COMPARISON OF ENVIRONMENTAL IMPACTS AND PHYSICAL PROPERTIES OF REFRIGERANTS

by

Ko Matsunaga

Advisor: Professor Nickolas J. Themelis

Department of Earth and Environmental Engineering
Fu Foundation of Engineering and Applied Science
Columbia University

May 2002

Research by the

EARTH ENGINEERING
Center

Columbia University

Comparison of environmental impacts and physical properties of refrigerants

Ko Matsunaga

EXECUTIVE SUMMARY

Even before the invention of refrigeration, people wanted to improve their life by using ice to provide cold drinks and preserve food. In the last two centuries, human ingenuity made it possible to control fully the temperature and humidity of the environment by means of air conditioning and refrigeration systems. The objective of this study was to establish an evaluation method that combines the environmental impacts of the most prominent refrigerants and their thermal properties as they apply to the vapor compression refrigeration cycle, that is used commonly. The desirable characteristics of "ideal" refrigerants are considered to be as follows:

1. Normal boiling point below 0 °C
2. Non-toxic
3. Non-flammable
4. Stable under operating conditions
5. Easily detectable in case of leakage
6. Relatively inexpensive to produce
7. Relatively large heat of evaporation
8. Easy to recycle or destruct after use
9. Low environmental impacts in case of accidental venting
10. Low gas flow rate per unit of cooling at compressor

To evaluate the environmental impacts of various refrigerants, the Eco-indicator 99 system for Life Cycle Analysis was used. The thermochemical and physical properties of each refrigerant were used to determine and compare heat carrying capacities and heat transfer characteristics (Prandtl and Nusselt numbers). With regard to environmental impacts, the preferable refrigerant is butane. In grouping environmental and performance characteristics, assuming the same weighting coefficients, the preferred refrigerant was R-32 (difluoromethane) followed by R-410A, ammonia, R-22, R-407C, propane, R-134a, R-125, and butane.

The ozone depletion is a global problem like global warming. However, the choice of alternative refrigerants is domestic issues involving recycling or disposal of refrigerants. Each government must decide which criteria for the ideal refrigerant should be relaxed in order to maximize the benefits of refrigeration systems and minimize the environmental impacts. This study has made it clear that the operation stage is the key factor for determining the environmental impact of various refrigerants. There is less impact to the environment in the production and disposal stages, even what refrigerants are assumed to be vented to the atmosphere. Therefore, the government and consumers should focus on energy saving programs, such as refund by New York State and the Energy Star Program by EPA and the U.S. Dept. of Energy, instead of accelerating changes of refrigerants that have less impact than the operation stage.

The information developed in this study on the environmental impacts and the properties of various refrigerants can be used by designers in seeking to provide better and environmentally friendlier refrigeration and air conditioning systems.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

The author gratefully acknowledges the warm support of his family, wife, Keiko, and son, Joe. The author also appreciates the kind support of Professor Nickolas J. Themelis, the Department of Earth and Environmental Engineering (Henry Krumb School of Mines), and all research associates of the Earth Engineering Center of Columbia University. Thanks are also due to Mitsubishi Heavy Industries whose support has made possible the author's studies at Columbia University. The author hopes that future generations can receive the same benefits as we have from mother Earth.

Ko Matsunaga
April, 2002

INTRODUCTION

The purpose of this research was to compare various refrigerants on the basis of their environmental impacts and thermal properties. Refrigerant fluids are a key component for air conditioners and refrigerators, both of which are essential for comfortable living. Since the 19^{th} century there have been many refrigerants developed and used but none of them has as yet become the standard fluid. The objective of this study was to establish an evaluation method that combined the environmental impacts of the most prominent refrigerants and their thermal properties as they apply to the refrigeration process.

In part, this work was motivated by the 1987 Montreal Protocol[3], an international agreement by most nations to stop or reduce the manufacture of chloro fluoro carbons (CFCs) and other ozone-depleting substances. This international treat required to stop using the widely used refrigerant, "Freon® ", that up to that time was considered as a "miracle compound". Since then, there have been many studies and much discussion about alternative refrigerants. However, as of now there is no single alternative refrigerant for air conditioners.

This report is divided into five sections. Section 1 is a brief history of the development of refrigerants. Section 2 discusses the environmental impacts of refrigerants through their life cycle (Life Cycle Assessment). Section 3 examines the thermal properties of refrigerants. Section 4 describes the overall evaluation of refrigerants based on the combination of their environmental impacts and thermal properties. Conclusions and recommendations are summarized in Section 5. Appendix A presents the history of various refrigerants and Appendix B their P-H diagram properties.

Note:
The trade name Freon® is a registered trademark belonging to E.I. du Pont de Nemours & Company (DuPont).

1. THE "FREON" FAMILY

"Freon" is a trademark created by Thomas Midgley for the chlorofluorocarbon compounds.[2] The original patents have expired long ago. According to one story, "freon" was picked up by throwing a dart on a board containing various potential trademarks. The names of chemical compounds are hard to remember, so people use common names such as salt for sodium chloride and vitriol for sulfuric acid. One of the most useful chlorofluorocarbon compounds is known as R-12. For ease of use and to avoid confusion, Midgley and the other developers of Freon proposed the following rule for naming these compounds: [2]

```
R- 0 1 2
|  | | |
|  | | + The first digit on the right is the number of fluorine atoms in the compound.
|  | |
|  | + The second digit from the right is one more than
|  |     the number of Hydrogen atoms in the compound
|  |
|  + The third digit from the right is one less than the number of carbon atoms
|    in the compound. When this digit is zero, it is omitted from the name
|    (i.e. R-12 for R-012).
|
+ "R" stands for refrigerant (it used to be F for Freon).
```

The various refrigerants derived from methane and ethane are shown in Figures 1 and 2.

		CH_4 (R-50)		
	CH_3Cl (R-40)	*CH_3F (R-41)*		
	CH_2Cl (R-30)	CH_2ClF (R-31)	*CH_2F_2 (R-32)*	
$CHCl_3$ (R-20)	$CHCl_2F$ (R-21)	$CHClF_2$ (R-22)	*CHF_3 (R-23)*	
CCl_4 (R-10)	<u>CCl_3F (R-11)</u>	<u>CCl_2F_2 (R-12)</u>	<u>$CClF_3$ (R-13)</u>	CF_4 (R-14)

Figure 1. Chlorofluorocarbon compounds derived from methane (CH_4) (see note below Figure 2.)

C_2H_6 (R-170)

C_2H_5Cl (R-160) | *C_2H_5F (R-161)*

$C_2H_4Cl_2$ (R-150) | C_2H_4ClF (R-151) | *$C_2H_4F_2$ (R-152)*

$C_2H_3Cl_3$ (R-140) | C_2H_3Cl2F (R-141) | $C_2H_3ClF_2$ (R-142) | *$C_2H_3F_3$ (R-143)*

$C_2H_2Cl_4$ (R-130) | $C_2H_2Cl_3F$ (R-131) | $C_2H_2Cl_2F_2$ (R-132) | $C_2H_2ClF_3$ (R-133) | *$C_2H_2F_4$ (R-134)*

C_2HCl_5 (R-120) | C_2HCl_4F (R-121) | $C_2HCl_3F_2$ (R-122) | $C_2HCl_2F_3$ (R-123) | C_2HClF_4 (R-124) | *C_2HF_5 (R-125)*

C_2Cl_6 (R-110) | C_2Cl_5F (R-111) | $C_2Cl_4F_2$ (R-112) | $C_2Cl_3F_3$ (R-113) | $C_2Cl_2F_4$ (R-114) | C_2ClF_5 (R-115) | CF_6 (R-116)

Figure 2. Chlorofluorocarbon compounds derived from ethane (C_2H_6)

Note
- CFC: Chloro fluoro carbon — Production was ended in 1996 in some countries
- HCFC: Hydro chloro fluoro carbon — Production will be ended by 2030 in some countries.
- *HFC: Hydro fluoro carbon — No restrictions at this time.*
- **HC: Hydrocarbon — Propane and butane**

The above taxinomy was accepted by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) and is widely applied to other refrigerants such as inorganic compounds, hydrocarbons, and azeotropic mixtures, as described in ASHRAE Standard 34. For example, R-290 is propane, R-600 is butane, R-400s are zeotropic and R-500s are azeotropic blends. In zeotropic blends or mixtures (non-azeotropic blends), the compositions of coexisting liquid and vapor differ and condensation and evaporation occur over a range of temperatures. In some applications, this property improves performance in plants with heating/cooling demand varying with temperature. On the other hand, azeotropic blends consist of one or more refrigerants of different volatilities that do not appreciably change in composition or temperature as the fluid evaporates or condenses under constant pressure.[22]

2. DEVELOPMENT OF REFRIGERATION

The main types of air conditioners and refrigerators are a) vapor compression-refrigeration cycle, and b) adsorption systems. The former is most commonly used and is known to Carnot cycle, conceived by Nicolas Carnot in 1824.[1] In the late 19th century and the beginning of the 20th century, air, ammonia, carbon dioxide, sulfur dioxide and methylene chloride were used as refrigerants even though they were far from "ideal" refrigerants. Prior to the invention of the "freon" compounds, nearly all of the early refrigerants were flammable, toxic, or both, and some were also highly reactive. Accidents were common, such as the killing of entire families by leaking of poisonous refrigerants. The first non-toxic and non-flammable refrigerant with good stability was invented by Midgley in 1928.[2] He had already attained fame by finding that tetraethyl lead improved the octane rating of gasoline.

The development of fluorocarbon refrigerants, Freon, was announced in April 1930. To demonstrate the safety of the new compounds, at a meeting of the American Chemical Society, Midgley inhaled it (R-12) and then blew out a lit candle by exhaling on it. The freon compounds offered several advantages, not only as refrigerants but also as solvents and in other applications such as:

- Foams for thermal insulation
- Medical aerosols
- Fire fighting (Halon)

A brief outline of the history of refrigeration and refrigerants is shown in Table 1.

Table 1. History of HVAC/R (Heating, Ventilating, Air Conditioning, and Refrigeration) [5, 6, 7, 8, and 9]

Year	Item	Comments
1748	Concept	William Cullen, in Scotland, initially developed the concept of mechanical / chemical refrigeration and demonstrated that the evaporation of ether in a partial vacuum produces cold
1755	Concept	William Cullen cooled water by drawing a vacuum over it. This was the earliest known attempt at vapor compression refrigeration.
1803	Word	Thomas Moore builds a box-within-a-box for the sole purpose of preserving food and calls it the "refrigerator."
1824	Concept	Michael Faraday discovers the principle of absorption type refrigeration.
1850	Product	The first successful continuous operating heat absorption machine, using ammonia as refrigerant and water as absorbent, was built. This was the only the absorption system to gain commercial importance during the 19th and 20th century.
1852	Concept	Lord Kelvin developed the heat pump concept.
1872	Refrigerant	Ammonia was first used in vapor-compression systems in 1873, sulfur dioxide and methyl ether in 1875, and methyl chloride in 1878.
1880	Product	Reciprocating compressors were developed. These compressors were used in commercial applications for ice making, fish processing, meatpacking and brewing.
1881	Refrigerant	The use of carbon dioxide was introduced.
1882	Topic	The first electric power plant in New York opened as an outgrowth of Thomas Edison's research and inventions.
1906	Word	Stuart W. Cramer coins the term "Air Conditioning" and uses the term in a patent claim for a humidifying head.
1920	Product	In 1920, GE began using a hermetically sealed compressor.
1923	Topic	Fast freezing to preserve food is developed.
1924	Product	The first hermetically sealed motor- compressor is developed by the General Electric Company for domestic refrigerators.
1930	Product	The first self-contained room air conditioner is developed by General Electric. It is a console- type unit with a hermetically sealed motor- compressor and water-cooled condenser, using sulfur dioxide as the refrigerant. Thirty units were built and sold the following year.
	Topic	The White House, the Executive Office Building and the Department of Commerce become air-conditioned.
1928	Refrigerant	Drs. Thomas Midgley, Albert L. Henne, and Robert R McNary invented the fluorocarbon "Freon-12" refrigerant, all employed in a small private research laboratory at Dayton, Ohio, sputtered by General Motors Corporation.
1931	Refrigerant	Freon-12 is introduced as a commercial refrigerant.
1936	Refrigerant	Albert Henne synthesized R-134A.
1940	Product	Practically all-domestic refrigeration units were now of the hermetic type.
1945	Refrigerant	Refrigerant R-13 is introduced.
1950	Refrigerant	Refrigerant R-500 is introduced.
1956	Refrigerant	A new refrigerant numbering system is adopted by the HVAC/R industry: R-12, R-22, R-502, etc. to have a standard designation for all the many different trade names of refrigerant.
	Ozone	Ozone measurements are started at the British Antarctic base at Halley Bay. Ozone levels are found to fall dramatically in September and October to 150 DU (Dobson Units) or about half the normal level. Thus the "Ozone Hole" is actually discovered at this time, but British scientists are not cognizant of this fact for many years to come.
1957	Product	The first rotary compressor is introduced, permitting units to be smaller, quieter, and weigh less. The rotary is more efficient than the reciprocating compressor.
1962	Refrigerant	Refrigerant R-502 is introduced.
1977	Ozone	On May 11, US Government announces ban on spray cans using "freon" to take effect in two years. The chemical is found to destroy the ozone layer.
1987	Ozone	The United Nations Monteal Protocol for protection of the Earth's ozone layer is signed, establishing international cooperation on the phase-out of CFC's.
1996	Ozone	CFC production in the US ends.
2030	Ozone	HCFC production will end in most of countries.

3. CONTROL OF CFCs and HCFCs

In 1974, James Lovelock discovered the presence of CFCs in the global atmosphere. In 1974, Rowland and Molina (awardees of the Nobel Prize for chemistry in 1995) published their concept of ozone depletion in the stratosphere by CFC emissions.[10] At that time, this was only a hypothesis. However, in 1977, the United Nations Environment Programme (UNEP) organized an international meeting to adopt the 'World Plan of Action on the Ozone Layer'. Twenty-eight countries agreed to the Vienna Convention for the Protection of the Ozone Layer planned in 1987. The "Montreal Protocol on Substances that Deplete the Ozone Layer" came into force on January 1st, 1989, by 29 countries.

The London Amendment (1990) added methyl chloroform, carbon tetrachloride and an additional range of CFCs to the phase-out schedules and established a mechanism for financial and technical assistance to developing country parties. The Copenhagen Amendment (1992) added hydrochlorofluorocarbons (HCFCs), hydrobromofluorocarbons (HBFCs), and methyl bromide to the phase-out schedules and formally created the Multilateral Fund as the route for financial and technology assistance. The Montreal Amendment (1997) created a system of licenses for imports and exports of ozone-depleting substances, mainly in order to tackle the growing illegal trade in the substances. It increased the number of controlled substances and accelerated the phase-out schedules for ozone-depleting substances. The most recent Beijing Amendment (1999) added bromochloromethane to the phase-out schedules and extended the controls on HCFCs to production in addition to the revised controls on consumption.

The latest Montreal protocol including the Beijing Amendment(1999) has several categories of ozone-depleting substances(Table 2). Some ozone-depleting potential for refrigerants are shown in Table 3.The phase-out schedules of Annex A Group I and Annex C Group II are important for regular refrigerants, which is shown in Figure 3 and 4.

Table 2. Control substances in the Montreal Protocol[3]

Annex	Group	Main substances
Annex A	Group I	CFCs
Annex A	Group II	Halon
Annex B	Group I	CFC for very low temperature refrigeration and certain cleaning uses
Annex B	Group II	Carbon tetrachloride
Annex B	Group III	Methyl chloroform
Annex C	Group I	HCFC
Annex C	Group II	Bromide compounds
Annex E	Group I	Methyl Bromide

Table 3. Ozone-depleting potential of some substances[3]

Group	Substance	Name	Ozone-depleting potential*
Annex A, Group I (CFC)	$CFCl_3$	R-11	1.000
	CF_2Cl_2	R-12	1.000
	$C_2F_3Cl_3$	R-113	0.800
	$C_2F_4Cl_2$	R-114	1.000
	C_2F_5Cl	R-115	0.600
Annex A, Group II (Halon)	CF_2BrCl	Halon-1211	3.000
	CF_3Br	Halon-1301	10.000
	$C_2F_4Br_2$	Halon-2402	6.000
Annex C, Group I (HCFC)	$CHFCl_2$	R-21	0.040
	CHF_2Cl	R-22	0.055

Note: * These ozone depleting potentials are estimates based on existing knowledge and will be reviewed and revised periodically.

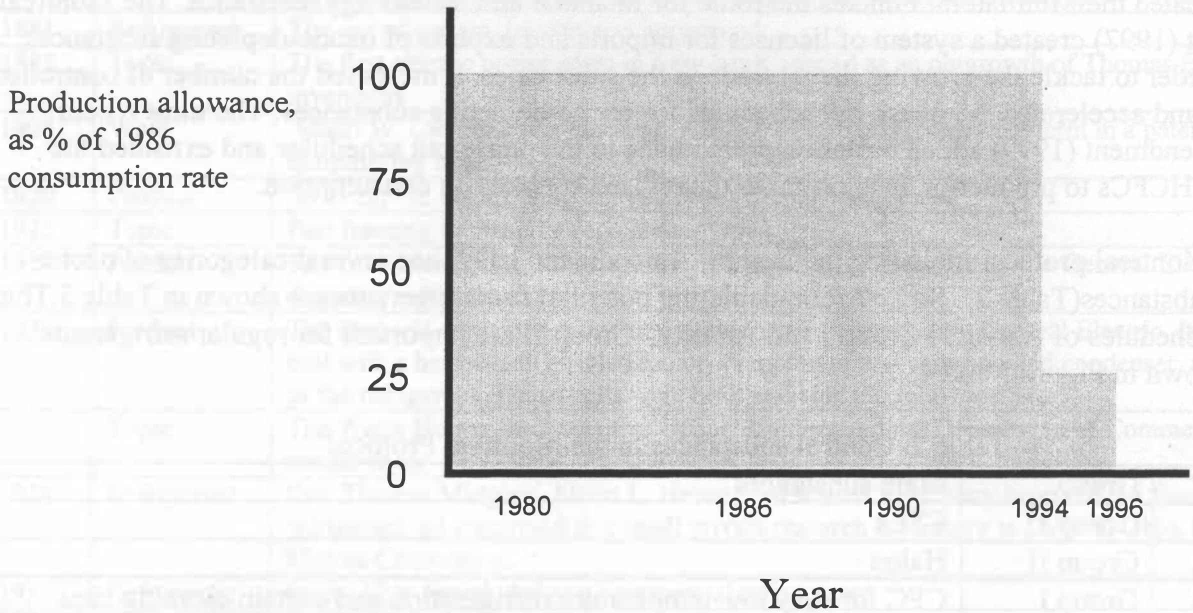


Figure 3. Phase out schedule for CFCs (Annex A, Group I compounds)[3]
Note: In 2010, production for basic domestic needs is prohibited.

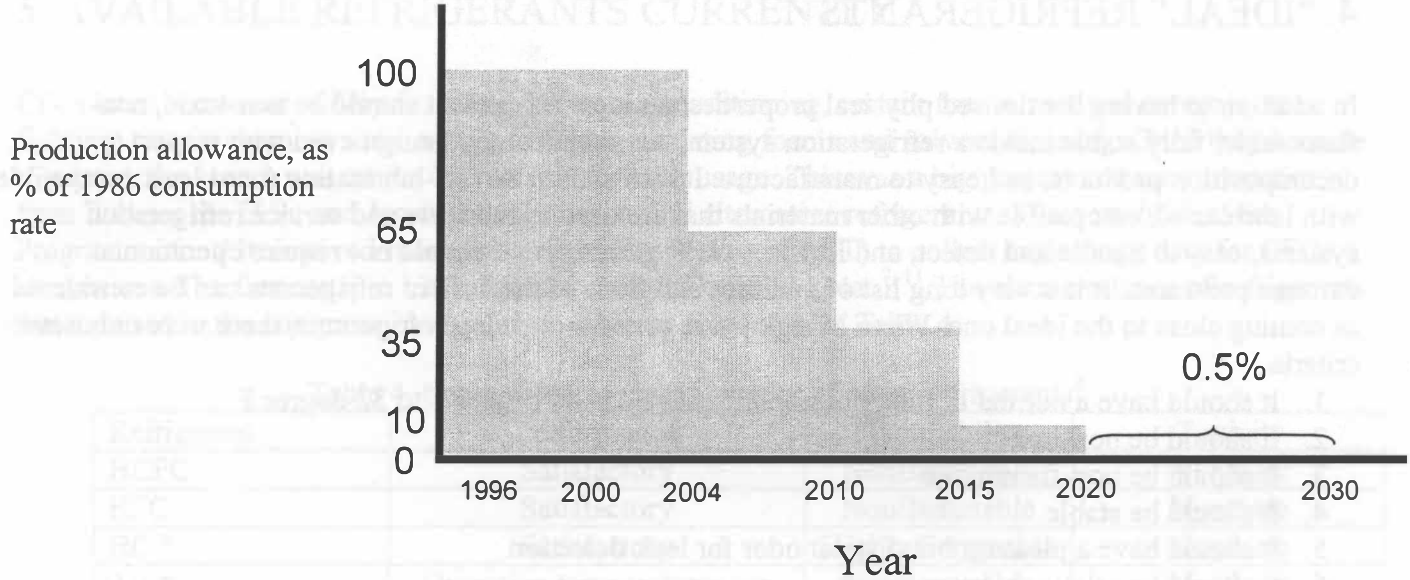


Figure 4. Phase out schedule for HCFCs (Annex C, Group I compounds) [3]

Note: In 2004, production for the basic domestic needs will be regulated.

For the protection of the ozone layer, many substances are controlled now under the Montreal Protocol on substances that deplete the ozone layer. However, some developing countries, China, India, etc, can delay for ten years to meet their basic domestic need, because their consumption was less than 0.3 kilograms per capita and they wanted to have the equal opportunity to use Freon in order to develop their economy.

4. "IDEAL" REFRIGERANTS

In addition to having the desired physical properties, an ideal refrigerant should be non-toxic, non-flammable, fully stable inside a refrigeration system, environmentally benign even with respect to decomposition products, and easy to manufacture. It also should be self-lubricating (or at least compatible with lubricants), compatible with other materials that are used to fabricate and service refrigeration systems, easy to handle and detect, and low in cost. Furthermore, it should not require operation at extreme pressures. It is a very long list of qualities and none of the current refrigerants can be considered as coming close to the ideal one. When Midgley was asked to develop refrigerants, there were only seven criteria

1. It should have a normal boiling point in the range of –40 degree F to 32 degree F
2. It should be non-toxic
3. It should be non-flammable
4. It should be stable
5. It should have a pleasant but distinct odor for leak detection
6. It should be relatively inexpensive
7. It should be have a relatively large heat of evaporation

The first four criteria were assigned top priority.[2]

Presently, there are several additional criteria for refrigerants:

8. Easy to be recycled or destructed
9. Low environmental impacts in case of accidental venting
10. The required flow rate, per unit of cooling provided, should be low in order to minimize the charging quantity and the size of compressor.

5. AVAILABLE REFRIGERANTS CURRENTLY

CFCs have been used widely for refrigeration, air-conditioning, certain foams, medical aerosols, fire-fighting, certain cleaning uses, energy-efficient insulating foams and solvent cleaning. Once they became regulated, the search was on for alternatives for each usage. This was a big project and nine countries from Europe, the U.S., and Japan got together to find alternative refrigerants. They established the Programme for Alternative Fluorocarbon Toxicity Testing (PAFT) to collect toxicology data for CFCs alternatives. The first tests, in 1987, focused on R-123 and R-134a. [7, 11] The characteristics of refrigerants that are used in the compression-expansion systems are shown in Table 4.

Table 4. Comparison of characteristics of some refrigerants[2]

Refrigerant	Performance	Flammability	Toxicity
HCFC	Satisfactory	Nonflammable	Nontoxic
HFC	Satisfactory	Nonflammable	Nontoxic
HC *	Satisfactory	Highly flammable	Nontoxic
Air *	Operation temperatures are limited	Nonflammable	Nontoxic
Ammonia *	Satisfactory	Very slightly flammable	Toxic but gives ample warning
Carbon dioxide *	Operation temperatures are limited	Nonflammable	Nontoxic but asphyxiant
Water *	Operation temperatures are limited and poor performance	Nonflammable	Nontoxic
Sulfur dioxide *	Satisfactory	Nonflammable	Toxic but gives ample warning
Methyl chloride *	Satisfactory	Slightly flammable	Toxic and gives no warning
Methyl bromide *	Operation temperatures are limited	Slightly flammable	Toxic and gives no warning

Not: * These substances were used before the 1930s when Freon was developed.

The consumption of CFCs was banned in 1996 and the consumption of HCFCs will be banned in 2030 in the U.S.. However HFCs, which do not contain chlorine and do not damage the ozone layer, are produced and used widely. Nevertheless, HFCs have a high Global Warming Potential (GWP, Table 5) Also, some scientists caution that HFCs may have as yet unknown environmental impacts because they are artificial substances. For this reason, the European Community (EU) has started using hydrocarbons (HCs), such as propane and butane, as refrigerants. As of now, there are no HC refrigerators manufactured in the US, for the following reasons:

- The law of product liability deters American manufacturers from using a flammable refrigerant
- Chemical companies have already invested a lot of money to produce HFCs
- Many design changes are required in order to change refrigerants

Table 5. Global Warming Potential of various refrigerants [18]

Substance	Lifetime (years)	Global Warming Potential		
		20 years	100 years	500 years
Ca bon dioxide	Uncertain	1	1	1
Methane	12.0	62	23	7
R-12 (CFC)	100	10200	10600	5200
R-22 (HCFC)	11.9	4800	1700	540
R-32 (HFC)	5.0	1800	550	170
R-125 (HFC)	29	5900	3400	1100
R-134a (HFC)	13.8	3300	1300	400
R-407C (HFC)	15.6 *	3605 *	1653 *	522 *
R-410A (HFC)	17 *	3850 *	1975 *	635 *

Note: * values are derived by combining their compositions

6. REFRIGERANTS COMPARED IN THIS STUDY

The present study has focused on HFCs, HCs, HCFCs and ammonia as being practical alternative refrigerants. These fluids were compared in terms of environmental impacts and physical properties. HCFCs can be used only until 2030 but they were included as a benchmark in the comparison of various alternative refrigerants. R-32 and R-125 are rarely used as refrigerants. However, they are blended in R-410A and R-407C.

6.1 Physicochemical properties

To avoid confusion, the chemical name, the chemical formula, the Chemical Abstracts Service (CAS) number, the ASHRAE name, and composition of ASHRAE standard are shown in Table 6. The chemical properties of these refrigerants are shown in Table 7.

Table 6. Classification of refrigerants[12]

Category	Chemical	Chemical formula	CAS#	ASHRAE	Composition of ASHRAE standard (%)
HCFC	Chlorodifluoromethane	$CHClF_2$	75-45-6	R-22	
HFC	Difluoromethane	CH_2F_2	75-10-5	R-32	
HFC	Pentafluoroethane	C_2HF_5	354-33-6	R-125	
HFC	1,1,1,2-tetrafluoroethane	CH_2FCF_3	811-97-2	R-134a	
HFC	HFC-32／HFC-125／HFC-134a			R-407C	23.0±2.0／25.0±2.0／52.0±2.0
HFC	HFC-32／HFC-125			R-410A	50.0+0.5-1.5／50.0+1.5-0.5
HC	Propane	C_3H_8	74-98-6	R-290	
HC	Butane	C_4H_{10}	106-97-8	R-600	
	Ammonia	NH_3	7664-41-7		
	Carbon dioxide	CO_2	124-38-9		

Table 7. Physicochemical properties of various refrigerants[12]

	Mole-cular weight	Triple point Temp. °C	Boiling point Temp. °C	Critical temp °C	Critical pressure MPa	Critical density kg/m³	Min. temp °C	Max. temp °C	Max Pressure MPa	Max density kg/m³
R-22	86.47	-157.42	-40.81	96.15	4.990	523.8	-157.4	276.9	60.0	1722
R-32	52.02	-136.81	-51.65	78.11	5.782	424.0	-136.8	161.9	70.0	1429
R-125	120.02	-100.63	-48.14	66.18	3.629	571.3	-100.6	226.9	60.0	1692
R-134a	102.03	-103.30	-26.17	101.06	4.059	511.9	-103.3	180	70.0	1592
R-407C	86.20	-------	-------	86.05	4.634	512.7	-------	-------	-------	-------
R-410A	72.59	-------	-------	70.17	4.770	551.9	-------	-------	-------	-------
Propane	44.10	-187.28	-42.09	96.70	4.248	220.5	-187.3	326.9	100.0	732.7
Butane	58.12	-138.29	-0.54	152.01	3.796	227.8	-138.3	226.9	70.0	735.3
NH_3	17.03	-77.66	-33.33	132.25	11.333	225.0	-77.7	426.9	1000.0	732.9
CO_2	44.01	-56.57	-78.40	31.06	7.384	466.5	-56.6	167.0	40.0	1223

Note: Triple point is the intersection where three phases coexist in equilibrium. Critical point is the state at which liquid and gas phases first become indistinguishable. Critical pressure and critical temperature are pressure and temperature at the critical point.

7. LIFE CYCLE ASSESSMENT

There are many methods to measure environmental impacts. This study opted for using the Eco-indicator 99 method developed by Pre Consultants in the Netherlands.[13] This methodology was applied in comparing the environmental impacts of each refrigerant through its life cycle (i.e. production, operation, disposal stages). The Eco-indicator 99 has defined the term "environment" as being subject to three types of damage: a) Human health, b) Ecosystem quality, and c) Resources. The higher the Eco-indicator numbers, the more adverse is the environmental impact. In this study, the Eco-indicators 99 were used. The indicators are numbers that express the total environmental load of a product or process and are included in the ISO 14042 standard (International Organization for Standardization). In the Eco-indicator 99 system, the unit of impact is the millipoint (mPt) and 1000 mPt are equal to 1 point (Pt). The value of 1 Pt has been defined to be one thousandth of the yearly total environmental load of one average European inhabitant.[13]

Some people use the total equivalent warming impacts (TEWI) as defined by the Alternative Fluorocarbons Environmental Acceptability Study and the U.S. Department of Energy (DOE). They represent the sum of the direct contribution of emissions of a product to the atmosphere as greenhouse gases plus the indirect contribution of the carbon dioxide emissions resulting from its operation, including electricity consumption.[14] Eco-indicators include TEWI concepts and focus on wider environmental impacts; therefore, they were chosen as the measurement system for this study.

7.1 Production stage

In the Eco-indicator 99, some of the refrigerants of interest are listed, such as ammonia, R-22, and R-134a, but not R-125, R-32, R-407C, R-410A, R-290 (propane), and R-600 (butane). R-125 and R-32 are pure HFC refrigerants and the Eco-indicator 99 describes their impact as a function of weight, so it is independent of the molecular weight of the fluid. R-134a is a HFC refrigerant and its chemical composition is $C_2H_2F_4$, HFC-32 is CH_2F_2, and HFC-125 is C_2HF_5. In this study, the Eco-indicator 99 of these three refrigerants was assumed to be 150 mPt per kg, i.e., the same as for R-134a. R407C and R410A are mixture of HFC refrigerants R-32, R-125, and R-134a(Table 6). The Eco-indicator 99 does not include the blending process, so Indicators must be assumed here. In the actual manufacturing process, these compounded refrigerants are blended in storage tanks according to the ASHRAE composition standard and they are mixed well. The blending process requires little energy and does not produce any residues or emissions, so the Eco-indicator 99 of the blending process was assumed to be negligible.

For R-290 (propane), and R-600 (butane), the production indicator, 180 mPt, of fuel oil and fuel diesel was used. The summary of environmental impacts at production stage is shown in Table 8.

Table 8. Environmental impacts of the production of each refrigerant (in mPt per kg) [13]

Refrigerant	The Eco-indicator 99
R-22	240
R-32	150 *
R-125	150 *
R-134a	150
R-407C	150 *
R-410A	150 *
Propane	180 *
Butane	180 *
Ammonia	160

Note: * values are derived by comparison with similar compounds

7.2 Operation stage

To determine the energy consumption during operation, the pressure and enthalpy diagram (P-H diagram) was used to determine the consumption of electricity for a given load of refrigeration. For example, the P-H diagram of R-22 is shown in Figure 5. The P-H diagrams of other refrigerants are shown in Appendix B. The bold line represents the cooling operation of the cycle and flow. The top horizontal line is the condensation process and the cycle proceeds from right to left side. The downward left vertical line is the expansion process. Finally, the bottom horizontal line, leading from left to right side, represents the evaporation process. The diagonal curved line stands for the compression process of the cycle. We need the difference of enthalpy in compressor process, h_{Hh}-h_{Hl} in Figure 5, to be cooled by the difference of the enthalpy, h_{Hl}-h_L in Figure 5. The ratio of h_{Hl}-h_L to h_{Hh}-h_{Hl} is called the Coefficient of Performance (C.O.P.) for cooling, i.e., the cooling capacity (joule or watt) divided by the energy input (joule or watt). The heating capacity divided by the energy input is the C.O.P. for heating. It should be noted that is in the U.S., the Energy Efficiency Ratio (EER) is used instead of C.O.P.. The EER is the cooling capacity (Btu/h) divided by the energy input (W). For example, a unit which has 10,000 Btu/h cooling capacity and requires 1000 W. EER has as of 10,000 Btu/h / 1000 W = 10. To compute the C.O.P. of the same machine, the 10,000 Btu/h is equivalent to 2930 W. Therefore, the C.O.P. = 2930 W / 1000 W = 2.93.

The results of theoretical calculations are shown in Table 9 and Table 10 for each refrigerant. This study focused on the cooling cycle and the operating conditions are shown below.[15] For reference, the P-H diagram for carbon dioxide is shown in Figure 6 to show that it is not a suitable refrigerant for air conditioners.

- Condensing process 41 °C
- Evaporating process 2 °C
- Superheat 5 °C
- Supercool 5 °C
- Compressor process is assumed to be isentropic
- All processes are theoretical and efficiency is 100 %
- Cooling capacity 1465 (W) (5000 Btu/h)
- 12 hours of operation in three summer months, ten-year life.
  Total operating time = 10,950 hours
- No frictional pressure drop

- No reverse flow
- Assumed zero heat losses to the surroundings

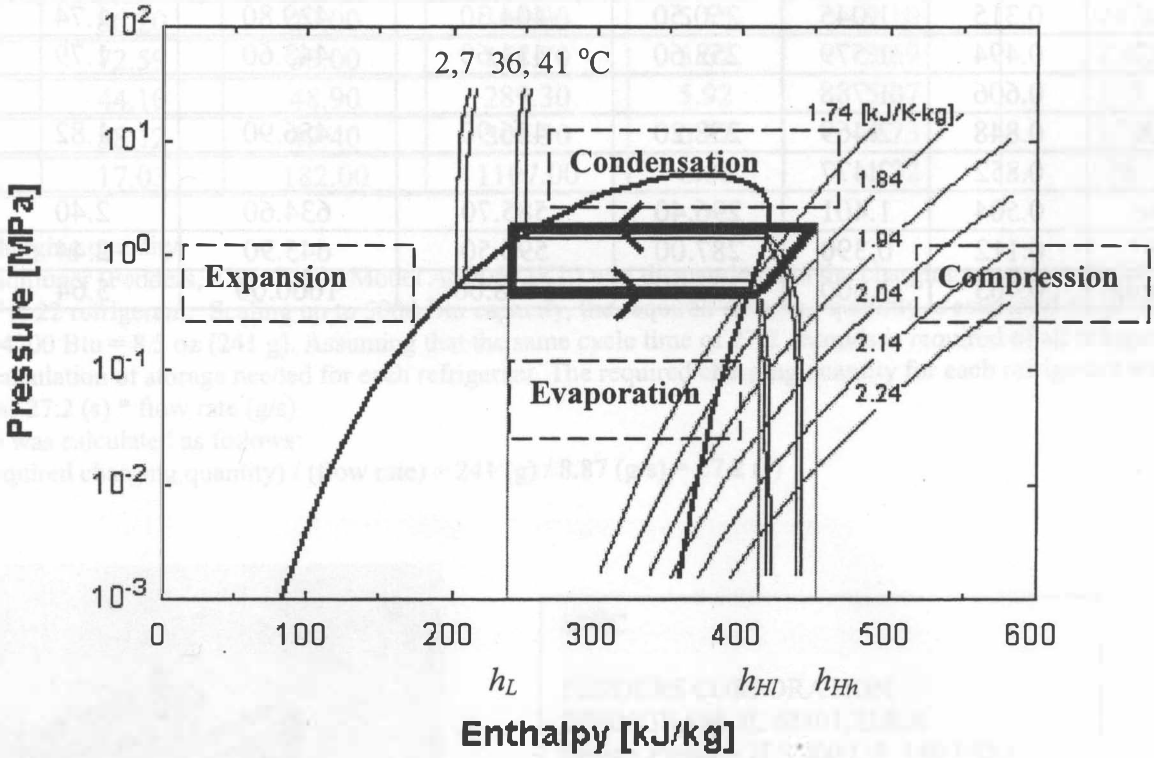


Figure 5. Pressure and enthalpy diagram for R-22. (Temp. levels: 2, 7, 36, and 41 °C)

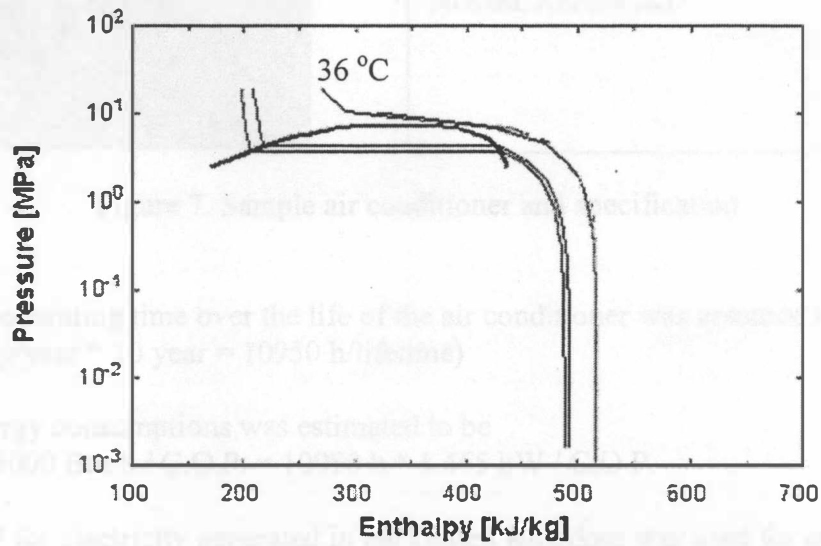


Figure 6. Pressure and enthalpy diagram for carbon dioxide (Temp. levels: 2, 7, and 36 °C [12])

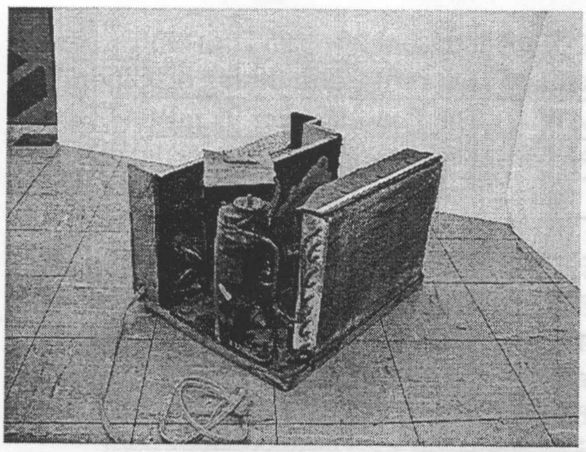
Table 9. Thermal properties of each refrigerant [12]

	Low Pressure MPa	High Pressure MPa	h_L kJ/kg	H_{Hl} kJ/kg	h_{Hh} kJ/kg	Compressor Entropy kJ/K-kg	Compressed temp. °C
R-22	0.532	1.572	244.30	409.50	437.20	1.76	63.28
R-32	0.867	2.540	267.10	521.80	566.40	2.17	76.15
R-125	2.055	0.715	248.70	338.30	355.10	1.50	46.84
R-134a	0.315	1.045	250.50	404.30	429.80	1.74	49.92
R-407C	0.494	1.579	253.60	414.60	443.60	1.79	57.01
	0.606	1.788					
R-410A	0.848	2.469	258.20	426.90	456.90	1.82	62.57
	0.852	2.477					
Propane	0.504	1.401	296.40	585.70	634.60	2.40	49.55
Butane	0.112	0.390	287.00	596.50	645.90	2.44	42.15
Ammonia	0.463	1.600	371.00	1478.00	1660.00	5.64	98.51

Table 10. Cooling efficiency of each refrigerant

Refrigerant	Molecular weight	Work Energy $h_{Hh} - h_{Hl}$ J/g	Cooling Energy $h_{Hl} - h_L$ J/g	C. O. P.	Required mass flow rate g/s	Required charging quantity g
R-22	86.47	27.70	165.20	5.96	8.87	241
R-32	52.02	44.60	254.70	5.71	5.75	156
R-125	120.02	16.80	89.60	5.33	16.35	444
R-134a	102.03	25.50	153.80	6.03	9.53	259
R-407C	86.20	29.00	161.00	5.55	9.10	247
R-410A	72.59	30.00	168.70	5.62	8.69	236
Propane	44.10	48.90	289.30	5.92	5.07	138
Butane	58.12	49.40	309.50	6.27	4.73	129
Ammonia	17.03	182.00	1107.00	6.08	1.32	36

Note:
Required charging quantity:
One air conditioner (Fedders, 4700 Btu/h, Model ASP05F2KL) was dismantled and the charging quantity was 8.0 oz (2270 g) of R-22 refrigerant. Scaling up to 5000 Btu capacity, the required charging quantity is estimated as 8.0 oz * 5000 Btu / 4700 Btu = 8.5 oz (241 g). Assuming that the same cycle time of 27.2 seconds is required of all refrigerants led to the calculation of storage needed for each refrigerant. The required charging quantity for each refrigerant was calculated as 27.2 (s) * flow rate (g/s).
Cycle time was calculated as follows:
(required charging quantity) / (flow rate) = 241 (g) / 8.87 (g/s) = 27.2 (s)



SPEC

FEDDERS CORPORATION
EFFINGHAM, IL 62401, U.S.A
Design Pressure H.S 400 L.S. 150 PSIG
REFRIGERANT R22
CHARGE 8 oz, under 6lbs.
MODEL ASP05F2KL

Figure 7. Sample air conditioner and specification

As noted earlier, the operating time over the life of the air conditioner was assumed to be 10,950 hours. (12 h/day * 365/4 day/year * 10 year = 10950 h/lifetime)

Accordingly, the energy consumptions was estimated to be
= 10950 h * 5000 Btu/h / C.O.P. = 10950 h * 1.465 kW / C.O.P.

The Eco-indicator 99 for electricity generated in the United Kingdom was used for energy consumption (33 mPt per kWh). In the Eco-indicator 99 list, there is no indicator for the U.S. electricity. This indicator depends on the energy source of each country. Figure 8 shows that the sources of the U.S. electricity are similar to those of the United Kingdom. The recalculated indicators of each refrigerant are shown in Table 11.

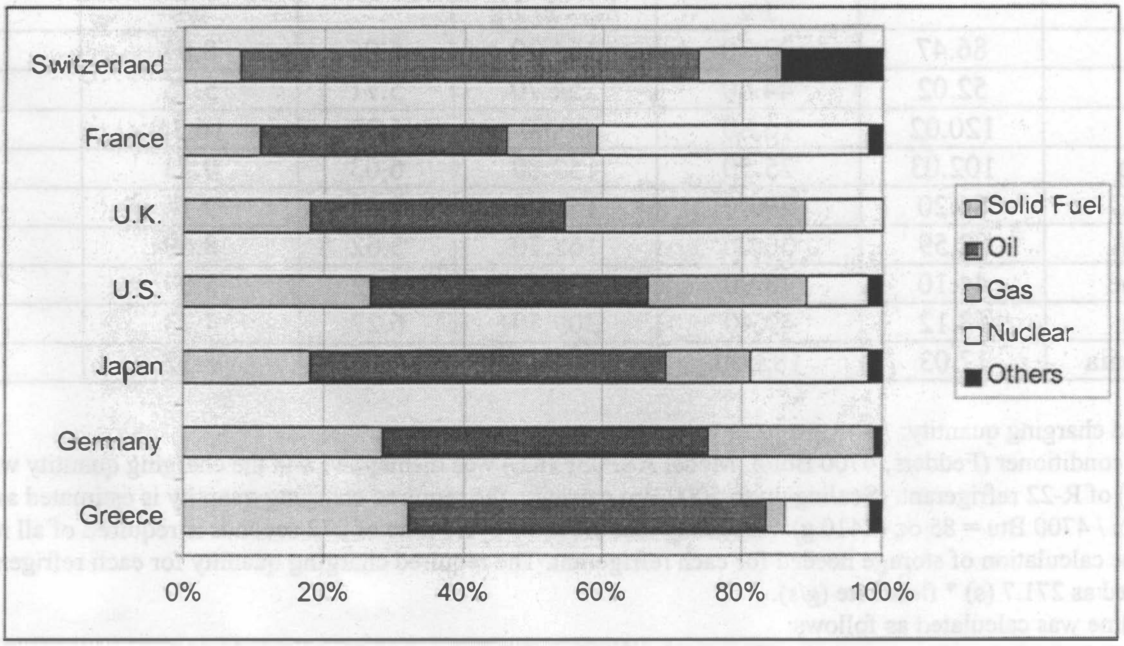


Figure 8. Energy supply by source, 1998 [16]

Table 11. Energy consumption and environmental impacts of each refrigerant during operation

Refrigerant	C.O.P	Required energy MW	The Eco-indicator 99 mPt
R-22	5.96	2.637	87027
R-32	5.71	2.754	90884
R-125	5.33	2.949	97316
R-134a	6.03	2.608	86053
R-407C	5.55	2.833	93488
R-410A	5.62	2.797	92298
Propane	5.92	2.658	87729
Butane	6.27	2.510	82842
Ammonia	6.08	2.586	85331

7.3 Disposal stage

When air conditioners are disposed of, refrigerants should be collected and handled properly. Some cities like New York City have freon recovery programs: refrigerants from all freezers, refrigerators, water coolers, dehumidifiers, air conditioners, or other types of appliances are collected separately. After collection, most of refrigerants should be destructed. CFCs and HCFCs cannot be used and reclaim of other refrigerants cannot be done when the refrigerant is contaminated or mixed with other refrigerants. The EPA has developed regulations requiring the recycling of ozone depleting chemicals (both CFCs and HCFCs) during the servicing, repair, or disposal of refrigeration and air conditioners.[17] HFC refrigerants are not required to comply with the EPA regulation. However, HFCs have a high GWP(Table 5), so intentional venting to the atmosphere is prohibited.

The environmental impacts of the destruction process of refrigerants is not included in the Eco-indicator 99. Assumed indicators are obtained. For CFCs, HCFCs, and HFCs destruction, three technologies are preferred in terms of destruction efficiency: Plasma Arc, Solvated Electron Process and Gas-Phase Chemical Reduction.[19] At this moment, the plasma arc technology is widely used. An electric current ionizes a gas flow and generates temperatures in excess of 5000 °C and decomposes used refrigerants to the constituent elements. Mitsubishi Heavy Industries has introduced a destruction equipment for refrigerants that injects water with refrigerant into plasma above 6000 °C, created by a 2.45 GHz microwave.[20] This equipment requires only 5.5 kW and lime ($Ca(OH)_2$) to destruct up to 2.3 kg R-12 per hour. However, this equipment is the most advanced equipment; less advanced equipment can be used. The destruction energy is calculated to heat up the refrigerant to 6000 °C. The specific heat is unknown through this process, so water is substituted to refrigerant. The specific heat at constant pressure of R-134a up to 400 °C is 1.399 J/(K g), but no data is available above 500 °C. Therefore, the specific heat of water was assumed for the refrigerants at higher temperatures.

$$1000 \text{ g} * 6000\,^{\circ}\text{C} * 4.2 \text{ J/(K g)} = 25.2 * 10^6 \text{ Joule} = 25.2 \text{ MJ}$$

From the Eco-indicator 99, the environmental impacts of heat from gas use in industrial furnaces is estimated at 5.3 mPt per MJ. Therefore, the indicators for destruction of HFC and HCFC refrigerants is

25.2 MJ * 5.3 mPt/MJ = 133.56 mPt per kilogram of refrigerant.

The Eco-indicator 99 estimates 7300 mPt for emission of 1 kg R-134a to air and 8400 mPt for emission of 1 kg R-22 to air. In this study, it was assumed that on the average there may be 10 % inadvertent emissions of each refrigerant including residue refrigerant, illegal venting to air, and leakage through operation.

Therefore, the total disposal indicator for R-22 is

133.56 * 0.9 + 8400 * 0.1 = 960 mPt

Also, the total destruction indicator for R-134a and other HFC refrigerants is

133.56 * 0.9 + 7300 * 0.1 = 850 mPt

The ammonia is assumed to become nitric acid (HNO_3). The Eco-indicator 99 estimates the environmental impact of ammonia to be 55 mPt per kilogram.

Other hydrocarbon refrigerants are assumed to be combusted and that the heat will be recovered.

For butane C_4H_{10}, the heating value is calculated from heating value of carbon and hydrogen

8100 * (48/58) + 28600 * (10/58) = 6703 + 4 931 = 11634 Joule /mol

Expected recovery heat for 1kg is 11634 Joule/mol * 1000 g / 58 g/mol = 200.6 kJ

For propane C_3H_8, the heating value is 8100 * (36/44) + 28600 * (8/44) = 6627 + 5200 = 11827 Joule / mol

Therefore, the expected recovery heat for 1 kg is 11827 Joule/mol * 1000 g / 44 g/mol = 268.8 kJ

From the Eco-indicator 99, the environmental impact of heat from gas use in industrial furnaces is estimated at 5.3 mPt per MJ.

So Butane can be recovered 0.2 MJ/kg * 5.3 mPt/MJ = 1.1 mPt/kg

So propane can be recovered 0.268 MJ/kg * 5.3 mPt/MJ = 1.4 mPt/kg

---

Note: When the Mitsubishi equipment is used for destruction, the Eco-indicator 99 is 79 mPt for electricity consumption and 13 mPt for 0.6 kg lime to capture the chlorine and fluorine from freon's decomposition for 1 kg R-12 destruction

7.4 Sum of environmental impacts

The cumulative Eco-indicator 99 impacts are calculated from the production, operation, and disposal stages considering the required charging quantity. The results are shown in Table 12. Also, Figure 9 shows the production stage, Figure 10 the operating stage, Figure 11 the disposal stage, and Figure 12 the Life Cycle Assessment. These results can be summarized as follows:

- The operation stage is the most important with regard to environmental impacts.
- With regard to least environmental impact, butane is the preferred refrigerant and is better than the present refrigerants such as R-22 and R-134a.
- The traditional refrigerant, ammonia, has a low environmental impact.
- The Eco-indicator 99 for use of electricity has a large effect on environmental impact.
  For example, 33 mPt per kWh is used to calculate the value assuming that U.S. electricity is similar to UK's one. However, if the U.S. source of electricity is assumed to be that of Switzerland, the indicator is only 8.4 mPt per kWh. On the other hand, it can be as high as 61 mPt per kWh for electricity is Greece.
- The destruction stage of HCFCs and HFCs has seven times more impact than the production process.
- For HC refrigerants, the destruction process is favored due to energy recovery.

Table 12. Summary of environmental impacts of each refrigerant

Refrigerant		Production		Operation		Destruction		Total
		mPt	%	mPt	%	MPt	%	mPt
Butane	R-600	23	0.0%	82842	100.0%	0	0.0%	82865
Ammonia		6	0.0%	85331	100.0%	2	0.0%	85339
R-134a		39	0.0%	86053	99.7%	220	0.3%	86312
R-22		58	0.1%	87027	99.7%	232	0.3%	87316
Propane	R-290	25	0.0%	87729	100.0%	0	0.0%	87754
R-32		23	0.0%	90884	99.8%	133	0.1%	91041
R410A		35	0.0%	92298	99.7%	201	0.2%	92534
R407C		37	0.0%	93488	99.7%	210	0.2%	93736
R-125		67	0.1%	97316	99.5%	378	0.4%	97761

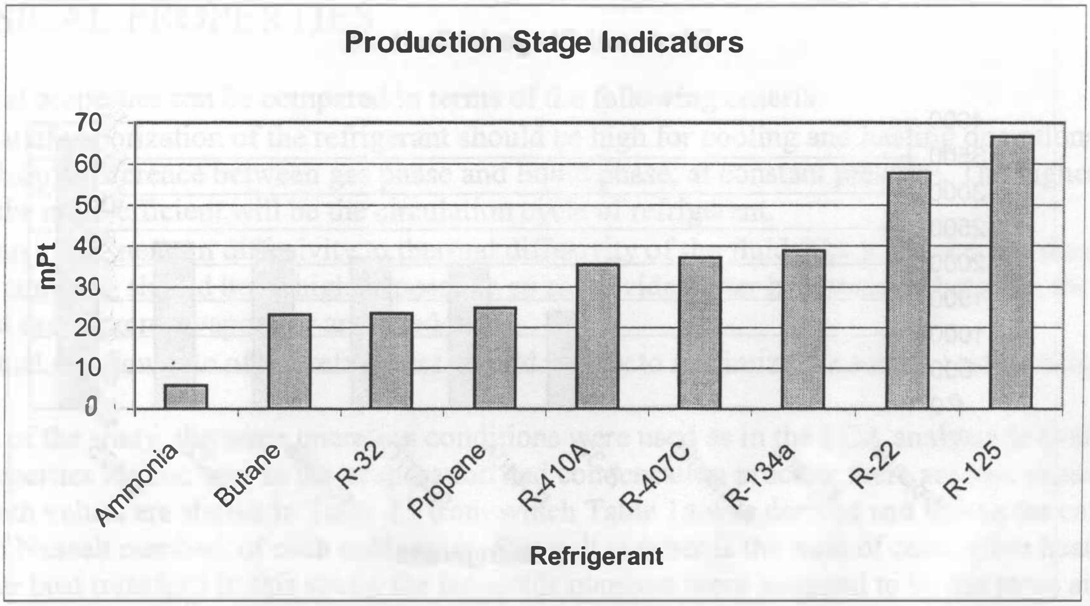


Figure 9. Production stage indicators for each refrigerant

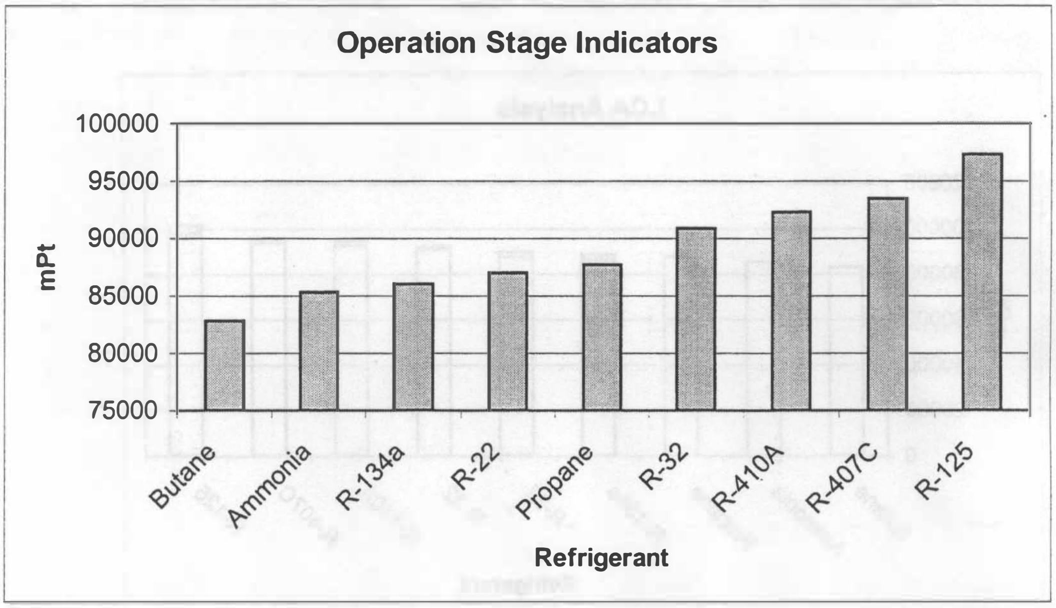


Figure 10. Operation stage indicators for each refrigerant

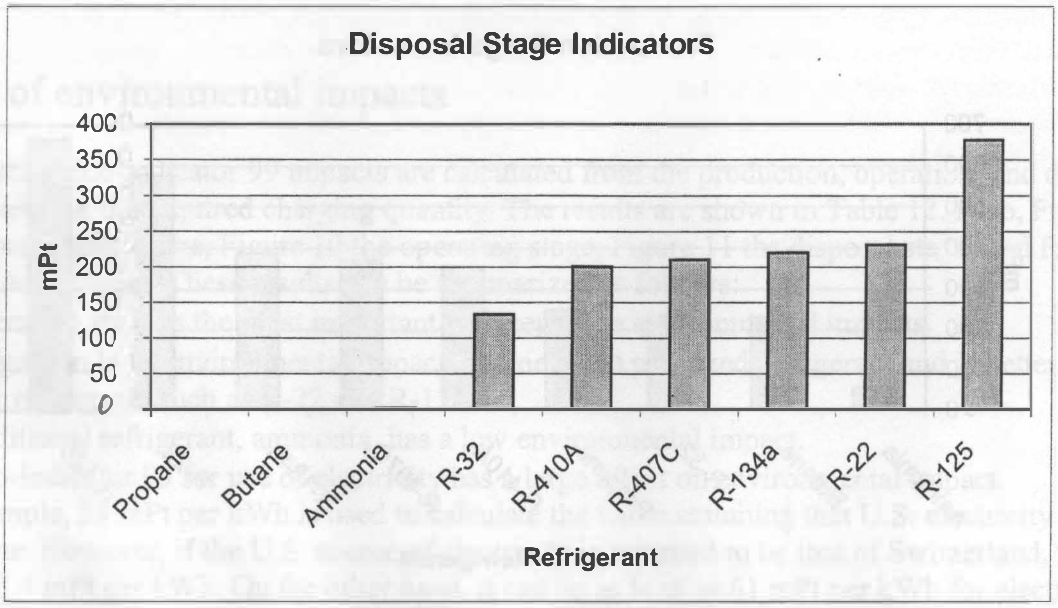


Figure 11. Disposal stage indicators for each refrigerant

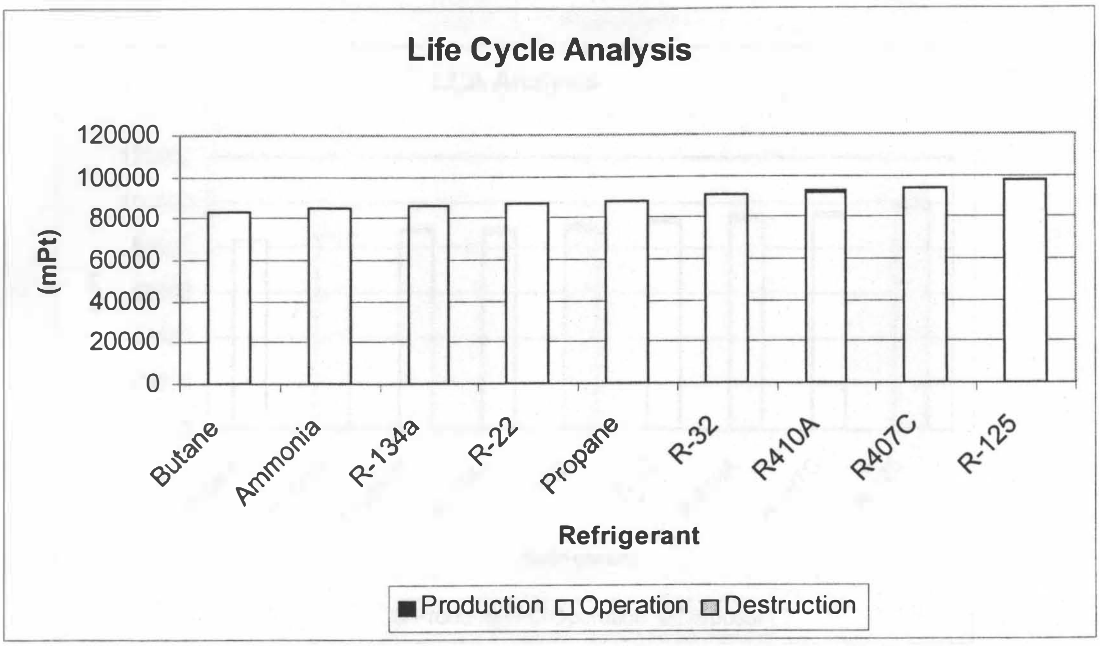


Figure 12. Life Cycle Assessments based on the summation of the Eco-indicators 99 for each refrigerant

8. PHYSICAL PROPERTIES

The physical properties can be compared in terms of the following criteria:

- The heat of vaporization of the refrigerant should be high for cooling and heating operations. This is the enthalpy difference between gas phase and liquid phase, at constant pressure. The higher is this value, the more efficient will be the circulation cycle of refrigerant.
- The ratio of momentum diffusivity to thermal diffusivity of the fluid ($Cp\ \mu/K$), i.e. the dimensionless Prandl numbers, should be as high as possible so as provide better heat transfer between the fluid and the heat exchangers, evaporator and condenser.
- The actual gas flow rate of the refrigerant should be low to minimize the work at compressor.

In this part of the study, the same operating conditions were used as in the LCA analysis to evaluate the thermal properties for cooling. In the evaporation and condensation process, there are two phases, liquid and gas. Both values are shown in Table 13 from which Table 14 was derived and shows the calculated Prandtl and Nusselt numbers of each refrigerant. (Nusselt number is the ratio of convective heat transfer to molecular heat transfer.) In this study, the Reynolds numbers were assumed to be the same and were calculated from the sample air conditioner using R-22 (Figure 7).

In addition, one of the examined parameters was the required flow rate of refrigerant since it affects the size of compressor. From practical experience, smaller equipment is easier to maintain and requires less energy to operate. In Japan, there are some air conditioners using R-410A instead of R-22, which according to the Montreal Protocol, is banned from use beyond 2030. The air conditioners with R-410A have achieved the better C.O.P., even though R-22 has better thermal properties than R-410A. This was mainly due to the use of smaller compressors, and lower flow rate than R-22. In Table 15, the actual gas flow rates are calculated from Table 13 and Table 14.

Table 13. Thermal properties of each refrigerant [12]

	Temperature °C	Pressure MPa	Density kg/m^3	Cv kJ/K*kg	Cp kJ/K*kg	Viscosity micro Pa-s	Thermal Cond. W/m-K	Phase
Ammonia	41	1.600	577.80	2.748	4.944	113.00	0.4408	liquid
	41	1.599	12.37	2.288	3.539	10.36	0.0286	gas
	2	0.463	635.80	2.797	4.628	166.50	0.5531	liquid
	2	0.462	3.71	1.933	2.709	9.12	0.0236	gas
Propane	41	1.401	465.50	1.738	2.959	81.56	0.0853	liquid
	41	1.400	30.94	1.703	2.298	9.46	0.0217	gas
	2	0.504	526.20	1.587	2.523	123.60	0.1044	liquid
	2	0.503	10.96	1.465	1.789	7.86	0.0160	gas
Butane	41	0.390	553.50	1.797	2.547	137.20	0.1008	liquid
	41	0.389	9.67	1.678	1.915	8.10	0.0183	gas
	2	0.112	598.40	1.654	2.326	198.50	0.1160	liquid
	2	0.111	2.95	1.480	1.657	6.97	0.0140	gas
R-22	41	1.572	1124.00	0.707	1.346	137.70	0.0764	liquid
	41	1.571	67.94	0.675	1.005	13.58	0.0132	gas
	2	0.532	1275.00	0.672	1.175	213.50	0.0940	liquid
	2	0.531	22.59	0.577	0.748	11.59	0.0096	gas
R-32	41	2.540	888.00	0.982	2.184	96.65	0.1216	liquid
	41	2.539	75.43	1.032	2.037	14.25	0.0200	gas
	2	0.867	1048.00	0.940	1.756	153.30	0.1526	liquid
	2	0.866	23.53	0.859	1.272	11.71	0.0120	gas
R-125	41	2.055	1081.00	0.871	1.635	104.80	0.0528	liquid
	41	2.054	146.30	0.869	1.387	15.11	0.0186	gas
	2	0.715	1311.00	0.793	1.270	196.00	0.0697	liquid
	2	0.714	44.85	0.742	0.906	11.98	0.0128	gas
R-134a	41	1.045	1142.00	0.935	1.504	161.30	0.0743	liquid
	41	1.044	51.51	0.889	1.153	12.60	0.0156	gas
	2	0.315	1288.00	0.882	1.347	264.30	0.0911	liquid
	2	0.314	15.43	0.767	0.906	10.81	0.0117	gas
R-407C	41	1.788	1063.00	0.926	1.661	123.40	0.0793	liquid
	41	1.579	70.06	0.904	1.302	13.70	0.0159	gas
	2	0.606	1229.00	0.870	1.416	203.90	0.0998	liquid
	2	0.494	21.08	0.772	0.960	11.51	0.0114	gas
R-410A	41	2.477	972.90	0.933	1.941	96.20	0.0869	liquid
	41	2.469	105.70	0.977	1.819	15.31	0.0209	gas
	2	0.852	1163.00	0.863	1.517	161.80	0.1127	liquid
	2	0.848	32.47	0.820	1.127	12.43	0.0119	Gas

Table 14. Comparison of Nusselt numbers

	Temp °C	Pressure MPa	Phase	Flow rate g/s	Reynolds -	Diameter m	Velocity m/s	Prandtl Number -	Nusselt number -
Ammonia	41	1.599	Gas	1.32	109.0	0.00187	48.9	1.282	7.5
	2	0.463	Liquid		8.3	0.00122	1.8	1.393	2.1
Propane	41	1.4	Gas	5.07	109.0	0.00750	4.4	1.002	6.9
	2	0.504	Liquid		8.3	0.00626	0.3	2.987	2.8
Butane	41	0.389	Gas	4.73	109.0	0.00681	13.4	0.848	6.6
	2	0.112	liquid		8.3	0.00365	0.8	3.980	3.0
R-22	41	1.571	Gas	8.87	109.0	0.00952	2.3	1.034	7.0
	2	0.532	liquid		8.3	0.00635	0.2	2.669	2.7
R-32	41	2.539	Gas	5.75	109.0	0.00698	3.0	1.451	7.8
	2	0.867	liquid		8.3	0.00574	0.2	1.764	2.3
R-125	41	2.054	Gas	16.35	109.0	0.05118	0.2	1.127	7.2
	2	0.715	liquid		8.3	0.01275	0.1	3.571	2.9
R-134a	41	1.044	Gas	9.53	109.0	0.01023	2.6	0.931	6.8
	2	0.315	liquid		8.3	0.00551	0.3	3.908	3.0
R-407C	41	1.579	Gas	9.10	109.0	0.00979	2.2	1.122	7.2
	2	0.606	liquid		8.3	0.00682	0.2	2.893	2.7
R-410A	41	2.469	Gas	8.69	109.0	0.00974	1.6	1.332	7.6
	2	0.852	liquid		8.3	0.00821	0.1	2.178	2.5

Note

- Diameters for R-22 determined from disassembled of R-22 air conditioner (Figure 7);
- Reynolds numbers are assumed to be the same for all refrigerants;
- Nusselt numbers are obtained from correlation $Nu = 0.664\ Re^{(1/2)}\ Pr^{(1/3)}$ [21]

Table 15. Comparison of thermal performance of each refrigerant[12]

	Molecular weight	C.O.P.	$h_{HI} - h_L$ J/g	Required mass flow rate g/s	Standard gas flow rate 10^{-6} m^3/s	Actual gas flow rate 10^{-6} m^3/s
Ammonia	17.03	7.08	1289.00	1.14	1495.28	115.01
Propane	44.10	6.92	338.20	4.33	2200.79	167.85
Butane	58.12	7.27	358.90	4.08	1573.59	421.23
R-22	86.47	6.96	192.90	7.60	1967.86	139.45
R-32	52.02	6.71	299.30	4.90	2108.21	96.00
R-125	120.02	6.33	106.40	13.77	2570.37	380.89
R-134a	102.03	7.03	179.30	8.17	1794.25	183.67
R-407C	86.20	6.55	190.00	7.71	2004.15	138.76
R-410A	72.59	6.62	198.70	7.37	2275.71	102.46

Note

- (Required refrigerant) (g/s) = (Cooling capacity) (J/g) / (cooling energy) (J/s = watts)
- (Required refrigerant in gas at standard condition) (cc/s)
  = (Required refrigerant) (g/s) * 22400 (cc) / (molecular weight)
- (Required refrigerant in gas in compressed temperature) (cc/s)
  = (Required refrigerant in gas at standard condition) (cc/s) *((273 + compressed temp)
  / (273 + 25)) / (Pressure after compressing * 10.13) (atm)

$1(cc) = 10^{-6} (m^3)$

9. OVERALL EVALUATION

Through out this paper, this study focused on environmental impacts and physical properties of various refrigerants. In order to combine the various ratings, the following method was used:

- In cases when the lower value was the preferred one (e.g. low mPt value in the case of environmental impacts and low flow rate in the case of the gas flow rate at compressor), all data were normalized by dividing by the lowest value; accordingly, in the rate of environmental impacts, butane was the lowest (normalized value =1) and all others were divided by the butane value to produce the 2nd column of Table 16.
- Where the highest value was the preferred one, the highest value was taken as the reference point and the relative values of all other refrigerants were obtained as the ratio of the highest Nusselt number divided by each number.
- The relative measures of environmental impact, required flow rate, required mass flow rate, and Nusselt number were then summed up. If the weighing coefficient for the three categories were the same, the lowest sum would represent the best refrigerant from all points of view.

It seems to be a simple method. However, it is hardly possible to provide a coefficient for each category, due to diversified cultures and importance assigned to environment or performance. On the assumption that all weighting coefficients were equal to 1, the results of the summation of impacts are shown in Table 16 and Figure 13.

Table 16. Overall evaluation

	Relative environment impact	Relative gas flow rate	Relative Nusselt number	**Summation for weighting coefficient = 1**
R-32	1.11	1.00	1.31	**3.42**
R-410A	1.14	1.07	1.22	**3.43**
Ammonia	1.03	1.19	1.42	**3.63**
R-22	1.08	1.44	1.14	**3.67**
R-407C	1.16	1.45	1.11	**3.72**
Propane	1.06	1.74	1.10	**3.90**
R-134a	1.07	1.90	1.01	**3.97**
R-125	1.22	4.01	1.04	**6.27**
Butane	1.00	4.33	1.00	**6.33**

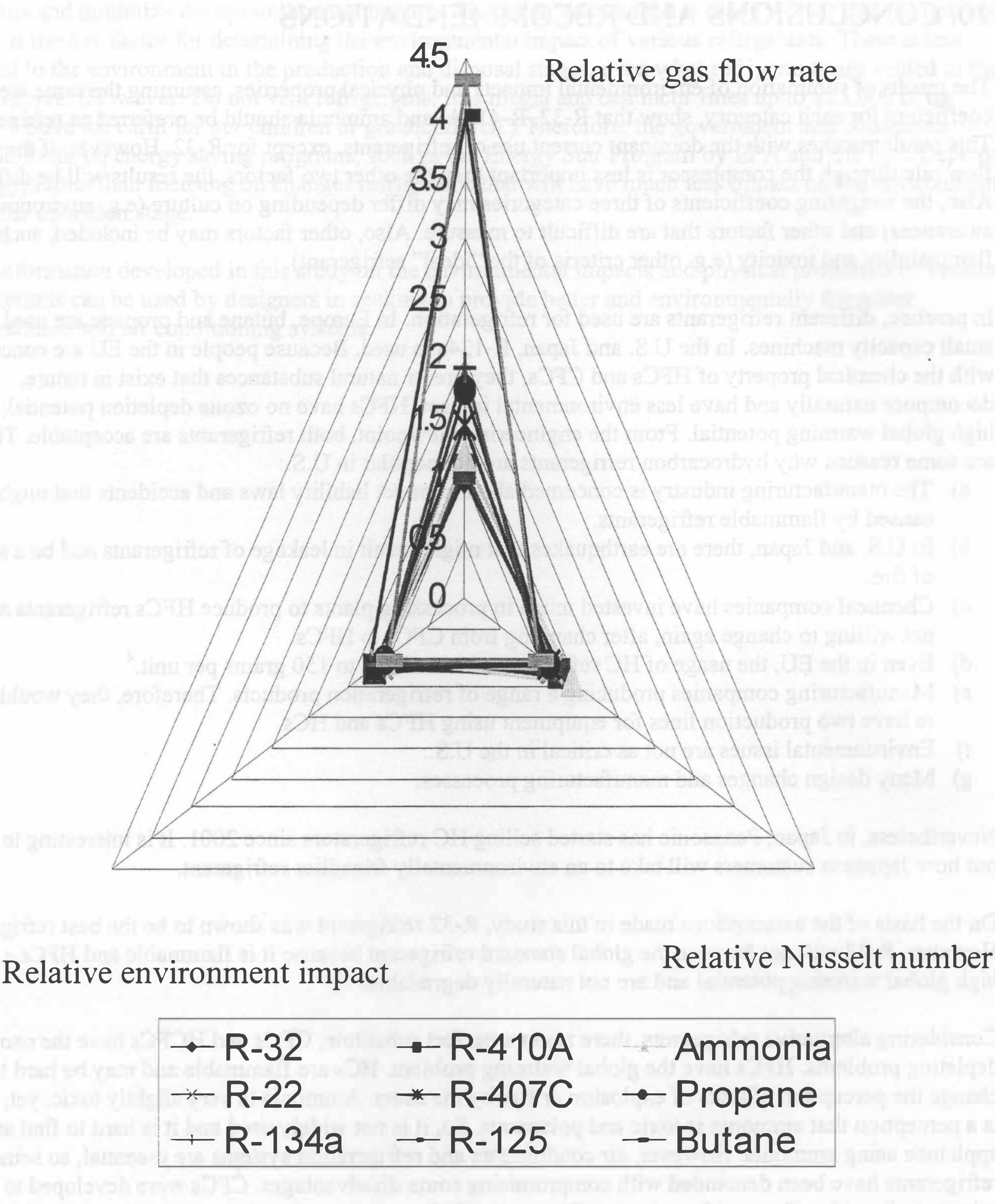


Figure 13. Overall evaluation

Note: It is vertically enlarged to make this figure see easier.

10. CONCLUSIONS AND RECOMMENDATIONS

The results of summation of environmental impacts and physical properties, assuming the same weighting coefficient for each category, show that R-32, R-410A, and ammonia should be preferred as refrigerants. This result matches with the dominant current use of refrigerants, except for R-32. However, if the mass flow rate through the compressor is less important than the other two factors, the results will be different. Also, the weighting coefficients of three categories may differ depending on culture (e.g. environmental awareness) and other factors that are difficult to measure. Also, other factors may be included, such as flammability and toxicity (e.g. other criteria of the "ideal" refrigerant).

In practice, different refrigerants are used for refrigeration. In Europe, butane and propane are used for small capacity machines. In the U.S. and Japan, R-134a is used. Because people in the EU are concerned with the chemical property of HFCs and CFCs, they prefer natural substances that exist in nature, decompose naturally and have less environmental impact. HFCs have no ozone depletion potential, but high global warming potential. From the engineering viewpoint, both refrigerants are acceptable. There are some reasons why hydrocarbon refrigerants are not popular in U.S.:

a) The manufacturing industry is concerned about product liability laws and accidents that might be caused by flammable refrigerants.
b) In U.S. and Japan, there are earthquakes that might result in leakage of refrigerants and be a source of fire.
c) Chemical companies have invested much in processing plants to produce HFCs refrigerants and are not willing to change again, after changing from CFCs to HFCs.
d) Even in the EU, the usage of HC refrigerants is restricted to 150 grams per unit.[4]
e) Manufacturing companies producing a range of refrigeration products. Therefore, they would need to have two production lines for equipment using HFCs and HCs.
f) Environmental issues are not as critical in the U.S..
g) Many design changes and manufacturing processes.

Nevertheless, in Japan, Panasonic has started selling HC refrigerators since 2001. It is interesting to find out how Japanese customers will take to an environmentally friendlier refrigerant.

On the basis of the assumptions made in this study, R-32 refrigerant was shown to be the best refrigerant. However, R-32 will not become the global standard refrigerant because it is flammable and HFCs a have high global warming potential and are not naturally degradable.

Considering alternative refrigerants, there is not a perfect substitute. CFCs and HCFCs have the ozone-depleting problems. HFCs have the global warming problem. HCs are flammable and may be hard to change the perception of risks of explosion or fire by the users. Ammonia is very slightly toxic, yet, there is a perception that ammonia is toxic and poisonous. So, it is not widely used and it is hard to find any appliance using ammonia. However, air conditioners and refrigeration systems are essential, so some refrigerants have been demanded with compromising some disadvantages. CFCs were developed to substitute for either flammable or toxic refrigerants. HFCs were introduced to protect the ozone-depleting problem. EU has started to use HCs to avoid the global warming problem caused by venting to the atmosphere. What will be next? Every few generations there is the use of new refrigerant.

The ozone depletion is a global problem like global warming. However, alternative refrigerants are domestic issues regarding recycling or disposal of refrigerants and good management of hazardous wastes. At this moment, global standardization is hard to achieve, so each government should decide which criteria for the ideal refrigerant should be relaxed in order to maximize the benefits of refrigeration systems and minimize the environmental impacts. However, this study has made it clear that the operation stage is the key factor for determining the environmental impact of various refrigerants. There is less impact to the environment in the production and disposal stages, even what refrigerants are vented to the atmosphere. (However: Do not vent refrigerants. It is illegal and can incur fines up to $25,000 in the U.S.!!! Save the earth for our children or grandchildren.) Therefore, the government and consumers should focus on energy saving programs, such as the Energy Star Program by EPA and the U.S. Dept. of Energy, rather than focusing on changes refrigerants that will have much less impact on the environment than the operation stage.

The information developed in this study on the environmental impacts and physical properties of various refrigerants can be used by designers in seeking to provide better and environmentally friendlier refrigeration and air conditioning systems.

11. REFERENCES

1. Carnot Foundation. (2000). http://www.carnot.org/ENGLISH/Default-Eng-5.HTM
2. Mohinder S. Bhatti, Ph.D.. (1999). A Historical Look at Chlorofluorocarbon Refrigerants, CH-99-21-3, ASHRAE Transaction: Symposia
3. The Montreal Protocol on Substances that Deplete the Ozone Layer : as either adjusted and/or amended in London 1990, Copenhagen 1992, Vienna 1995, Montreal 1997, Beijing 1999. UNEP, Ozone Secretariat, United Nations Environment Programme. ISBN: 92-807-1888-6
4. Peter Baz., Klaus Meyersen., and Dirk Legatis. (1996). Hydrocarbon Technology" The Use of Hydrocarbons as Foaming Agents and Refrigerants in Household Refrigeration". Deutsche Gesellschaft für Technische Zusammenarbeit
5. Refrigeration service engineers society, http://www.rsestc.org/hvactimeline.htm
6. Air conditioning | Heating | Refrigeration the NEWS. (2001). http://www.achrnews.com/CDA/ArticleInformation/features/BNP__Features__Item/0,1338,24844,00.html
7. Environmental Protection Agency, http://www.epa.gov/ozone/title6/snap/safety.html
8. St. Simon's Anglican Church. (2002). http://www3.bc.sympatico.ca/st_simons/cr0003.htm
9. Enchanted Learning Software. (2001). http://www.enchantedlearning.com/inventors/indexr.shtml
10. Ozone Secretariat, United Nations Environment Programme (2000 edition). Action on Ozone
11. Alternative Fluorocarbons Environmental Acceptability Study. (http://www.afeas.org/)
12. Refprop program, National Institute of Standards and Technology
13. Mark Goedkoop, Suzanne Effting and Marcel Collignon. The Eco-indicator 99: A damage oriented method for Life Cycle Impact Analysis. PRe Consultants B.V.
14. Alternative Fluorocarbons Environmental Acceptability Study. (http://www.afeas.org/tewi.html)
15. Lecture Note, Microelectronics Heat Transfer Laboratory, Department of Mechanical Engineering, University of Waterloo, Waterloo, Ontario, Canada http://www.mhtl.uwaterloo.ca/courses/me354/lectures/pdffiles/ch6.pdf
16. OECD, OECD Environmental Indicators 2001. (2001). pp.82.
17. Billy C. Langley. Refrigerant Management(1994): The recovery, Recycling, and Reclaiming of CFCs. DELMAR. ISBN 0-8273-5590-4.
18. IPCC, Climate Change 2001: The Scientific Basis. ISBN 0521014956
19. Greenpeace (7 October 1998). Technical criteria for the destruction of stockpiled persistent organic pollutants. ISBN 90-73361-47-8
20. Masahiro Bessho., Toshio Hattori., Minoru Danno., Tetsuya Ikeda., and Yuji Okada. Mitsubishi Heavy Industries, Ltd. Technical Review Vol.37 No.3 (Oct. 2000). Pp.83-87.
21. Robert S. Brodkey., and harry C. Hershey.. Transport Phenomena: A unified Approach. (1988). McGraw Hill. pp.575. ISBN 0-07-007963-3
22. UNEP DTIE's OzonAction Programme. http://www.uneptie.org/ozonaction/faq/abc.html#ac

Appendix A Refrigerant history

1748		William Cullen, in Scotland, initially developed the concept of mechanical / chemical refrigeration. He demonstrated that the evaporation of ether in a partial vacuum produces cold. (Up until almost the 20th century, early refrigeration consisted solely of using natural ice for food preservation.)
1755		William Cullen cooled water by drawing a vacuum over it. This was the earliest known attempt at vapor compression refrigeration.
1777		The principles of absorption were discovered.
1803		Thomas Moore builds a box-within-a-box for the sole purpose of preserving food and calls it the "refrigerator."
1805		Oliver Evans proposed a closed circuit vapor compression system.
1820		Artificial ice was made for the first time in an experiment
1824		Michael Faraday discovers the principle of absorption type refrigeration.
1834		Jacob Perkins patents an ice-producing machine.
		Artificial ice manufacturing becomes practical.
1844		Jacob Perkins, an American engineer, invented and built the first practical refrigerating machine which later led to the modern compressor systems. This was the first workable refrigeration system to be built using the vapor compression cycle.
		Dr. John Gorrie (1803-1855), director of the U.S. Marine Hospital at Apalachicola, FL, designed the first commercial reciprocating refrigeration machine.
1845		First air machine was developed.
1850		An absorption machine was developed using water and sulfuric acid.
		The first absorption machine was developed by Edmond Carr, in 1850, using water and sulfuric acid.
		The first successful continuous operating heat absorption machine, using ammonia as refrigerant and water as absorbent, was built. This was the only the absorption system to gain commercial importance during the 19th and 20th century.
1851		Dr. John Gorrie was granted U.S. Patent 8080 for building the first commercial machine in the world used for refrigeration and air conditioning. Gorrie's machine subsequently received worldwide acclaim, recognition and acceptance.
1852		Lord Kelvin developed the heat pump concept.
1855		A German engineer built the first absorption type refrigeration system.
		Commercial refrigeration began to take off shortly thereafter, as American civil engineer Alexander Twining advanced the work of others in vapor-compression refrigeration. Twining's ice-making plant in Cleveland, OH, in 1855 was perhaps the earliest success in manufacturing ice in commercial quantities.
1856		Azel Lyman of New York invents a "Method of Cooling and Ventilating Rooms" using air blown over ice in racks at a room's ceiling.
1857		Ether was used widely as a refrigerant in the brewing and meat processing industries.
		Edmond Carr 's brother, Ferdinand Carr, demonstrated an ammonia/water refrigeration machine in 1859. Patented in France in 1859 and in the usa in 1860
1866		A mixture called chemogene, consisting of petrol ether and naphtha, was patented as a refrigerant for vapor-compression systems in 1866. Carbon dioxide was introduced as a refrigerant in the same year.
1872		David Boyle designs the original ammonia compression refrigeration machine.

		Ammonia was first used in vapor-compression systems in 1873, sulfur dioxide and methyl ether in 1875, and methyl chloride in 1878.
		The first practical, portable compressor refrigeration machine was built in 1873 in Munich, Germany by Carl Linde. His early prototypes used methyl ether, but he switched to ammonia in 1877, and his refined design was commercially manufactured in 1879.
1876		Sulfur dioxide compressor was developed.
1880		Reciprocating compressors were developed. These compressors were used in commercial applications for ice making, fish processing, meat packing and brewing.
1881		The use of carbon dioxide was introduced.
1882		The first electric power plant in New York opened as an outgrowth of Thomas Edison's research and inventions. For the first time, there is an inexpensive source of energy available to commercial and residential buildings.
		Nikola Tesla and George Westinghouse receive a patent for their invention of the electric fan.
1883		Warren Johnson invents the first automatic temperature control, leading to the formation of Johnson Electric Service Company, the predecessor to Johnson Controls.
1885		Al Butz creates an automatic furnace value opener, the Damper Flapper, which is the forerunner of the thermostat. His company, Butz Thermo-Electric Regulator Company is a predecessor to Honeywell.
1890		Demand for small units for home and store use developed. A very warm winter resulted in a severe shortage of natural ice for refrigeration. Prior to this time, little artificial ice was produced, but this single event helped to start the mechanical ice-making industry.
1900		* Professor C.F. Marvin, US Weather Bureau devised "Psychometric Tables for Obtaining the Vapor Pressure, Relative Humidity and Temperature and the Dew Point of Air."
		* Warren Johnson invents the humidostat.
1901		Alfred Wolff designs a cooling system for the New York Stock Exchange using a 300-ton cogeneration system that provided free cooling.
1902		* Dr. Willis H. Carrier (1876-1950), who is recognized as the "Father of Air Conditioning," discovers the relationship between temperature and humidity, and how to control them.
		* Dr. Willis H. Carrier builds the first air conditioner to combat humidity inside a printing company.
1904		* Dr. Willis H. Carrier develops the "air washer," a chamber installed with several banks of water sprays for air humidification and cleaning. Carrier's method of regulating humidity and temperature, by controlling the dew point of supply air, is still used today in many industrial applications like lithographic printing plants and textile mills.
		* A direct expansion cooling system is installed in a building at the St. Louis World's Fair, introducing thousands of fair visitors to comfort cooling.
		* Refrigeration engineer Gardner T. Voorhees first introduced the public to the cooling side of air conditioning at the 1904 World's Fair in St. Louis, MO — the same World's Fair at which ice cream was introduced.
1906		* Stuart W. Cramer coins the term "Air Conditioning" and uses the term in a patent claim for a humidifying head.
		* Other mechanically refrigerated comfort cooling systems installed around this time

		included the St. Nicholas Garden in New York City in 1906 and the system designed by Arthur Feldman for the bank offices of Kuhn, Loeb & Co. in New York City. In 1907, a carbon dioxide direct-expansion air cooling system, designed by Andrews & Johnson Co. and Fred Wittenmeier of Kroeschell Bros. Ice Machine Co., was installed for the Chicago Congress Hotel's banquet and meeting rooms.
1906		Willis Carrier patents his new invention calling it an "Apparatus for Treating Air."
1908		Carrier Air Conditioning Company of American, a wholly owned subsidiary of Buffalo Forge Co., begins operation.
1910		* The first automotive heater was introduced as an accessory for the "horseless carriage." The small heater burned coal or charcoal to warm the passenger compartment continuously -- all for the paltry sum of $4.00 for this latest new gadget!
		* Mechanical domestic refrigeration first appears.
1911		* Willis Carrier formally presents an epoch making paper dealing with the properties of air. His assumptions are formulas formed the basis for the first psychometric chart which in turn becomes the authority for all fundamental calculations involving air conditioning.
		* Folies Berger Theater, New York City, installs the first air-conditioning system in a theater.
1913		* J.M. Larsen produces a manually operated household refrigeration machine.
		* Fred W. Wolf Jr. began manufacturing a refrigerating machine called the "DOMELRE," short for DOMestic ELectric REfrigerator, in 1914. Packard Motor Car Co. bought the rights to it in 1916, founded the Isko Corp. to manufacture the units, and moved its facilities from Chicago, IL to Detroit, MI.. Ultimately, the DOMELRE was a failure
1918		Kelvinator produces the first automatic domestic refrigerator for the American market. 67 Kelvinator machines are sold this year.
1920		* The domestic refrigeration industry emerges as a very important new industry.
		* In 1920, GE began using a hermetically sealed compressor. The "General Electric Refrigerator" was announced in 1925. The company decided to sell the refrigerator as a whole unit, rather than trying to retrofit iceboxes. Later, GE came out with the "Monitor Top," which sold well.
1921		Willis Carrier first introduces the open-type gear-driven centrifugal refrigeration machine, in which the motor is housed separately from the compressor.
1922		* Willis Carrier is acknowledged as having invented the centrifugal refrigeration machine. * The first air conditioned movie theater opens in Los Angeles, California (Grauman's Metropolitan Theatre). Not to be outdone by LA, NYC movie houses get into the act by providing "Cooled by Frosted Air" creature comforts to their patrons at such famous movie houses such as Rivoli, Paramount, Roxy, and the Loew's Theaters on Times Square.
1923		Fast freezing to preserve food is developed.
1924		The first hermetically sealed motor- compressor is developed by the General Electric Company for domestic refrigerators.
1925		Carrier Corporation introduces "Weathermaker," a high-efficiency residential gas furnace incorporating a blower and filter. This was invented by Carlyle Ashley.
1926		Dichloroethene (dilene) was used in Willis Carrier's first centrifugal compressors, and was replaced with methylene chloride in 1926.
1927		* Automatic refrigeration units, for the comfort cooling part of air conditioning

		appear.
		* "The Electrolux," an automatic domestic refrigeration absorption unit, appears.
		* The first practically applied heat pump was installed in Scotland.
1928		* General Electric introduces the "Monitor Top," the first sealed or "hermetic" automatic domestic refrigeration unit.
		* Frigidaire develops and installs the first room cooler.
		* The first fully air conditioned office building was built in San Antonio, Texas. Named the Milan Building, it was designed by George Willis. The building's air conditioning system consisted of one centralized plant to server the lower floors and numerous other small units to serve the top office floors.
		* The Chamber of the House of Representatives becomes air conditioned.
1929		* The Senate Chambers in the Capital become air conditioned. By the end of the year, the entire US Capitol is air conditioned. The conditioned air is supplied from overhead diffusers that maintain a temperature of 75 F and a relative humidity of 40% during summer, and an 80 F and 50% relative humidity during winter. The volume of supply air is controlled by a pressure regulator to prevent cold drafts in the occupied zones.
1930		* The first self-contained room air conditioner is developed by General Electric. It is a console- type unit with a hermetically sealed motor- compressor (an arrangement in which the motor and compressor are encased together to reduce the leaking of refrigerant) and water cooled condenser, using sulfur dioxide as the refrigerant. Thirty units were built and sold the following year.
		* The White House, the Executive Office Building and the Department of Commerce become air-conditioned.
		Drs. Thomas Midgley and Henne of the DuPont Company develop the fluorocarbon "Freon-12" refrigerant. This major discovery led to a new nontoxic, nonflammable refrigerant that was widely used on reciprocating and centrifugal compressors.
		1930-1939 Dr. Willis Carrier develops the conduit induction system for multi-room buildings, in which recirculation of space air is induced through a heating/cooling coil by a high-velocity discharge air stream. Carrier's system supplies only a limited amount of outdoor air for the occupants.
1931		* Freon-12 is introduced as a commercial refrigerant.
		* The "Atmospheric Cabinet" is developed by Carrier Engineering Company and is installed in May of this year.
1931		Lincoln automobiles are introduced with the first "modern" heaters. The Lincolns' heater housing contained finned tubes through which hot engine coolant was circulated. An electric fan blew air over the fins; volume and direction were controlled with flaps.
		Columbian run on the Baltimore and Ohio railroad becomes the first air-conditioned train route.
1932		The Thorne company introduces the first window air conditioner.
1933		The Refrigeration Service Engineers Society (RSES) is founded and organized through the efforts of Herbert Herkimer, J.F. Nickerson and Harold T. McDermott.
1934		* Carrier introduces the hermetic centrifugal chiller, with a hermetically sealed motor- compressor assembly.
		* The Ford Motor Company introduces an after market heater to "air condition your V-8"; most cars prior to this point had no heater. The new heater is installed or mounted directly to the engine exhaust manifold. Hot exhaust gases from the engine pass through flues in a small boiler-like compartment, before exiting through the

		exhaust pipe. Much of the heat from the exhaust is absorbed into the flue walls. The engine fan acts as a blower to force fresh air into an intake pipe and past the flue walls. This air picks up the heat from the flue walls and delivers it to the registers via tubing run to the front and rear passenger compartments. It only cost $14.00 and was installed "while you wait."
1935		* Frederick McKinley Jones produces an automatic refrigeration system for long-haul trucks. The system was, in turn, adapted to a variety of other common carriers, including ships and railway cars.
		* The first hermetic compressor for air-conditioning duty is introduced. The outer shell is bolted instead of being completely welded like present-day compressors. Motor speed is 1750 rpm versus 3600 rpm of modern units. Although the first hermetic compressor is pretty large by today's standards, the concept of passing cooling suction gas over the motor windings became universally accepted by all compressor manufacturers.
1936		* Chrysler Corporation's Airtemp Division introduces its "Store Coolers," self-contained unitary packages for commercial applications. The early models used a water-cooled condenser and were in the three to five tons capacity range.
		* Albert Henne synthesized R-134A.
1937		The capacity of centrifugal chillers increases to 700 tons.
1938		* The direct-driven hermetic centrifugal chiller is introduced by the Trane Company.
		* Nash (automobile) offers the "Weather Eye Conditioned Air" option which was actually a fan- boosted, filtered ventilation system, not true air conditioning. Nash continues offering this option through the post WWII years.
1939		* Packard (automobile) markets the first true mechanical air conditioning system and it was controlled only by the blower switch. During the winter, the owner had to remove the belt to turn the compressor off and the cooling coils filled half of the trunk!
		* Bacharach markets the first heating service instruments -- a portable gas analyzer name the "Fryite."
1940		* Practically all domestic refrigeration units were now of the hermetic type.
		* Servel introduces a unit using water as refrigerant and lithium bromide as the absorbing solution. The capacities of these units ranged from 15 to 35 tons.
1941		Cadillac (automobile) not to be outdone by Packard, introduces a similar air conditioning system of its own as an option. Both systems were very expensive, did not incorporate a clutched compressor, took trunk space, and had limited availability.
1942		* R.S. Gaugler develops the basic principles of the heat pipe. The heat pipe is later used in aerospace, industrial and pipeline applications.
		* Pepco becomes the nation's first summer peaking utility.
1945		* Carrier introduces the first large commercial lithium bromide absorption chillers. These units were developed with 100 to 700 ton capacity, using low-pressure steam as the heat source.
		* There are over 6,400 Locker plants now in existence. In 1936, there was less than a million pounds of frozen food processed, but by 1945, this industry has grown to over 7,000,000 pounds of frozen food processed. Over 300 firms are now making equipment for the frozen food industry.
		* Refrigerant R-13 is introduced.
1946		* After World War II, the demand for room air- conditioners began to increase dramatically. Some 30,000 were produced this year.
		* Prior to World War II, it was estimated that there were 30,000 refrigeration

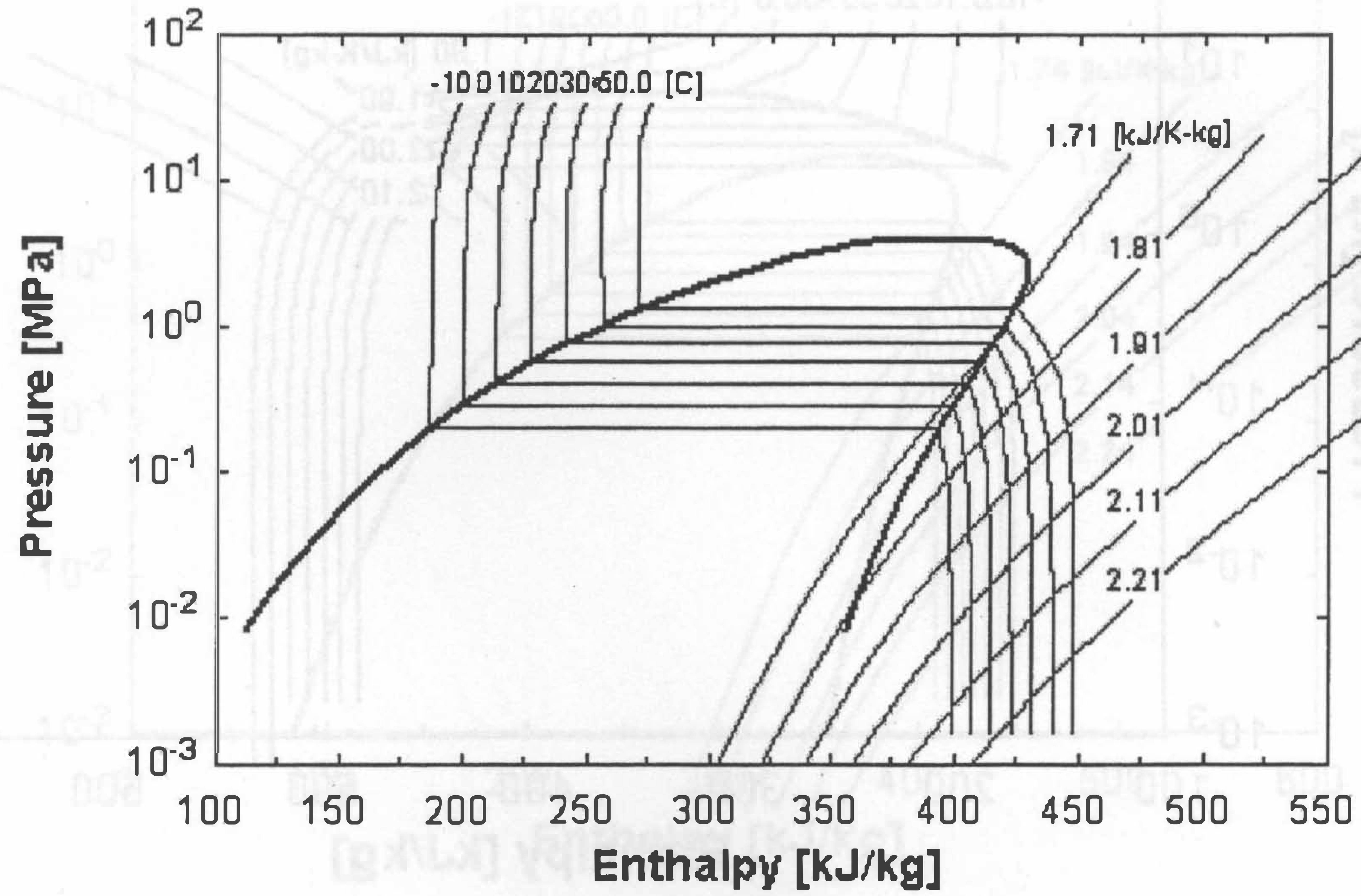
		servicemen. During the war, that number was reduced to 10,000. After the war, only 25,000 refrigeration service personnel are available in the manpower pool. However, pent up delayed consumer demand requires a workforce of 50,000 refrigeration servicemen. Critical shortages result due to lack of good, qualified service personnel, which continue until to this day.
1946-1949		Texas millionaires around the Dallas/Fort Worth area begin demanding air conditioning for their Cadillacs and Lincolns. Local area shops start improvising "Hang On" units to meet the demand. They use Chieftan Compressors with no drive clutches – thus compressor speed varies with engine rpm. Condensers are mounted in front of the radiator. Blower coils are placed against the back seat cushion in front of the trunk. This heavy consumer demand drives the post war surge towards automotive air conditioning.
1946-1953		Post World War II HVAC/R products consist mainly of applied machinery systems for large buildings, water-cooled store conditioners, and window air-conditioners.
1950		* Annual sales of room air conditioners exceeds 100,000 units for the first time, and never drops below this level again.
		* Dr. Willis H. Carrier (1876-1950), regarded as the "Father of Air Conditioning" dies in October. HVAC/R industry leaders and historians alike acknowledge Dr. Carrier as having contributed more to the advancement of the industry than any other individual.
		* Refrigerant R-500 is introduced.
1950-1955		Heat pumps are built and marketed by companies in Southern US for local markets. However, many units are sent North to be installed in colder climates and unsuitable applications. As a result heat pumps have a high failure rate and get a very bad reputation. This dismal failure practically destroys the heat pump market – which does not recover until the 1970's.
1950-1970		Large builders like Levitt and Sons of Levittown, PA; Ryan Homes of Pittsburgh, PA, and Fox and Jacobs of Dallas, TX begin building large tract housing developments with central air conditioning as standard equipment. This major development forces other builders and the financial community to get on the bandwagon to go to central air conditioning as a marketing tool to sell houses.
1953		* Industry introduces air-cooled operating systems instead of water cooled for condensing purposes. This major break through causes sales to skyrocket. Early systems are primarily horizontal package units for mounting in attics or on slabs at ground level. There are many advantages: no refrigerant piping, factory charged, minimum electrical, and little or no plumbing. * Room air conditioner sales exceed one million units with demand still exceeding supply.
		* Air-Conditioning and Refrigeration Institute (ARI) is formed through a merger of two related trade associations. ARI is a trade association of HVAC/R manufacturing companies.
1954		Nash automobile teams up with Kelvinator to produce the Nash-Kelvinator "Weather Eye." This is the first true refrigerated air conditioner for the mass market. All components are installed under the hood or in the cowl area. The new A/C system is compact, easily serviceable and relatively inexpensive.
1955		* R-12 becomes the standard refrigerant in automobile air conditioners.
		* Other manufacturers join E.I. Dupont de Nemours and Company in manufacturing fluorocarbon refrigerants.
		* By now nearly a dozen companies have sprung up in Texas to meet the demand for

		automobile air conditioning. A popular economy model came out which is mounted under the dash and it is dubbed the "crotch cooler" by the public.
1956		* Erling Berner brings the most advanced European air curtain technology to the US from Sweden.
		* A new refrigerant numbering system is adopted by the HVAC/R industry: R-12, R-22, R-502, etc. to have a standard designation for all the many different trade names of refrigerant.
		* Ozone measurements are started at the British Antarctic base at Halley Bay. Ozone levels are found to fall dramatically in September and October to 150 DU (Dobson Units) or about half the normal level. Thus the "Ozone Hole" is actually discovered at this time, but British scientists are not cognizant of this fact for many years to come.
1957		The first rotary compressor is introduced, permitting units to be smaller, quieter, and weigh less. The rotary is more efficient than the reciprocating compressor.
1957-1963		Industry introduces the "rooftop" combination gas heating and electric cooling unit in the 2 to 5 ton system range to be installed on the rooftops of low-rise commercial structures. This major innovation still accounts for the most dramatic growth sales rate of all packaged year- round conditioners.
1957-1973		Residential packaged unitary system sales start a dramatic growth from over 200,000 units this year to 2,767,792 by 1973.
1959		* The first gas valve with a built-in pressure regulator valve that truly merited the name "combination gas control valve" is introduced by Honeywell.
		* The American Society of Air-Conditioning Engineers merges with the American Society of Refrigeration Engineers to form ASHRAE.
1960		Cadillac introduces a bi-level HVAC system in their automobiles. This is the first modern automotive HVAC system which could cool the top level of the car while heating the lower level. Consequently this method provided a means of controlling in-vehicle humidity levels.
1962		* A little over 11% (756,781 units) of all cars sold in the US are equipped with air conditioning. This includes both factory installed and after market systems.
		* Refrigerant R-502 is introduced.
		* Air conditioning plays a vital role in John Glenn's mission as the first American to orbit the earth.
1963		York installs a three-pipe air conditioning system in the Library of Congress. Built in 1897, the building contained masonry ducts, formally used for warm air heating. York induction units are installed under windows with piping running through the ducts, resulting in a very inconspicuous installation. Chilled water is supplied from chillers totaling 17,000 tons of refrigeration, which delivers water to all capitol buildings.
1965		* Dr. Irving Selikoff studies over 1,500 insulation workers who have been engaged in their trade for a number of years. Dr. Selikoff finds that of workers with more than 40 years work experience in the industry, more than 90% have asbestosis related medical problems. Thus a link between asbestos and cancer is first established.
		* On November 9 - 10, the greatest power failure in history strikes seven northeastern states and Ontario, Canada. About 30,000,000 people are plunged into total darkness over an 80,000 square mile area. Con. Ed.'s (of NY) power grid collapses and as other utilities rush into bolster the failing grid, they are also pulled down with Con Ed. In NYC, the power failed at 5:27PM and is not fully restored for 13.5 hours. Two people die as a result of the blackout. On a brighter note, nine

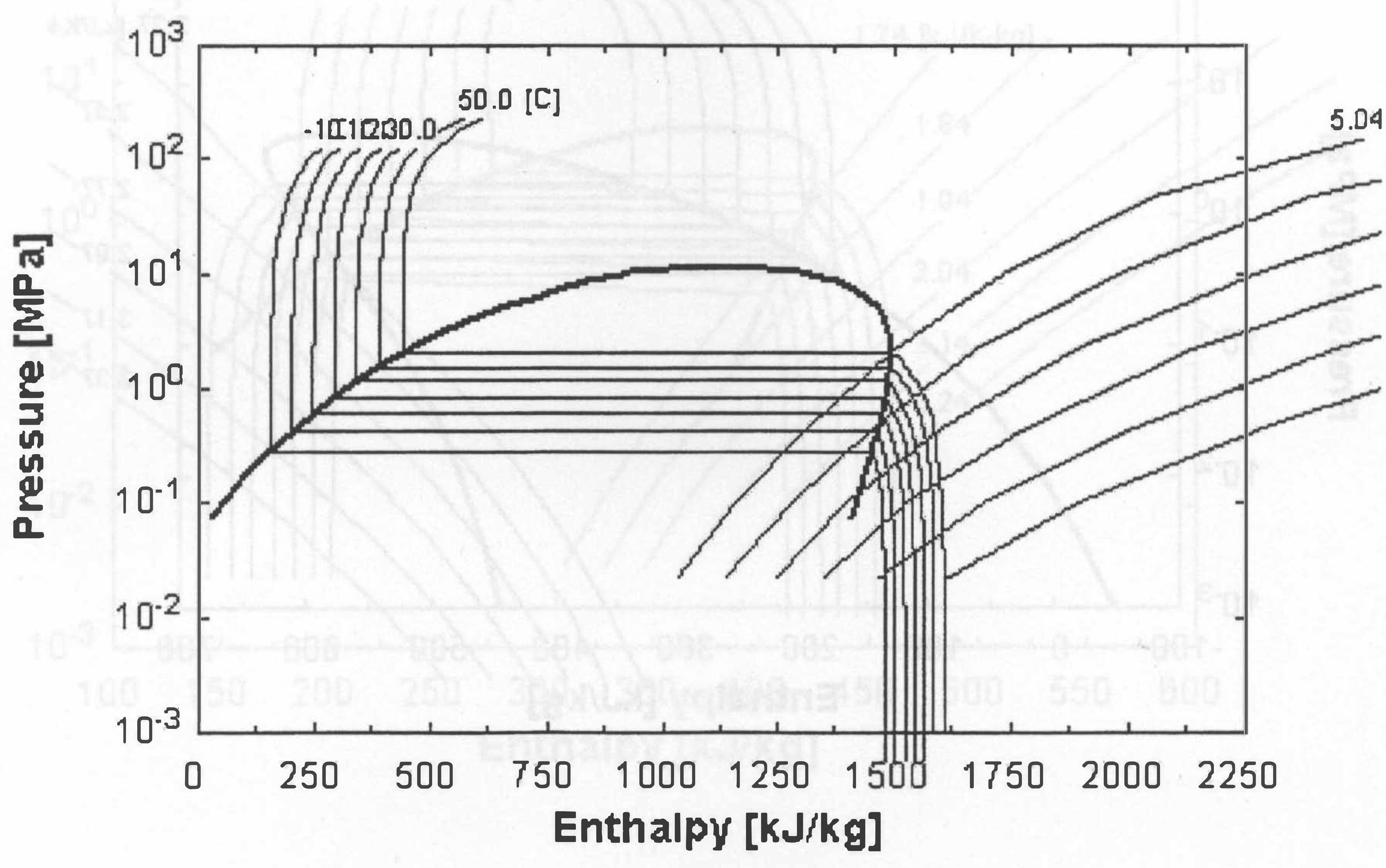
		months later there is a surge in new births at the area's hospitals.
1967		The total number of cars sold in the US that are equipped with air conditioners has increased to 3,546, 255 units. This represents an astounding increase of 469% over sales five years earlier.
1968		38% of all US automotive domestic production is delivered with the air conditioner option.
1976		* The World's largest cooling tower is completed in Uentrop, Germany. Rising some 590 feet, the cooling tower is adjacent to a nuclear plant.
		* York produces the first computer-controlled heat pump.
		* In August, 27 persons die from a mysterious legionnaire's disease after attending an American Legion convention at the Bellevue Stratford Hotel in Philadelphia. The cause of the deaths is later determined by the CDC in Atlanta to be a bacteria in the water of the hotel's cooling tower. Indoor Air Quality (IAQ) begins to be debated as a serious area of concern.
1977		* On May 11, US Government announces ban on spray cans using "freon" to take effect in two years. The chemical is said to destroy the ozone layer.
1987		* The United Nations Monteal Protocol for protection of the Earth's ozone layer is signed, establishing international cooperation on the phase-out of CFC's.
		* The Programme for Alternative Fluorocarbon Toxicity Testing (PAFT) is a cooperative effort sponsored by the major producers of CFCs from nine countries. PAFT was designed to accelerate the development of toxicology data for fluorocarbon substitutes, as refrigerants and for other purposes. Examples of the other uses include as blowing agents, aerosol propellants, and solvents. The PAFT research entails more than 100 individual toxicology tests by more than a dozen laboratories in Europe, Japan, and the United States. The first tests were launched in 1987, to address R-123 and R-134a (PAFT I).
1996		CFC production in the US ends.
2030		HCFC production will end in most countries.

Appendix B P-H diagram of each refrigerant

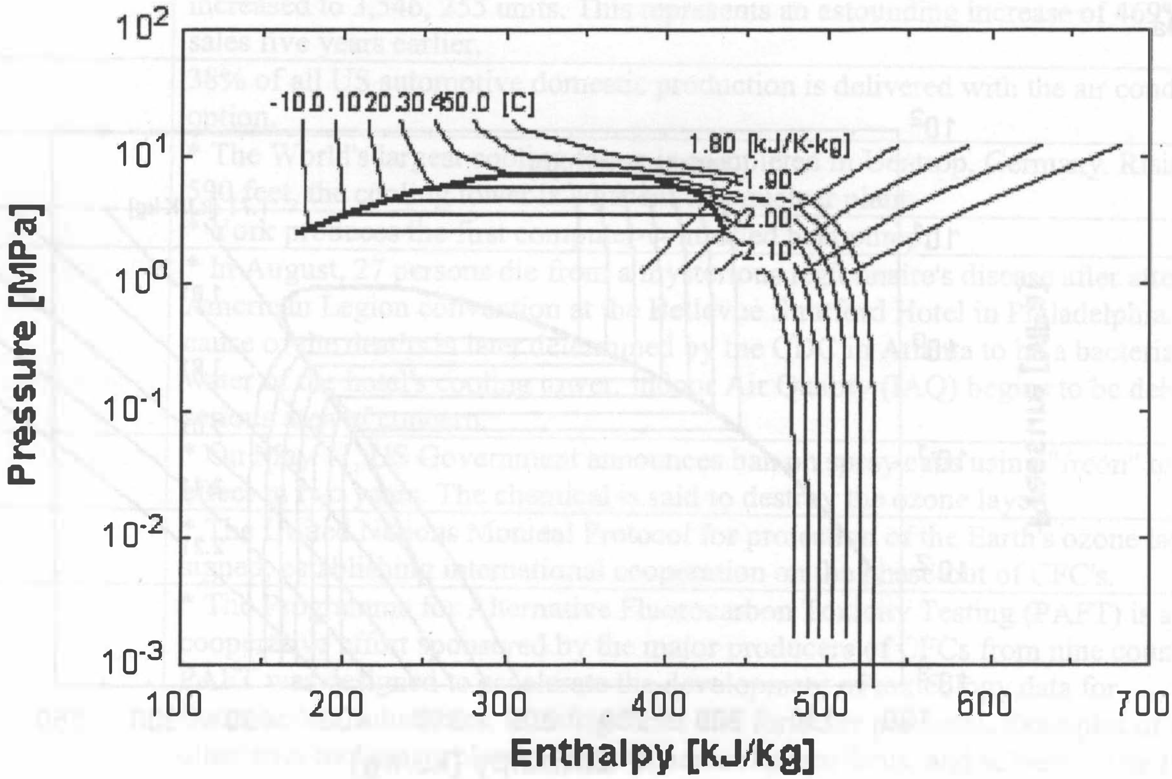
R134a



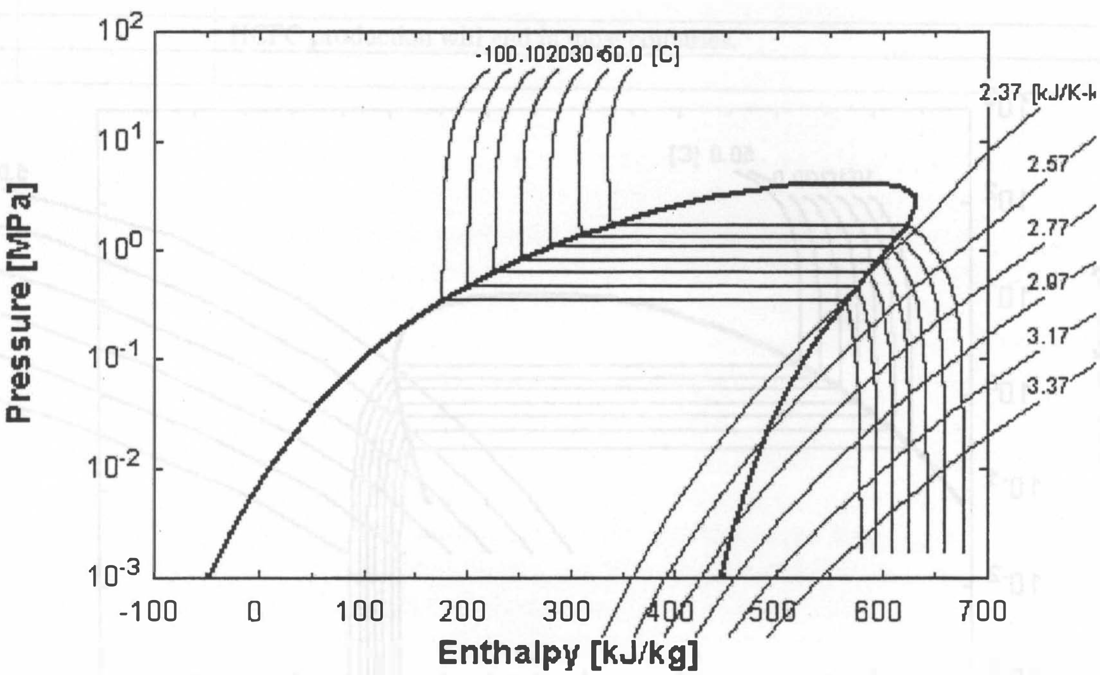
Ammonia



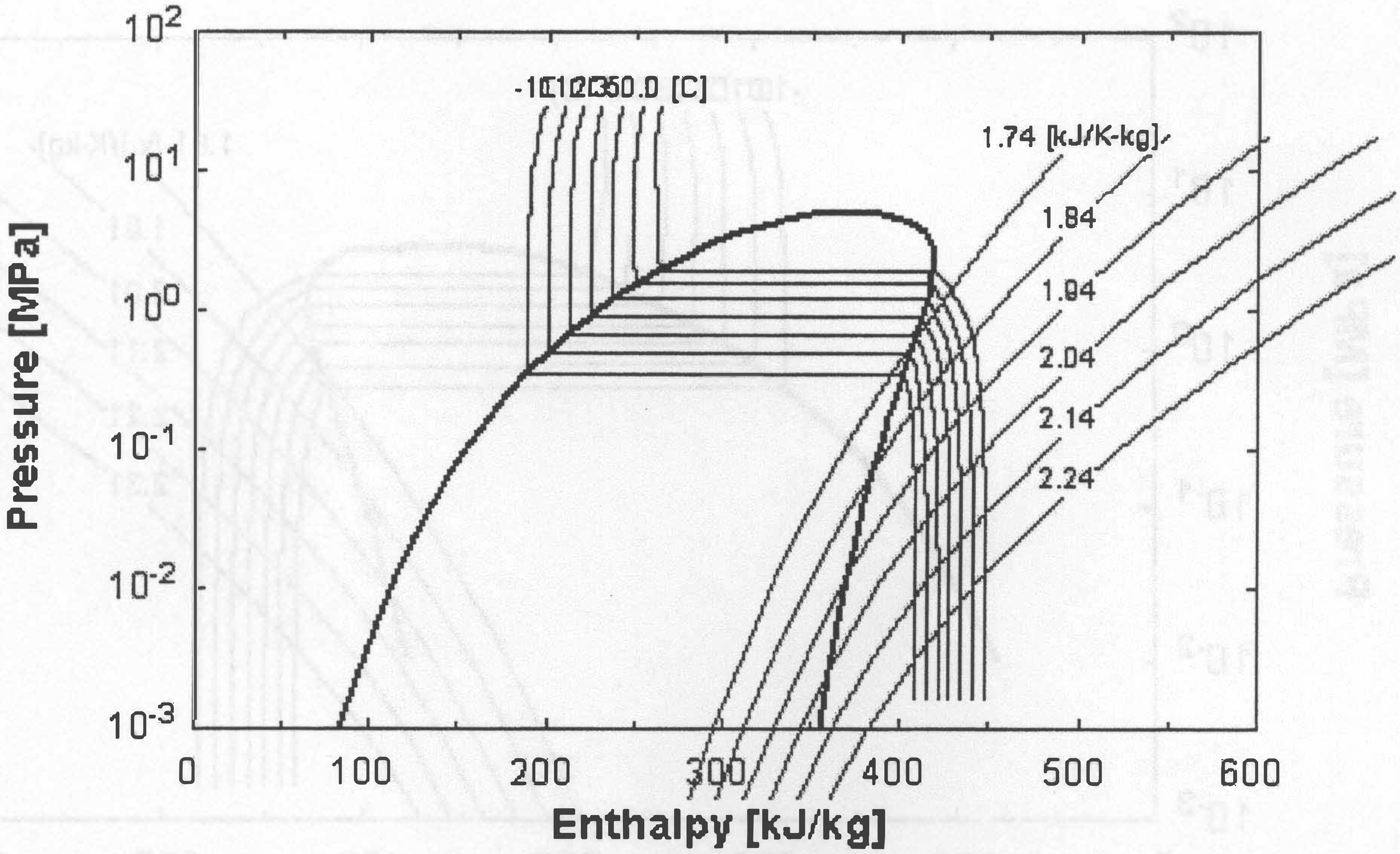
Carbon dioxide



Propane

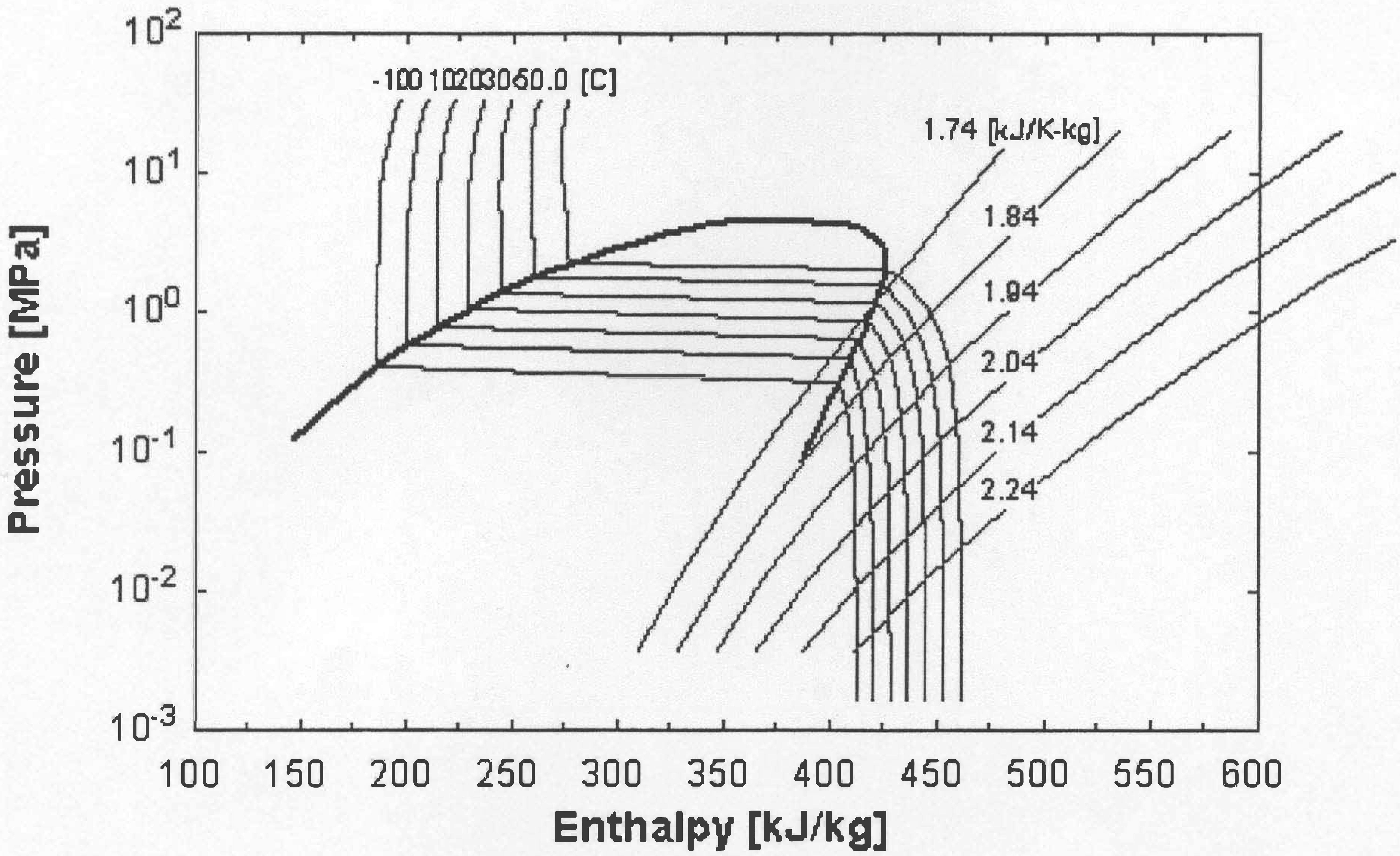


R-22



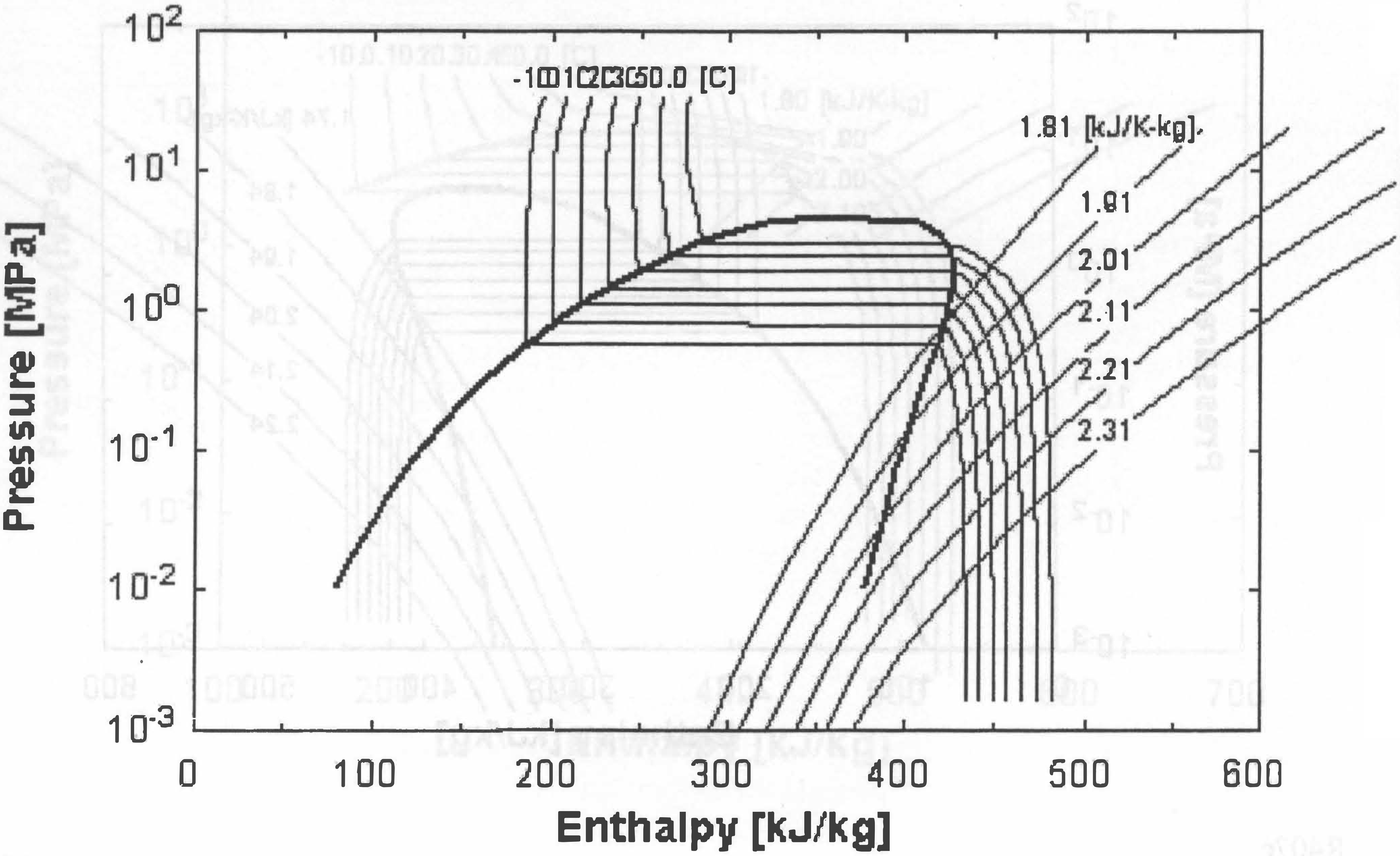
-10 0 10 20 30 50.0 [C]
1.74 [kJ/K-kg]
1.84
1.94
2.04
2.14
2.24
Pressure [MPa]
Enthalpy [kJ/kg]

R407c



-10 0 10 20 30 40 50.0 [C]
1.74 [kJ/K-kg]
1.84
1.94
2.04
2.14
2.24
Pressure [MPa]
Enthalpy [kJ/kg]

R410a


-10.0 10 20 30 50.0 [C]
1.81 [kJ/K-kg]
1.91
2.01
2.11
2.21
2.31
Pressure [MPa]
Enthalpy [kJ/kg]
10^2
10^1
10^0
10^-1
10^-2
10^-3
0
100
200
300
400
500
600