, considering the accuracy of physical property information used for the equation-of-state calculations and the simplicity of the idealized cycle model used in estimating refrigerant performance.

Blank spaces in Table 4 indicate sections where insufficient data have been found to generate the equation-of-state coefficients for the indicated compounds and/or where experimental measurements have not been made on synthesized samples. This work is proceeding in our laboratory. The relatively poor performance indicated for R125, R218, and C318 is worth noting. R125 is known to have a low critical temperature (approx. 68°F, 341 K), which severely hampers its performance at the rating conditions specified. Additionally, perfluorinated compounds like R218 and C318 show relatively low latent heats of vaporization that are reflected in decreased refrigeration performance. Attempts to use larger molecules such as R218 and C318, which have larger volumetric heat capacities, can lead to "wet compression" and greater throttling losses in conventional systems without regenerative superheating. The larger molecular weights of these compounds also indicate that higher mass flow rates are needed to obtain comparable capacities.

Conclusions

The impending CFC restrictions necessitate evaluation of new compounds as potential alternatives to regulated refrigerants. Research and development efforts are required to measure the physical and thermodynamic properties of potentially useful compounds and their mixtures.

The potential for discovering and developing nonazeotropic blends of refrigerants which can function as CFC replacements is encouraging. Refrigerant property subroutines based on various equations of state are available for estimating the thermodynamic performance of these alternative fluids (pure fluids and mixtures) from a minimum of physical property information.

Sample quantities of the most promising of these materials should be tested and compared to modeled performance. This work should continue as

	-8°C (17°F) HEATING		35°C (95°F) COOLING	
	COP	CAPACITY (W)	COP	CAPACITY (W)
R32				
CALCULATED [1]	2.4	3227	2.6	5781
EXPERIMENTAL	2.4	2941	—	—
R125				
CALCULATED [1]	2.1	1675	2.0	3001
EXPERIMENTAL	2.4	2320	—	—
R143a				
CALCULATED [1]	2.3	1864	2.3	3761
EXPERIMENTAL	2.5	2413	—	—
R22				
CALCULATED [1]	2.5	2057	2.6	3353
EXPERIMENTAL	2.6	2132	2.1	2977
R218				
CALCULATED [1]	1.7	887	1.4	1546
EXPERIMENTAL	2.0	1424	1.5	1614
R134a				
CALCULATED [1]	2.3	902	2.5	2157
EXPERIMENTAL	—	—	2.4	2191
R152a				
CALCULATED [1]	2.5	884	2.7	1990
EXPERIMENTAL	3.0	576	1.9	1817
R134				
CALCULATED [1]	2.3	680	2.5	1652
EXPERIMENTAL	—	—	—	—
R124				
CALCULATED [1]	2.3	416	2.4	1138
EXPERIMENTAL	2.2	361	2.0	1227
R142b				
CALCULATED [1]	2.4	478	2.6	1214
EXPERIMENTAL	—	—	2.0	1176
R318				
CALCULATED [1]	2.1	363	2.2	903
EXPERIMENTAL	1.6	284	1.6	931
R143				
CALCULATED [2]	—	—	—	—
EXPERIMENTAL	—	—	—	—

1. SIMPLE IDEAL CYCLE MODEL

2. NOT ENOUGH PROPERTY DATA FOR EQUATION OF STATE COEFFICIENTS

Table 4. Modeled/experimental performance of CFC alternatives (CSD refrigerant property routines)

new alternatives are identified for various applications.

Atmospheric lifetimes, acute toxicity, and flammability of alternatives can be approximated from molecular structure and composition. Long-term exposure and inhalation toxicity are virtually impossible to predict accurately at this time from first principal information. These evaluations are only justified after extensive, preliminary testing has indicated encouraging results.

Beyond thermodynamic, thermophysical, and toxicity considerations, extensive material compatibility information is necessary to fully assess the utility of new refrigerants or refrigerant mixtures in refrigeration/air conditioning equipment.

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Global Warming - What Are The Best Options? Cogeneration? Conservation? Industrial Heat Pumps?

This paper discusses some of the options available for achieving a reduction in CO_2 emissions in industry. The options are ranked as follows: 1-conservation, 2-heat exchanger based energy recovery, 3-heat pumps, and 4-cogeneration. Some of the other advantages of heat pump use over cogeneration include possibility for achieving reduced waste water temperatures, less need for government incentives, conservative designs, and lower technical risk.

While the final determination of all causes for global warming is still in question, there seem to be a few unarguable premises. In some way, carbon dioxide is a major contributor. Clearly, the largest changeable producer is the combustion of fuels both in the production of electricity and in industrial process heat. The nuclear power option is receiving renewed consideration, but the time required to get new nuclear capacity on line and fears concerning the consequent cost take this off the short-term options menu. Over the long haul, however, experts agree that increased reliance on uranium as a fuel seems likely, especially if the design of new plants can be finalized and fears about plant operational safety can be settled.

In the interim, energy professionals and even the United States' Congress have come to the conclusion that cogeneration (the co-production of power and useful heat) at appropriate industrial sites should be encouraged to reduce the production of carbon dioxide, especially when using natural gas. This conclusion stems from the combination of improved energy performance attributable to thermally efficient cogeneration designs and the lower carbon dioxide emissions associated with natural gas.

But is cogeneration the best choice? Are there other energy options that can make an even bigger difference?

This paper examines the facts supporting cogeneration and alternative energy design options and illustrates which cogeneration system designs do achieve the desired objectives. Examples of improper cogeneration system designs (seeking mostly electric revenue benefits and sacrificing much in the way of thermal co-production efficiencies) could actually run counter to the noble objectives of reducing global warming.

Finally, this report confirms what will appear all too obvious once examined in relation to cogeneration - that conservation (both of electricity and thermal energy) is the first objective for any appropriate system design.

Cogenerated energy not used efficiently should not be generated in the first place. This makes steam conservation even more important. One might even argue that steam traps should be made available free much as lighting efficiency is being paid for by electric utilities in the United States. The bottom line is that heat should be used wisely and recovered from waste heat sources if possible. Since heat exchange is one of the least expensive options, customers should consider this before considering cogeneration.

After heat exchanger-based heat recovery has been implemented consistent with the economics, the next item worth consideration is the heat recovery heat pump. After that, the provision of industrial plant electric and thermal energy might be economically generated in a properly designed cogeneration system. This paper will review the impact of each of these measures and illustrate how they can be "stacked up" much like an electric utility's generation stacking order to help customers reduce energy costs while making a dramatic reduction in our nation's release of carbon dioxide.

The emphasis should be on alternatives

When natural gas is substituted for coal and natural gas-fired cogeneration is used make power, there can be a 66% reduction in carbon dioxide emissions! Even simply substituting natural gas for coal at an industrial facility or an electric utility reduces carbon dioxide production by about 44%. These certainly are rather impressive results.

But what about alternatives? After all, cogeneration is just about the most capital intensive energy alternative a customer could choose. What about simple heat recovery? Doesn't that deserve even greater emphasis and consideration as well? And why are almost all large cogeneration projects sited in the US at this time foregoing the efficient thermal balance between power and waste heat and seeking maximum electric production which forces the design into thermal waste? Why is it that most of these larger projects secure a steam host as only a token element in the energy design?

Our observation is that most large projects fail to live up to the original intent of the 1978 legislation (PURPA) in fuel conservation. They are made as large as possible to maximize project financial revenues . . . not to achieve maximum fuel reduction. In fact, most of these projects give away the steam to gain the PURPA rights to site a power plant exempt from regulatory status as a utility. What kind of signal does that send to plant operating management about steam conservation?

	Per MM Btu Burned	Per MM Btu Steam Used	Per kWh Gen At Util
Natural Gas	122	152	1.37
No 2 Oil	173	204	1.84
Coal	229	270	2.43
Wood	259	344	3.50

Table 1. Pounds of carbon dioxide released per 1000 lbs of steam

Some interesting CO_2 production rules of thumb

How much CO_2 is produced when fuel is burned? Table 1 summarizes a few rules of thumb. Notice that natural gas releases much less carbon dioxide to the atmosphere than any other common fuel. But what happens when you combine the impact of cogeneration with source energy fuel use? Assume a 3 MW gas turbine for an example cogeneration plant. It is a hypothetical engine always operating at full capacity and producing 18,000 pounds of steam from a waste heat boiler. Assume as well that this steam is fully used at the industrial facility thereby displacing steam currently generated in boilers.

Before cogeneration, the 18,000 pounds of steam would normally have resulted in 152 pounds of CO_2 per thousand pounds, 2736 pounds of CO_2 per hour. Generating 3000 kW would consume approximately 10,600 Btu/kWh or 31.8 million Btu/hr at a typical US electric utility power plant. Each million Btu of natural gas would have formed 122 pounds of CO_2. Therefore, if the electric utility burning natural gas to generate this power produces 3880 pounds of CO_2 each hour, the total CO_2 emitted before cogeneration is 6616 pounds per hour.

With a 3000 kW cogeneration system, the customer would burn about 39.4 million Btu of natural gas in a gas turbine producing both this power and steam. The cogeneration system would produce 4807 pounds per hour and displace the previous 6616 pounds per hour, yielding a CO_2 reduction of 1807 pounds per hour (27%).

	Electric Utility Fuel Burned		
Customer Fuel Burned	Nat Gas	Fuel Oil	Coal
Natural Gas	-1807	-3461	-5221
Fuel Oil	-2980	-4627	-6387
Coal	-4225	-5872	-7632
Wood Waste	-4912	-6559	-8319

Table 2. Hourly carbon dioxide formation reductions (in pounds) possible assuming an efficient cogeneration system

Reductions would be even larger if the customer were burning fuel oil or coal and the electric utility was as well. These results are shown in Table 2 for the typical range of assumptions.

But what happens if the cogeneration system is not thermally efficient? What would the results be if the system were just minimally compliant under the current PURPA regulations? The biggest impact is in the amount of steam credit taken by the design. This analysis produced the following results shown in Table 3. Notice that the CO_2 reduction potential attributable to cogeneration for the case where the customer and the utility currently burn natural gas is virtually destroyed. This should be intuitively appealing to those readers familiar with the original intent of PURPA efficiencies, since they were formulated to assure some source energy Btu conservation.

Well then, what about alternatives?

Steam conservation conserves CO_2 emissions! Therefore, long before anyone considers the expense of cogeneration, the conservation of existing steam users deserves renewed emphasis. And when that has run its economic course, what about the industrial heat pump to recover waste heat not economically recoverable using heat exchange? Can this device more than offset increased electric utility loads (and consequent increase in CO_2 emissions) with thermal reduction? Tables 4 and 5 summarize these calculations. As you might expect, the results are a strong function of the industrial heat pump coefficient of performance (COP) which defines the amount of thermal energy delivered back to the process in relationship to the power consumed by the device.

Tables were prepared for two common COP situations: Closed-cycle designs achieving COPs of about 6 (typical of food processing and textile waste water heat recovery situations), and open-cycle designs that normally achieve COPs of 12 or more (we used 12) typified by process evaporators. A sensitivity analysis indicated assumptions of COPs higher than assumed values produced only secondary influence. This should come as no surprise since the heat pump was computed for a fixed thermal load (the 18,000 pounds of steam) and could, therefore, only save a given CO_2 emission.

	Electric Utility Fuel Burned		
Customer Fuel Burned	Nat Gas	Fuel Oil	Coal
Nat Gas	- 553	-2200	-3960
Fuel Oil	-1181	-2828	-4588
Coal	-1852	-3499	-5259
Wood Waste	-2222	-3869	-5629

Table 3. Hourly carbon dioxide formation reductions likely if a minimally compliant cogeneration system is used

Table 4 illustrates the results for closed-cycle industrial heat pumps. Notice that results are comparable to the 3000 kW cogeneration system when the electric utility and the customer are burning natural gas. Not surprisingly, the results deteriorate as the serving electric utility moves to fuels heavier in percent carbon.

Open cycle heat pumps usually achieve COPs well in excess of 12, but for that COP, the results shown in Table 5 demonstrate the majority of the impact. Notice that the largest improvement over lower COP designs comes in the situation where the serving electric utility burns coal. This is a direct result of the lower kW consumption attributable to industrial heat pumps at these high COP levels. Analyses similar to these might be used to guide energy strategies for marketing departments within electric utilities that have no operating natural gas-fired capacity.

If carbon dioxide emissions alone were the reason for considering the industrial heat pump, the concept would go nowhere. There are a host of other advantages accruing to the industrial heat pump, especially in relation to cogeneration. For example, consider some of the following as a sample:

Coping with environmental pressures

The textile finishing industry, pulp and paper and others reject large quantities of warm water and are undergoing increased pressure to reduce both discharge quantity and the temperature of these streams. The industrial heat pump concepts recover otherwise unavailable heat and reduce plant boiler fuel consumption, thereby paying for the environmental compliance. Cogeneration will not do that.

Incentives are generally not required

When one looks at the number of incentives used in the United States to get cogeneration where it is today, and at the number of lawyers involved in the unending differences of opinion, it is refreshing to consider the simple task of helping an industrial firm evaluate and install heat recovery systems. The appropriate use of an industrial heat pump is derived directly from this evaluation and does not create the emotional battlefield so prevalent with cogeneration in this country.

Systems are designed conservatively

Industrial heat pump designers do not try to go after the entire heating load. Industrial heat pump systems are, of intrinsic necessity, sized very carefully. Customer proposals are not merely glowing claims about system performance. Heat pump systems require careful engineering judgement. And, when proper design judgement is taken to consider performance characteristics, these heat pump designs prove economically viable across a broader range of energy prices than do cogeneration systems.

Lower technical risk

Cogeneration systems are much more complicated to operate than an industrial heat pump. Closed-cycle designs are essentially chillers running at higher temperatures, and open-cycle designs are simply vapor compressors and heat exchangers. While certain operational cautions are essential for low operating maintenance and assured system longevity, heat pumps are intrinsically simple to own and operate.

Load management vs. base load erosion

Electric utilities are increasingly concerned about the management of their electric loads. Most cogeneration systems are deteriorating electric utility load factors by generating base load. The industrial heat pump represents one of the best electrotechnologies in that it can be easily interrupted in most designs. At those times, the existing boiler senses the increased heating requirements and meets the need. Therefore, the industrial heat pump can act as a valley fill device and improve an electric utility's load factor.

Reduced dependence upon future fuel price increases

The current high level of interest in cogeneration is partly spawned by a very low price for fuel. If natural gas were at the prices of just a few years ago, very

	Electric Utility Fuel Burned		
Customer Fuel Burned	Nat Gas	Fuel Oil	Coal
Nat Gas	-1532	-1119	- 600
Fuel Oil	-2697	-2284	-1766
Coal	-3943	-3529	-3011
Wood Waste	-4629	-4216	-3698

Table 4. Hourly carbon dioxide formation reductions for a closed cycle industrial heat pump (COP of 6)

Customer Fuel Burned	Electric Utility Fuel Burned: Nat Gas	Electric Utility Fuel Burned: Fuel Oil	Electric Utility Fuel Burned: Coal
Nat Gas	-2134	-1927	-1668
Fuel Oil	-3299	-3093	-2834
Coal	-4545	-4338	-4079
Wood Waste	-5232	-5025	-4766

Table 5. Hourly carbon dioxide formation reductions for an open cycle industrial heat pump (COP of 12)

few of the projects being considered today would be economic. Worse yet, some of the projects already in place cannot survive a doubling of current fuel prices. Electric rates in those areas are less a function of future fuel price increases due the electric utility's diverse fuel mix. Some customers will abandon the thermally-unbalanced systems when they need a major overhaul . . . all too reminiscent of the total energy days of the late 1960s in this country.

By contrast, industrial heat pumps become increasingly more economic with higher fuel prices. They are even economic today in cases where the industrial firm burns coal. Cogeneration using natural gas is almost never economic in these circumstances. And considering that no forecaster or energy expert is predicting fuel to rise slower than electricity, it seems that a customer should be betting on the side of heat recovery and heat pumps, not on the side of increased fuel cost sensitivity (cogeneration).

And, some final issues

Industrial heat pumps are only a small fraction of the cost of a cogeneration system design. Therefore, the capital required to achieve CO_2 reductions is lower and can be paid off through energy savings. Additionally, an industrial heat pump does not operate out of the designed efficiency (COP) without obvious operational indications. This assures an industrial firm that they are actually saving money and making the hoped for return on investment. In contrast, minimally compliant cogeneration systems can and often do operate out of anticipated design and have generally returned much lower financial performance than predicted.

But industrial heat pumps are not for everyone. They work very well in those situations where competing energy efficiency concepts prove inferior. This situation is identical to that of cogeneration. So Congress and the energy profession should not leap on the cogeneration bandwagon as the answer to the CO_2 release question.

Let's take a look at **all** the options for our customers, and let's get back to the basics.

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W. Ritter*

The Impact of Heat Pumps on the Greenhouse Effect

The author presents the results of a comparison of two house heating systems and their contribution to the greenhouse effect. The two systems, an oil-fired boiler and a monovalent electric compression heat pump, are analyzed based on electricity generating conditions prevalent in Austria. The results show that the heat pump system has a significantly lower contribution to the greenhouse effect even when the release of the CFC working fluid is accounted for.

Due to the dramatic price increases in crude oil, oil products, and natural gas after the first and second oil crises (1973/1979), the heat pump entered quickly into the field of space heating and hot tap water production. This was true for small heat loads in newly constructed houses and for retrofitting, as well as for larger projects up to the several MW_{th} range. The most important motivation to install a heat pump at this time was the possibility for reducing the operating costs. The investments, even though they were and are still presently very high due to small production volumes and lack of good dissemination of basic installer expertise, etc., were able to achieve very short payback periods. These basic economic criteria had a more important rank than high seasonal performance factors.

During this period of excellent price relations between the different energy sources (high oil costs and low electricity costs), the argument for environmental protection which could be

Gas	Concentration (ppmv)		Increase Rate (%/year)	Relative Share %	Relative Greenhouse potential compared to CO_2
	A.D. 1750	A.D. 1988			
CO_2	280	350	0.4 - 0.5	50	1
CH_4	0.65	1.7	1.0	19	32
N_2O	0.28	0.31	0.2 - 0.3	4	150
$CFC1_3$ (CFC-11)	0	0.0002	5	5	14000
CF_2Cl_2 (CFC-12)	0	0.00032	5	10	17000

Table 1. Heat trapping gases: concentration, increase rates, greenhouse potential

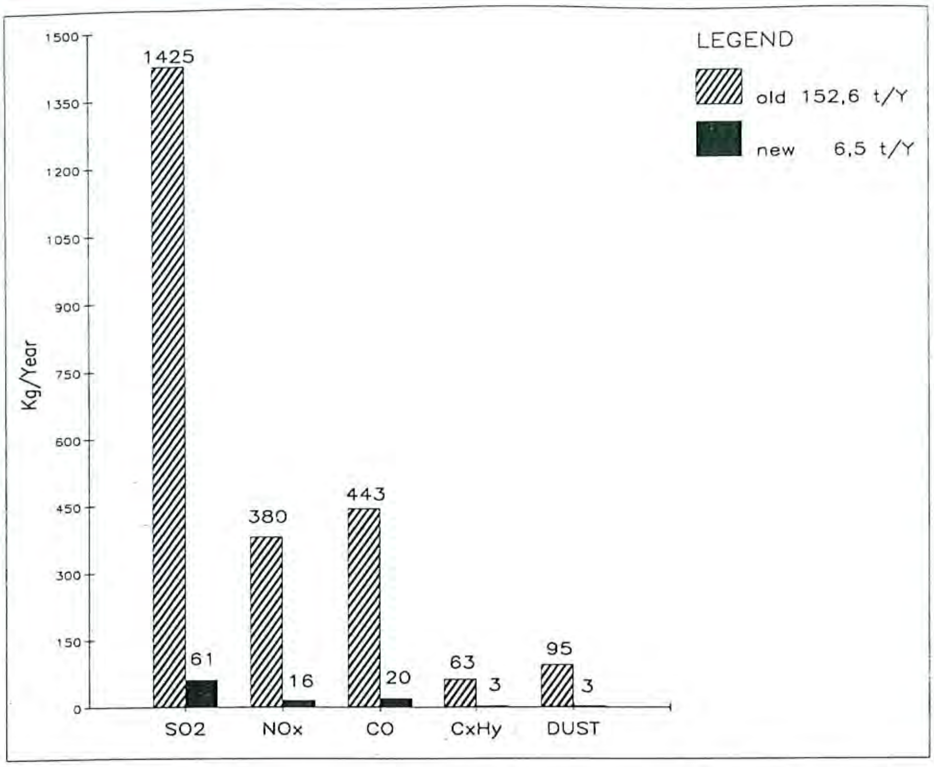

Figure 1. Heat pump installation in community center and indoor bath in Ebensee, Austria -- fuel oil and emission reduction

achieved by operating heat pumps was of secondary importance. On the other hand, the question of primary energy efficiency was already an important consideration. For these reasons, the electricity-production mix is very important.

In the special case of Austria, one must consider the quantity of electricity produced by hydro power stations and by thermal power stations. In the latter case, the primary fuel is domestic lignite or imported hard coal. From year to year, this distribution is very different because it depends on the water supply of the rivers. In addition, the distribution is also different over the year. In winter, the water supply is a function of autumn rainfall and outdoor temperatures.

Calculation of the long-term mean values results in a distribution of about 75% electricity from hydro power stations and about 25% from coal-fired thermal power stations, if the values are taken for a complete year. If only the winter months are considered, then the share of electricity production changes to 60% hydro power and 40% thermal power.

The detailed analysis of the distribution of the electricity production from sources without emissions (from hydropower stations and in other countries also nuclear power stations) and from sources with emissions (from power stations using fossil fuels such as lignite, hard coal, oil, and gas) is important for determining the environmental benefits of heat pump application.

This type of analysis is of less importance for determining the effect on local emissions at the place of heat pump operation. For this, a comparison with the substituted fuel and the related emissions is more essential. For local analyses it is reasonable to not consider the carbon dioxide (CO_2) emissions.

An example of local emission reduction by use of the heat pump can be seen from the heat pump installations in the community center of Ebensee, Upper Austria (Figure 1). This is a retrofit installation of a water-water heat pump (Figure 2) which is used in a bivalent-parallel mode with an existing oil-fired boiler and supplies heat for space heating of the offices, a restaurant, and an indoor bath. Industrial waste heat is used as the heat source.

Figure 1 shows the effect that reducing oil consumption from approx. 150 t/year to approx. 6 t/year has on the flue gas emissions. The reduction per year for SO_2 is approx. 1460 kg (the sulphur content of the oil is 0.5% max), for NO_x about 360 kg, for CO about 420 kg, for C_xH_y about 60 kg, and for dust about 90 kg.

If the area considered for the analysis of emissions reduction would be widened, the figures must be corrected to take

Space heating system Heat load: 15kW Operating hours per year: 1750 System lifetime: 15 years			
		System A	System B
	Type	Oil fired boiler	Ground coupled, monovalent, heat pump
	Efficiency/SPF	η= 80%	SPF = 3.0
	Fuel use	3281 lt/year	8750 kWh/year (electricity)
	Yearly CO_2 production (Kg)	9270	3394*
	Lifetime CO_2 production (Kg)	139000	50925
	Total CO_2 molecules emitted	$1.9406 \text{x} 10^{30}$	$6.9767 \text{x} 10^{29}$
Greenhouse effect	% relative contribution without accounting for refrigerant leakage	100%	36%
	% relative contribution taking into account refrigerant leakage		62% (R12)** 42% (R22)**

* Thermal power station η = 38% using 50% lignite and 50% hard coal, production mix: 60% hydroelectric, 40% thermal

**Factors used as shown in Table 1, 6 Kg leakage over 15 year system lifetime

Table 2. Comparison of heating system contribution to the greenhouse effect

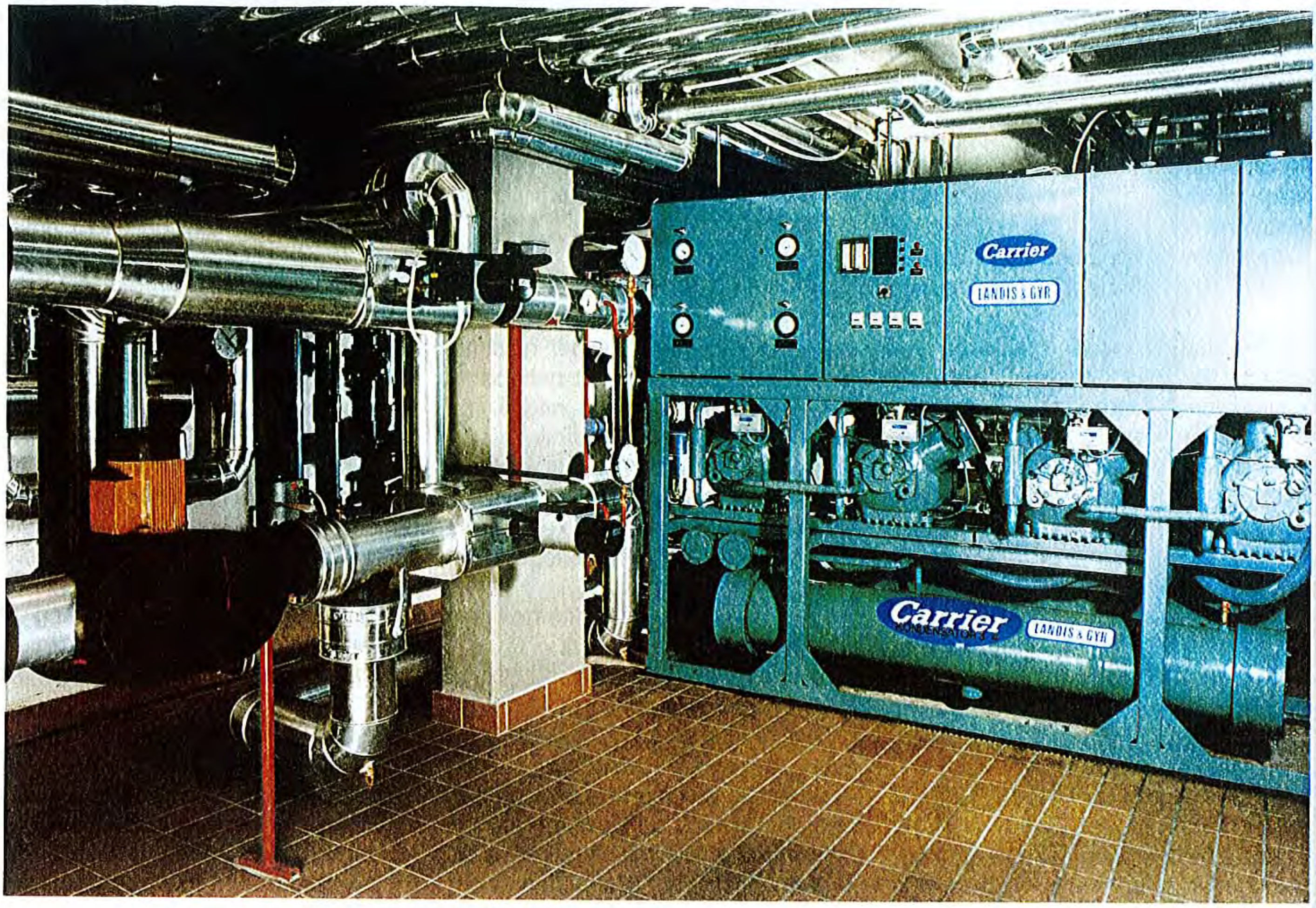

Figure 2. Heat pump installation at community center, Ebensee, Austria

into consideration the contribution from thermal electricity production with fossil fuels. This mainly concerns the factors for SO_2, NO_x, C_xH_y, and dust.

Furthermore, in the last years the discussion about the greenhouse effect has spread. These discussions have centered on the heat trapping greenhouse gases. Questions arise such as which share of the global effect is caused by each specific gas, what is the rate of increase of the concentration of the particular substance today and what will it be in the future, and how big is the relative influence of the most important gases to the greenhouse effect?

In the course of these discussions, the chlorofluorocarbons (CFCs) receive special attention because they are also responsible for ozone layer depletion in the stratosphere. The CFCs are also an important reason for a detailed analysis of heat pump use in relation to the greenhouse effect. Various types of CFCs are used as working fluids in heat pumps. In the majority of cases, R12 or R22 are used. If the comparison between two different heating systems should be done according to their contribution to the greenhouse effect, a rating of the single components as well as the whole system is necessary.

As shown in Table 1, one molecule of R12 is approx. 17,000 times as effective as one CO_2 molecule in contributing to the greenhouse effect. This means that 17,000 CO_2 molecules have an effect identical to one R12 molecule. Some studies from a few years ago gave the information that R22 had only 1/20th the effect of an R12 molecule. Current data shows that R22 has 1/4 the effect of R12.

With a relative rating of the different heat trapping greenhouse gases available, one can compare different heating systems. In Table 2 (see previous page), the influence on the greenhouse effect from a house heated by an oil-fired boiler or a ground-coupled heat pump is compared.

The overall lifetime of the heating system is assumed to be 15 years. The model house has a heat load of 15 kW, which represents a yearly heat demand of 26,250 kWh_{th} at typical climate conditions in Austria. A modern oil-fired boiler and heat pump are compared having a yearly efficiency of 80% and a SPF of 3.0, respectively. The quantity of working fluid in the heat pump is 6.0kg CFC (R12 or R22).

The yearly heat demand requires 3281 liters of fuel oil for the oil boiler, causing a CO_2 emission of 9270 kg/year. Over the 15 year lifetime of the heating system, more than 49,200 liters of heating oil are used and a total CO_2 emission of

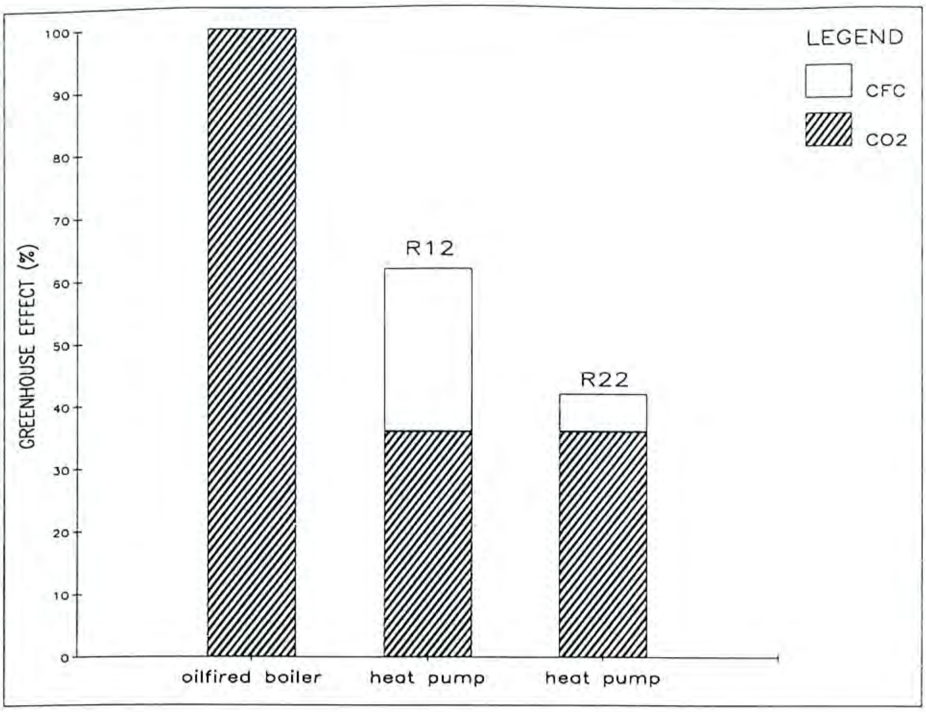

Figure 3. Comparison of heating systems according to the greenhouse effect (base case: oil-fired boiler)

about 139,000 kg (1.9406 · 10^{30} CO_2 molecules) takes place. This is the base case for compariosn and represents 100% of the greenhouse effect caused by the model house heated with oil.

If this model house is heated by a heat pump in the monovalent mode, the electricity demand is 8750 kWh/year. For winter conditions in Austria, 60% of the electricity comes from hydropower stations without emissions of CO_2. The remaining 40% is produced by thermal power stations where the fuel is lignite and hard coal. For these fossil fuels, the operation of the heat pump causes a CO_2 emission of 3394 kg/year. Projected over the lifetime of the system, the result is approx. 50,900 kg of CO_2 emissions.

If the comparison of the two systems is made only on the basis of CO_2 emissions, the outcome is a reduction of the greenhouse effect of 60% by use of the heat pump. For the heat pump, though, it is sometimes necessary to make repairs. Corresponding to this the influence of the working fluid on the greenhouse effect must also be considered. Here it is assumed that the total quantity of refrigerant (6 kg) escapes into the atmosphere once during the 15 year lifetime of the heat pump.

As shown in Table 1, the refrigerant R12 is 17,000 times more effectve than CO_2 in causing the greenhouse problem. Considering the effect of 6 Kg of R12 alone, the contribution to the greenhouse effect is only 26% of that of the CO_2 emissions from the oil-fired boiler. If the working fluid in the heat pump is R22 instead of R12, the contribution to the greenhouse effect is 1/4 as much, or approx. 6%.

For an overall comparison of both heating systems, the influence of the CO_2 emissions from the oil-fired boiler must be compared to the total of the CO_2 emissions from the thermal power station caused by electricity used to drive the heat pump and the equivalent effect of the heat pump working fluid. The final result is a reduction of the 100% contribution to the greenhouse effect caused by the oil-fired boiler to about 60% with R12 or about 40% if R22 is used in the heat pump.

These results are summarized in Figure 3 showing that even over the lifetime of the heating system and including the effect of the working fluid, a large positive effect and a great reduction of the heat trapping greenhouse gases exists. This result is important because it was reached in spite of the much stronger contribution of CFC gases to the greenhouse effect. Consequently, it has been shown that according to the current state of knowledge an important positive contribution to reducing the greenhouse effect can be realized by heat pump operation. This result is conservative because the probability for complete leakage of the working fluid is assumed to be 100%.

Conclusions

After the first and second oil crises, the immediate economic aspects concerning heat pump installations had the highest priority. Now and in the future the environmental possibilities of heat pumps will become more and more important. The heat pump is, in terms of emission reductions, the winner when compared with an oil-fired boiler. This is the case for "conventional" flue gases like SO_2, NO_x, C_xH_y, CO and dust, whose reduction on both a local and regional level are of importance.

As the calculations in this paper have shown, the heat pump is also able to provide an important positive contribution to reducing the greenhouse effect which is being more and more actively discussed and analyzed. This is the case even when the contribution of CFCs to the greenhouse effect is accounted for.

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K. Takemoto*

District Heating and Cooling Systems from the Viewpoint of Air Pollution Abatement

In Japan, air pollution from nitrogen dioxide in large cities has increased to a serious extent, requiring those concerned to take countermeasures. In these circumstances, it is effective to introduce district heating and cooling systems in office buildings and hotels, which are expected to increase in large cities, since they are superior to individual heating and cooling systems in improving air quality. The author intends to make clear the background, environmental improvement effect, and considerations to be given to environmental preservation, in conjunction with introduction of district heating and cooling systems. It should be emphasized that the views given in this article are entirely those of the author and do not represent the official views of the Japanese Environment Agency.

State of air pollution in large cities

In Japan, target values to be maintained for air quality preservation are based on five items: sulfur dioxide, nitrogen dioxide, carbon monoxide, suspended particulate matters, and photochemical oxidants. In order to achieve the environmental standards, various countermeasures against air pollution have been implemented. For nitrogen oxides, emission control has been carried out since 1973 on soot and smoke emitting facilities in factories and places of work. Furthermore, effective 1982, total quantity control has been carried out in Tokyo, Yokohama, and Osaka.

Total quantity control is such that, in order to lower the environmental concentration values to the levels specified in the environmental air standards in an area where it is difficult to secure the specific levels merely by emission control of each unit of facilities, the total allowable quantity of air pollutants from generating sources in the area is calculated by means of a certain set of scientific techniques. These techniques take into account regional characteristics, such as meteorology, topography and conditions of pollutant generating sources. In this way emission control is implemented at a factory or place of business as a unit, so that the emission quantity is kept within the said total quantity.

Despite these efforts, acceptable nitrogen dioxide levels have not been achieved, mainly in large cities. The unfavorable situation is thought to be attributable to increasing automotive traffic and nitrogen oxide emissions from smaller sources such as buildings. The energy consumption and nitrogen oxides emissions of buildings in major cities is shown in Table 1. The contribution from heating boilers to the concentration levels in Tokyo is estimated to reach 20% during the winter. Therefore, in order to decrease air pollution from nitrogen oxides in urban areas, it is required that countermeasures against smaller generating sources centering around building air conditioning be taken.

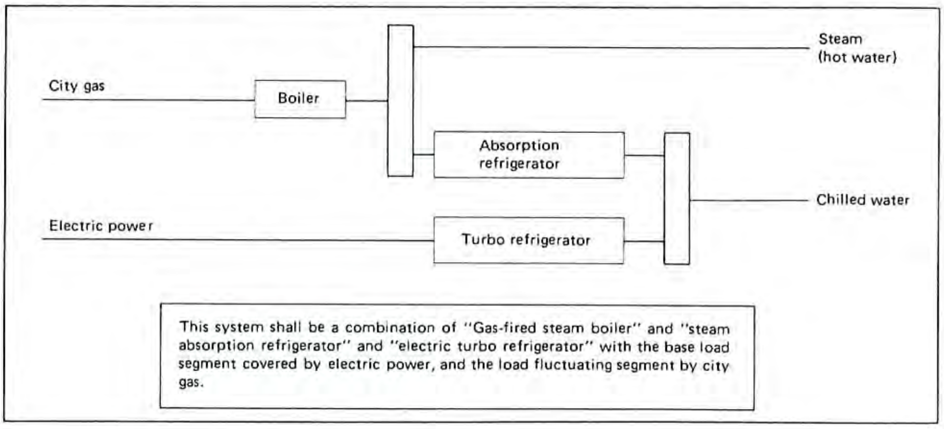
Air pollution abatement effect of district heating and cooling systems

Since a district heating and cooling system can centralize the heat generat-

City	Floor area of office (Km^2)	Quantity of energy used for heating (10^9 kcal/h)	NOx emission (Nm^3/h)
Sapporo	18.7	2.0	420
Tokyo	101.6	7.1	1,490
Yokohama	21.1	1.5	320
Kawasaki	7.5	0.53	110
Nagoya	28.1	2.0	420
Kyoto	15.4	1.1	230
Osaka	44.1	3.1	650
Kobe	14.2	0.99	210
Hiroshima	11.0	0.77	160
Kita-Kyushu	10.0	0.70	150
Fukuoka	15.5	1.1	230

Note Average quantity of energy used for unit floor area: 70 kcal/h·m^2 (source: "Survey of Optimization of Decentralized Power Supply Systems" conducted by the Energy Conservation Center)

Table 1. Floor area and consumption of energy for heating at places of work in large cities



This system shall be a combination of "Gas-fired steam boiler" and "steam absorption refrigerator" and "electric turbo refrigerator" with the base load segment covered by electric power, and the load fluctuating segment by city gas.

Figure 1. Heat source system in model plant

Nox t/year (%)

System / Area	Individual	District cooling/heating
Commercial housing complex	6.53 (100)	4.57 (70)
Public office housing complex	4.71 (100)	3.30 (70)
Redevelopment area in front of station	0.76 (100)	0.55 (72)

Note: Figures in ( ) denote the ratio with the individual system (gas combustion) as 100.

Table 2. Comparison of nitrogen oxide emissions in three model areas

ing section, compared to multiple installations, each being a smoke source, it allows (1) adequate combustion control, (2) effective exhaust gas treatment, (3) conversion to high quality fuel, and can therefore help in abating air pollutants.

In Japan, district heating and cooling systems have been introduced in Tokyo and Sapporo since the latter half of the 1960s. In Tokyo, the promotion of district heating and cooling systems is recognized as a countermeasure against air pollution in the Prefectural Ordinance for Environmental Pollution Control of 1967.

In order to quantitatively grasp the air pollution abatement effect resulting from the introduction of a district heating and cooling system, three model areas in Osaka (commercial housing complex, public office housing complex, and redevelopment area in front of a station) have been selected to compare an individual heat source system and a district heating and cooling system in each area. In this model, the heat source system for heating and cooling is as shown in Figure 1. With this system, the base load segment of cooling in summer is covered by electric power, and the load fluctuation segment is covered by city gas.

The results are as shown in Table 2. In all areas, nitrogen oxides emissions from the district heating and cooling systems are smaller than those from the individual heat source systems, thus demonstrating that the former is more effective for air pollution abatement in cities where there are many smaller heat sources.

Characteristics dependent on heat source systems

Since heat source systems for district heating and cooling systems comprise boilers, absorption refrigerators, and heat pumps, as well as their combinations, a variety of systems are available (Figure 2).

As for heat source systems, when looked at from prevention of air pollution, it is necessary to take into account the fact that pollution load characteristics differ depending on the type of heat source system. Generally speaking, the air pollution load is smallest with a heat pump applied system, and is largest with a system using an internal combustion engine (gas turbine, gas engine, diesel engine), while it is likely to lie somewhere between them with a boiler applied system. Introducing a district heating and cooling system, it is necessary to take full account of the present state of the air environment in the area installed, location of emission

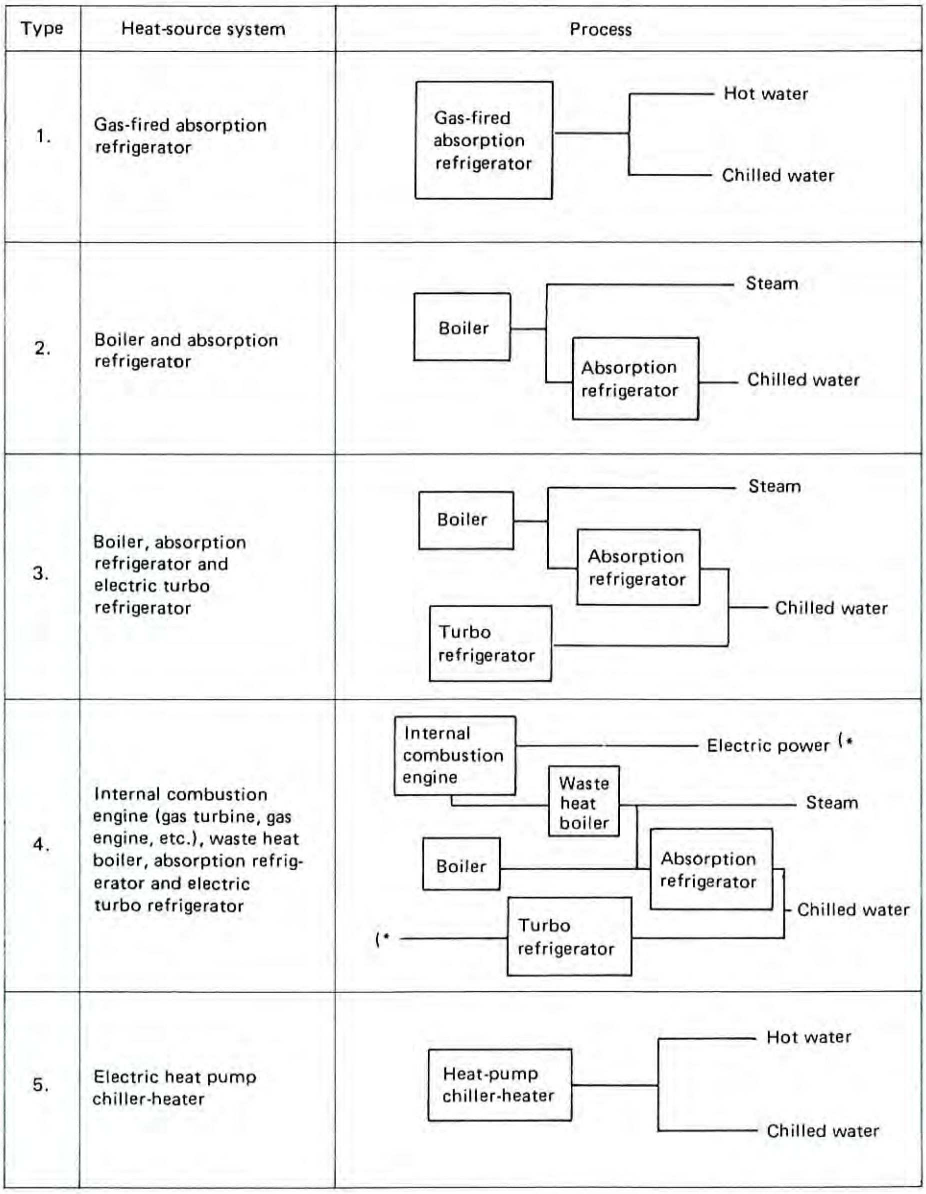


Figure 2. Varieties of heat-source system

sources, and carefully select an optimum heat source system to avoid an adverse influence upon the neighboring air quality. Where necessary, countermeasures for the pollution load must be taken.

Considerations to be given to air pollution prevention

In introducing a district heating and cooling system, it is necessary to take the following steps for prevention of air pollution:

1. In cases where heat demand is expected to increase due to execution of city redevelopment, utmost care must be exercised not to aggravate the environmental condition of the area covered.
2. In view of the fact that the air pollution load differs depending on the type of heat source system, considerations must be given in selecting a heat source system so that it may not adversely affect the surrounding air environment. Special considerations should be given to the fact that a heat pump applied system has no air pollution load at the area covered, and as such is the best from the view point of air pollution abatement.
3. Since buildings varying in height stand close to each other in an urban area, pollutants may descend to the ground due to down-wash and down-draft. Therefore, in setting the stack height, due considerations must be given.
4. In introducing a district heating and cooling system in an urban area, it is desirable to use as high a quality fuel as possible.
5. Since there are many waste heat sources in an urban area, it is desirable to effectively utilize them as much as possible so that air pollutant emissions may be reduced.

Conclusion

It has been demonstrated that the introduction of a district heating and cooling system is effective as a measure for reducing smaller generating sources in urban areas. However, even with the district heating and cooling system, heat source systems vary and the air pollution load differs accordingly. It is necessary to carefully select a heat source system while taking account of the surrounding environmental situation. In particular, since a heat pump applied system features the smallest air pollution load, it is desirable to employ it. In introducing a district heating and cooling system, consideration must be given to environmental preservation.

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Gustav Lorentzen*

Future Prospects of the Heat Pump

Resource considerations and pressure on the environment make it imperative to limit primary energy usage in the future. The heat pump can be a major tool in this process. However, to exploit its possibilities fully, it is necessary to improve its performance. Present systems have an efficiency in the order of typically 20 percent only, and great improvements are possible, using available technology. Detailed exergy analysis is a good means to separate the thermodynamic losses as a guide to optimize system design and make it more cost effective.

Background

Nearly half a million years ago, man discovered the use of fire for heating. The same general principle is still applied, although the combustion is now normally enclosed in cast iron or steel and the heat distribution more elaborate. Since the advent of the "second law" by the middle of last century, many generations ago, we now know that this practice is extremely wasteful in fuel. The true efficiency is actually less than 5 percent on an average in house heating. It is high time that something is done about this by introducing some form of thermodynamic heating. The heat pump is, of course, one of the obvious possibilities. The theory has been with us for well over a hundred years, and time is ripe to apply it effectively.

The resource situation

Mankind has increased in numbers and technological sophistication to a level where energy is used in an amount which is significant in comparison with the processes of nature itself. We can foresee the exhaustion of fossil fuel resources, which it has taken nature millions of years to produce. And perhaps even more ominous, the changes to our biosphere as a result of human activities are becoming rapidly more apparent. It is time to start thinking, to plan for the future in order to stave off the ultimate catastrophe.

Except for the senseless piling up of ever greater arsenals of nuclear weapons, the uncontrolled release of gasses to the atmosphere is probably the most dramatic threat to our future in a short time perspective. It influences the so-called "greenhouse effect," which controls the climate of the earth by reducing the radiation of heat to space. With a completely transparent atmosphere in the infrared spectrum, the mean temperature would have been about -18°C. If the absorption is increased above the present level, the temperature will rise, causing drastic changes to the global climate. The trick is to keep the balance just right.

A large number of gases, including the CFCs, are responsible for the heat radiation shield. By far the most important one is CO_2, which now contributes about 50 percent of the total. Its concentration has been increasing steadily over the years as a result of the growing

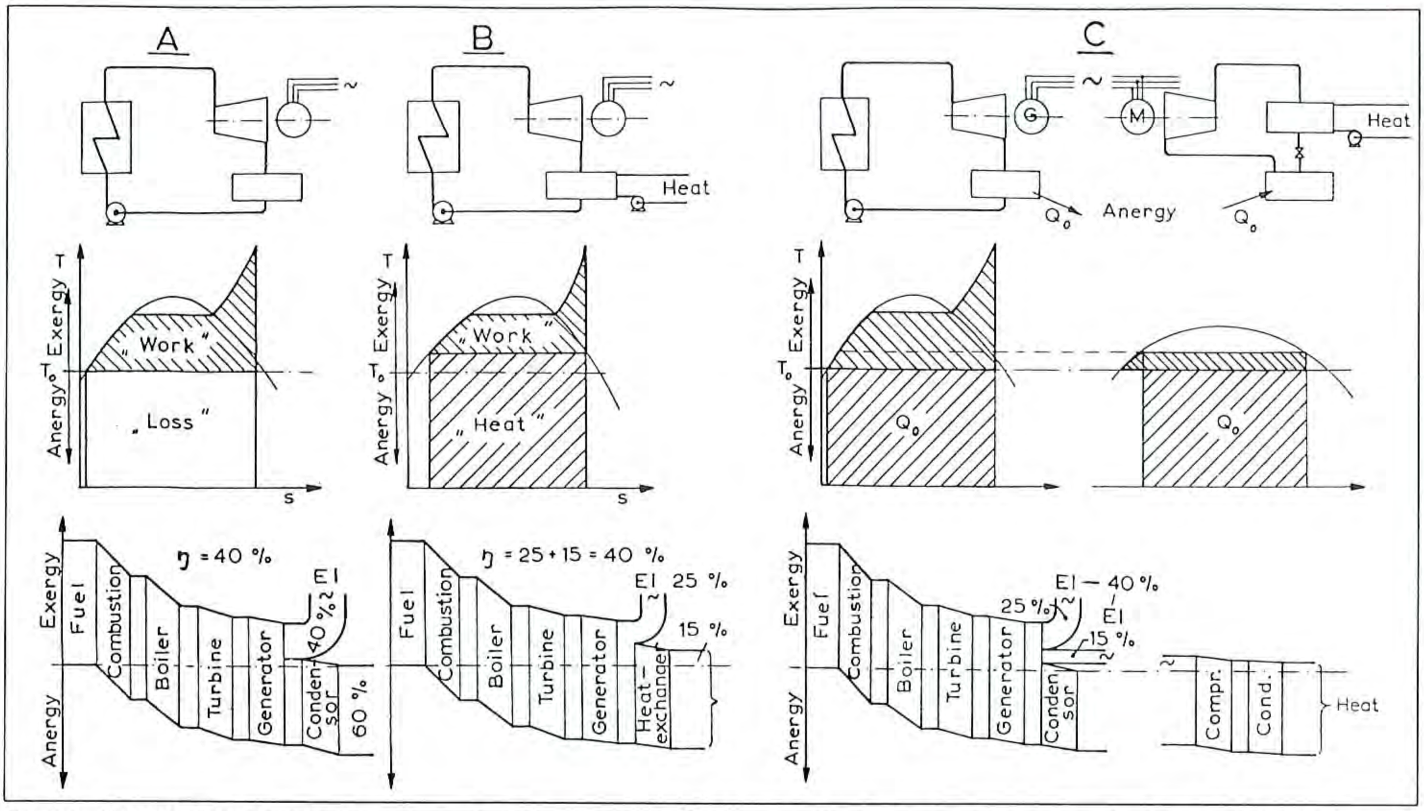

Figure 1. Theoretical comparison of power generation, cogeneration and heat pump at the same temperature assumption. The total efficiency is exactly the same.

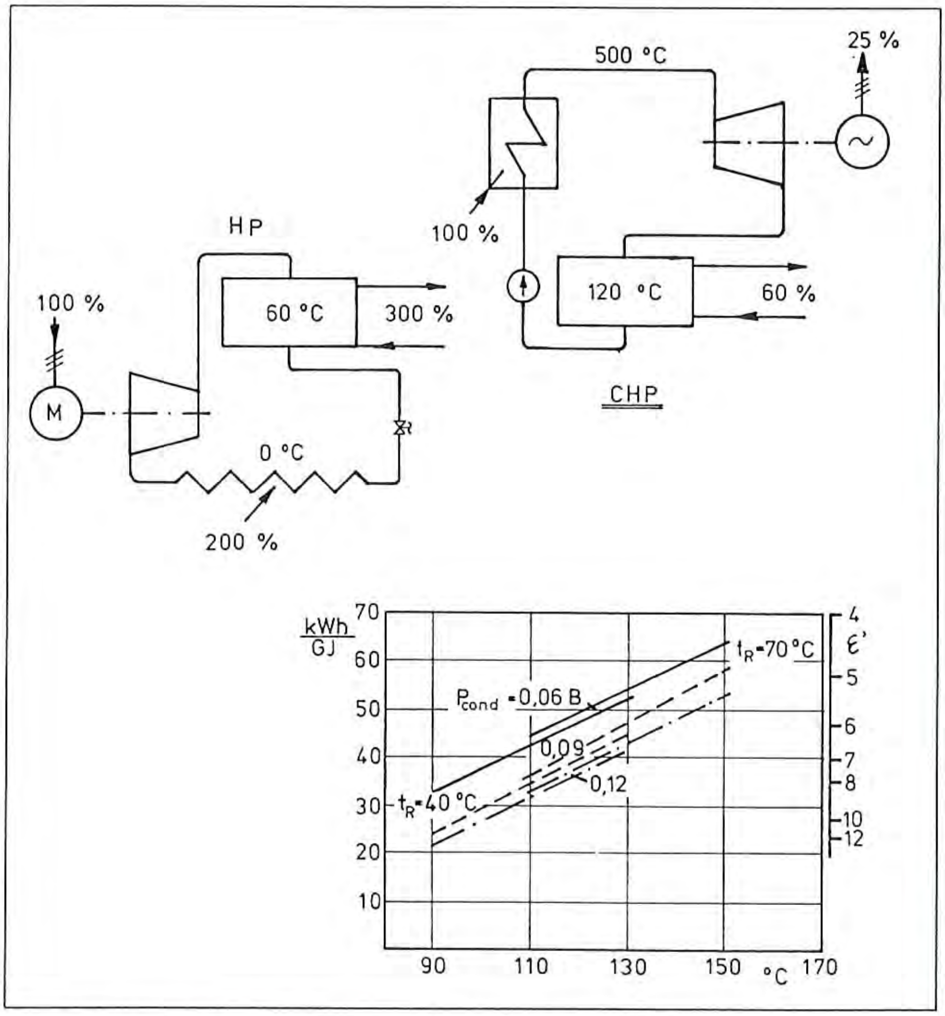

Figure 2. Reduction in power generation and apparent COP in ideal cogeneration with balance load conditions

use of fossil fuels and rapid deforestation in the tropics. This process must not be allowed to accelerate beyond control.

The most prestigious prognoses, such as those by the World Energy Conference, International Institute of Applied Systems Analysis, IEA and others, predict an increase of fuel consumption by a factor of 2 to 3 by the year 2020. This would mean a doubling of the atmospheric CO_2 by about 2030 and increase of the average temperature by 3 ± 1.5K and up to 8-10K in the polar regions. Such a development is clearly unacceptable. A radically different energy strategy has to be developed, to limit the use of fuels to the present level or even reduce it, as required.

This could be achieved, in principle, by a rapid change to nuclear power. Such a development seems to be completely impossible for economic and political reasons. A more sensible approach must be to improve our traditional energy processes. All the exergy which we use, is lost sooner or later in grim consequence of the second law. It is fundamentally possible to reduce the consumption as much as we like by developing more efficient technology. In this way economic growth and human welfare can be maintained with much reduced energy flow, as shown by a recent analysis of a large number of processes involved.[1] Future energy use is largely a matter a choice.

The heat pump is one important element in building a sustainable energy system for the future.

The present heat pump situation

Among the several million heat pumps in the world, the great majority are really refrigeration machines for summer cooling, which are also used for heat production in the winter time. In this way the problem of first cost is overcome and there may even be a saving over the installation of a separate fireplace. With a normal seasonal performance factor (SPF) of 2-3 and a generating efficiency as measured in the electric grid of perhaps 30 percent, there is actually no saving of fuel compared with conventional combustion heating.

In the case of "heating only" in a colder climate the electric heat pump is much less attractive. A small, single house unit will rarely save fuel at all in a heat power country. Even when electricity is supplied from water power or nuclear sources, such installations are not normally cost effective at present price relations. Larger units may be marginally profitable for comfort heating when the conditions are favorable, in particular when the yearly utilization season is long. In industrial applications the situation is often different, and heat pumps for evaporation, drying, or hot water production may be very advantageous.

Heat driven heat pumps, absorption or motor driven are, of course, better adapted to the situation in fuel energy countries and may give a real saving in the order of 30-40 percent. This is rarely enough to offset the increased first cost and operational troubles. A motor-driven compressor system in a way combines the problems of a small power station and a heat pump. It might seem a better solution in many cases to use small motor or gas turbine type cogeneration block units and, eventually, connect them to operate electric heat pumps in the periferic areas.

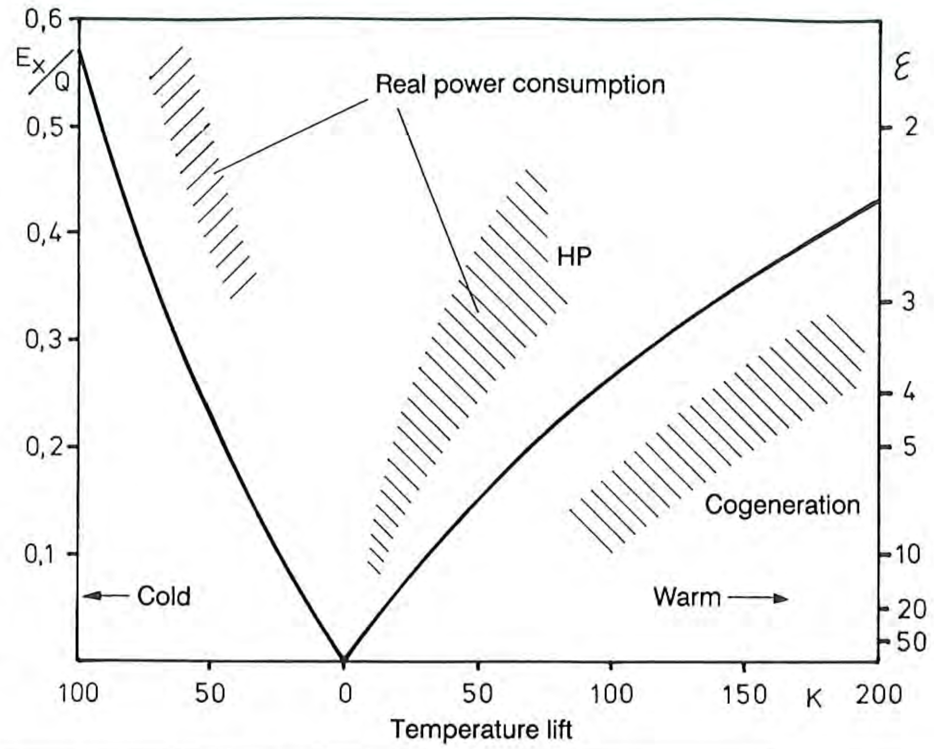

Figure 3. Theoretical power consumption for thermodynamic heating as a function of temperature lift and range of performance for cogeneration and heat pumps

In view of what has just been said, it is not surprising that the enthusiastic marketing of heat pumps in many countries has been met with heavy setbacks. The heat pump is just not good enough as yet, with a real thermodynamic efficiency of only 15-20 percent, or perhaps a little bit more in the very best cases of large machines. In order to reach a general breakthrough, and make the heat pump the universal method of heating worldwide, an average COP in the order of 5 will be required. The system is capable of considerable improvement, as will be discussed later, and this seems a reasonable aim.

Alternative methods of thermodynamic heating

The traditional method of thermodynamic heating is the so-called "cogeneration system," which has actually been used since the early days of steam engines, when exhaust from the atmospheric discharge was used to feed radiators. Today the typical installation is a normal steam power plant, where a more or less important part of the vapor is bled off at a high enough pressure and temperature to supply a district heating network. Recently smaller systems using gas turbines or internal combustion engines are being used occasionally.

There is a great deal of misconception about the efficiency of cogeneration systems. It is often heard that "when the efficiency of a condensing power plant may be 40 percent, the cogeneration system has an efficiency of 80 or 90." To those with even a rudimentary knowledge of thermodynamics this is clearly nonsense. By the same philosophy it would be correct to say that "the efficiency of a heat pump is 300 percent."

In reality the efficiency of a combination condensing power plant and a heat pump system is theoretically the same as for the cogeneration plant, when the temperature of heat production and ambience is the same (Figure 1).

Practice presents an entirely different picture, however. In cogeneration some losses in the low pressure part of the power cycle are avoided, as are the losses in the heat pump system. As a result the apparent coefficient of performance under balanced load condition is quite high (Figure 2). This advantage is largely eliminated by the fact that the power and heat loads are rarely matched, and that the temperature

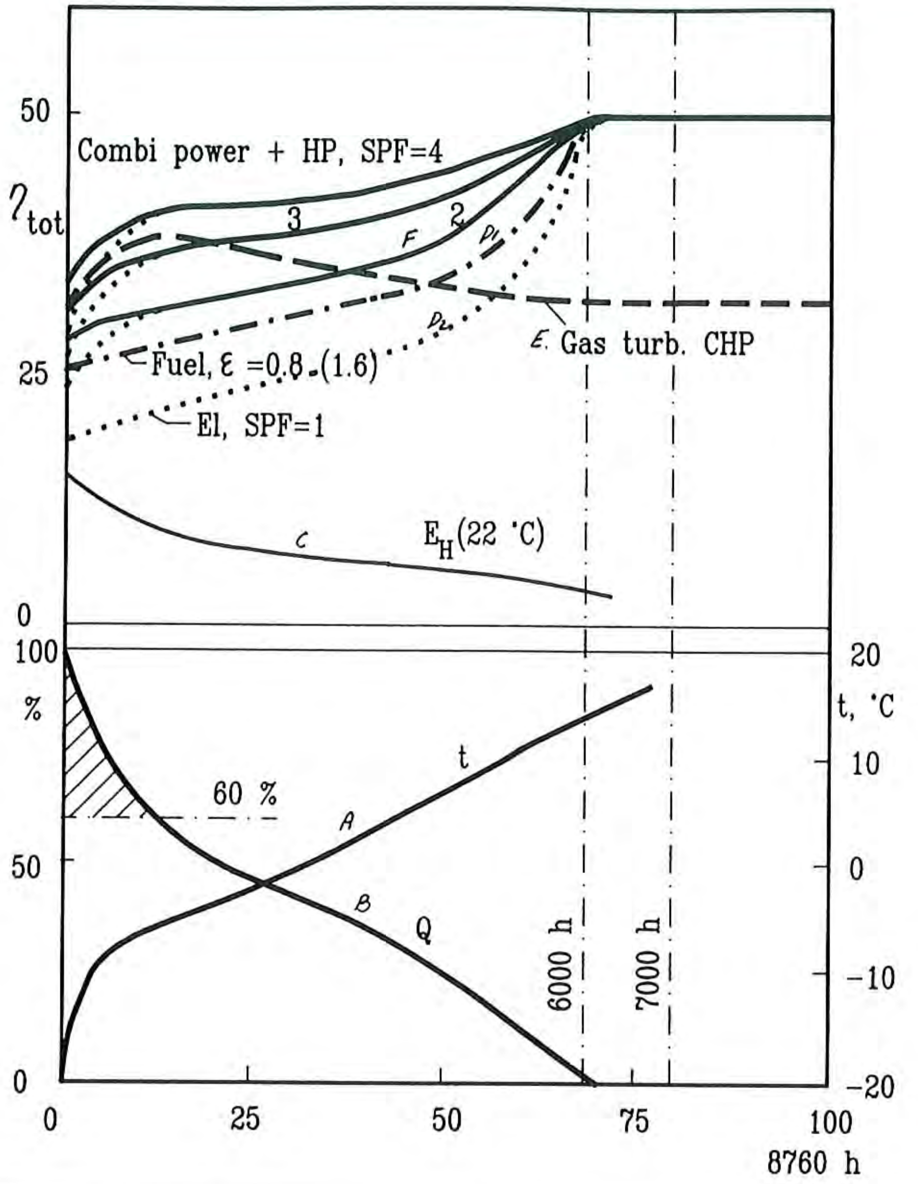

Figure 4. Comparison of the seasonal efficiency of some methods of combined heat and power production

level of heat extraction is usually much higher than for heat pumps (Figure 3).

The traditional cogeneration system is steadily becoming less attractive for a number of reasons:

- The size of a steam power plant to be energy and cost efficient is very high, at least several hundred MW electric. This means that it can only serve effectively for cogeneration if it is built very close to a large district of concentrated consumption. This means an extensive and very costly culvert system, which is often difficult to construct in a densely built-up area. To keep costs within reason, a high heat supply temperature is needed at the expense of reduced efficiency.
- These problems have increased dramatically during later years as a result of greatly reduced heat requirement due to improved insulation and heat recovery, and thus less heat density.
- Heat demand varies enormously and is quite small most of the year, when the power plant operates on the condensing cycle. The heating season is becoming shorter as a result of the development mentioned.
- The changing in building technology leads to increasing need for summer air conditioning and installation of a refrigeration plant, which can also be used for heating. One can envisage a future where the insulation and heat recovery is dimensioned to balance the heating and cooling load to give effective utilization of the same heat pump equipment summer and winter alike.

It is obvious that a system which can be decentralized without loss of energy or cost effectiveness has very important and increasing advantage. Time definitely works for the heat pump.

In order to overcome some of the drawbacks mentioned above, there is a certain interest in smaller and simplified cogeneration or "total energy" schemes using gas turbines or reciprocating combustion engines. Such plants will have a much reduced power generating efficiency and retain some of the shortcomings of the larger systems. In my opinion they are rarely a match to a good heat pump system.

It may be of interest to have a look at a concrete example, the heating of an area in Oslo with a peak load demand of about 200.000 kJ/s (kW). North Sea gas is assumed as the primary energy source. Some results are given in Figure 4 for the following alternative schemes:

1. Electricity generation in large combi-cycle power plants with an efficiency η = 50% and conventional combustion heating with a fuel COP ϵ = 0.8. An alternative dotted curve also indicates the situ-

System		Mean efficiency (η_m) for time power production 6000h	7000h	8760h	Fuel saving relative conventional fuel 6000h	7000h	8760h
1. Combi power/combust.		33.9	36.2	39.0	--	6.8	15.0
2. Gas turbine - CHP		34.8	34.4	33.9	2.6	1.5	0
3. Combi power-resist. el.		29.2	32.2	35.7	-13.9	-5.0	5.3
4. Combi power/HP	SPF=2	36.9	38.8	41.1	8.9	14.5	21.2
	SPF=3	39.7	41.1	42.9	17.1	21.2	26.6
	SPF=4	44.1	45.0	46.0	30.1	32.7	35.7

Table 1. Efficiency and fuel consumption for alternative heat/power systems

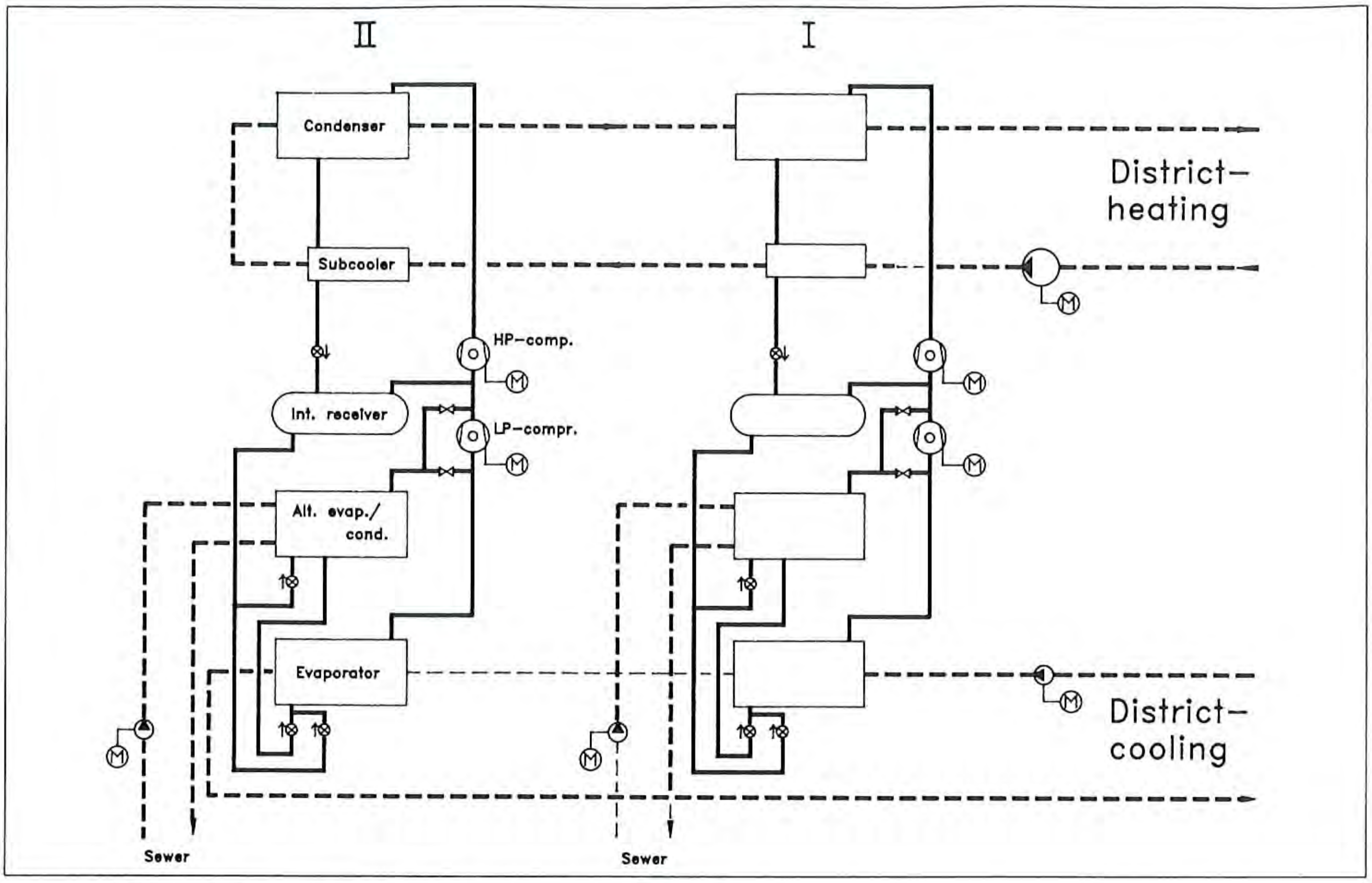

Figure 5. Schematic piping diagram of heat pump for district heating, Sandvika

ation with electric resistance heating, $\epsilon_{el} = 1$, $\epsilon_{fuel} = 0.5$.

2. CHP system consisting of a standard gas turbine with full load efficiency $\eta = 32\%$ and waste heat utilization.

3. Electricity generation in large gas power plants with $\eta = 50\%$ and decentralized heat pumps with $\epsilon_{el} = 2$, 3 and 4.

The lower diagram shows the cumulative temperature curve for a normal year and the corresponding variation of the heat demand, corrected for solar radiation effect in the spring time. The exergy fraction in the heat, assuming a room temperature of 22°C, is indicated by curve C. For systems 2 and 3 it is assumed that the peak demand above 60% of the design load is supplied by direct combustion heating in order to limit the investment in equipment to a level near the economic optimum. The other curves represent the variation of the overall exergy efficiencies of the various systems when the electricity production is the same as for system 2. This means that the comparison relates only to the combined energy production in connection with the heating requirement in a CHP plant and not the total electricity generation, which is always much larger.

The variation of the efficiency for system 1 is indicated by curve D_1. It is naturally falling off as the heat load increases due to the poor thermodynamic efficiency of fuel heating. This is even more the case when electric resistance heating is used, curve D_2.

The CHP (sys 2) has a different characteristic. The relatively low efficiency in electricity production is improved by increasing use of waste heat, curve E. At peak load it drops off again as a result of the additional fuel heating (or electric peak heating). But it appears for the whole year the gain over the traditional system 1 is very slight, if any.

System 3 is similarly represented by the curves F for different values of the average COP or seasonal performance factor (SPF) of the heat pumps. Again there is a more rapid efficiency drop at peak load condition due to fuel heating (fully drawn curves) or electric resistance heating (dotted curves). This effect is quite limited, however.

It is evident from the diagram, and indicated more accurately in Table 1, that the heat pump solution is much superior to the alternatives with regard to primary fuel consumption. This is true even when relatively poor heat pumps are used and much more so with modern and more efficient machines. Today SPFs of 3 to 4 are readily attainable with standard large equipment and even higher values can be expected in the future.

In practice the development is dictated by economic considerations rather than energy efficiency, and investment costs play an important part. Without going into detail here it can be stated that the heat pump system is markedly more cost effective than the alternatives in a long term perspective. This is the case for heating only in individual systems of more than 50-100 kW capacity and even much more so when summer cooling is also required. This is increas-

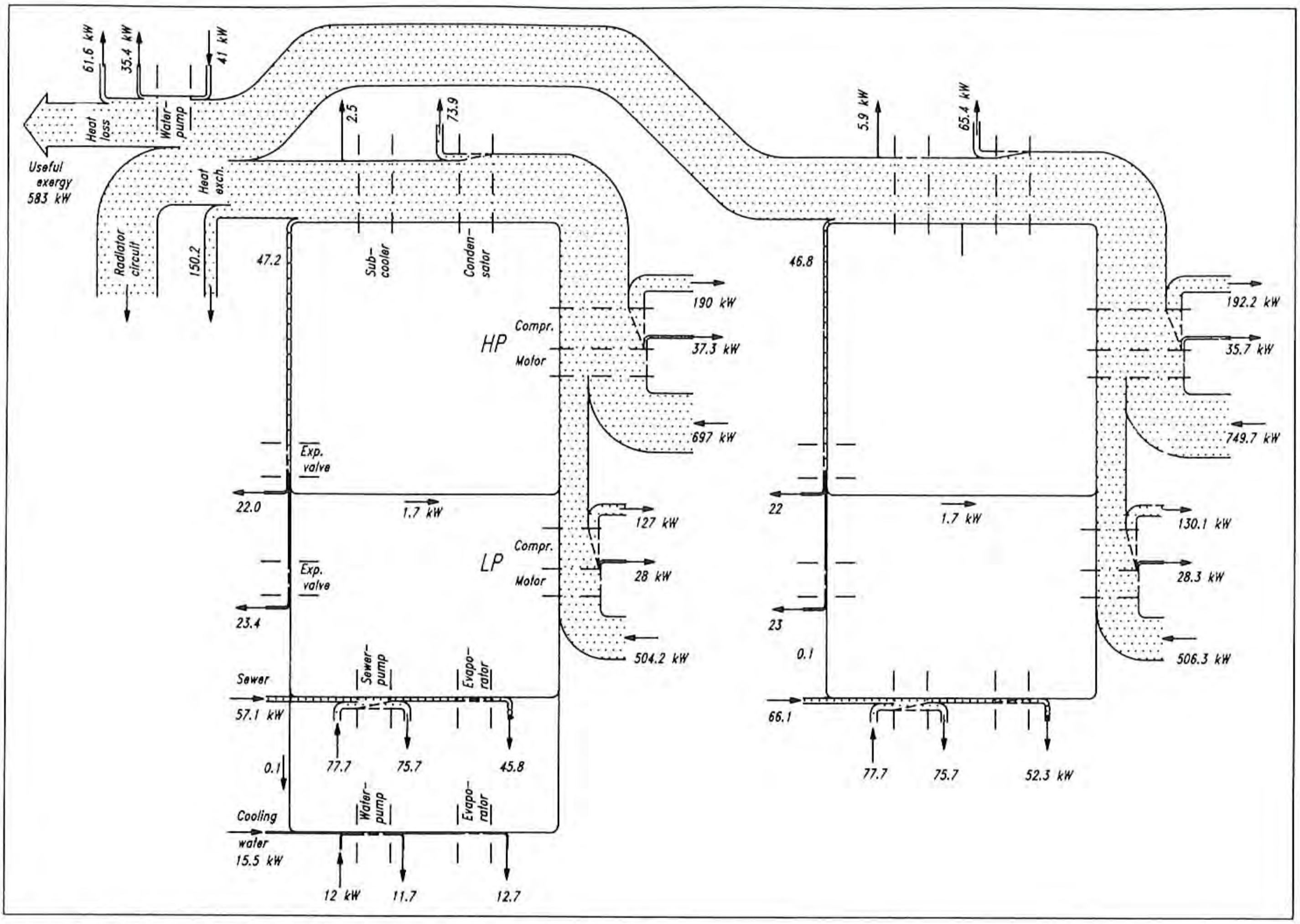

Figure 6. Exergy flow chart for heat pump system, showing distribution of thermodynamic losses (in kW)

ingly so in commercial buildings, even in the Nordic countries. A rising energy price level in the future will make the advantage even more clear. The cost of strengthening the electricity distribution system is marginal. To reconstruct a gas distribution network for domestic consumption, which was done away with in the Scandinavian countries 50 years ago, does not make sense.

Item	Absorbed Power kW	Exergy Loss kW	Loss %
Evaporator system			
Pumps for sewer and water	167.4	163.2	
Exergy from sewer and recovery	138.7		
Loss in heat transfer		110.8	
Total for evaporator system	306.1	271.0	9.8
Compressor plant			
Electric power to motors	2457.4		
Exergy losses in motors		134.3	
Exergy losses in compressors		640.1	
Total for compressor plant	2457.4	774.4	27.6
Condenser system, losses in heat transfer		147.5	5.2
Throttling losses		92.2	3.3
District heating system			
Circulation pump	41.0	35.4	
Heat loss in transfer		61.6	
Heat transfer in exchangers		150.2	
Temp loss in secondary circuit		687.2	
Total district heating system	41.0	934.4	33.3
Consumption/useful exergy	2804.5	582.9	20.8

Table 2. Exergy flow account, summary

Heat pump improvement possibilities

It was stated before that the present heat pumps are capable of vast improvement. A COP of say 3 is considered a fairly good value today, but corresponds to a thermodynamic efficiency of only 20 percent or so, depending on the conditions of operation. The losses are thus very important.

In order to study the distribution and relative importance of losses, an exergy analysis is a good method. As an example we can consider a new heat pump, which has just been put in operation in a district heating and cooling scheme in Sandvika, outside Oslo, (Figure 5).[2] It can be considered a very good plant according to present standards, with an overall system COP at medium load conditions of 3.7. In spite of this the thermodynamic efficiency is not much over 20 percent. One reason for this is the relatively low theoretical temperature lift, raw sewage being used as a heat source.

The distribution of losses is shown in detail in the exergy flow diagram (Figure 6) and in more exact figures in Table 2. This gives a good basis for deciding where improvements are most worthwhile and how the performance can be increased by appropriate changes towards a better cost-benefit optimization. The following main conclusions can be drawn:

- The largest item of loss is due to irreversible heat transfer in the distribution system. Only the heat exchangers at the intake of the consumers, which are in principle superfluous, increase the power consumption by 150 kW. The radiator heat transfer loss is close to 700 kW. The heat distribution losses increase the theoretical power requirement by a factor of 2.6 and enlarge the motor-compressor losses correspondingly. There is thus a tremendous possibility of improvement by redesigning the heating system to match the requirement of the heat pump, abandoning old practice from the time of direct fuel heating.
- The most important loss item for the heat pump itself occurs in the motor-compressor units. Their loading includes most of the other losses in the system and an improvement in their efficiency can therefore give very good effect.
- The other various losses are more marginal and the possibilities of improvement limited. It is apparent from the figures, however, that the individual sizing of the various heat exchange surfaces could have been better optimized. For instance, the effect of the subcoolers is very limited in a low lift two-stage system like this, when the temperature difference in the condensers is so small. They are hardly cost effective at all and could have been omitted.

Conclusions

The situation can be summarized as follows:

- Heat pumps are very cost effective when they are combined with summer cooling at matching capacity. However, Present electric drive units hardly save any fuel in a heat energy system.
- For heating only large heat pumps are marginally cost effective in many situations for house heating in a water or nuclear power system, when the yearly time of utilization is reasonably long. Increasing demand for summer air conditioning in office buildings improves the economy enormously. In many industrial applications large heat pumps are highly competitive.
- Present heat pumps are capable of great improvement in performance. This is necessary to make this system the universal method of house heating in the future.

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First Results of Cycle Experiments with Ethyl Chloride in Compression Heat Pumps

The Department of Chemical Engineering Fundamentals of the Institute of Chemical Engineering of the Graz University of Technology screened 940 substances as to their suitability as compression heat pump media. Based on this study, ethyl chloride was chosen as a possible media and tests were carried out on an actual laboratory compression cycle. The measurements and tests indicate that ethyl chloride is well suited as a heat pump medium and better than R114 in terms of COP and η. An acceptable lubricating oil has also been identified for use with ethyl chloride.

CFC replacement

As the fatal impact of chlorofluorocarbon (CFC) compounds on the ozone layer in the world's atmosphere was confirmed, urgent calls were made for the reduction of the output of these substances. In compression heat pump cycles there are different approaches to achieve this goal. First, incompletely substituted CFCs like R21 and chlorine-free compounds like R134a can replace the more dangerous completely substituted ones. Secondly, research work can be done to find other well-suited alternative substances well suited as compression heat pump media.

Ethyl chloride as a heat pump medium

The Department for Chemical Engineering Fundamentals of the Institute of Chemical Engineering of the Graz University of Technology chose the second approach. M. Narodoslawsky and F. Windisch[1,2,3] screened 940 substances contained in the data bank of a commercial flowsheeting program (PROCESS) for their applicability in heat pump cycles by applying the criteria found by Unterleutner[4] and by simulating a compression heat pump for three cases: with the temperature of the heat source at 20°C and a temperature boost of 50°C, and with the temperature of the heat source at 60 and 90°C and a temperature boost of 60°C. This study showed that ethyl chloride is applicable to the lower and medium temperature cases, where ethyl bromide and propyl chloride may be used

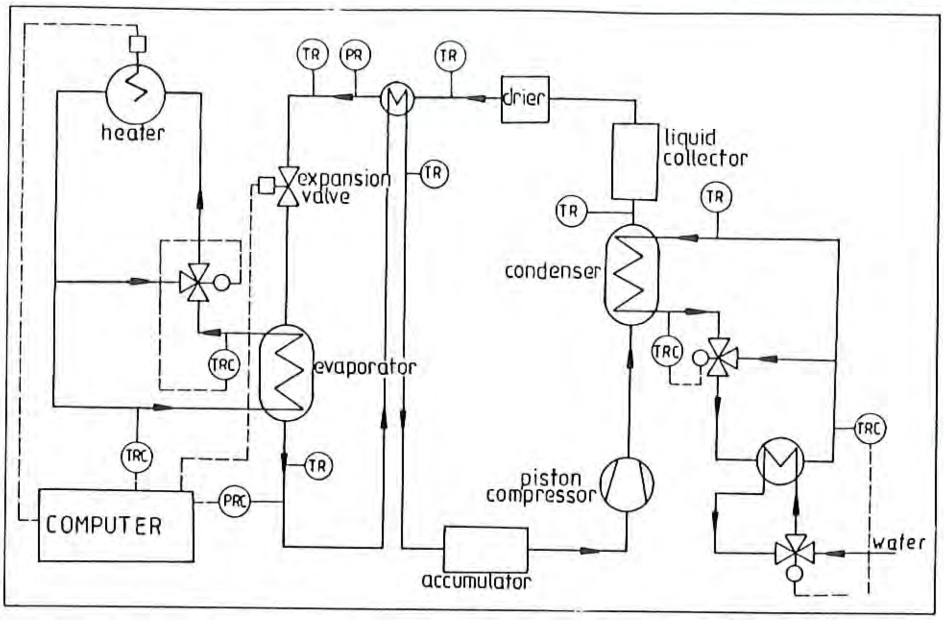

Figure 1. Test heat pump

for the medium and high temperature cases. It was decided to run the first experimental tests with ethyl chloride.

The test facility

Figure 1 shows a flowsheet of the single stage compression heat pump used in the experiments at the Institute. This plant was designed as a multi-purpose compression heat pump for use in evaluating the performance of non-azeotropic mixtures of R114 and R12 in 1985. Therefore, it has no specific design for ethyl chloride.

The compressor is an open compressor (Bitzer Type V), driven by a 2.6kW electric motor. The isentropic efficiency of this unit was approximately 0.6 in our tests, as this is not a proper field of application for a compressor normally used in a refrigeration plant. The plant further consists of a coaxial evaporator (Wieland V8), a coaxial condenser (Wieland KWG6), and an internal double pipe heat exchanger. Both the evaporator and the separator are reliably oversized. Between evaporator and compressor there is an accumulator; a liquid collector and a drier are installed after the condenser.

The evaporator pressure is controlled by a modified thermostatic expansion valve. Normally the temperature detector (a cartridge filled with refrigerant) is attached to the evaporator outlet and therefore generates pressure (dependent on the evaporator outlet temperature) which adjusts the membrane working on the valve. In our modification, the cartridge is separated from the evaporator outlet and heated electrically. The current for the heating wire is controlled by a computer program using a PID-algorithm. This gives independence from the working pressure and the tested medium.

Two water cycles work as heat sink and heat source. The water inlet temperature into the evaporator is controlled by an electric boiler. The heat load of the boiler is determined by a computer program. The inlet temperature into the condenser is controlled by a separate water cooler circuit using a plate heat exchanger, a PID-controller and a three-way mixer, which acts upon the fresh water flow. The water outlet temperatures of the evaporator and the condenser are adjusted by independent PID-controllers operating on three-way mixers.

The measuring points of temperatures and pressures are given in Figure 1. Pt80 and Pt100 resistance feelers are used for determining temperatures in the refrigerant cycle and water cycles, respectively, piezofeelers meter the pressures. The water flow in the heat source and heat sink is measured by turbine flow meters. Shaft torque, speed, and power input of the motor are metered. The data acquisition is done by a computer program running on a PDP-11 using an Epson HX-20 as interface. The shaft power of the motor is calculated from the shaft torque and the motor speed. Heat input and heat output are calculated from flows and temperatures.

As mentioned above, the design of this heat pump was not optimized for testing ethyl chloride. As the insulation was not optimized either, heat losses in the condenser and compressor have to be expected, their amount depending on the compressor outlet temperatures and the condensing temperature.

Compressor lubrication

Thermal and chemical stability and the mixing behavior of oil-refrigerant mixtures are important points in selecting a suitable oil. Sealed Tube Tests (ASHRAE 97 P) at 175°C at the Shell laboratories in Hamburg qualified CLAVUS G 100 as proper lubricant in connection with ethyl bromide, propyl chloride, and ethyl chloride. It was chosen as the compressor oil.

Results of cycle experiments

For the graphic representation, an entropy temperature diagram was calculated using a package of thermodynamic computer programs based on the Benedict-Webb-Rubin-Starling equation of state developed by Unterleutner[4] and plotted. The calculated data agreed well with data from the literature and measurements.

Table 1 shows the temperatures of evaporator and condenser, the outlet

EXP	T_{eva} [C]	T_{con} [C]	T_{sup} [C]	P_{con} [bar]	Q_1 [kW]	COP_1	COP_2	η_1	η_2	π
1	12.50	44.35	90.93	2.98	0.410	4.08	4.59	0.41	0.46	2.93
2	30.70	69.08	109.90	5.90	1.004	4.30	5.09	0.48	0.57	3.15
3	33.75	73.00	112.50	6.64	0.940	4.17	4.87	0.47	0.55	3.11
4	43.97	88.34	123.65	9.34	1.310	4.03	4.80	0.49	0.59	3.24
5	19.95	68.00	113.64	5.74	0.730	2.95	3.55	0.42	0.50	4.42
6	34.35	88.89	121.21	9.46	1.121	3.00	3.71	0.45	0.57	4.50

Table 1. Experimental results with ethyl chloride

EXP	T_{eva} [C]	T_{con} [C]	T_{sup} [C]	P_{con} [bar]	Q_l [kW]	COP_1	COP_2	η_1	η_2	π
1	8.73	44.90	71.68	3.66	0.257	3.81	4.10	0.43	0.47	3.07
2	31.66	70.70	84.34	7.28	0.497	4.07	4.40	0.46	0.50	2.92
3	34.82	75.30	89.26	8.15	0.671	3.79	4.21	0.44	0.49	3.00
4	43.48	89.55	104.21	11.25	0.860	3.50	3.93	0.45	0.50	3.20

Table 2. Experimental results with R114

temperature of the compressor, the condenser pressure, the pressure ratio, COPs, performance factors and cumulated heat losses of six characteristic experiments.

The COPs were calculated as follows:

$$COP_1 = \frac{Q_{mes}}{P_{shaft}}$$

$$COP_2 = \frac{Q_{mes} + Q_l}{P_{shaft}}$$

$$COP_{Car} = \frac{T_{con}}{T_{con} - T_{eva}}$$

The performance factors were calculated as follows:

$$\eta_1 = \frac{COP_1}{COP_{Car}}$$

$$\eta_2 = \frac{COP_2}{COP_{Car}}$$

Abbreviations used

COP = coefficient of performance
η = performance factor
π = pressure ratio
P = power
p = pressure
Q = heat load
T = temperature

Subscripts used

Car = Carnot
con = condenser
eva = evaporator
l = losses
mes = measures
shaft = shaft
sup = superheated

The heat losses to the surroundings were found by measuring the surface temperature of the insulation and subsequent calculation and checked by comparing the cycle with the entropy-temperature diagram. Inspecting the cumulated heat losses showed their expected dependence on the compressor outlet temperature. As these losses would not occur in a well-designed system, the computer acquired performance data had to be corrected to make the results comparable with other media. This calculation yielded COP_2 and

$_2$.

Comparison with R114

To compare ethyl chloride to a commercially available working medium suited for a higher working temperature, region experiments were done with R114 in the same test plant with identical condenser and evaporator temperatures. The results are shown in Table 2.

As ethyl chloride is more superheated at the compressor outlet, heat losses in the compressor and the condenser are higher than with R114. Therefore, the two series of experiments become comparable only if the measured COPs (COP_1) are properly corrected by the heat losses (COP_2).

The comparison between ethyl chloride and R114 shows that ethyl chloride achieves better COPs and performance factors in the higher temperature range. The condensing pressures are lower with ethyl chloride, pressure ratios and volumetric heat storage similar. As calculations by M. Narodoslawsky et al[2] showed, the required heat transfer area for ethyl chloride is higher than for R114. The oil proved stable in 100 hours of operation, but there were problems with the binder in the drier and the conventional seals and packings.

Conclusions

The heat pump has been run now for 100 h with ethyl chloride as a medium. The results show that ethyl chloride is well suited as a heat pump medium. The comparison with R114 indicates that ethyl chloride works better than R114 in terms of COP and . The oil, CLAVUS G 100, has proved its stability up to 150°C. The conventional valve packings and the binder in the drier turned out to be inadequate. Better suited materials are being tested. A continuous test in a commercial heat pump is being prepared at the Institute.

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Proposal for New Sorption Cycle Working Pairs Based on Thermodynamic Considerations

Energy recovery systems based on sorption cycles are getting more attention from industry and academia. The reasons for this attraction are manyfold. Reliability and flexibility in operation are some of the most important advantages, appealing to industrial users.[1] Besides this, the CFC discussion somewhat helped to establish sorption systems as a technical solution with great potential for the future. However, sorption systems have serious drawbacks. For industrial applications, high temperature levels for the rejected heat are frequently called for. The conventional working pairs LiBr-water and water-ammonia, however, pose limits to the attainable temperature levels. This gives the rationale for a search for working pairs, which will be applicable in a wider temperature range and will permit greater temperature boosts. This report gives the results of a thermodynamically based search for alternative absorption heat transformer (AHT) and absorption heat pump (AHP) working pairs.

Thermodynamic properties determine to a great extent the performance of a sorption cycle. Moreover, the basic thermodynamic data are readily available for a great number of pure substances and some mixtures. It therefore seems appropriate to take thermodynamic properties as the base for a first screening of the almost infinite number of mixtures in order to narrow the field of possible contenders for alternative working pairs.

The method

In order to find optimal working fluids for sorption cycles, one has to consider two major levels of influence. These are:

-- Influences exerted by the pure component properties of the refrigerant and the absorbent, respectively, and

-- Influences by the properties of mixing of the working pair

None of these influences may be neglected at first sight. So both have to be described by appropriate properties and models and their influence on the complex system of a sorption cycle must be carefully assessed and compared.

This leads directly to the next question. What are the properties describing the processes and interdependencies in a sorption cycle? The properties chosen for representing the pure components and the mixtures should fulfill certain requirements. They should:

-- Significantly influence the performance of the sorption cycles

-- Be available for a great number of substances and mixtures

-- Be the base for predictive methods describing the actual thermodynamic states (pressures, temperatures, concentrations, etc.) of the working pair adequately in the whole range of operation.

The first two requirements are obvious. The third, however, needs some explanation. As the aim of the search is to find hitherto unknown working pairs, one cannot expect to have a data base exceeding the most fundamental information. Therefore, predictive methods are the only way to estimate the behavior of a presumptive working pair. Although the results of calculations based on predictive methods do not show sufficient accuracy to allow for construction of sorption heat pumps, they nevertheless give good and quite reliable estimates.

From the above mentioned considerations, the critical data and the latent heat at normal boiling point emerged as the most interesting pure component data. For the properties of mixing, the functions of the excess free enthalpy g^E and the heat of mixing h^E are the most influencing properties. They were characterized by the extremum of the g^E function.

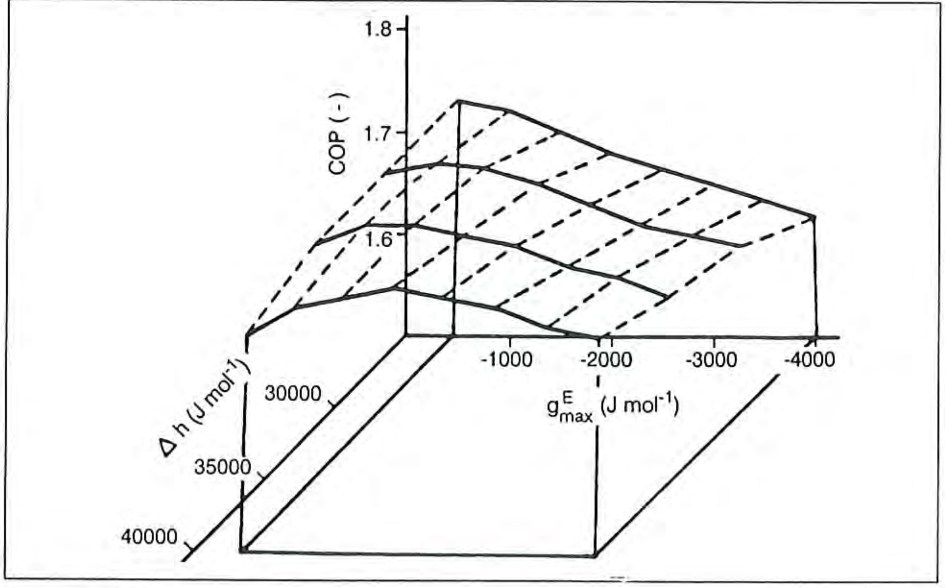

Figure 1. COP of an Absorption Heat Pump (AHP)

The second step after establishing the set of properties on which to base the screening, is to derive criteria for these properties. These criteria have to be fulfilled by optimal working pairs. To obtain these criteria, a systematic simulation of sorption cycles has to be made. In this simulation, the values of the most important properties have to be varied gradually. Thus, optimal values and sensitivities can be deduced which subsequently are formulated into criteria.

The third step now is to apply these criteria to a great number of possible alternatives. In this process, the most promising pairs have to be selected for further investigations.

The criteria

A detailed report on the thermodynamic criteria for optimal working pairs for AHP and AHT is already published elsewhere.[2,3] However, it may be of some interest to give a short summary of the various thermodynamic requirements which have to be fulfilled by optimal sorption cycle working pairs to obtain high coefficients of performance (COP).

One aspect of this criteria derived from thorough computer simulations of simple, one stage sorption cycles is that the sensitivity of the COP to the change of a property is different for the AHP and the AHT. The most important discrimination between these two cycles is that the AHP is sensitive to the properties of mixing, whereas the COP of an AHT changes more significantly with pure component properties.

Figure 1 shows the COP of an AHP as a function of the extreme value for the Gibbs Excess Free Enthalpy g^E of the working pair and the latent heat at normal boiling point of the refrigerant. The latter property turned out to be by far the most important pure component property. One can easily observe the strong influence of the mixing property g^E. An optimum of the COP may be obtained by working pairs showing extreme Gibbs Excess Free Energies between -1,500 and -2,000 kJ/kmol. These are mixtures with a strong negative deviation from Raoult's law. However, lower extreme values for g^E reduce the COP again. It is also important to note that the extremum of g^E should occur at high concentrations of the refrigerant.

		Pure component property				
		p_c	T_c	$T_{b,r}$	ω	Δh_{ev}
AHP	Refrigerant	high	low	high	high	high
	Absorbent	low	high	low	low	high
AHT	Refrigerant	low	high	low	low	high
	Absorbent	low	high	low	low	high

p_c = critical pressure
T_c = critical temperature
$T_{b,r}$ = reduced boiling point temperature
ω = azentric factor
Δh_{ev} = latent heat at normal boiling point

	Property of mixture		
	g^E_{max}	x_{max}	Δh^E
AHP	-1000 to -2000 J/mol	high	moderate exothermic to slightly endothermic
AHT	low	medium to high	exothermic

g^E_{max} = extreme value of Gibbs Free Energy
x_{max} = corresponding refrierant mole fraction
Δh^E = enthalpy of mixing

Table 1. Criteria for the pure component and mixture properties

A high latent heat of the refrigerant enhances the coefficient of performance for single stage AHP. The excess heat of mixing for optimal AHP working fluids should be moderately exothermic.

If we now turn to the AHT, the situation is markedly different. The influence of properties of mixing on the COP somewhat fades. However, strongly negative extreme values of g^E at medium to high refrigerant concentrations are still desirable. In contrast to AHP media, optimal AHT working pairs should exhibit strongly negative (exothermic) heats of mixing.

The most influencing properties in this case are pure component properties, mainly of the refrigerant. Besides the latent heat, which is of some importance for AHT, too, the critical pressure and the normal boiling point influence the COP of an AHT.

Table 1 gives a summary of thermodynamic criteria for optimal working pairs for AHP and AHT. These criteria were subsequently used to find promising sorption machine working fluids. To screen a great number of possible mixtures for the best combinations of refrigerant and absorbent, an extensive computer simulation was employed. As there are only scarce data on the thermodynamic properties of mixtures, predictive methods[2] were used to estimate the values of the criterias. For the properties of mixing, the UNIFAC group contribution method[4] was used in a first screening.[2] After narrowing down the field of possible candidate pairs to some ten contenders, the cycles were simulated, again using the predictive methods to estimate the state variables (pressure, density, temperature, etc.) in different parts of the cycles. However, for this close up look, the more accurate "Extended UNIFAC" concept[5] was used. Thus, temperature dependence of vapor-liquid equilibria and heats of mixing could be estimated. The results of this screening will now be presented.

AHT working pairs

The working pair water-LiBr is very close to an optimal working pair for AHT. Water fulfills the pure component properties for a good refrigerant (high

Refrigerant/absorbent	Temperature of heat source/sink (°C)					
	20/60	20/70	20/80	60/100	60/110	60/120
methylamine/ethylenglycol	1.60	1.54	1.46	-	-	-
methylamine/1,4 butanediol	1.59	1.51	1.44	-	-	-
ethanediamin/glycerol	-	-	-	1.57	1.50	1.41
ethanol/dihydroxibenzol	-	-	-	1.74	1.68	1.61
ethanol/trihydroxibenzol	-	-	-	1.74	1.68	1.62

Table 2a. COP of alternative AHP working pairs

Refrigerants	T_b [°C]	p [bar] 20°C	80°C	110°C	Δh_v [J/mol]	LTV[1] ppm
methylamine	-6.2	2.94	17.1	32.75	24570	10
ethanol	78.4	0.06	1.08	3.15	38760	1000
ethandiamine	117.3	0.01	0.25	0.78	41860	10
ammonia	-33.6	8.53	41.26	75.53	23375	50
water	100	0.02	0.47	1.43	40617	-

Absorbents	T_b [°C]	LTV [ppm]
ethylenglycol	197	-
1,4 butandiol	235	-
glycerol	289	-
dihydroxibenzol	285	2
trihydroxibenzol	309	2

([1] Limit Threshold Value)

Table 2b. Properties of pure refrigerants and absorbents

latent heat at normal boiling point, high critical temperature, etc.), and the mixture exhibits both, high negative deviations from Raoult's law and strongly exothermic heats of mixing. No organic mixture is able to top the performance of water-LiBr as a working pair for AHT. In the case of the AHT, the highest temperature in the cycle is only a few degrees above the actual temperature level of the rejected heat. Thus, this working pair is well suited for industrial applications with temperature levels of up to 160°C. Given the optimal set of properties of the water-LiBr pairs, it is not probable that a new working pair much better than this will emerge anytime soon.

Alternatives for conventional AHP working pairs

The situation is markedly different for the AHP cycle. The classic working pair ammonia-water exhibits high condenser pressures for industrial applications (heat sink above 70°C). Its COP in this case is poor, too. Though water-LiBr shows good COP for most industrial applications, there are limits for its application. Corrosion does not allow temperatures in the generator to exceed 180 to 200°C, thus limiting the temperature of the heat rejected to just above 100°C. The second severe limitation is posed by the crystallization of LiBr. It limits the possible temperature boost for an AHP.

From the screening of organic fluids, there are mainly two alternatives for low temperature industrial heat recovery systems by AHP. This low temperature industrial application may be characterized by heat sources of 20°C and temperatures of heat sinks of 60 to 80°C. These are the pairs methyl amine-ethylenglycol and methyl amine-1,4 butandiol. Both show quite good COP. Methyl amine has considerably lower pressure levels than ammonia at the same temperatures and smaller vapor volumes than water. Both mixtures display a much broader solution field than the system water-LiBr, thus allowing for higher temperature boosts. For more details on the properties of the working fluids see Table 2.

Besides the low temperature applications, AHP cycles are interesting alternatives for medium and high temperature heat recovery systems in an industrial environment. However, for these applications the lack of suitable working pairs is obvious. Apart from other ionic solutions a possible choice could be the working pair ethane diamine-glycerol. Other possible candidates could be mixtures of ethanol and methanol with aromatic alcohols like dihydroxy benzene or trihydroxy benzene. Although the latter two mixtures show good COP, they are only long-shot alternatives. There is next to nothing known about stability and corrosivity of these mixtures. However, their high potential should induce enough interest as to warrant a thorough investigation in the physical and chemical properties of these mixtures.

Conclusion

Thermodynamic considerations lead to criteria to be fulfilled by optimal sorption cycle working fluids. A screening of organic mixtures by these criteria renders no alternatives to the conventional water-LiBr systems for AHT. However, there are at least two reasonable options for AHP cycles in low temperature industrial applications. These are the mixtures of methyl-amine with either ethylenglycol or 1,4 butandiol. Both seem to be superior to the ammonia-water system and more versatile than the water-LiBr working pair.

An extension to the field of application of AHP to higher temperature levels could be possible with these and other working fluids like ethane diamine-glycerol. This would be especially interesting for industrial heat recovery. However, tests of stability and compatibility with materials of construction at high temperatures have to be carried out before a final verdict on the merits of these alternative fluids can be spoken.

Acknowledgments

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R.A. Macriss*

Recommended Thermodynamic Data for NH_3-H_2O in the Temperature Range of -50° to 316°C and Pressure Range of 0.05 to 170 bar

The objective of this study has been to critically assess past NH_3-H_2O thermodynamic data and the results of predictive methods, and to include most recent data that extend to higher temperatures and pressures, in order to provide an accurate, consistent, and comprehensive set of data to be used in the design and assessment of advanced absorption heat pumps and refrigeration. The recommended thermodynamic data cover a range of temperatures from -50° to 316°C and a range of pressures from 0.05 to 170 bar. The recommended values for equilibrium properties (p-t-x-y) have been based on the measurements by Wilson (1925), Macriss et al (1964), and Gillespie et al (1985). It is believed that this study has eliminated the long standing confusion about the accuracy of existing vapor-liquid-equilibrium data for NH_3-H_2O, has extended the range of data from the NH_3-H_2O three-phase boundary to 170 bar, across the entire concentration range, and can serve to avoid costly duplication of effort.

Introduction

The ammonia-water binary fluid system is the oldest successfully employed absorption fluid in many applications and processes, ranging from industrial refrigeration to residential absorption heat pumps and air conditioners. Because of its importance, over 30 different researchers, in the United States and abroad, have attempted to develop experimentally or define analytically thermodynamic and other properties data for equipment design purposes. The earlier investigations began in 1901 and have continued until recent times, with at least three major investigations having been published during 1985.

Some of the reasons for the at times repetitive investigations stem from the highly nonideal nature of this fluid sys-

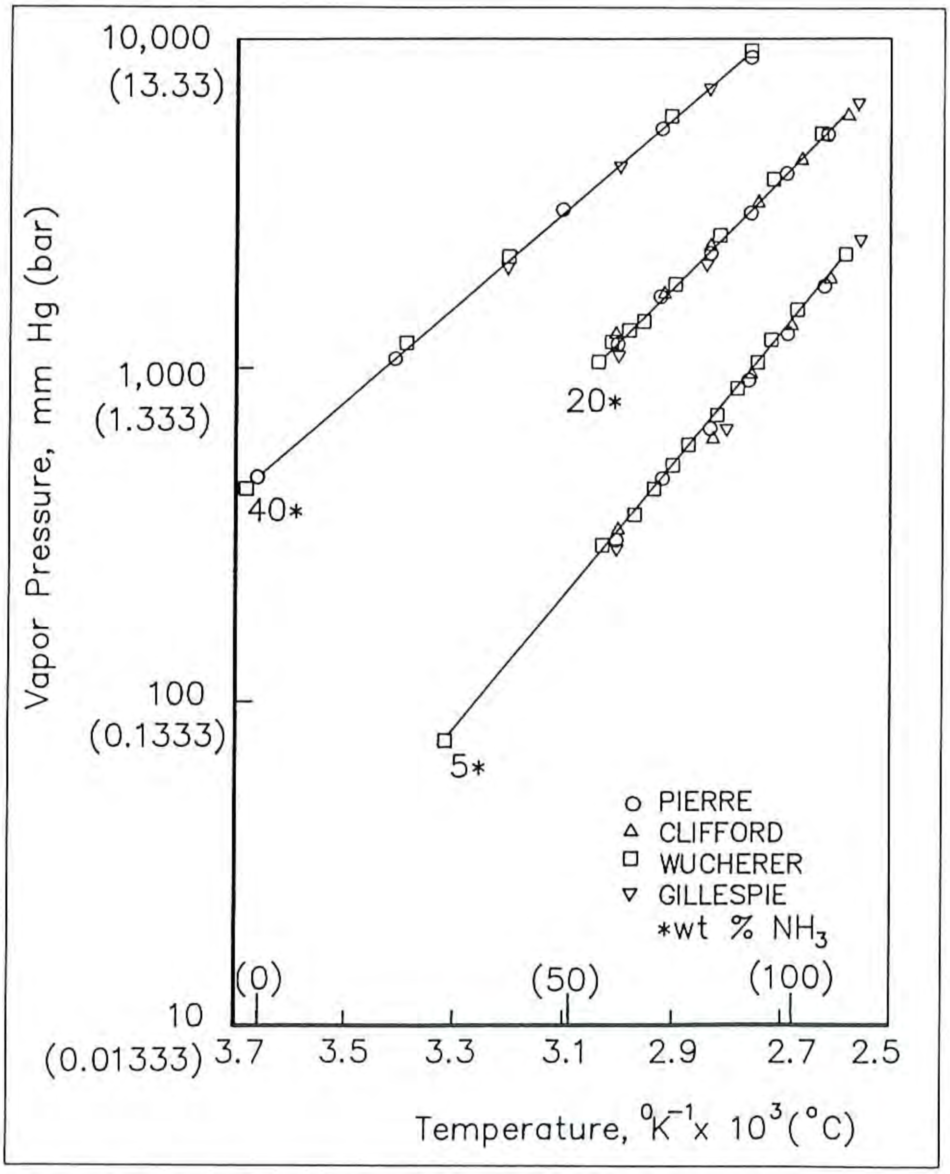

Figure 1. Comparison of NH_3 + H_2O vapor pressure-concentration data

tem and the lack of standard equipment and procedures for proper measurement of thermodynamic and other properties data, especially at high pressures. The most recent investigations have produced data at extended ranges of temperature and pressure, needed for advanced absorption heat pump cycles and other applications.

Serious disagreements have been identified over the years between actual measurements and thermodynamic projections for important properties of the NH_3-H_2O fluid. This study, supported by Oak Ridge National Laboratory for the U.S. Department of Energy, was undertaken to resolve these differences and consolidate the available data into a consistent set of recommended values in tabular, graphical and analytical forms. More so, to expand the applicability of the recommended values with the most recent, accurate data covering the range of conditions from the three-phase NH_3-H_2O boundary to 170 bar.

The basic approach was to compare primary experimental data sets from the various sources with each other, and then with thermodynamic predictions and empirical polynomial estimates. Based on the results of this screening, a set of recommended phase equilibrium data was compiled covering saturation temperature (t), pressure (p), liquid-phase composition (x) and vapor-phase composition (y) and the details are discussed in this paper.

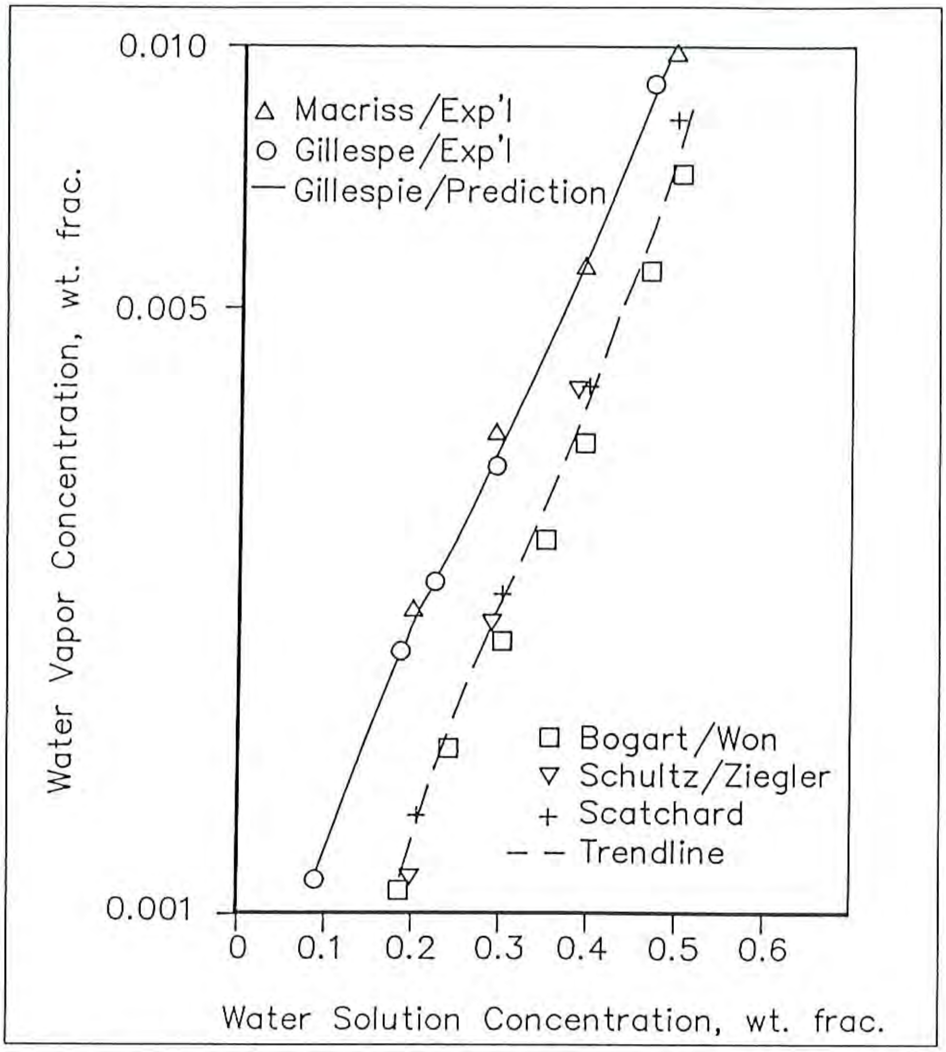

Figure 2. Comparison of measured and predicted water vapor concentration of the NH_3 + H_2O pair at 60°C

Experimental data

Several NH_3-H_2O experimental studies were carried out in Europe, some prior to 1932. Contributions include Perman 8 (1901), Mollier 7 (1908), Wucherer 14 (1932), Clifford and Hunter (1932) 1 and Pierre 9 (1959). In the U.S.A, Wilson 13

Source	Data* Type	Basis	Temperature °C	Pressure bar	Concentration Range Liquid Wt % H_2O	 Vapor
Equilibria						
Gillespie	S	PTxy	40 - 316	0.07 - 210	7.0 - 99.0	0.057 - 85.0
Gillespie	E	PTxy	40 - 316	0.07 - 210	7.0 - 99.0	0.057 - 85.0
Macriss	S	PTxy	-75 - 204	0.07 - 29.9	10.0 - 90.0	0.013 - 68.0
Macriss	E	PTy	61 - 116	14.8 - 37.0	(16.2 - 57.2)**	0.47 - 3.59
Wucherer/Jennings	S	PTxy	-75 - 185	0.07 - 20.7	10.0 - 90.0	2.0 - 55.0
Perman	E	PTxy	0 - 60	0.02 - 0.81	77.0 - 95.0	2.5 - 53.0
B. Pierre	S	PTx	-20 - 150	0.1 - 10.0	50.0 - 90.0	NA
Guillevic	E	PTx	130 - 230	13.4 - 71.7	31.0 - 92.0	NA
Guillevic	E	PTy	130 - 230	7.8 - 67.1	(35.8 - 95.0)**	2.75 - 35.9
Polak	E	PTxy	91 - 147	1.0 - 4.8	96.0 - 99.9	66.0 - 99.9
Clifford & Hunter	S	PTxy	60 - 140	0.7 - 18.8	70.0 - 90.0	7.0 - 46.0
Wilson	S	PTxy	4 - 93	0.07 - 20.7	10.0 - 90.0	0.019 - 33.4

* S - smoothed data, E - experimental data
** Calculated
NA Not available

Table 1. Range of data used for comparisons

(1925) obtained a significant amount of p-t-x-y data. In 1964, Macriss et al 6 presented a side-by-side comparison of the data measured earlier by several investigators. They also presented a set of recommended values for vapor pressures based on their analysis. Recently, Gillespie et al 3, (1985), Guillevic, 4 (1983) and Rizvi 11, (1985) obtained and presented new data that span a wider range of pressure and temperature than previously reported.

Source	Data* Type	Basis	No. of Points	Average ------	Deviation S.D. %	S.E. ------
Gillespie	S	Tx	62	0.053	1.95	0.25
Gillespie	E	Tx	42	0.123	3.58	0.55
Macriss	S	Tx	41	0.297	2.08	0.33
Macriss	E	Ty	16	0.30	4.82	1.20
Wucherer/Jennings	S	Tx	28	1.00	1.71	0.32
Perman	E	Tx	42	0.34	3.50	0.54
B. Pierre	S	Tx	17	1.30	2.79	0.68
Guillevic	E	Tx	18	4.01	4.13	0.97
Guillevic	E	Ty	26	4.16	11.52	2.26
Polak	E	Tx	23	-1.08	1.04	0.22
Clifford & Hunter	S	Tx	24	1.79	2.34	0.48
Wilson	S	Tx	16	-4.23	6.05	1.52
TOTAL			355	-0.86	4.30	0.23

* S - smoothed data, E - experimental data
S.D. Standard deviation
S.E. Standard error
Deviation (calculated value - measured value)/measured value

Table 2. Comparisons of preferred values of total pressure to literature data

p-t-x Data

A comparison of the equilibrium pressures measured by four (9, 1, 14, 3) investigators over three distinct solution concentrations (5, 20, and 40 Wt % NH_3) is illustrated in Figure 1. The data shown in the figure are actual experimental data. For all practical purposes, there are no significant differences between the data gathered by the four investigators, indicating that for the specific concentrations and temperatures shown, there are no conflicts in the data. Some differences in the data, however, exist at relatively high temperatures and pressures.

p-t-x-y Data

As previously mentioned, Macriss et al evaluated the data obtained by Wucherer, Clifford and Hunter, and Wilson, and determined and recommended a "best" set of p-t-x values for use in process calculations up to 34.5 bar. With the aid of several directed experimental measurements in the ammonia-rich solution region, Macriss et al also compiled a recommended set of values for equilibrium vapor concentrations over the range of pressure from 0.07 to 34.5 bar and temperatures from 60°to 116°C. Most recently, Gillespie et al obtained similar data in the range of 40° to 316°C and 0.074 to 313.3 bar. The comparison of vapor composition data of Macriss et al and Gillespie et al at 60°C is shown in Figure 2. Very good agreement is shown on the left side of the figure labeled "measured" between the two data sets.

Thermodynamic predictions

A major thrust of U.S.A. and European investigations has been to thermodynamically analyze historical data in order to determine consistency. For example, in 1947 Scatchard et al 28 calculated equilibrium vapor compositions that were significantly different than the measured values. Scatchard reached this conclusion through a Gibbs-Duhem integration, assuming water was essentially non-volatile.

More recently, Edwards 16 (1978) and then Won et al 33 (1980) evaluated the thermodynamic consistency of the tabulated values presented earlier by Macriss et al. Again, as did Scatchard, Won projected water vapor concentrations, in equilibrium with ammonia-rich solutions, significantly below the measured data. European researchers, specifically Schultz 29 (1971) and Ziegler and Trepp 32 (1984) have also thermodynamically analyzed the NH_3-H_2O system and again concluded that the reported measured water vapor concentrations are higher for ammonia-rich solutions than their predictions.

Figure 2 presents the results of several thermodynamic predictions of the equilibrium vapor composition of the NH_3-H_2O fluid at 60°C. Good agreement is indicated between the five different estimations (Edwards, Won, Schultz, Ziegler and Trepp, and Scatchard), shown on the right side of Figure 2 labeled "predicted".

Comparisons

Figure 2 shows the disagreement between the actual experimental data of

(Vapor Composition)

Source	Data* Type	Basis	No. of Points	Average ------	Deviation S.D. %	S.E. ------
Gillespie	S	Tx	55	0.44	2.56	0.35
Gillespie	E	Tx	52	-0.16	4.80	0.65
Macriss	S	Tx	32	0.89	12.90	2.28
Macriss	E	PT	16	2.10	8.90	2.22
Wucherer/Jennings	S	Tx	14	-3.38	3.17	0.85
Perman	E	Tx	42	1.76	4.48	0.69
Guillevic	E	PT	16	3.89	11.57	2.27
Polak	E	Tx	23	-0.76	4.82	1.00
Clifford & Hunter	S	Tx	21	-4.49	6.95	1.52
Wilson	S	Tx	16	-1.71	22.75	5.52

* S - smoothed data, E - experimental data
S.D. Standard deviation
S.E. Standard error
Deviation (calculated value - measured value)/measured value

Table 3. Comparisons of preferred values of vapor composition to literature data

Macriss et al and Gillespie et al at 60°C versus the thermodynamic predictions of the previously listed investigations. It is evident that the calculated water vapor compositions are substantially lower than the measured values in the ammonia-rich solution region by as much as a factor of 2. This pattern appears to also hold true at other temperatures in the ammonia-rich region of concentration. From these comparisons, we have concluded that the thermodynamic projections of vapor composition of Scatchard, Edwards, Won, Schultz, and Ziegler and Trepp must be in error.

	Ammonia in liquid, WT%										
Temp. °C	0	10	20	30	40	50	60	70	80	90	100
	Saturation pressure, bar										
250	39.7	62.3	88.5	114.0	138.0	170.0	NA	NA	NA	NA	NA
252	41.1	64.2	90.7	116.0	141.0	175.0	NA	NA	NA	NA	NA
254	42.5	66.0	92.9	119.0	145.0	NA	NA	NA	NA	NA	NA
256	43.9	68.1	94.9	120.0	155.0	NA	NA	NA	NA	NA	NA
258	45.4	70.0	97.3	122.0	144.0	NA	NA	NA	NA	NA	NA
260	46.9	72.0	99.6	124.0	147.0	NA	NA	NA	NA	NA	NA
262	48.4	74.1	102.0	127.0	149.0	NA	NA	NA	NA	NA	NA
264	50.0	76.1	104.0	129.0	151.0	NA	NA	NA	NA	NA	NA
266	51.6	78.2	107.0	131.0	153.0	NA	NA	NA	NA	NA	NA
268	53.3	80.4	109.0	134.0	156.0	NA	NA	NA	NA	NA	NA
270	55.0	82.5	112.0	137.0	159.0	NA	NA	NA	NA	NA	NA
272	56.7	84.7	114.0	139.0	161.0	NA	NA	NA	NA	NA	NA
274	58.5	87.0	117.0	142.0	164.0	NA	NA	NA	NA	NA	NA
276	60.3	89.3	120.0	145.0	166.0	NA	NA	NA	NA	NA	NA
278	62.2	91.6	123.0	147.0	169.0	NA	NA	NA	NA	NA	NA
280	64.1	93.9	125.0	150.0	171.0	NA	NA	NA	NA	NA	NA
282	66.1	96.3	128.0	153.0	174.0	NA	NA	NA	NA	NA	NA
284	68.1	98.7	131.0	157.0	180.0	NA	NA	NA	NA	NA	NA
286	70.1	102.0	133.0	163.0	NA	NA	NA	NA	NA	NA	NA
288	72.2	104.0	135.0	165.0	NA	NA	NA	NA	NA	NA	NA
290	74.4	107.0	138.0	167.0	NA	NA	NA	NA	NA	NA	NA
292	76.6	109.0	141.0	172.0	NA	NA	NA	NA	NA	NA	NA
294	78.8	112.0	144.0	176.0	NA	NA	NA	NA	NA	NA	NA
296	81.1	115.0	147.0	177.0	NA	NA	NA	NA	NA	NA	NA
298	83.4	118.0	150.0	181.0	NA	NA	NA	NA	NA	NA	NA

Table 4. Saturated vapor pressures of ammonia-water mixtures as a function of temperature and liquid composition

	Ammonia in liquid, WT%										
Temp. °C	0	10	20	30	40	50	60	70	80	90	100
	Water in saturated vapor, WT%										
50	100.0	23.6	8.86	3.61	1.58	0.755	0.403	0.237	0.147	0.0826	0.0
52	100.0	24.1	9.11	3.75	1.65	0.799	0.431	0.256	0.159	0.0903	0.0
54	100.0	24.5	9.35	3.89	1.73	0.845	0.460	0.275	0.173	0.0987	0.0
56	100.0	24.9	9.61	4.03	1.81	0.893	0.490	0.296	0.188	0.108	0.0
58	100.0	25.3	9.86	4.17	1.89	0.943	0.523	0.319	0.203	0.118	0.0
60	100.0	25.8	10.1	4.32	1.98	0.996	0.557	0.343	0.220	0.128	0.0
62	100.0	26.2	10.4	4.47	2.07	1.05	0.593	0.368	0.238	0.140	0.0
64	100.0	26.6	10.6	4.63	2.16	1.11	0.632	0.395	0.258	0.152	0.0
66	100.0	27.1	10.9	4.78	2.26	1.17	0.672	0.424	0.279	0.166	0.0
68	100.0	27.5	11.2	4.94	2.35	1.23	0.714	0.454	0.301	0.180	0.0
70	100.0	28.0	11.4	5.11	2.45	1.30	0.759	0.487	0.325	0.195	0.0
72	100.0	28.4	11.7	5.27	2.56	1.36	0.806	0.521	0.351	0.213	0.0
74	100.0	28.8	12.0	5.44	2.67	1.43	0.558	0.558	0.379	0.231	0.0
76	100.0	29.3	12.3	5.62	2.78	1.51	0.907	0.597	0.408	0.251	0.0
78	100.0	29.7	12.5	5.79	2.89	1.58	0.962	0.638	0.440	0.273	0.0
80	100.0	30.2	12.8	5.97	3.01	1.66	1.02	0.682	0.474	0.296	0.0
82	100.0	30.6	13.1	6.16	3.13	1.75	1.08	0.729	0.510	0.321	0.0
84	100.0	31.0	13.4	6.34	3.25	1.83	1.14	0.778	0.549	0.348	0.0
86	100.0	31.5	13.7	6.53	3.38	1.92	1.21	0.829	0.591	0.377	0.0
88	100.0	31.9	14.0	6.73	3.51	2.02	1.28	0.884	0.635	0.409	0.0
90	100.0	32.3	14.3	6.93	3.65	2.11	1.35	0.943	0.682	0.443	0.0
92	100.0	32.8	14.6	7.13	3.79	2.21	1.43	1.00	0.733	0.480	0.0
94	100.0	33.2	14.9	7.33	3.93	2.31	1.51	1.07	0.787	0.520	0.0
96	100.0	33.7	15.2	7.54	4.07	2.42	1.59	1.14	0.844	0.564	0.0
98	100.0	34.1	15.5	7.75	4.23	2.53	1.68	1.21	0.906	0.611	0.0

Table 5. Saturated vapor compositions of ammonia-water mixtures as a function of temperature and liquid composition

Methodology for recommended values

Fourteen potential sources of data were initially scanned to obtain vapor-liquid-equilibrium data. Of these, four sources (2, 7, 11, 12) contained no useful data for this study. A summary of acceptable data from the remaining ten sources is shown in Table 1. The type of data and range of conditions are also included on the table and show that both primary and smoothed experimental data were used in the comparative assessment.

Total pressure data are available from 0.02 bar up to 210 bar (critical envelope), temperatures from -75° to 316°C and liquid compositions from 7.0 to 99.9 Wt % H_2O. Precise vapor composition data are not as extensive, particularly in the ammonia-rich region. For example, above 40°C, only Gillespie et al and Macriss et al provide accurate data in the vapor composition range of 0.057 to 3.59 Wt % H_2O. Below 0°C, however, there are no precise data available.

Verification of analytical methodology

To facilitate the development of recommended values for vapor liquid-equilibrium of the NH_3-H_2O fluid, we utilized the Gillespie et al general approach. It includes an equation of state with a hard sphere expansion term and second and third virial coefficients, analogous to the Redlich-Kwong 40 equation, and the Redlich-Kister 39 activity coefficient equation, respectively.

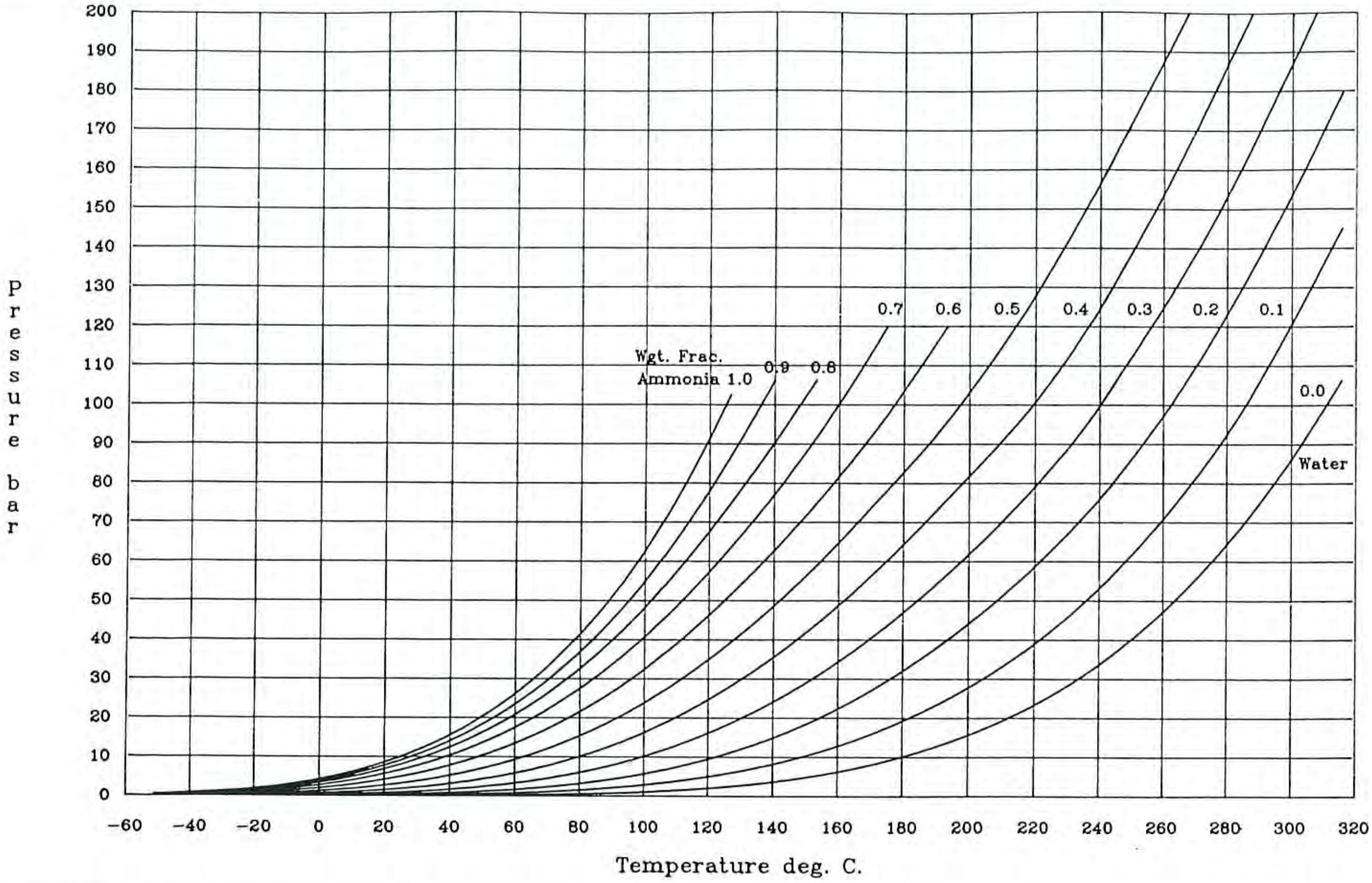

Figure 3. Pressure-concentration diagram (ammonia/water system)

We reviewed the Gillespie et al equations and made several modifications, as follows:

- Added an equation for fugacity, as none was provided by Gillespie et al.
- Substituted pure ammonia properties obtained by Doring 33 for similar values in the Matheson Gas Data Book, used by Gillespie et al.
- Substituted the liquid volume data of Jennings 5 for the liquid volume data developed by Gillespie et al.

With these modifications included, a new methodology for generating NH_3-H_2O vapor-liquid equilibrium data was formulated and compared to the data to ascertain its accuracy.

p-t-x Data

For convenience, equilibrium vapor pressures were calculated using the new methodology and compared to literature values on the assumption that temperature and composition were without error and, therefore, all experimental error was attached to the vapor pressure. A total of 355 individual comparisons were made covering all the data over the entire range of conditions shown in Table 1. Individual deviations between projected and measured values were averaged. The standard deviation and standard error of estimate were computed (shown in Table 2).

On the average, agreement is excellent between the projected values and data of Gillespie, et al (0.053% and 0.123% for smoothed and experimental values) and Macriss et al (0.297% and 0.3% for smoothed and experimental values). Good agreement, within 1% to 2%, was also obtained with data of Wucherer, Perman, Polak, and Clifford and Hunter. Including all data sources, average agreement was within + 5%.

p-t-x-y Data

The results of the comparison of vapor composition projections and data are presented in Table 3. Similar to total pressure calculations, it was assumed that temperature and liquid composition were without error, when computing vapor composition and pressure and, therefore, all experimental errors were attached to the vapor composition. The results of the comparison are shown below:

- Good agreement was obtained between values developed with the new methodology and the data of Gillespie et al, and Macriss et al, -0.16% to 2.1% on the average.
- General agreement was also obtained for all other data sources with deviations from experimental data ranging from -3.4% (Wucherer) to 3.9% (Guillevic).
- Using all the data, standard deviations were generally higher than those obtained for vapor pressure comparisons.
- The solid line in Figure 2 represents the thermodynamic prediction of vapor composition by the Gillespie et al approach as modified by the authors of this paper.

Recommended values

The recommended values for vapor-liquid-equilibrium are essentially based on the data of Macriss et al and Gillespie et al, for temperatures of -50° to 316°C and

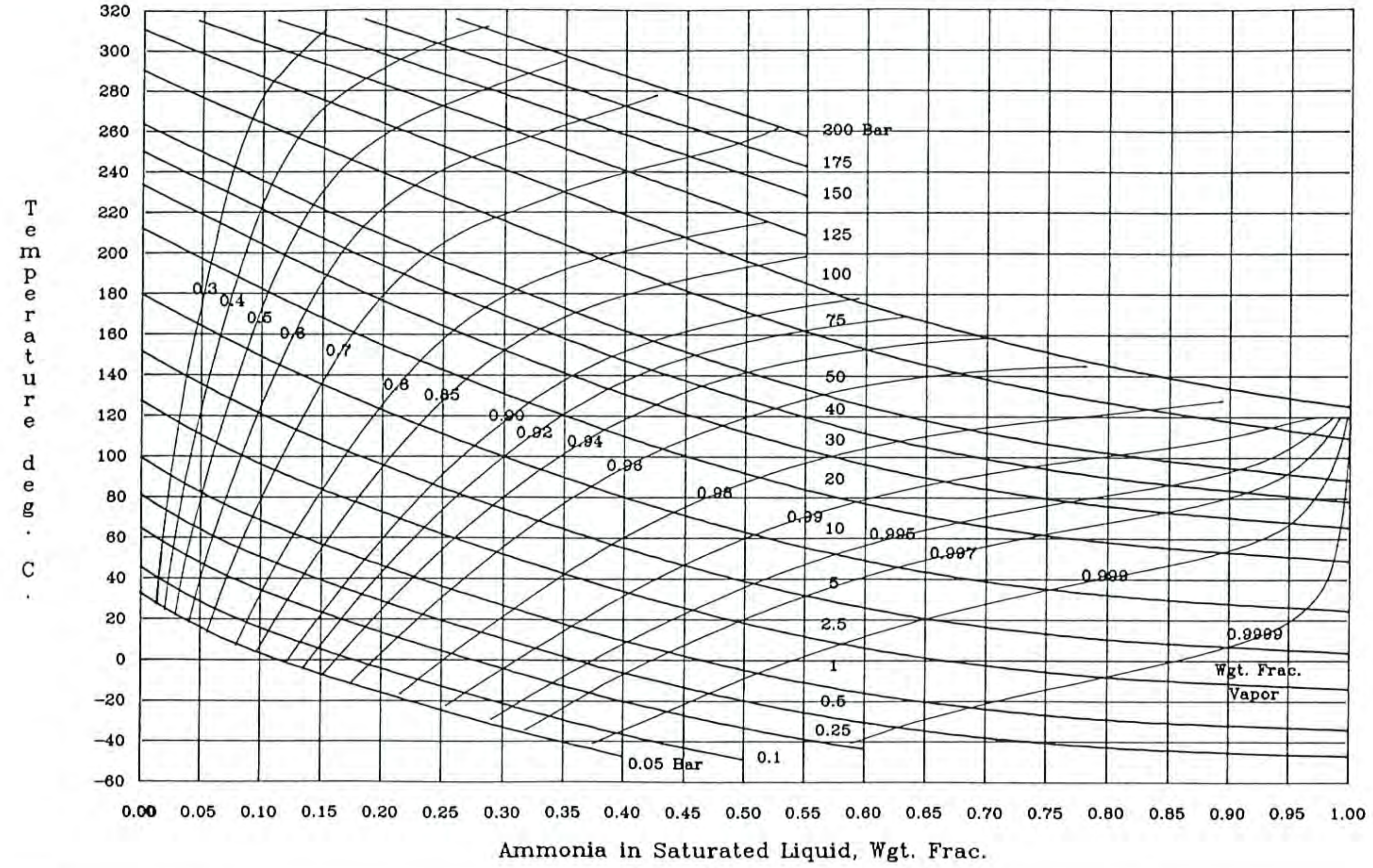

Figure 4. Temperature-concentration diagram (ammonia/water system)

pressures of 0.05 to 170 bar. To facilitate the generation of tabular values at regular intervals of temperature, pressure and concentration, the new equations of state were utilized, with coefficients derived by comparison to the actual data.

For the tables, small increments of temperature (2°C), liquid concentration (10 wt% NH_3), and pressure (1 bar, above 1 bar pressure) were used to present the data in detail. Examples of the tabular data are shown in Tables 4 (vapor pressure data) and 5 (vapor composition data). The equations were also used to present the data in various chart forms (p-t-x and t-x-p-y, etc.) over the entire range of conditions. Examples of the charts are shown in Figures 3 (p-t-x) and 4 (p-t-x-y).

The core of the new analytical methodology consists of the basic equation of state of Gillespie et al; correlating equations for the vapor phase (mixing rules, second and third virial coefficients and fugacity coefficients) and for the liquid phase (activity coefficients); vapor liquid density equations and correlations for partial molal volume; and equations for the fugacity of the pure compounds 33, 34, 35 (water and ammonia).

Liquid-phase density and enthalpy, and vapor-phase density and enthalpy recommended values have also been developed. Density values are based in part on the data of Jennings (liquid phase). Enthalpies of both phases are based on the heat of mixing data of Mollier 37, specific heat data of Macriss et al and equations of Ziegler and Trepp. Additional values for liquid phase viscosity (Pinovich 38) and thermoconductivity (Miller 36) have also been developed.

Space limitations do not permit comprehensive coverage of methodology development and results for the above mentioned properties. However, all of the above data will be published by IIR (International Institute of Refrigeration) in the near future.

Conclusions

- New data for NH_3-H_2O vapor-liquid-equilibria have extended the range of applicability of this fluid to advanced absorption heat pumps, refrigeration and power cycles. (e.g. Kalina).
- This study has consolidated all of the available data on vapor-liquid-equilibria, covering a range of conditions from the NH_3-H_2O three-phase boundary to 170 bar.
- Attempts to estimate equilibrium vapor compositions in the past, by means of empirical equations of state or polynomial expressions, have not been successful, probably due to the non-ideal nature of the NH_3-H_2O solutions. Large discrepancies were found between estimated values and actual data.
- These differences have been assessed and a recommended set of NH_3-H_2O vapor-liquid-equilibrium data has been formulated based on actual data.

References available upon request from the Heat Pump Center.

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Second Law Analysis for an Absorption Chiller

Second Law Analysis should not be confused with an Exergy-Analysis. Instead of calculating exergy losses, one can use a second law analysis to quantitatively determine the loss in refrigeration output or the required additional heat input caused by each loss mechanism. The results do not depend on the choice of a reference state.

Introduction

Absorption technology presently experiences an intensive renewed interest caused by the ozone and other environmental problems of several working fluids used in compression technology. Building energy efficient and cost effective advanced machinery requires pinpointing the major loss mechanisms to establish the connection between additional running costs caused by these loss mechanisms and investment costs required to reduce them. It has been proposed in the past that an exergy analysis may be helpful to achieve these goals.[1]

Yet doubts have been raised[2,3] that the exergy concept, representing a very special and limited formulation of the second law, would in general be as helpful as exergy analysts suggest. Instead of calculating exergy losses (i.e., the loss in power output of a reversible power station operating against a fictitious reference temperature level) it has been proposed that the quantitative knowledge about the loss in product output caused by individual irreversibilities or about the additional input required to run a process at a given output level would be more informative and helpful for optimization. These quantities can be calculated by applying a rigorous second law analysis. In contrast to exergy analysis, this analysis is free from any assumption about an "ambient state" or a "dead state."

To demonstrate the application of the method, a simple single-stage chiller working with $LiBr/H_2O$ will be analyzed. Since confusion in terminology exists about concepts like efficiency, effectiveness, exergy efficiency, second law efficiency, etc., we will first define in general terms the quantities we are using to apply second law analysis.

The efficiency or coefficient of performance (COP) is the ratio of the desired product output to the input required to run the process. If both quantities have the same dimension, like energy, this efficiency is a dimensionless quantity. But this is not a must. For an ammonia factory this quantity may have the dimension kg ammonia/kJ heat. In energy conversion systems, this efficiency is usually called "First Law Efficiency" or for absorption heat pumps sometimes "heat ratio." The following definitions are used:

$$\eta = \frac{\text{Product (real)}}{\text{Input (real)}} \quad (= \text{COP}) \qquad (1)$$

$$\eta\,(\text{max}) = \frac{\text{Product (max)}}{\text{Input (real)}} = \frac{\text{Product (real)}}{\text{Input (min)}} \qquad (2)$$

The maximum product output for the given real input can be found by applying second law and considering the limit of reversibility - at least for those loss mechanisms which one wants to evaluate. The same holds for the minimum input, required to achieve the given output.

No assumptions have to be made about a process with which the real process must be compared. The operational procedure defines the "ideal process" as the process considered yet in the limit of reversibility. This limit by no means must be a Carnot process. By what technical means reversibility can be achieved is a separate question.

For the "second law efficiency" or the "quality factor" g for a process we are using the following definition:

$$g = \frac{\eta}{\eta(\text{max})} \qquad (3)$$

$$= \frac{\text{Product (real)}}{\text{Product (max)}} \quad \text{(for fixed input!)}$$

$$= \frac{\text{Input (min)}}{\text{Input (real)}} \quad \text{(for fixed output!)}$$

η(max) is the maximum efficiency which would exist if the irreversibilities in consideration causing losses in product output are thought to be zero. Although η(max) quite often consists of Carnot type factors, it was not assumed that the ideal process is a Carnot process. For a Lorenz-process one also gets for η(max) Carnot type factors, yet the temperatures are entropic averages.

The quality factor g measures how close the performance of the real process is approaching the limits imposed by the second law. It signifies how much improvement is still possible, at least in principle. How much additional investment is required to achieve this improvement is certainly the next question. It should be noted that the second law efficiency as defined in Equation (3) is not identical to those definitions used for exergy efficiencies. Equation (3) does not depend on assumptions about an ambient state.

For optimization it would be desirable to know the impact of the individual loss mechanism on the product output or on the required additional input to achieve a given product output. For this purpose it is useful to realize that the quality factor g has a further simple but rather instructive interpretation: Using the definition Equations (1) to (3), one finds for the loss in product output due to irreversibilities Equations (4) and (5). Similarly, one finds for the required additional input Equations (6) and (7).

Equations (4) to (7) are useful relations to establish quantitatively the connections between the individual loss mechanisms and the loss in product output and/or the additional input required. In contrast to exergy for the input and product output, real market prices exist. Thus the connection to economy by considering the correlation between the required investment cost and the increase in product output or decrease in the required input can be established.

$$\frac{\text{Product(max)} - \text{Product(real)}}{\text{Product(max)}} = \frac{\Delta P}{P(\text{max})} = 1 - g \tag{4}$$

$$\frac{\text{Product(max)} - \text{Product(real)}}{\text{Product(real)}} = \frac{\Delta P}{P} = \frac{1}{g} - 1 \tag{5}$$

$$\frac{\text{Input(real)} - \text{Input(min)}}{\text{Input(min)}} = \frac{\Delta I}{I(\text{min})} = \frac{1}{g} - 1 \tag{6}$$

$$\frac{\text{Input(real)} - \text{Input(min)}}{\text{Input(real)}} = \frac{\Delta I}{I} = 1 - g \tag{7}$$

$$\eta_{(\text{real})} = \frac{\eta_{(\text{max, T})}}{1 + \eta_{(\text{max, T})} \cdot \frac{T_1 T_2}{T_2 - T_1} \sum_{1}^{6} \delta s_i / q_0} \tag{8}$$

With:

$$\eta_{(\text{max, T})} = \frac{T_2 - T_1}{T_2} \Big/ \frac{T_1 - T_0}{T_0} \tag{9}$$

$$\frac{\Delta q_2}{q_2(\text{real})} = \eta_{(\text{real})} \cdot \frac{T_1 T_2}{T_2 - T_1} \sum_{1}^{6} \delta s_i / q_0(\text{real}) \tag{10}$$

$$\frac{\Delta q_0}{q_0(\text{real})} = \eta_{(\text{max, T})} \cdot \frac{T_1 T_2}{T_2 - T_1} \sum_{1}^{6} \delta s_i / q_0(\text{real}) \tag{11}$$

$$\eta_{(\text{real})} = \frac{\eta_{(\text{max, t})}}{1 + \eta_{(\text{max, t})} \cdot \frac{t_1 t_2}{t_2 - t_1} \sum_{i-1}^{10} \delta s_i / q_0} \tag{12}$$

With:

$$\eta_{(\text{max, t})} = \frac{t_2 - t_1}{t_2} \Big/ \frac{t_1 - t_0}{t_0} \tag{13}$$

Although Equations (4) and (5) look very similar to Equations (6) and (7), one should keep in mind that the first two relations are derived under the condition of fixed input whereas for the other two relations fixed output has been assumed. This restriction is not of relevance if the total changes P or I are considered. Yet it is important when g is broken up into the contributions of individual loss mechanism.

In a former publication[4] the second law was applied to absorption devices. For terminology, see Figure 1 (for simplicity it will be assumed $T_1 = T_1$). The following irreversibilities causing an entropy increase si have been identified:

δs_1 = desuperheating of the fluid between T_2 and T_1

δs_2 = cooling of the fluid from T_1 to T_0 (throttling)

δs_3 = heating of the fluid from T_0 to T_1

δs_4 = heating or cooling of the weak (in respect to absorbent) solution to T_2

δs_5 = cooling or heating of the strong (in respect to absorbent) solution to T_1

δs_6 = entropy generation in the solution heat exchanger

δs_7
δs_8 = heat transfer between heat
δs_9 carrier fluids and working
δs_{10} fluids

δs_{11} = all the rest, e.g., irreversibilities of the solution pump pressure drops, heat conduction, radiation losses, etc.

With the internal temperatures T_0, T_1, T_2 given, the real efficiency $\eta = q_0/q_2$ can be written as Equation (8).[4]

The sum over the irreversibilities includes in this case only internal irreversibilities, i.e., not the heat transfer to the heat carrier fluids.

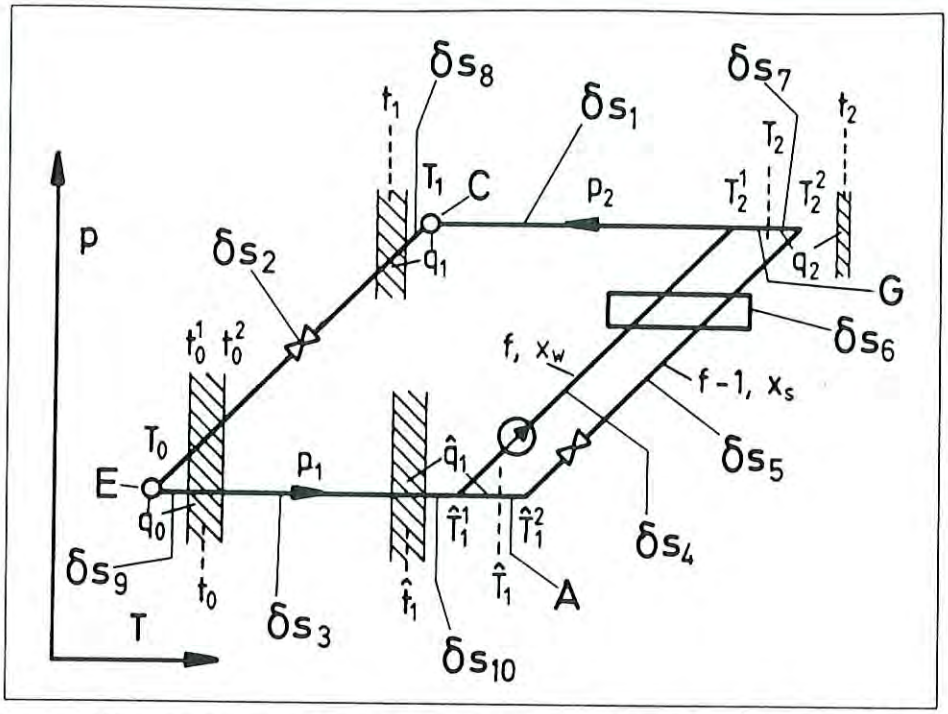

Figure 1. Temperatures and pressures for an absorption refrigerator (the δ s_i indicate loss mechanism, as described in the text)

With Equation (7) one finds Equation (10) for the additional input Δq_2 due to internal irreversibilities in units of the real existing input q_2(real). This equation can also be interpreted as the real reduction in heat input Δq_2 by removing the irreversibility labelled with the index i.

Similarly the increase in refrigeration Δq_0 in units of the real refrigeration output (at constant input q_2) can be calculated as Equation (11).

It should be noted that Equations (10) and (11) depend only on real process temperatures and not on an additional reference temperature as exergy losses do. (Note: If someone has more practice in calculating exergy losses, he still may apply Equations (10) and (11) by inserting $\delta s_i = \delta Ex^{(i)}/T_{amb}$. Dividing the exergy loss by T_{amb} removes the ambiguous reference state involved in the exergy concept.)

Equation (11) multiplied by the quality factor g (Equation [3]) yields Equation (10), as it must be according to Equations (5) and (7).

In Reference 4 the following data have been used:

T_0 = 2°C
T_1 = 38°C
T_2 = 80°C
x_s = 0.595
x_w = 0.570 (i.e., f = 16)
c = 4.19 kJ/kg K
c_p = 1.90 kJ/kg K
r = 2490 kJ/kg
c_s = 1.97 kJ/kg K
c_w = 2.09 kJ/kg K
solution heat exchanger efficiency η_s = 0.80.

With this data one finds for η(real) = 0.76 and η(max, T) = 0.91. The quality factor g(T) therefore amounts to g(T) = 0.835. g(T) measures the quality of the process taking into account the internal irreversibilities 1 to 6 only.

Table 1 shows the results for Equations (10) and (11) using the data of Reference 4. The largest contribution comes from the solution cycle, where the desuperheating, the cooling of the liquid working fluid by flashing and the heating up of the vapor add up to only about 6%. This is only the case for water for which the characteristic quantities cT/r and c_pT/r are the smallest for all so far known working fluids. Improving the solution heat exchanger efficiency to 100% would yield η = 0.83 and thus g(T) = 0.91. The column 4-6 would be lowered to 4.2% in the refrigeration loss and to 3.8% in the heat input.

As the next step, heat transfer to the heat carrier fluids is included. The temperature t_0, t_1, t_1 and t_2 are entropic averages, each over the temperature span of the corresponding heat carrier fluid. In general, the mean temperature, e.g., $t_0 = (t_0^{(1)} + t_0^{(2)})/2$, is a very good approximation. (It should be noted that the entropic temperature difference $|T_i\text{-}t_i|$ is in general not identical with the mean logarithmic temperature difference, determining the heat transfer surface.)

Irrev. Nr.	1	2	3	4 - 6		
$\frac{\Delta q_0}{q_0(\text{real})}$ [%]	1.55	3.28	1.45	13.80	$\sum_1^6 = 20.1$	$\frac{1}{g(T)} - 1 = 19.8$
$\frac{\Delta q_2}{q_2(\text{real})}$ [%]	1.25	2.75	1.20	11.50	$\sum_1^6 = 16.7$	$1 - g(T) = 16.5$

Table 1. Gain in refrigeration output (in units of the existing refrigeration output) and reduction of heat input (in units of the existing heat input), with the corresponding irreversibility being eliminated; η(real) = 0.76, η(max,T) = 0.91, g(T) = 0.835

Irrev. Nr.	7	8	9	10		
$\frac{\Delta q_0}{q_0(\text{real})}$ [%]	17.3	21.0	25.7	22.7	$\sum_1^{10} = 106.8$	$\frac{1}{g(t)} - 1 = 105.6$
$\frac{\Delta q_2}{q_2(\text{real})}$ [%]	7.0	8.5	10.4	9.2	$\sum_1^{10} = 51.8$	$1 - g(t) = 51.4$

Table 2. [Continuation of Table 1] Additional possible gain in refrigeration output (in units of the existing refrigeration output) and reduction of heat input (in units of the existing heat input) if the internal temperatures T_I would approach the external temperatures t_i; η(real) = 0.76, η(max,t) = 1.566, g(t) = 0.486

In terms of the external temperatures t_i the real efficiency $\eta(\text{real}) = q_0/q_2$ can be written as Equation (12).[4]

Equation (12), taking into account the heat transfer, yields exactly the same result $\eta(\text{real}) = 0.76$ as Equation (8), which certainly must be the case as long as t_i and $|T_i\text{-}t_i|$ are given.

Yet the quality factor g(t) is different, since the maximum efficiency now refers to the external temperatures. (To achieve the maximum efficiency with a single stage machine would require operating the unit with a new fluid corresponding to vapor pressure lines connecting the external temperatures!)

With $|T_i\text{-}t_i| = 5$ K, i.e., $t_0 = 7°C$, $t_1 = 33°C$ and $t_2 = 85°C$, Equation (11) yields η (max, t) = 1.565 and thus g(t) = $\eta(\text{real})/\eta(\text{max, t})$ is reduced to 0.486.

In Table 2 the additional gain in refrigeration output at constant heat input and the reduction of the heat input at constant refrigeration output are shown. These values are of the same order of magnitude as that for the solution cycle in Table 1. The sum of the possible gain in refrigeration in Tables 1 and 2 adds up to 106.8%, which must be identical to (1 - g(t))/g(t). The reduction of heat input in Tables 1 and 2 must add up to 1 - g(t).

As already indicated the losses due to heat transfer are not independent from the internal loss mechanisms. These correlations will be discussed elsewhere in more detail.

Summary

This article can be summarized as follows: Second law analysis can predict quantitatively how large the contribution of individual loss mechanisms to the total loss in product output is. Vice versa: For given product output it can be predicted how much additional input is required due to individual irreversibilities. The results do not depend on assumptions about a reference state, as do the analyses given by Keenan[5], by Ch. Cheng and Y. Shih[6] and by R. Braun et al[7] for absorption cycles. These papers are examples for an exergy analysis. The recent article by Bŏsnjaković et al[8] is closer to a second law analysis. Besides exergy losses the loss in heat output is calculated.

A second law analysis for compressor heat pumps can be found in References 8, 9, and 10.

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Bibliographic Review

Heat Pumps in Japan, Products and Technical Trends (Second Edition), December 1988. Published by the Heat Pump Technology Center of Japan. 232 pages.

This publication is an update of a previous report published in early 1987. As indicated by the title the report gives an overview of the products and technical trends in the field of heat pumps in Japan. The topics covered include the general situation of heat pumps, production and shipment statistics, trends of equipment and systems, trends of heat pump utilization, research and development, promotional measures, measures for the CFC problem, and cogeneration. A section on statistical data gives an overview of some important energy statistics in Japan. Contact the HPC to obtain a copy of this report.

Japan HVAC & R Directory (15th Edition). This directory is produced yearly and contains information on the HVAC & R industry in Japan. Information is given on manufacturers, importers and exporters, products and services, and associations. Of particular interest are the detailed production and shipment statistics given for the time period 1983-1988 for 56 different product types. Tables of detailed import and export statistics are also given. To order a copy, contact JARN Ltd., Hosokawa Bldg., 1-16, Akasaka, 1-chome, Minato-ku, Tokyo 107, Japan.

World Energy Conference, Report 1988. Environmental Effects Arising from Electricity Supply and Utilisation and the Resulting Costs to the Utility. Published by World Energy Conference, 34 St. James' Street, London, SW1A 1HD, United Kingdom, October 1988.

This study was initiated by the Conservation Commission (now the Conservation & Studies Committee) of the World Energy Conference (WEC) and was prepared by the WEC Study Committee on The Environmental Effects Arising from Electricity Supply and Utilisation and the Resulting Costs to the Utility. The first main task of this study was to compare the impact on the environment and on man of the supply and utilisation of electric energy with the impact of systems using fuels locally. The second main task of the study was to investigate the cost to the utility of environmental control measures in the power plant.

In approaching the first main task, emphasis was placed on comparing the direct path of local fuel use to the indirect path via conversion of the same fuel to electricity. Regarding the scope of environmental effects, all kinds had to be discussed; quantitative data and worked examples could, however, be given only as far as atmospheric emissions are concerned.

Regarding actual atmospheric conditions, it was found that for most of the emissions and most of the regions, the relative contribution to total emission from power stations with modern emission control technology is small. In order to deduce ground level concentrations (GLC) from emissions, computer calculations using dispersion models based on dry deposition were performed in the Netherlands and in Austria. Taking the small furnace as the basis, the following relative GLC increases for the same source term (i.e., dispersion ratios, and - assuming no conversion - transfer ratios) were obtained: about 1% for a large (combined heat and power, CHP) plant and less than 0.5% for a very large (power) plant.

A number of examples comparing the environmental effects (atmospheric emissions as well as ground level concentrations) of energy paths - direct fuel use and use of electricity - are worked out. It is found that the electric path generally causes emissions that are considerably lower if the same fuel is considered by the two paths leading to the same energy service. In terms of GLC, the advantage of the electric path is even more pronounced.

For more information, contact the World Energy Conference.

Swedish Heat Pump Projects 1986-1987. Research - Development - Full-scale Experiments. BFR Document D5:1989. Bertil Malmqvist, editor. Published by the Swedish Council for Building Research, Sankt Goeransgatan 66, S-11233 Stockholm, Sweden.

Several government organizations and civil service departments provide grants and loans for energy research in Sweden.

This catalog of projects is a compilation of the heat pump projects being carried out on government grants and/or loans in Sweden. Only projects involving research work are listed. Subsidized heat pump installations for general energy conservation, not research, are not included.

Privately financed heat pump projects have not been listed, because such sources are generally disinclined to inform third parties of their future products.

This is a continuation of the earlier compilation of heat pump projects "Swedish Heat Pump Projects 1979-1983" (BFR Report D24:1984) and "Swedish Heat Pump Projects 1984-1985" (BFR Report D6:1986).

For more information, contact the Swedish Council for Building Research (BFR).

Preliminary Equations of State for the Non-ozone Depleting Refrigerant R134a. (Vorläufige Zustandsgleichungen für das ozonunschädliche Kältemittel R134a.) *Ki Klima-Kälte-Heizung* 2/1989, p. 69-71.

The stratospherically safe refrigerant tetrafluoroethane (R134a) is a possible substitute for R12. Following the publication of the first measurements of R134a's vapor pressure, saturated liquid density, and pressure on five isochores in the gas range, in this work fairly simple equations are formulated by which the following properties in the region important to refrigeration can be calculated: vapor pressure, specific volume, specific enthalpy, and specific entropy. These new equations fit the experimental values very well. They must be regarded, however, as preliminary because they rely only on relatively few measurements. For the liquid range, only a few measurements for the saturated liquid are available.

Proceedings of the JAR International Symposium on Recent Developments in Heat Pump Technology, March 9-10, 1988, Tokyo Garden Palace, Tokyo, Japan. Published by the Japanese Association of Refrigeration (JAR), San-ei Bldg., 8 San-ei-cho, Shinjuku-ku, Tokyo 160, Japan.

Thirty-two papers are included in these proceedings. A total of 228 individuals attended the symposium including 78 from outside of Japan. The symposium consisted of six sessions. Two of these were panel discussions with the following themes: "Towards Higher Performance Domestic Heat Pumps" and "Current State and Future Prospects of Large Industrial Heat Pumps." Following are abstracts of articles which appear in these proceedings.

Thermophysical Properties of NARBs and Their Effectiveness in Heat Pump Applications. Koichi Watanabe, Department of Mechanical Engineering, Keio University, pp. 99-109.

This paper presents an overview of the thermophysical properties of nonazeotropic refrigerant blends (NARBs) which have been considered prospective especially for advanced vapor-compression heat pump systems. After introducing some general backgrounds on the thermodynamic behaviors of NARBs, the current state of the art on thermophysical properties research for NARBs which are also considered as possible candidates for CFC alternatives is reviewed. Thermophysical properties discussed include not only thermodynamic properties such as PVTx properties, vapor-liquid equilibria, critical parameters, etc., but also essential transport properties such as viscosity and thermal conductivities. The emphasis, however, is given to the most updated results due to extensive research projects partially supported by the Japanese Association of Refrigeration (JAR) on the occasion of its 60th anniversary of foundation in 1985.

Recent Advances in Compressor Technology. Raymond Cohen, Ray W. Herrick Laboratories, Purdue University, Indiana, USA, pp. 26-31.

An annotated review of the recent literature is presented, covering for the most part the 1986 Purdue compressor conference, and previewing the 1988 Purdue compressor conference. A few other survey papers are highlighted. Comments are presented about the most common positive displacement refrigerant compressors; namely, reciprocating, rotary, screw and scroll compressors. Comments are also made concerning the engineering technologies related to these compressors; namely, valves, modeling and simulation, noise and vibration, performance and efficiency measurement and prediction, etc.

Development of Absorption Heat Pumps with Organic Working Fluids for Refrigeration and Heating Applications. Irene Borde, The Institutes for Applied Research, Ben-Gurion University of the Negev, Israel, pp. 123-132.

The need to utilize industrial waste heat and low-grade energy sources has stimulated the search for organic working pairs having both the thermodynamic, heat transfer and transport properties and the chemical stability required for cost-effective absorption heat pumps. In this context, the latest developments in heat pumps using organic working fluids are surveyed. After systematic investigation of many potentially interesting working fluids, our research focused on halohydrocarbon fluids (especially monochlorodifluoromethane) as the volatile component. Among absorbents examined for possible combination with the halohydrocarbons were representatives of various classes of organic compounds, all of which are commercial available and relatively inexpensive. The ultimate evaluation and selection of a promising working fluid combination is based on the totality of the expected performance characteristics as calculated from advanced cycle and systems analysis and predicted by computerized simulation models. The basic thermodynamic data for the new working fluids were measured and evaluated in terms of enthalpy-concentration diagrams. For monochlorodifluoromethane, amide compounds were found to be most promising group of absorbents. To verify the evaluations made with the simulation model, a demonstration unit was designed and operated with several refrigerant-absorbent pairs. A number of industrial units are at various stages of construction and running in. The main features of these units are nontoxicity of fluids, low energy cost, low installation and maintenance costs, low electricity consumption, and reliability.

Hyperabsortion - a New Absorption Heat Pump Concept. Robert A. Macriss, Energy Utilization, Institute of Gas Technology, Chicago, Illinois, USA, pp. 134-143.

The conventional absorption cycle has been commercialized for at least 30 to 40 years and has played a significant role in current developments of gas-fired, absorption-type heat pumps for residential and commercial applications. The major inherent limitation of the conventional absorption cycle is its relatively low coefficient of performance (COP) even under the best of conditions. Potential approaches to achieving higher efficiencies are either advanced, multistage-multieffect cycles, new working fluids or radically new cycles. The level of complexity of advanced cycles, the requirement for larger heat transfer surfaces, and the need for some to operate at high temperatures and pressures, may prolong the time that such equipment could reach the market. On the other hand, new working fluids to date have been less than satisfactory when compared to the traditional NH_3-H_2O and H_2O-LiBr absorption fluids. Insufficient absorption rates, stability and corrosion, large heat transfer requirements, large solution pumping rates, toxicity and cost represent the new fluid drawbacks. This paper presents a preliminary assessment of a radically new cycle, termed the "Hyperabsorption" cycle, which uses saturated salt solutions (three phases present). Literature data on fluid systems, cycle formulations and conceptualization, and performance calculations are presented.

Current and Future Perspectives of Absorption Heat Pumps in Commercial Applications in Japan. Shigekichi Kurosawa, Total Energy System Development and Service Dept., Tokyo Gas Co., Ltd., Japan, pp. 145-155.

Absorption heat pumps embody optimum heat recovery technologies that recover low temperature waste heat and convert it into high temperature thermal energy. All-out development of absorption heat pumps in Japan began 10 years ago when the Agency of Industrial Science and Technology, Ministry of International Trade and Industry, took it up as one of its major objectives for 1977. Driven by heat energy, absorption heat pumps have made their way into commercial and industrial field alike. Recent trends include the use of heat recovery systems in district cooling and heating plant and "intelligent" building applications, some systems even recovering the heat from river water. This paper first introduces some examples of utilizing absorption heat pumps in urban energy systems amid Japan's active city redevelopment boom at present. Currently deployed absorption heat pumps are of a water heat source type. They are mostly used in cases where their heat source system is relatively large, relying on readily available waste heat. Instead, we are aiming ultimately at implementing an air heat source absorption heat pump. As a first step toward this goal, we have successfully developed the world's first H_2O-LiBr based, air-cooled, gas-fired absorption water chiller-heater using a double effect cycle. This is what this paper discusses following introductory descriptions of absorption heat pumps. The new water chiller-heater belongs to the next generation of heat pumps we are working on. The paper concludes by outlining current and future perspectives of the ongoing research and development of absorption heat pumps.

News Briefs

HPC Internal

IEA Heat Pump Center Newsletter Mailing List Update. The IEA Heat Pump Center has started with the September and December 1988 Newsletter issues an updating of its subscriber mailing list. The response to this effort has shown us that there is a broad interest in the Newsletter. It has also shown us the need for a revision of the existing five year old mailing list. With this phase of the updating now complete, the National Teams in each member country are undertaking efforts to insure that the Newsletter reaches more interested institutions and individuals to help support the diffusion of heat pump technology. Encouraging results from this latter effort have already been obtained in Canada, Norway, the USA, and the Federal Republic of Germany. The Heat Pump Center would like to thank all new and continuing Newsletter subscribers for their continued interest in the Newsletter.

Information Exchange. Information exchange has been established between the IEA Heat Pump Center and the International Center for Energy Storage (ICES).

Heat Pumps combined with energy storage are of interest for building heating and or cooling applications. It is well known that thermal storage allows the system to operate efficiently by serving as a buffer between the heating requirements of the building and the heat pump. Use of a thermal store allows the heat pump to operate during periods when electricity tariffs are lower or enables the heat pump to meet short duration load peaks (for example during cold weather). For more information on ICES write: CISE (Centre International Pour Le Stockage D'Energie), Place Sopie Laffitte, Sophia Antipolis, F-06560 Valbonne, France.

North America

ARI Appoints Director of Research and Technology. The Air Conditioning and Refrigeration Institute (ARI) has appointed Mr. J.M. Calm as its Director of Research and Technology. This position was established in early 1988 by ARI's Board of Directors to assist ARI's Technical Committee in identifying government and utility research projects and in targeting these towards the research needs of its members. ARI plans to coordinate the research being funded by the public sector with that being done by its member companies. This will help to avoid duplication of work. The new Director of Research will work with ARI member companies to identify research needs which the public sector could carry out in the future. One of the priorities is research on new CFC refrigerants. At ARI's request the National Institute for Standards and Technology, NIST, (formerly the National Bureau of Standards) has expanded their data collection on new refrigerants. Eleven manufacturers have agreed to provide data to the NIST. (The NEWS, November 28, 1988 and February 6, 1989)

Europe

Workshop Proceedings Available. Workshop Proceedings, The IEA Heat Pump Center's Future Activities and Organization. HPC-WR-4, January 1989, Published by the IEA Heat Pump Center, 150 pages. (This publication is free-of-charge; see back cover for ordering information.)

To develop a detailed program of work and organization for the next working period which begins in 1990, the Center's governing body (Steering Committee) established a special Subcommittee. One of the activities of the Subcommittee was the organization of a Workshop on the Heat Pump Center's Future Activities and Organization. This Workshop was held in Mainz, Federal Republic of Germany, on January 23 and 24, 1989.

At the Workshop thirty-six invited representatives from governmental organizations, research institutions, and industry from twelve IEA/OECD countries discussed improvement of the future role of the Center in directing available heat pump technologies and developments into environmentally sound and acceptable applications.

As a basis for the Workshop a questionnaire, prepared by the Subcommittee, was sent to the representatives of the Heat Pump Center in the member countries.

The results of the questionnaire as well as the discussions at the Workshop showed that the continuation of the Heat Pump Center as a forum for international cooperation was unanimously supported. Of the past and present activities the quarterly IEA Heat Pump Center Newsletter was identified as the most important and productive. Workshops for the evaluation of priority areas, possibly followed by more detailed analysis work, were largely supported as major elements of a future program. The questionnaire answers also indicated the need for a strengthening of the governing body of the Center and the role of the National Teams. The present organization and financing of the Center was also seen as adequate but more heat pump industry involvement is needed.

Additional input to the Workshop came through six keynote speeches. Two of these, from the United States of America and the Federal Republic of Germany, analyzed the heat pump industries future needs for international cooperation and how the Heat Pump Center could meet these needs. A second presentation from Germany dealt with the need for new refrigerants to replace those which adversely affect the environment. This is a need shared by the refrigeration and air conditioning industries. Of interest was the presentation from Japan on experiences with their National Heat Pump Technology Center. Suggestions for the future direction of the Heat Pump Center and funding from private industry were made. The views of the IEA Committee on Research and Development Review Team, as presented by T. Boström, generally confirmed the results of the questionnaire. The strong support of the Review Team for the Heat Pump Center's role as the secretariat of the Implementing Agreement on Advanced Heat Pumps was also identified during the Workshop. Finally, G. Lorentzen in his presentation identified the heat pump as an important element in building a sustainable energy system for the future.

An important aspect of the Workshop was the discussions among the four working groups concerning six specific topics. The results of these discussions form an important element for the final report of the Subcommittee on the Heat Pump Center's future activities and organization.

The Workshop in Mainz has provided a framework for a new IEA Heat Pump Center. The task remaining is to establish a work program and organizational structure which will be able to support the increasingly important role of heat pumps in energy conservation and environmental protection.

JIGASTOCK 88. An international conference on thermal storage and geothermics (JIGASTOCK 88) was held October 18-21, 1988 in Versailles, France. Approximately 250 persons participated in this conference. Of interest to the heat pump community was a general impression from the workshop that there has been a slow down in new initiatives and projects in the area of thermal storage worldwide. On the other hand, application of thermal storage to commercial building heating and cooling systems having heat pumps "seems to have a future in certain cases." (ICES Newsletter No. 9, January 1989.)

55900 Electric Heat Pumps in Germany. A recent survey performed and published at the end of 1988 by the VDEW (Vereinigung Deutscher Elektrizitätswerke), an association of electric utilities in the Federal Republic of Germany, showed that at the end of 1987 there were 55900 electrically driven heat pumps in operation for building heating. The survey was based on data and best estimates supplied by the 643 member utilities of the VDEW. The total number of electric heat pumps in 1987 decreased by 121 systems amounting to 660 residences. This is a 0.2% decrease compared to 1986. The total installed capacity has decreased by 1.3MW (0.35%). The detailed survey also revealed that 90% of the electric heat pumps are in one or two family residences and 3.5% are installed in multifamily houses. 90% of the installed systems fall into the two capacity ranges of 2-5kW and 5-10kW. Fifty-six percent of the systems in operation are bivalent, 54% use air as a heat source, 31.5% water, 10.6% ground, and 4.3% other sources (waste heat, solar absorbers, etc.). For more information the VDEW can be contacted at: Postfach 701151, 6000 Frankfurt 70, Federal Republic of Germany.

ISH Frankfurt, March 14-18, 1989. At the ISH (International Trade Fair, Sanitation, Heating and Air Conditioning) in Frankfurt, Federal Republic of Germany, 45 manufacturers and suppliers of heat pump units and components were represented. Twenty-two of these offered domestic hot water heat pumps. The interest in these systems has remained stable in Europe. Twenty-four companies offered air-to-water heat pumps, seventeen water-to-water, thirteen air-to-air, and ten brine-to-water units. Of the 45 manufacturers and suppliers 30 were from the Federal Republic of Germany; four from Italy; two each from Austria, Denmark, and Greece; and one each from France, Switzerland, Belgium, Turkey, and the German Democratic Republic. Impressions gained from the Fair indicate that the market for heat pumps in Europe is still limited to small volume manufacturing.

Editor's Note:

For subscribers in Germany and Austria, two German language brochures dealing with heat pumps are enclosed. The titles are "Dieselmotor-Wärmepumpenanlagen in Kfz-Betrieben" and "Abwärmenutzung in kleinen und mittleren Betrieben." If you are a subscriber in another member country and are interested in receiving these brochures, contact the Heat Pump Center.

Schedule of Conferences

July 5-7, 1989

Bristol (UK); **Meeting on the Impact of Electrotechnology on the Refrigeration/Heat Pump Industries (IMPEL).** Contact: Univ. of Bristol, Faculty of Engrg, ATTN: Dr. R.T. Moses, Queen's Bldg., Clifton, Bristol BS8 1TR, UK.

July 11-13, 1989

Nancy (France); **2nd European Conference on Thermoelectrics.** Sponsored by Ecole des Mines de Nancy; Lab. de Physique du Solide; Institut National Polytechnique de Lorraine. Contact: Ecole des Mines de Nancy, Attn: Prof. S. Scherrer, Parc de Saurupt, F-5400 Nancy, France.

August 6-9, 1989

Philadelphia, Pennsylvania (USA); **National Heat Transfer Conference and Exhibition.** Contact: American Society of Mechanical Engineers, United Engineering Center, 345 East 47th St., New York, NY 10017 USA.

August 27-September 1, 1989

Sarajevo (Yugoslavia); **CLIMA 2000 (The 2nd World Congress on Heating, Ventilating, Refrigerating and Air Conditioning).** Sponsored by the Federation of Representatives of European Heating and Ventilating Associations (REHVA), ASHRAE, and IIR. Contact: Organizing Committee of CLIMA 2000, Masinski fakultet, Prof. Dr. Emin Kulic, 71000 Sarajevo, Omladinsko setaliste bb, Yugoslavia, telephone 071/642071, telex 41 529 IPES YU.

September 4-8, 1989

Kobe (Japan); **ISES Solar World Congress and Exhibition: Clean and Safe Energy Forever.** Sponsored by International Solar Energy Society (ISES), Japan Solar Energy Society (JSES), and New Energy Development Organization (NEDO). Contact: International Solar Energy Society, 19 Albemarle St., London W1X 3HA, United Kingdom.

September 18-21, 1989

Seoul (Republic of Korea); **International Conference and Exhibition on Energy Sources Management and Energy Saving Technology and Equipment (KORENERGY '89).** Contact: SHK International Services Ltd., 22/F, 151 Gloucester Rd., Hong Kong.

September 27-28, 1989

Gaithersburg, Maryland (USA); **ASHRAE CFC Conference.** Sponsored by the American Society of Heating, Refrigerating and Air-Conditioning Engineers. Contact: ASHRAE International Headquarters, 1791 Tullie Circle, N.E., Atlanta, Georgia 30329, USA, telephone 01-404-636-8400, telex 705343.

Sep 28 - Oct 5, 1989

Moscow (USSR); **Energotechnika '89** (Exposition on Energy Technology and Power Generation). Contact: Nowea International GmbH, Stockumer Kirchstr. 61, 4000 Düsseldorf 30, Federal Republic of Germany.

October 26-28, 1989

Kuala Lumpur (Malaysia); **2nd Far East Conference on Air Conditioning in Hot Climates.** Contact: ASHRAE International Headquarters, 1791 Tullie Circle, N.E., Atlanta, Georgia 30329, USA, telephone 01-404-636-8400, telex 705343.

November 7-11, 1989

Paris (France); **International Heating, Refrigerating and Air-Conditioning Exhibition (INTERCLIMA '89).** Contact: CEP 7, Rue Copernic, F-75782 Paris, Cedex 16, France.

November 22-24, 1989

Hannover (FR Germany); **DKV - Kälte-Kilma - Tagung 1989.** Contact: Deutscher Kälte- und Klimatechnischer Verein (DKV), Pfaffenwaldring 10, D-7000 Stuttgart 80, FR Germany.

Nov 28 - Dec 1, 1989

Atlanta, Georgia (USA); **Meeting Customer Needs With Heat Pumps - 1989: A Conference and Equipment Show.** Sponsored by American Public Power Association, Edison Electric Institute, Electric Power Research Institute, International Ground Source Heat Pump Association, and the National Rural Electric Cooperative Association. Contact: David P. Ross, Policy Research Associates, Inc., 12121 Basset Lane, Reston, Virginia 22091, USA, telephone 703/620-1008.

March 12-15, 1990

Tokyo (Japan); **The 3rd International Energy Agency Heat Pump Conference.** Contact in **Japan**: Secretariat, Heat Pump Technology Center of Japan, Azuma Shurui Bldg., 9-11 Kanda Awaji-cho, 2-chome, Chiyoda-ku, Tokyo 101, Japan, telephone 03-258-1035, telefax 03-258-1037, telex 222-4601 hptcj. Contact in **North America**: R.L.D. Cane, Energy Systems Centre, ORTECH International, 2395 Speakman Drive, Mississauga, Ontario, Canada L5K1B3, telephone 416/822-4111 x238, telefax 416/823-1446. Contact in **Europe**: W. Hochegger, Energiesparhaus Graz, Petersgasse 45, A-8010 Graz, Austria, tel 316-822045, telefax 316-826371, telex 31-2305.

Services & Publications

Inquiries

Have a specific question about heat pumps?

Contact the Heat Pump Center directly with your questions on all non-commercial aspects related to heat pump topics. HPC staff members will do their best to answer directly or point you to the right expert.

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Please note new telephone and telefax numbers!

Reports

The following reports are published by the HPC:

Report No.	Report Title	
HPC-WR2	Proceedings of the Workshop on Ground-Source Heat Pumps (1987), 245 pages	DM 50,--/U.S. $30
HPC-WR3	National Reports on the Status of Heat Pumps (1987), 105 pages	DM 40,--/U.S. $25
HPC-R2-1	Heat Pump RD&D Projects Summary Report, Edition 2 (Dec. 1986), 514 pages	DM 50,--/U.S. $26
HPC-R3-1	Comparison of National Standards Testing and Rating Procedures for Heat Pumps (December 1986), 162 pages	DM 50,--/U.S. $30
HPC-R-4	Inverter-Driven Heat Pumps (September 1988), 109 pages	DM 50,--/U.S. $30
HPC-LR-3	HPC Bibliography - Sorption Heat Pump Systems (Oct. 1986), 372 pages	DM 20,--/U.S. $11
HPC-LR-2	HPC Bibliography - Industrial Heat Pumps (July 1986), 378 pages	DM 20,--/U.S. $11
HPC-WR-1/1-12	Workshop: Electric Heat Pumps for Retrofit in Existing Small Residential Buildings (1985), 13 separate reports, 506 pages	DM 70,--/U.S. $36
HPC-R-5	Report on the Application of Heat Pumps in Industry (1989), 62 pages	DM 50,--/U.S. $30
HPC-WR-4	Workshop Proceedings: The IEA Heat Pump Center's Future Activities and Organization (1989), 145 pages	Free of charge

Write to the HPC for a complete listing of HPC publications.

The IEA Heat Pump Center Newsletter is published quarterly.

Subscribers from countries participating in the IEA Heat Pump Center (Austria, Canada, Fed. Rep. of Germany, Italy, Japan, the Netherlands, Norway, Sweden, and the USA) will receive the newsletter free of charge. Subscribers from other countries will be billed DM 80,-- per year.

Subscription cancellation is possible with one month's notice to the end of the calendar year.

ORDER FORM AND SUBSCRIPTION CARD

NEWSLETTER SUBSCRIPTION:

Member Countries: ☐ start my subscription to the HPC Newsletter (no charge)

Non-Member Countries: ☐ start my subscription to the HPC Newsletter in 1989 (DM 80/year) (you will receive all four issues for this calendar year)
☐ also send me back issues through the end of 1988 (DM 80 additional)

PLEASE SEND ME THE FOLLOWING:

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☐ Payment enclosed. ☐ Please bill me later.

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Please fill in address on reverse side

06/89

Future Issues:

Vol/No	Topic	Deadline for Contributions
7/3	Heat pumps - heating and cooling	July 7, 1989
7/4	Planning for the future: national R,D&D programs, incentives, codes, and standards	September 7, 1989

If you would like to contribute an article on any of these topics, please contact the Heat Pump Center to obtain a copy of our author guidelines. Our regular features (feedback, bibliographic review, news briefs, and schedule of conferences) are included in each issue.

International Energy Agency

The International Energy Agency (IEA) was established in 1974 within the framework of the Organisation for Economic Cooperation and Development (OECD) to implement an International Energy Program. A basic aim of the IEA is to foster cooperation among the 21 IEA participating countries to increase energy security through energy conservation, development of alternative energy sources and energy research, development, and demonstration (RD&D). This is achieved in part through a program of collaborative RD&D consisting of 42 Implementing Agreements, containing a total of over 80 separate energy RD&D projects. IEA's address is 2 Rue André-Pascal, 75775 Paris Cedex 16, France.

Heat Pump Center

The IEA Heat Pump Center (HPC) was established in 1982 as Annex IV of the "Implementing Agreement for a Programme of Research and Development on Advanced Heat Pump Systems." Operating agent for the center is the Fachinformationszentrum Karlsruhe GmbH. Presently, nine countries are members of the HPC. These are: Austria, Canada, Federal Republic of Germany, Italy, Japan, the Netherlands, Norway, Sweden, and the USA. The language used in all material published by the HPC is English. Please write us at the address below if you would like to receive more information on the activities of the center.

Name
Company
Address
City
Country

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