國立交通大學
National Chiao Tung University

高溫熱泵產製蒸汽之低溫廢熱回收

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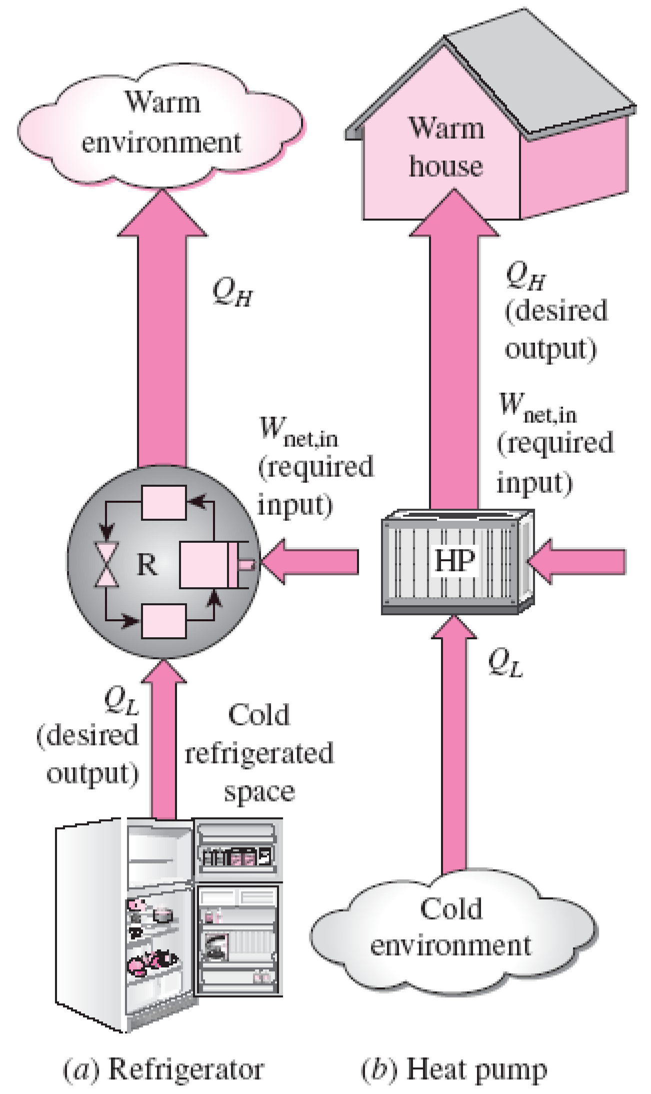
Outline

- Introduce the concepts of refrigerators and heat pumps and the measure of their performance.
- Heat Pump – General Overview and Some Applications
- Working Fluids for the Heat Pump.
- Review the factors involved in selecting the right refrigerant and related environmental concerns.
- High temperature and Industrial Heat Pumps
- Evaluate the performance of the high temperature heat pump using vapor-compression refrigeration systems.
- Discuss the special heat pumps (absorption, adsorption..)
- Introduce the concepts of heat driven refrigeration systems.

REFRIGERATORS AND HEAT PUMPS



(*a*) Refrigerator (*b*) Heat pump

The transfer of heat from a low-temperature region to a high-temperature one requires special devices called **refrigerators**.

Another device that transfers heat from a low-temperature medium to a high-temperature one is the **heat pump**.

Refrigerators and heat pumps are essentially the same devices; they differ in their objectives only.

$$\text{COP}_\text{R} = \frac{\text{Desired output}}{\text{Required input}} = \frac{\text{Cooling effect}}{\text{Work input}} = \frac{Q_L}{W_{\text{net,in}}}$$

$$\text{COP}_\text{HP} = \frac{\text{Desired output}}{\text{Required input}} = \frac{\text{Heating effect}}{\text{Work input}} = \frac{Q_H}{W_{\text{net,in}}}$$

$$\text{COP}_\text{HP} = \text{COP}_\text{R} + 1$$

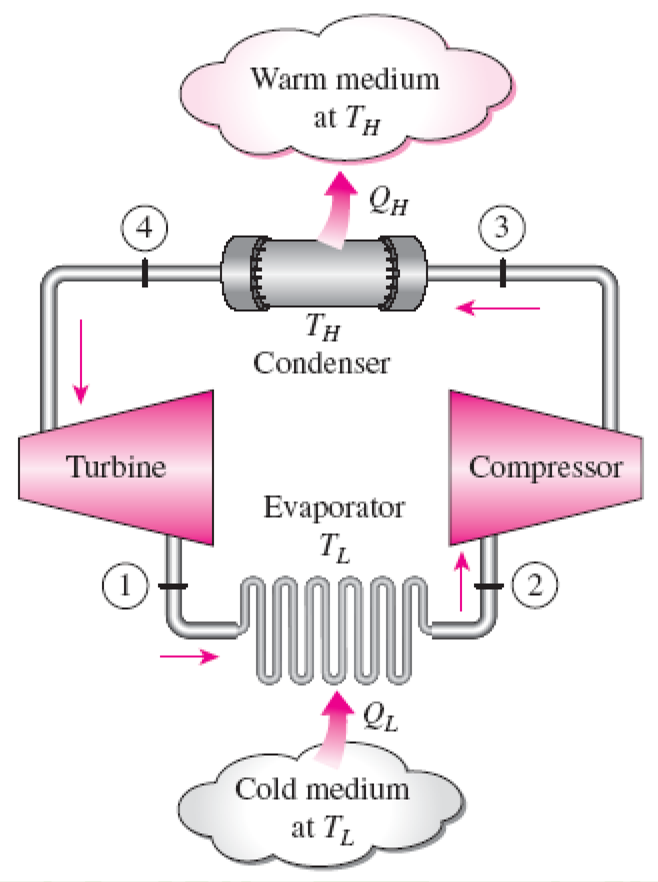
for fixed values of Q_L and Q_H

The objective of a refrigerator is to remove heat (Q_L) from the cold medium; the objective of a heat pump is to supply heat (Q_H) to a warm medium.

THE REVERSED CARNOT CYCLE

The reversed Carnot cycle is the *most efficient* refrig. cycle operating between T_L *and* T_H.

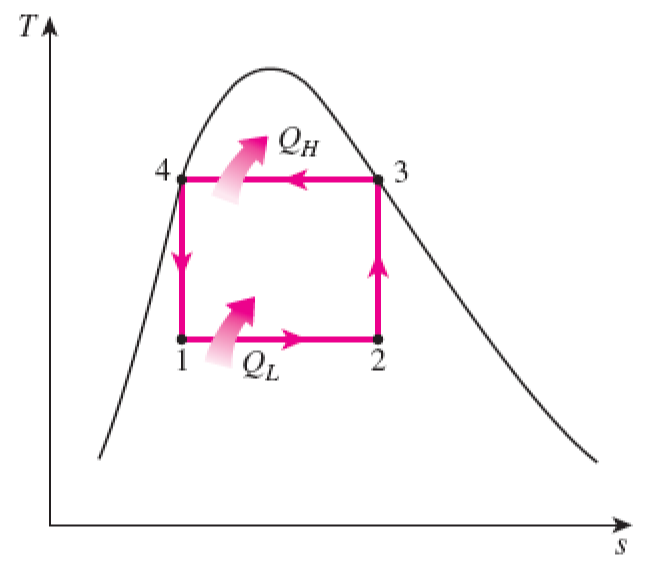
It is not a suitable model for refrigeration cycles since processes 2-3 and 4-1 are not practical because ***Process 2-3 involves the compression of a liquid–vapor mixture, which requires a compressor that will handle two phases***, and process 4-1 involves the expansion of high-moisture-content refrigerant in a turbine.



$$\text{COP}_{\text{R,Carnot}} = \frac{1}{T_H/T_L - 1}$$

$$\text{COP}_{\text{HP,Carnot}} = \frac{1}{1 - T_L/T_H}$$

Both COPs increase as the difference between the two temperatures decreases, that is, as T_L rises or T_H falls.

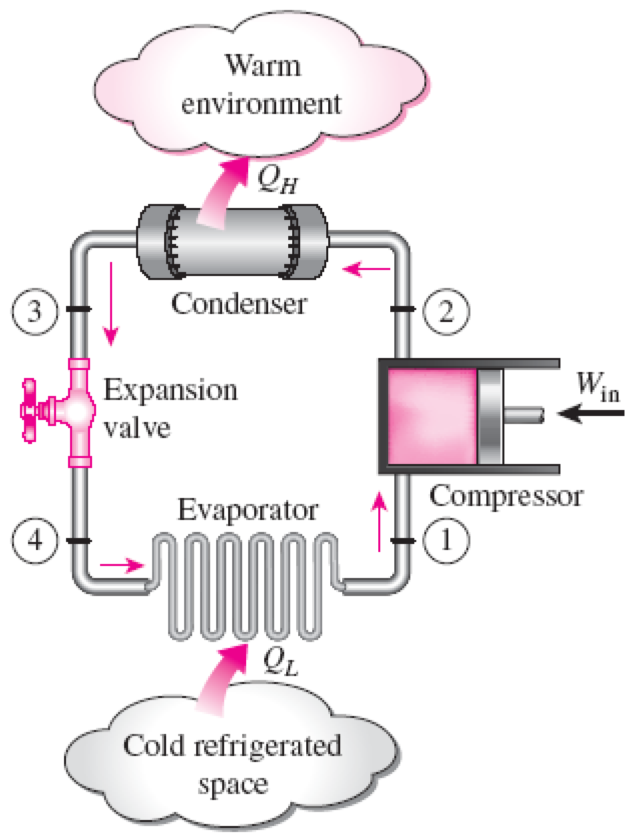


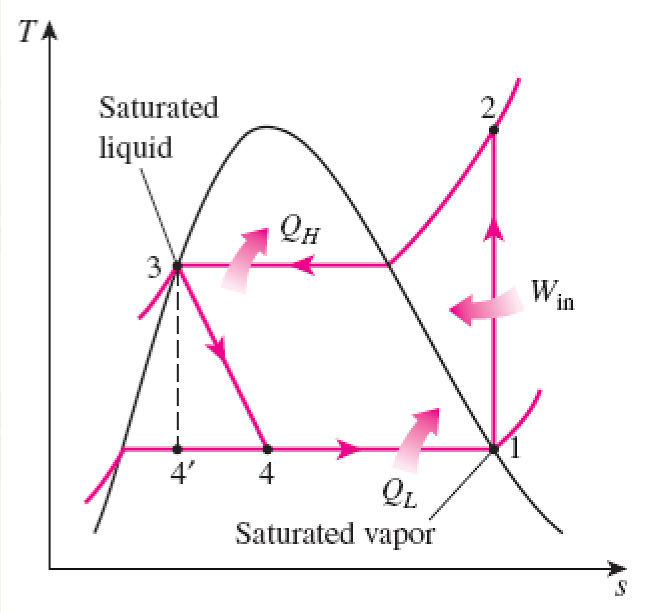
Schematic of a Carnot refrigerator and *T-s* diagram of the reversed Carnot cycle.

THE IDEAL VAPOR-COMPRESSION REFRIGERATION CYCLE

The **vapor-compression refrigeration cycle** is the ideal model for refrigeration systems. Unlike the reversed Carnot cycle, the refrigerant is vaporized completely before it is compressed and the turbine is replaced with a throttling device.

1-2	Isentropic compression in a compressor
2-3	Constant-pressure heat rejection in a condenser
3-4	Throttling in an expansion device
4-1	Constant-pressure heat absorption in an evaporator





This is the most widely used cycle for refrigerators, A-C systems, and heat pumps.

Schematic and *T*-*s* diagram for the ideal vapor-compression refrigeration cycle.

The ideal vapor-compression refrigeration cycle involves an irreversible (throttling) process to make it a more realistic model for the actual systems.

***Replacing the expansion valve by a turbine is not practical since the added benefits cannot justify the added cost and complexity*.**

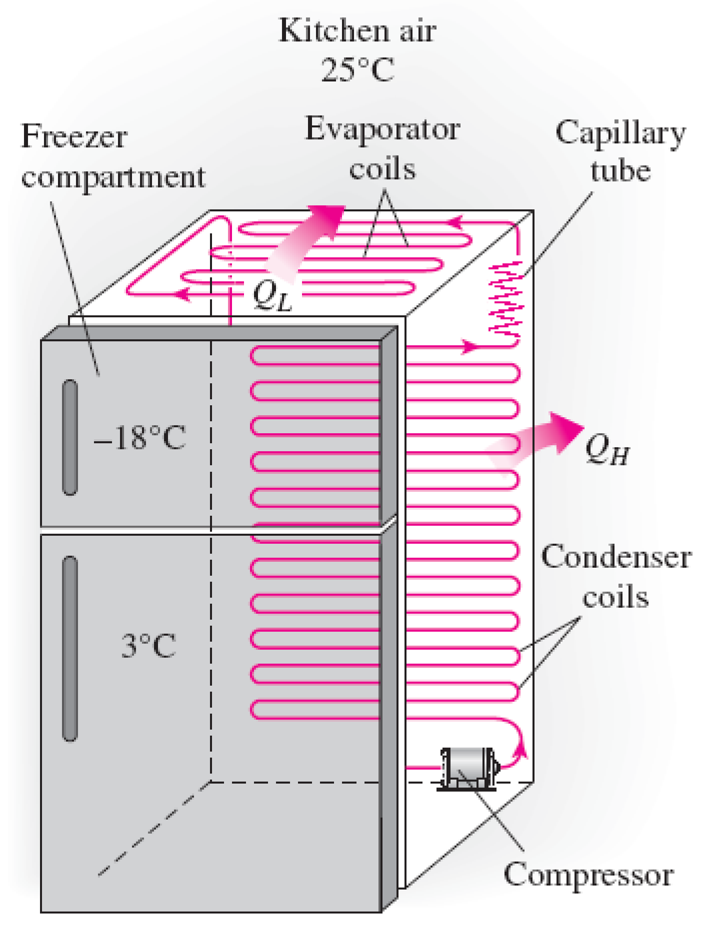
Steady-flow energy balance

$$(q_{\text{in}} - q_{\text{out}}) + (w_{\text{in}} - w_{\text{out}}) = h_e - h_i$$

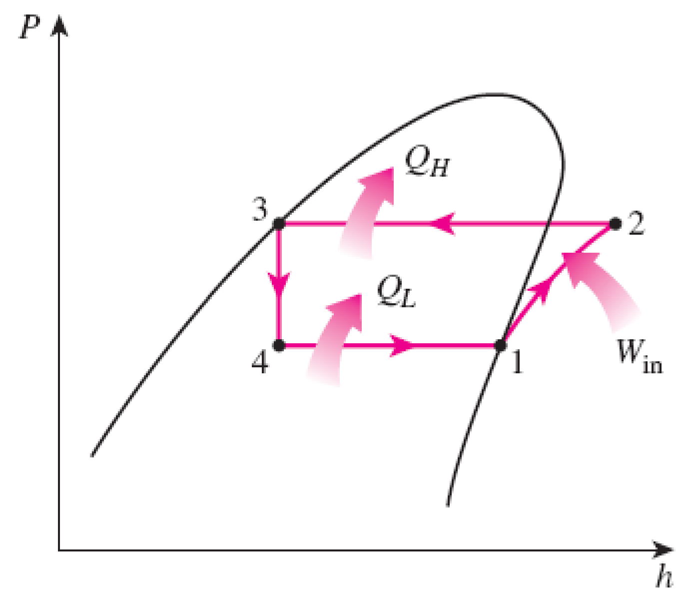
$$\text{COP}_{\text{R}} = \frac{q_L}{w_{\text{net,in}}} = \frac{h_1 - h_4}{h_2 - h_1}$$

$$\text{COP}_{\text{HP}} = \frac{q_H}{w_{\text{net,in}}} = \frac{h_2 - h_3}{h_2 - h_1}$$

$h_1 = h_{g\,@\,P_1}$ and $h_3 = h_{f\,@\,P_3}$ for the ideal case



An ordinary household refrigerator.



The *P-h* diagram of an ideal vapor-compression refrigeration cycle.

ACTUAL VAPOR-COMPRESSION REFRIGERATION CYCLE

An actual vapor-compression refrigeration cycle differs from the ideal one owing mostly to the irreversibilities that occur in various components, mainly due to fluid friction (causes pressure drops) and heat transfer to or from the surroundings.

The COP decreases as a result of irreversibilities.

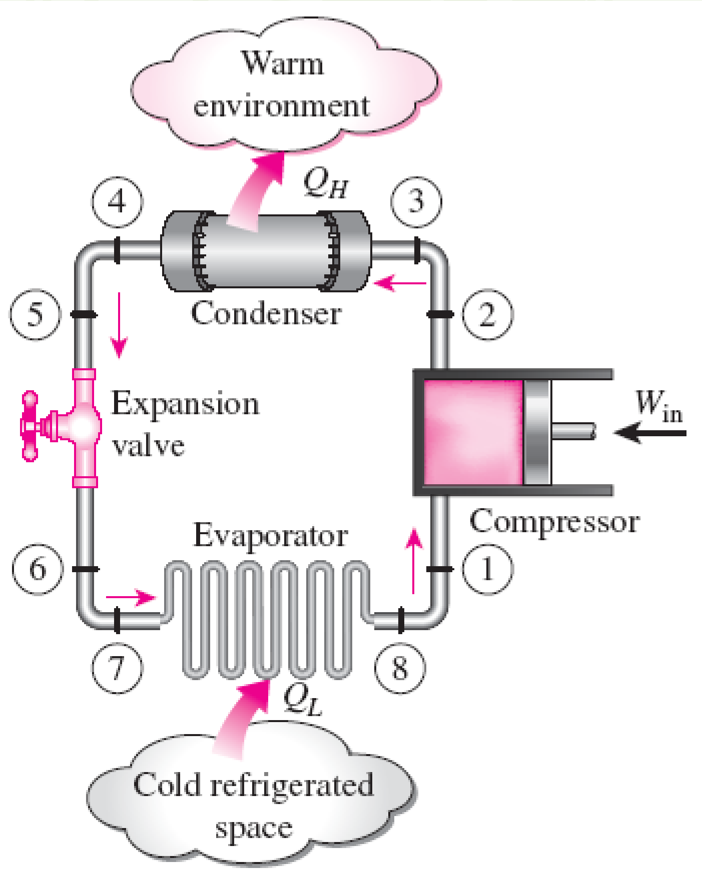
DIFFERENCES

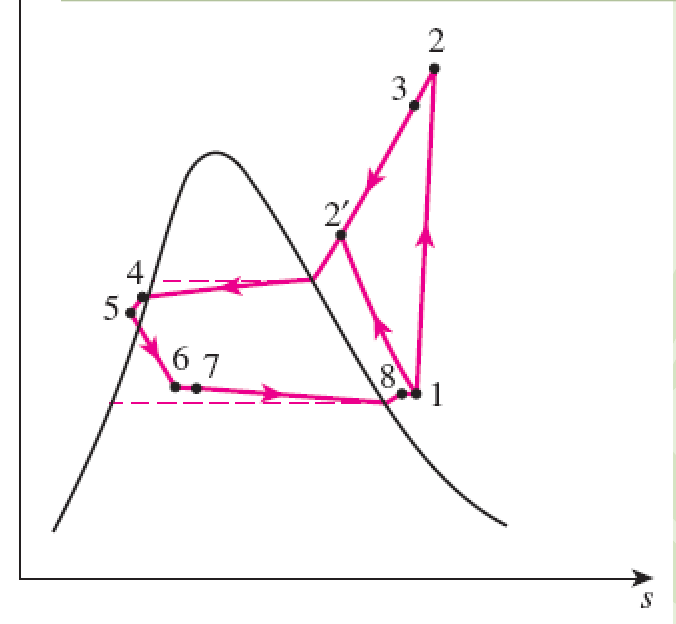
Non-isentropic compression

Superheated vapor at evaporator exit

Subcooled liquid at condenser exit

Pressure drops in condenser and evaporator





Schematic and *T*-*s* diagram for the actual vapor-compression refrigeration cycle.

Heat pump technology

- Reducing CO_2 emissions
- Reducing primary energy consumption
- Increasing the amount of renewable energy used

Scope of industrial applications

- Expected to expand further enhancing these effects

Typical applications

- for hot water supply
- for hot air supply
- for heating of circulating hot water
- for steam generation

Industrial heat pumps are mainly used for:

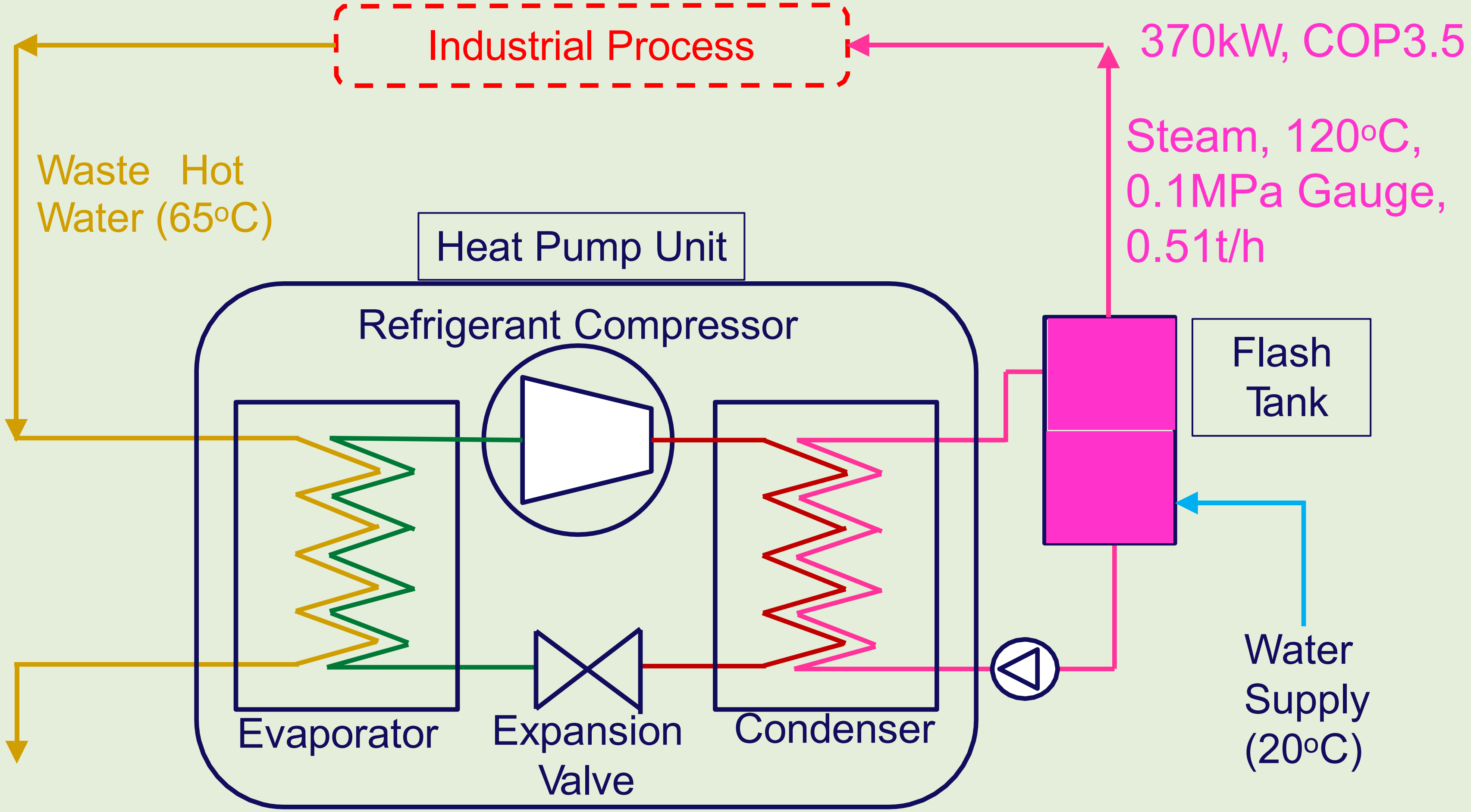
- space heating;
- heating and cooling of process streams;
- water heating for washing, sanitation and cleaning;
- steam production;
- drying/dehumidification;
- evaporation;
- distillation;
- concentration.

- **Space heating:**
  Heat pumps can utilize conventional heat sources for heating of greenhouses and industrial buildings, or they can recover industrial waste heat that could not be used directly, and provide a low- to medium temperature heat that can be utilized internally or externally for space heating. Mainly electric closed-cycle compression heat pumps are used.

- **Process water heating and cooling:** Many industries need warm process water in the temperature range from 40-90ºC, and often have a significant hot water demand in the same temperature range for washing, sanitation and cleaning purposes. This can be met by heat pumps. Heat pumps can also be a part of an integrated system that provides both cooling and heating. Mainly electric closed-cycle compression heat pumps are installed, but a few absorption heat pumps and heat transformers are also in use.

- **Steam production:**
Industry consumes vast amounts of low-, medium- and high-pressure steam in the temperature range from 100-200ºC. Steam is used directly in industrial processes, and for heat distribution. Current high temperature heat pumps can produce steam up to 150ºC (a heat pump prototype has achieved 300ºC). Both open and semi-open MVR systems, closed-cycle compression heat pumps, cascade (combination) systems and a few heat transformers are in operation.

Steam-generating heat pump SGH 120 model, Kobe Steel, Ltd.



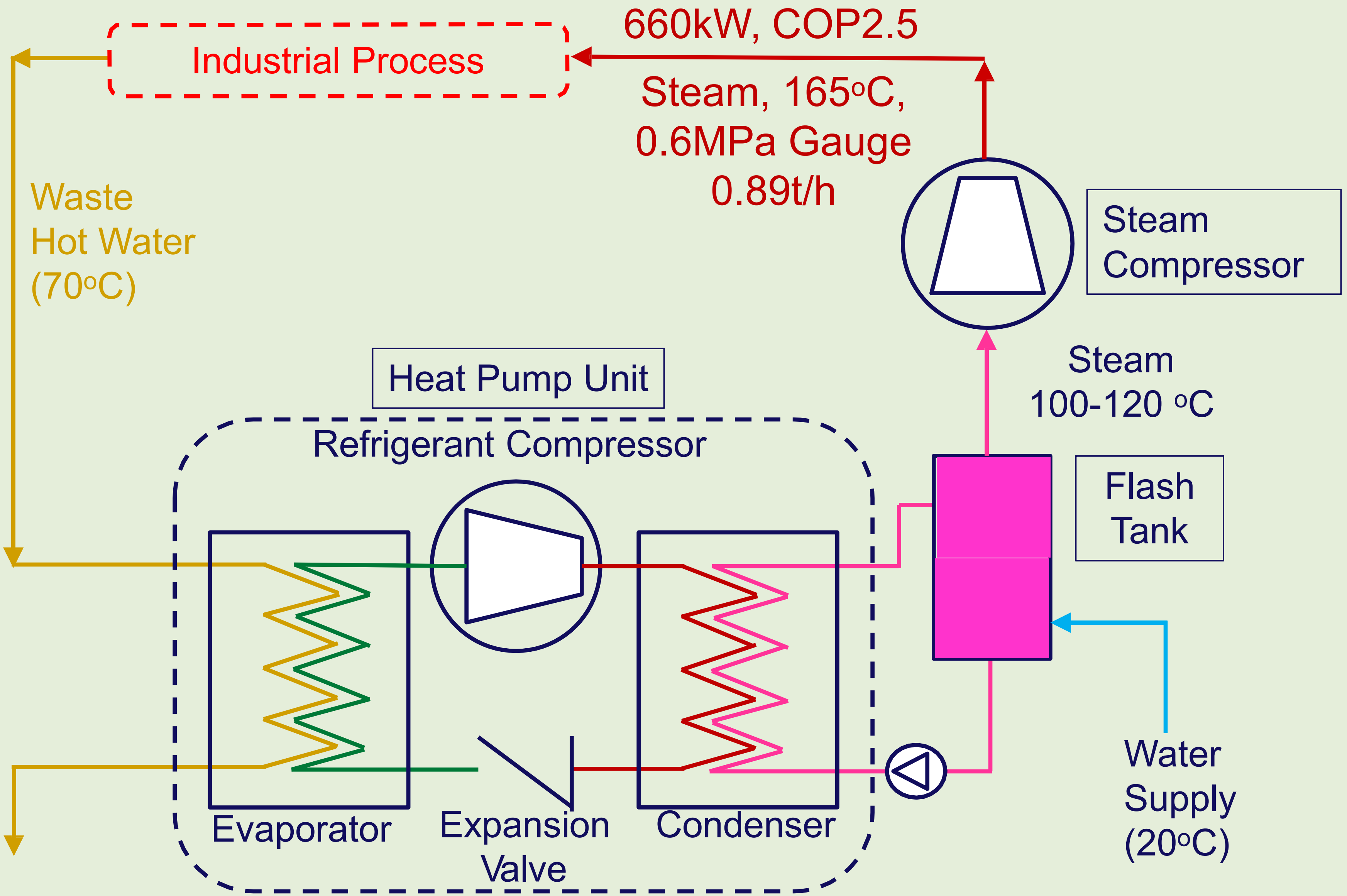
Steam-generating heat pump SGH 120 model, Kobe Steel, Ltd.

Supply 0.0 to 0.1 MPa Gauge steam, lifting up waste heat at 35 to 65^{o}C

Flash Tank

Heat Pump Unit

Steam-generating heat pump SGH 165 model, Kobe Steel, Ltd.



660kW, COP2.5

Industrial Process

Steam, 165^{o}C,
0.6MPa Gauge
0.89t/h

Waste
Hot Water
(70^{o}C)

Steam Compressor

Heat Pump Unit

Refrigerant Compressor

Steam
100-120 ^{o}C

Flash Tank

Evaporator

Expansion Valve

Condenser

Water Supply
(20^{o}C)

Steam-generating heat pump SGH 165 model, Kobe Steel, Ltd.

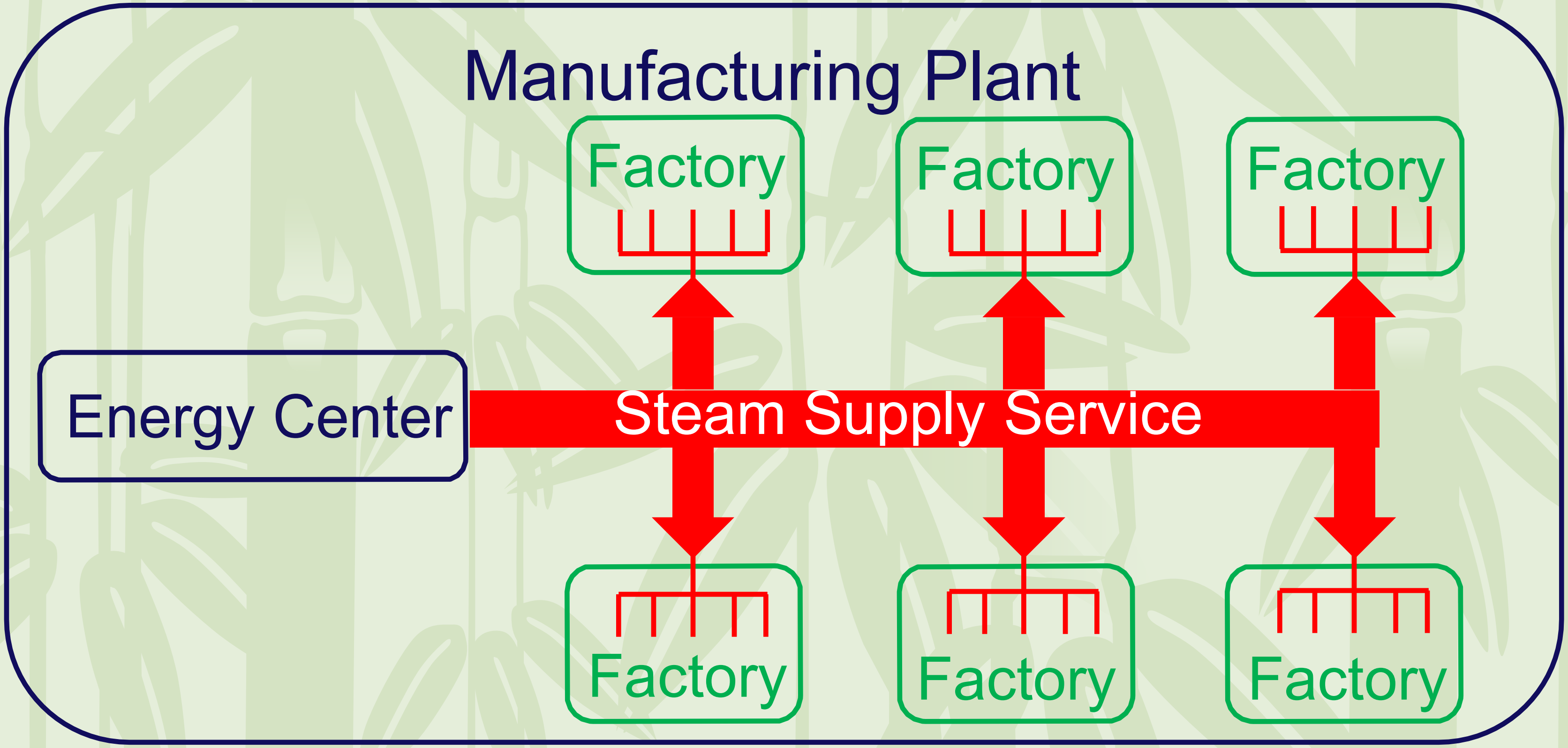
Supply 0.2 to 0.8 MPa Gauge steam, lifting up waste heat at 35 to 70^{o}C

- **Drying process:**
  Heat pumps are used extensively in industrial dehumidification and drying processes at low and moderate temperatures (maximum 100ºC). The main applications are drying of pulp and paper, various food products wood and lumber. Drying of temperature-sensitive products is also interesting. Heat pump dryers generally have high performance (COP 5-7), and often improve the quality of the dried products as compared with traditional drying methods. Because the drying is executed in a closed system, odours from the drying of food products etc. are reduced. Both closed-cycle compression heat pumps and MVR systems are used.

- **Evaporation and distillation processes:** Evaporation and distillation are energy-intensive processes, and most heat pumps are installed in these processes in the chemical and food industries. In evaporation processes the residue is the main product, while the vapour (distillate) is the main product in distillation processes. Most systems are open or semi-open MVRs, but closed-cycle compression heat pumps are also applied. Small temperature lifts result in high performance with COPs ranging from 6 to 30.

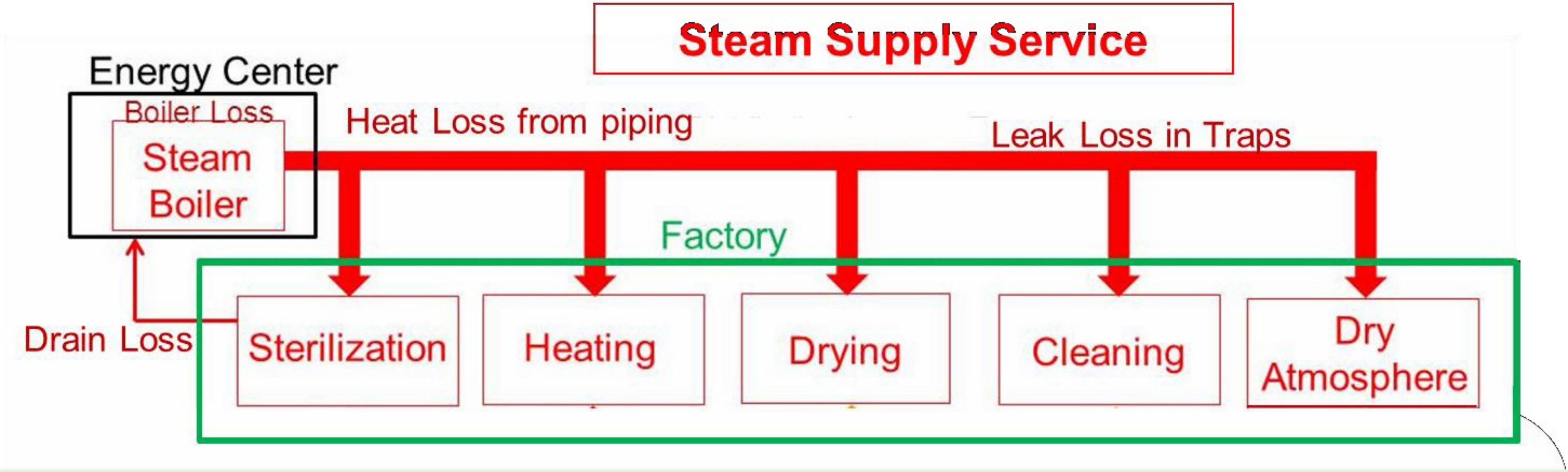
Steam supply service in a manufacturing plant

- Producing cars, auto parts, electrical equipment, food, etc.
- Steam is produced in the energy center
- Supplied to some factories and all areas of each factory
- Used in the manufacturing process



Total energy efficiency of steam supply service

- generally low (e.g. 20-40%) due to
- Boiler losses
- Heat losses from piping
- Steam leakage losses in traps
- Drain recovery losses



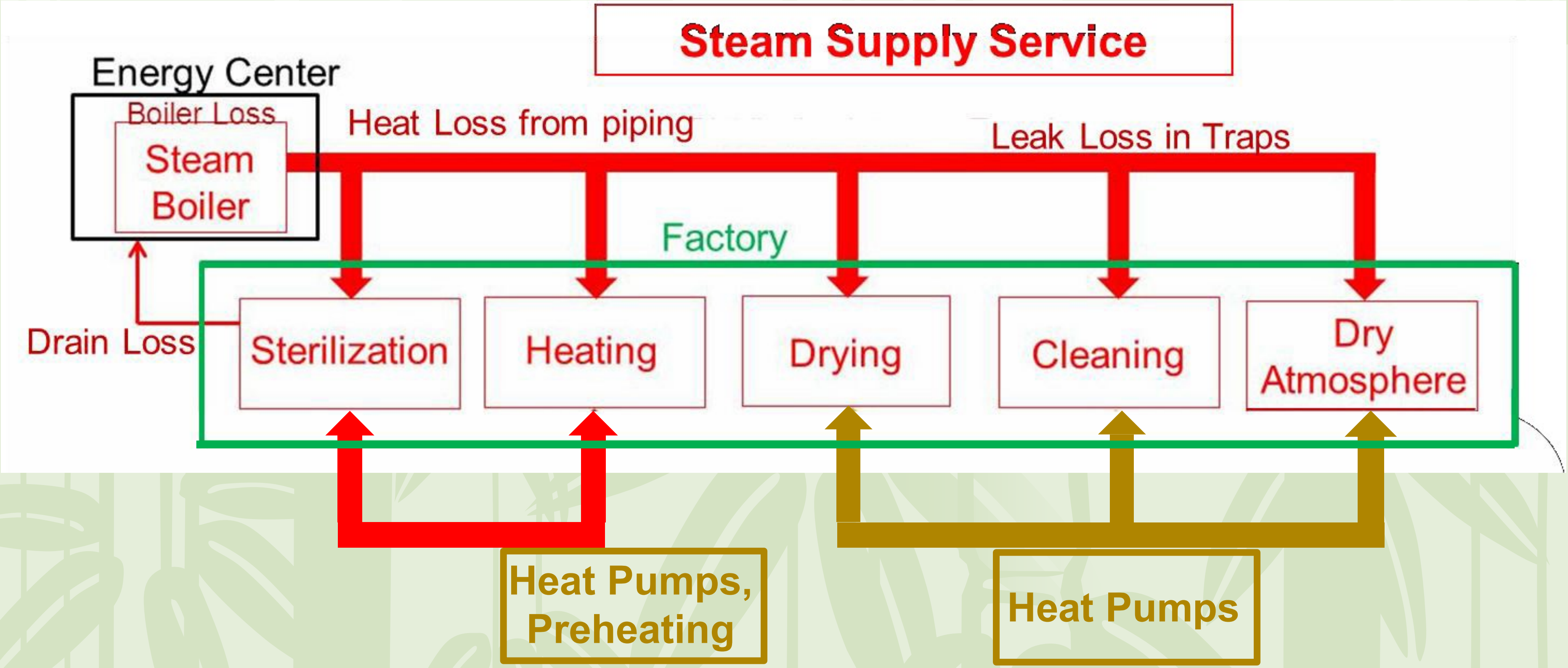
Steam supply service in a factory

- The most commonly used steam temperature zone is in the range e.g. 55-80°C
- Many electric heaters are used for these processes for which temperature control is required

Distributed heat pumps

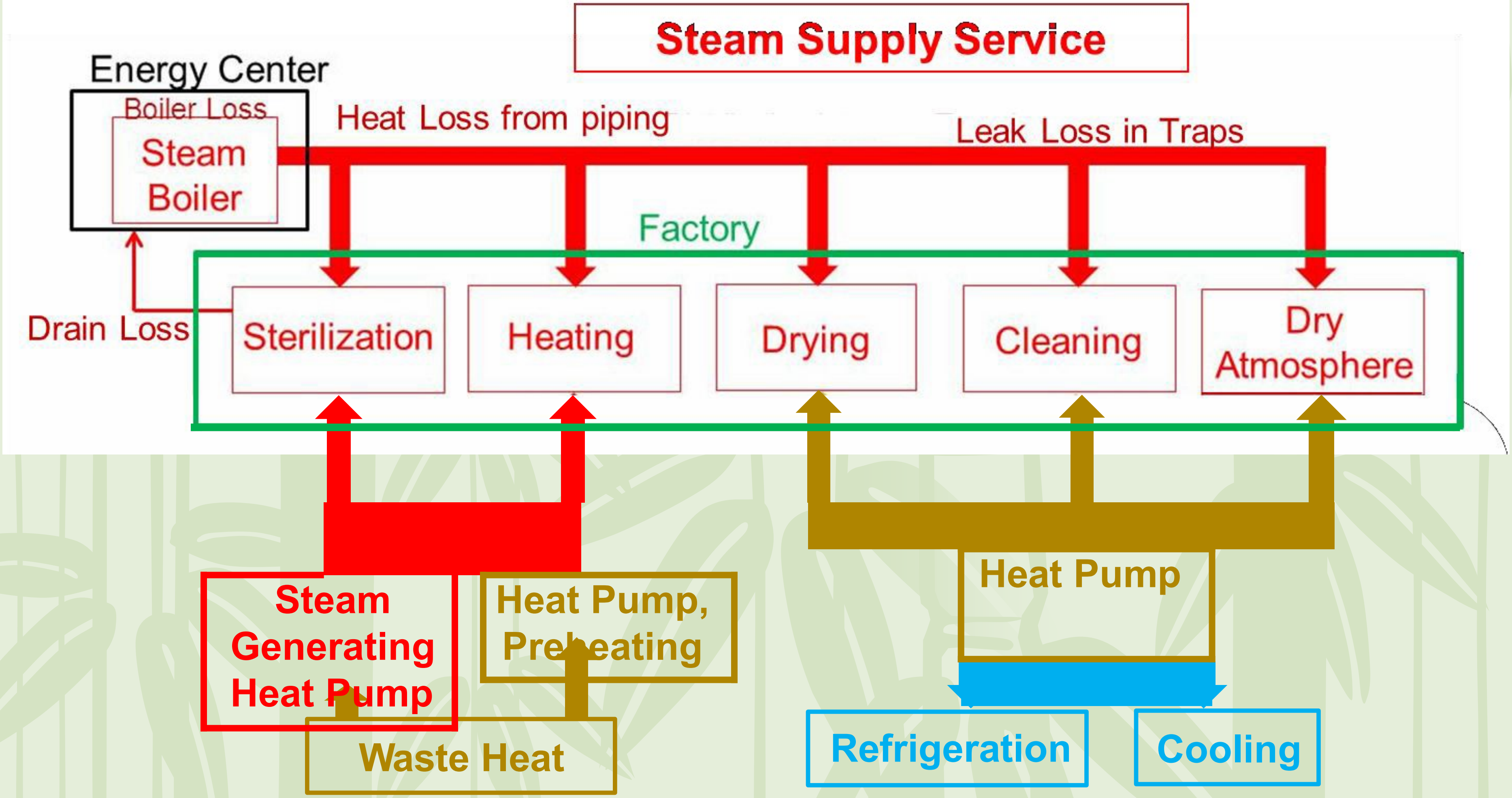
Significant energy savings are expected by

- Replacing some steam supply service and electric heaters
- With distributed high-temperature heat pumps



Heat recovery

- ◆Simultaneous utilization of cooling and heating
- ◆Utilization of waste heat



Steam Supply Service

Energy Center

Boiler Loss

Steam Boiler

Heat Loss from piping

Leak Loss in Traps

Factory

Drain Loss

Sterilization

Heating

Drying

Cleaning

Dry Atmosphere

Steam Generating Heat Pump

Heat Pump, Preheating

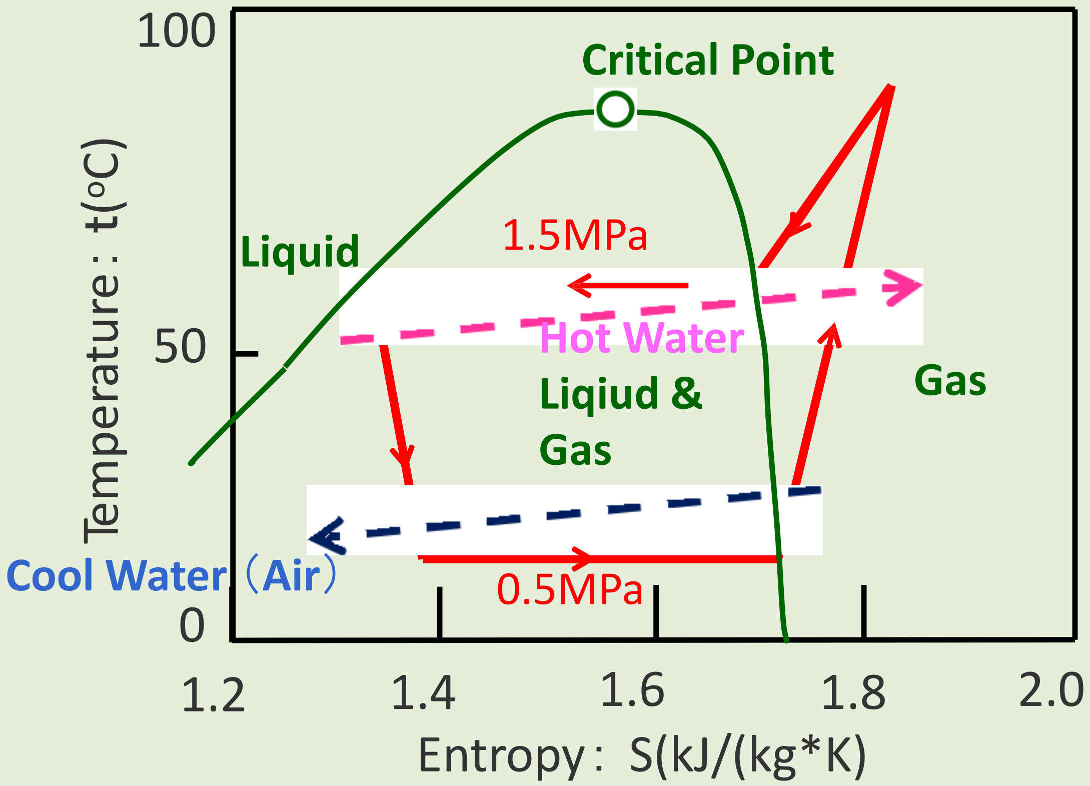
Waste Heat

Heat Pump

Refrigeration

Cooling

Reverse Rankine cycle (HFC-134a)



Heating of Circulating
Hot Water（60⇒65oC）

Cooling of Circulating
Cool Water（25⇒20℃）

Heat pump for washing process

Zeneral Heat Pump Industry Co., Ltd.

Cutting and washing process of machinery parts

- Cooling water-soluble cutting oil by chiller
- Heating washing liquid by boiler steam

Simultaneous cooling and heating by heat pumps The total COP in heating and cooling mode reaches 5

Three operating modes

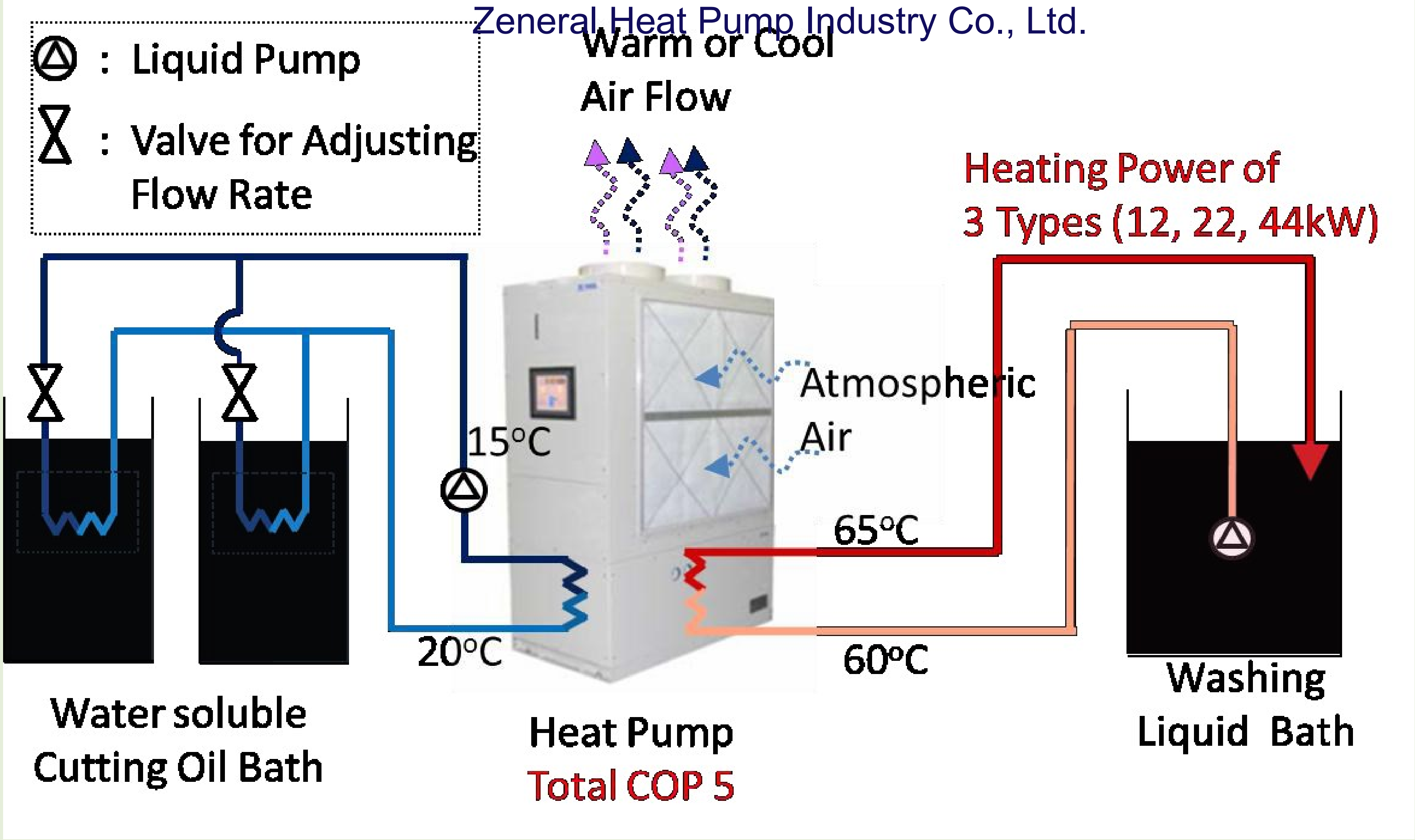
-1) Heating mode, 2) Cooling mode

-3) Heating and cooling mode

-Available using the heat exchanger between the air and refrigerant

Heat pump for washing process

Zeneral Heat Pump Industry Co., Ltd.



△ : Liquid Pump

⧖ : Valve for Adjusting Flow Rate

Warm or Cool Air Flow

Heating Power of 3 Types (12, 22, 44kW)

Atmospheric Air

15°C

20°C

65°C

60°C

Water soluble Cutting Oil Bath

Heat Pump

Total COP 5

Washing Liquid Bath

Heat pump for washing process

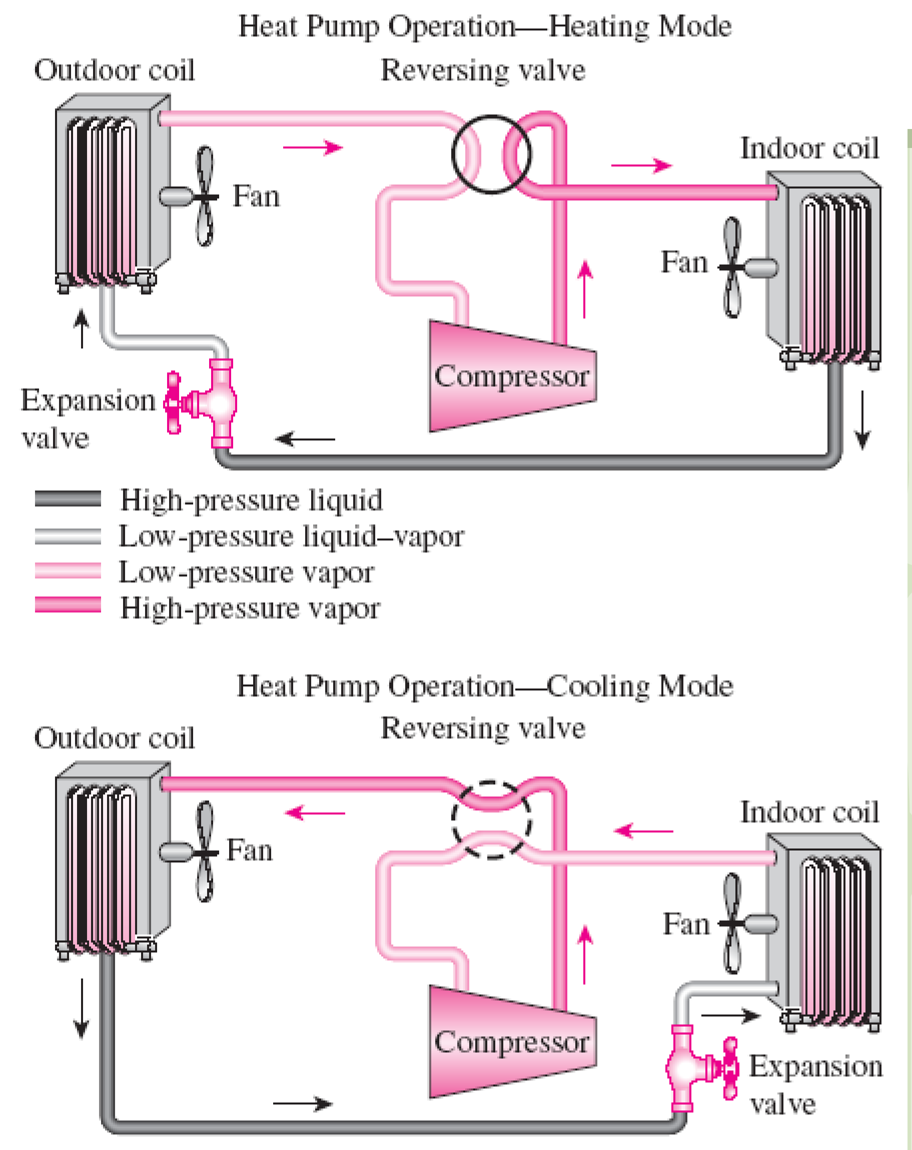
Zeneral Heat Pump Industry Co., Ltd.

As an example of the effect achieved using these heat pumps

- a reduction of 73 % in primary energy consumption
- a reduction of 86 % in CO_2 emissions

compared with the conventional method

HEAT PUMP SYSTEMS



A heat pump can be used to heat a house in winter and to cool it in summer.

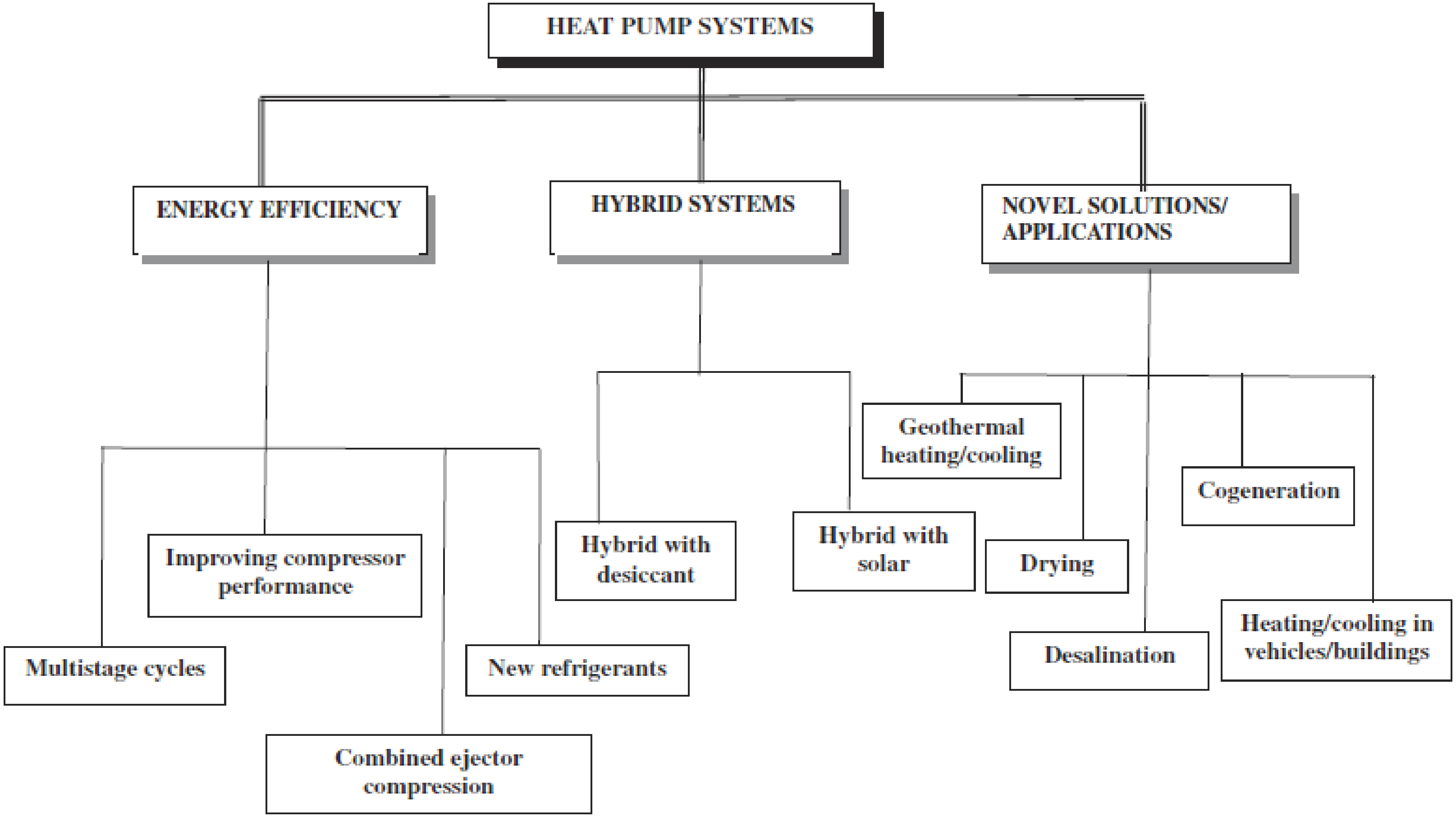
The most common energy source for heat pumps is atmospheric air (air-to-air systems).

Water-source systems usually use well water and ground-source (geothermal) heat pumps use earth as the energy source. They typically have higher COPs but are more complex and more expensive to install.

Both the capacity and the efficiency of a heat pump fall significantly at low temperatures. Therefore, most air-source heat pumps require a supplementary heating system such as electric resistance heaters or a gas furnace.

Heat pumps are most competitive in areas that have a large cooling load during the cooling season and a relatively small heating load during the heating season. In these areas, the heat pump can meet the entire cooling and heating needs of residential or commercial buildings.

Generalized Heat Pump System



- HEAT PUMP SYSTEMS
  - ENERGY EFFICIENCY
    - Multistage cycles
    - Improving compressor performance
    - Combined ejector compression
    - New refrigerants
  - HYBRID SYSTEMS
    - Hybrid with desiccant
    - Hybrid with solar
  - NOVEL SOLUTIONS/ APPLICATIONS
    - Geothermal heating/cooling
    - Drying
    - Desalination
    - Cogeneration
    - Heating/cooling in vehicles/buildings

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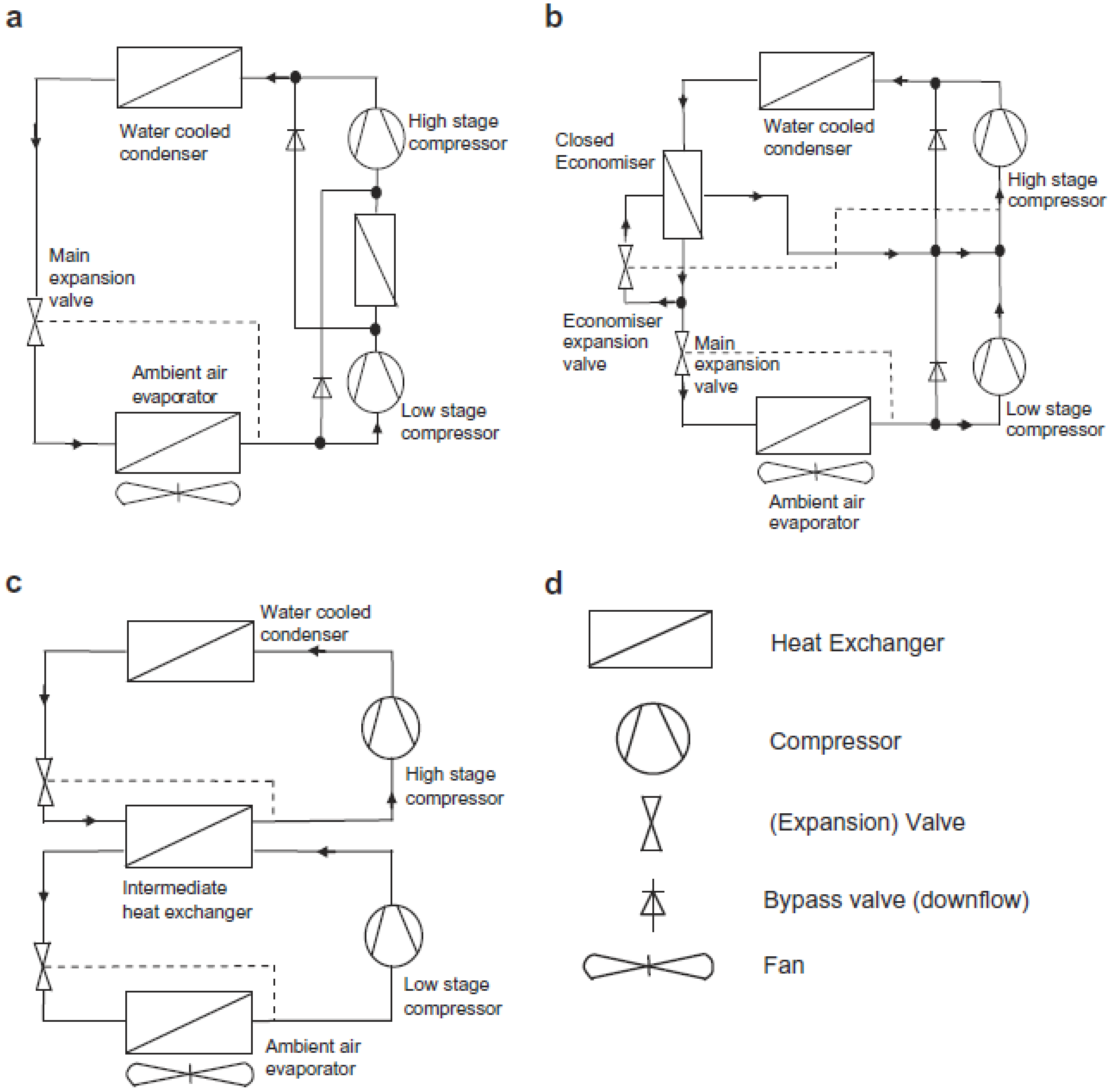
Schematics of (a) two-stage cycle with intercooler, (b) two-stage cycle with closed economizer, (c) cascade cycle, and (d) legend

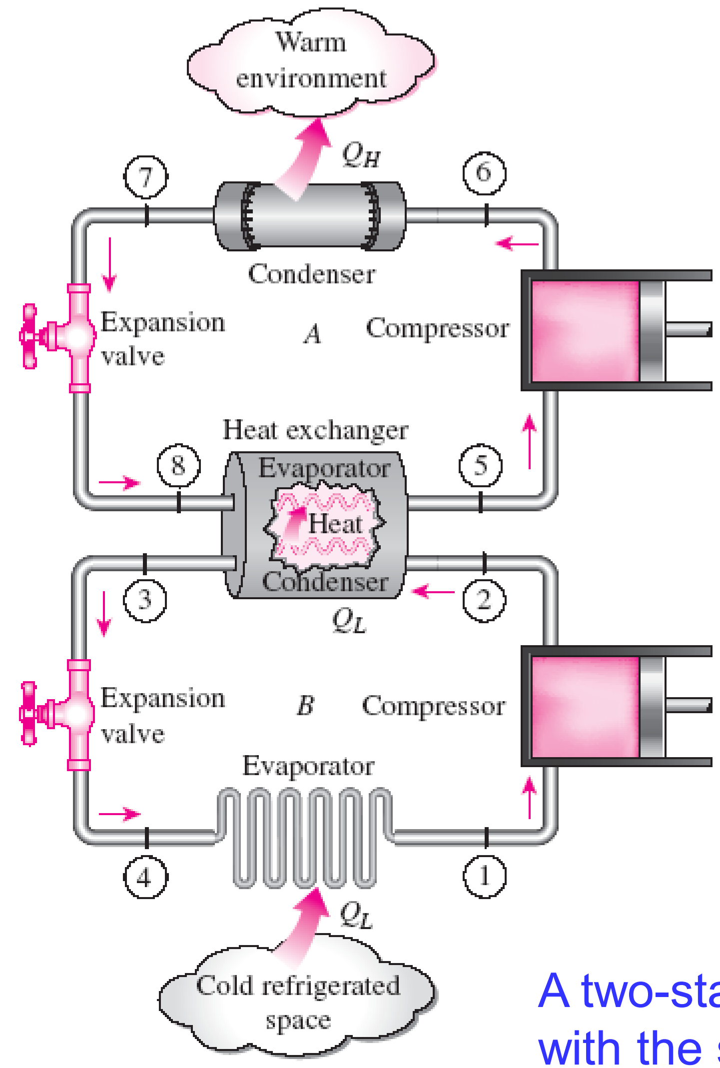


INNOVATIVE VAPOR-COMPRESSION REFRIGERATION SYSTEMS

- The simple vapor-compression refrigeration cycle is the most widely used refrigeration cycle, and it is adequate for most refrigeration applications.
- The ordinary vapor-compression refrigeration systems are simple, inexpensive, reliable, and practically maintenance-free.
- However, for large industrial applications *efficiency*, not simplicity, is the major concern.
- Also, for some applications the simple vapor-compression refrigeration cycle is inadequate and needs to be modified.
- For moderately and very low temperature applications some innovative refrigeration systems are used. The following cycles will be discussed:
  - Cascade refrigeration systems
  - Multistage compression refrigeration systems
  - Multipurpose refrigeration systems with a single compressor
  - Liquefaction of gases

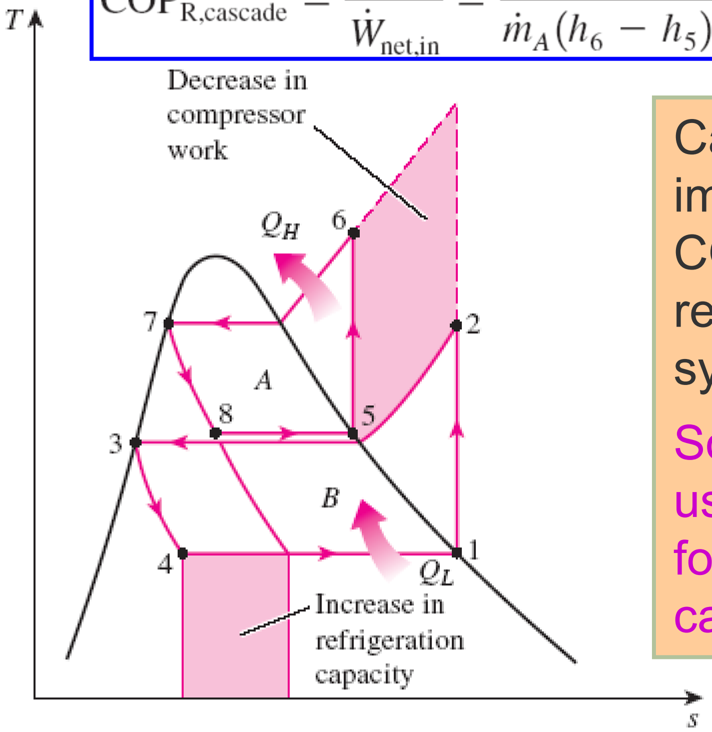
Cascade Refrigeration Systems

Some industrial applications require moderately low temperatures, and the temperature range they involve may be too large for a single vapor-compression refrigeration cycle to be practical. The solution is **cascading.**



$$\dot m_A(h_5-h_8)=\dot m_B(h_2-h_3) \longrightarrow \frac{\dot m_A}{\dot m_B}=\frac{h_2-h_3}{h_5-h_8}$$

$$\mathrm{COP}_{\mathrm{R,cascade}}=\frac{\dot Q_L}{\dot W_{\mathrm{net,in}}}=\frac{\dot m_B(h_1-h_4)}{\dot m_A(h_6-h_5)+\dot m_B(h_2-h_1)}$$



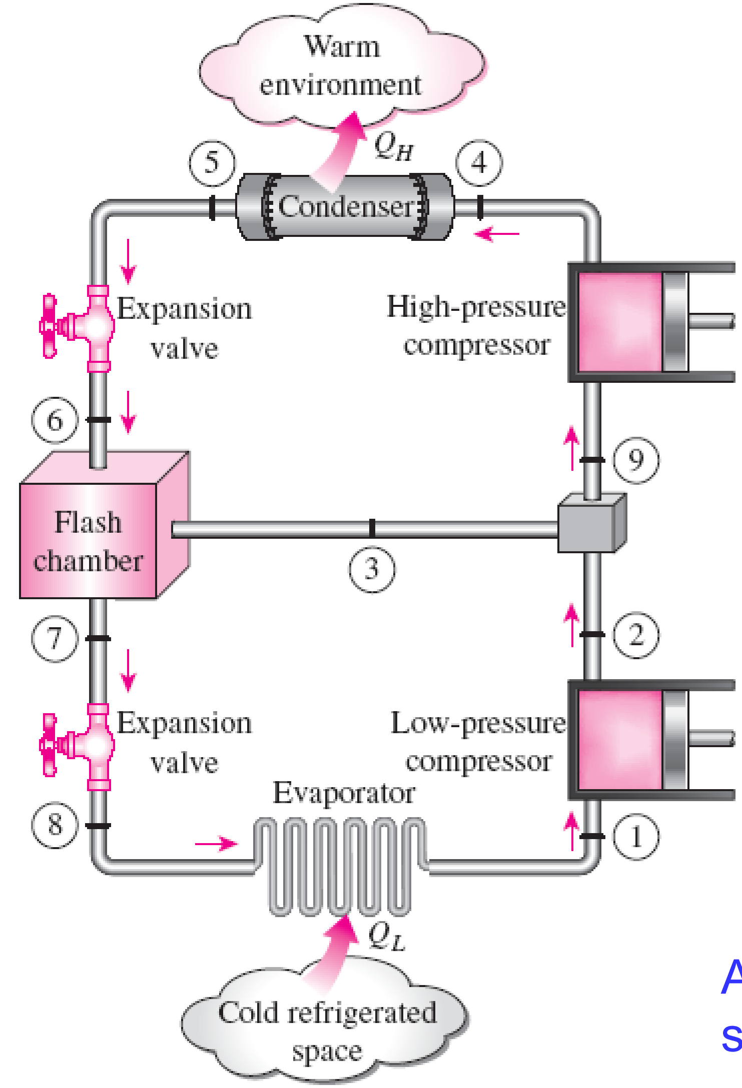
Cascading improves the COP of a refrigeration system.

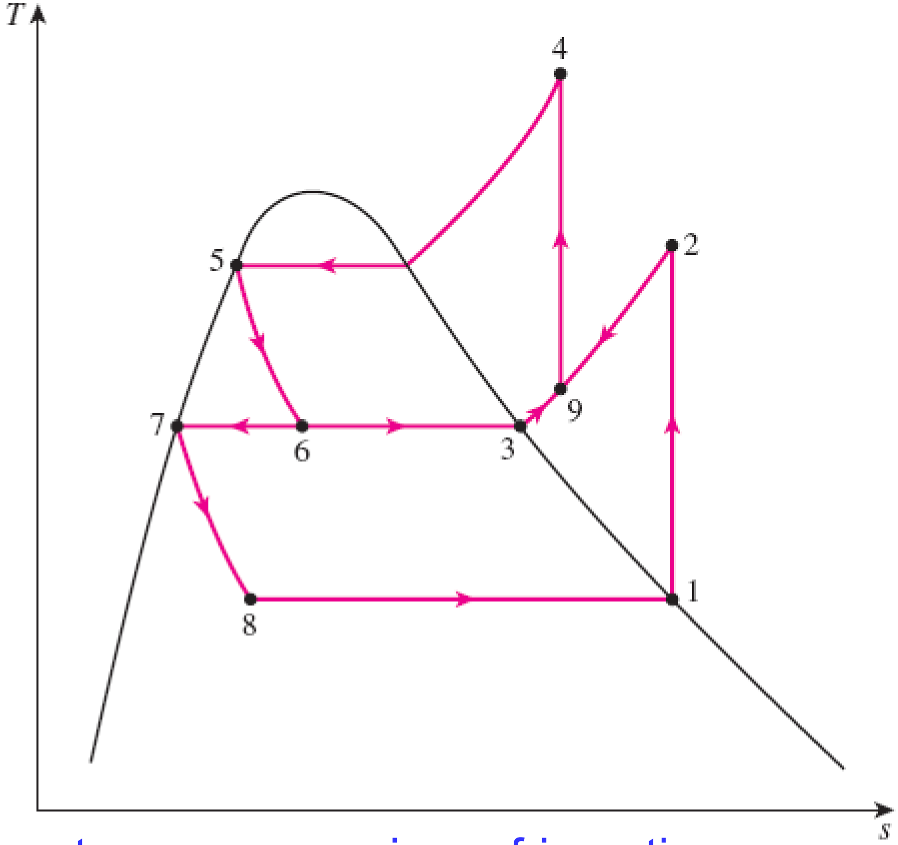
Some systems use three or four stages of cascading.

A two-stage cascade refrigeration system with the same refrigerant in both stages.

Multistage Compression Refrigeration Systems

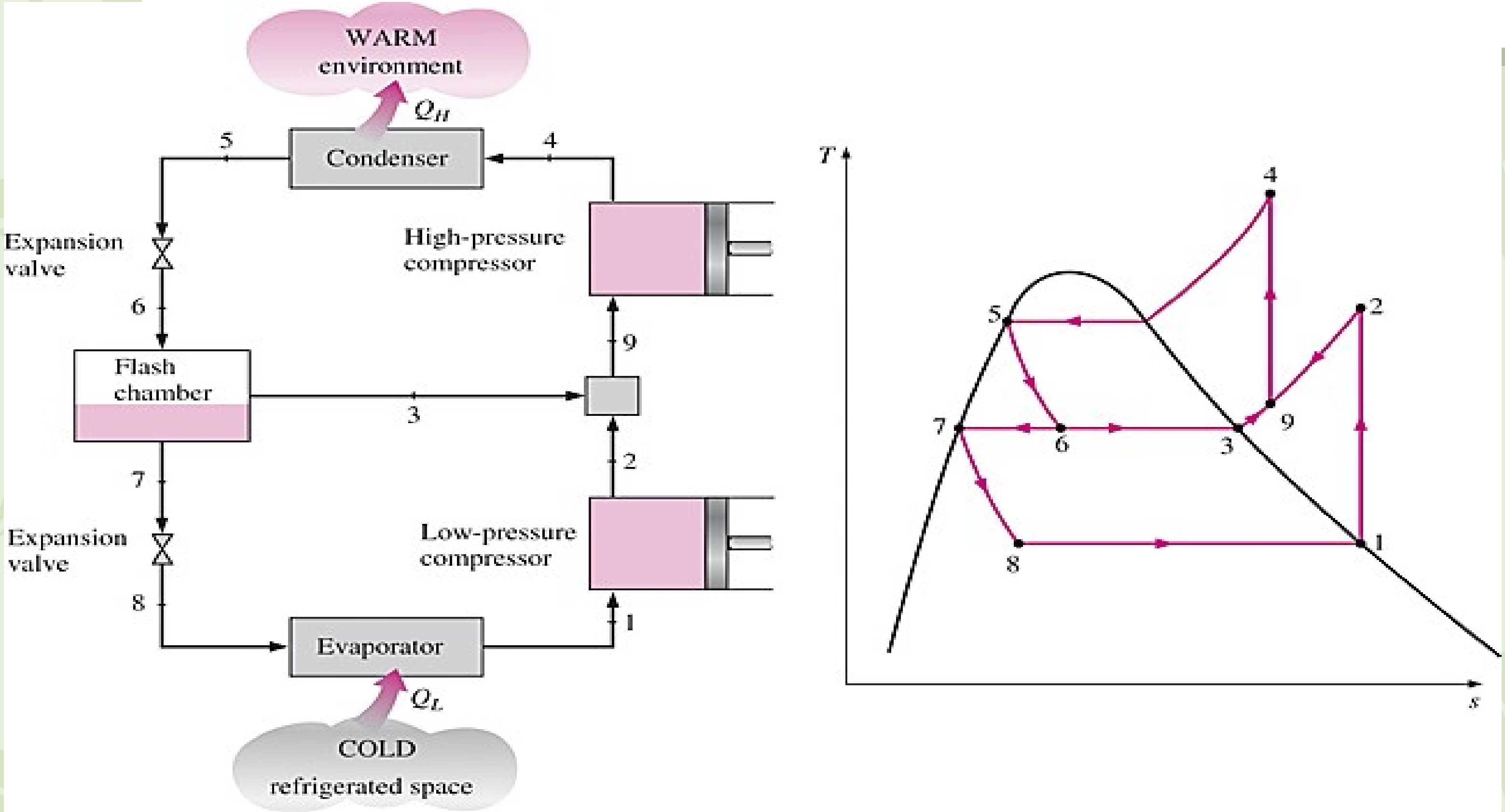
When the fluid used throughout the cascade refrigeration system is the same, the heat exchanger between the stages can be replaced by a mixing chamber (called a *flash chamber*) since it has better heat transfer characteristics.





A two-stage compression refrigeration system with a flash chamber.

Multistage Compression Refrigeration Systems



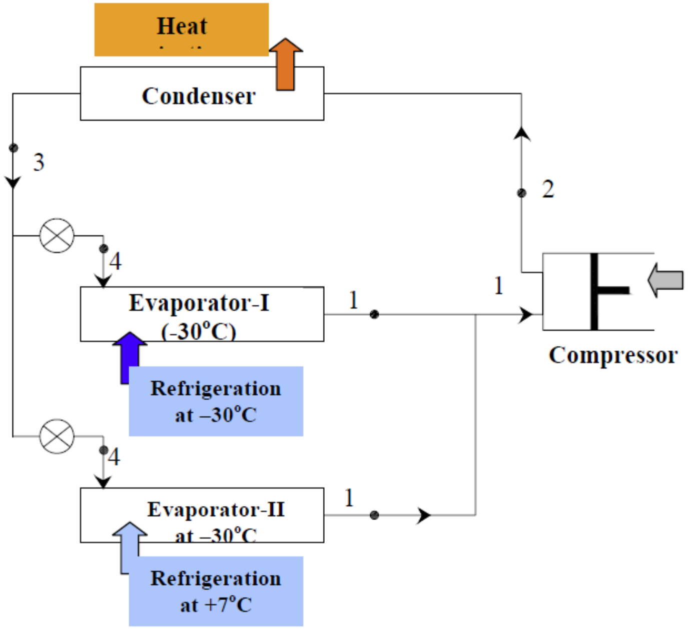
$$q_L = (1 - x_6)(h_1 - h_8) \quad \text{(kJ/kg)}$$

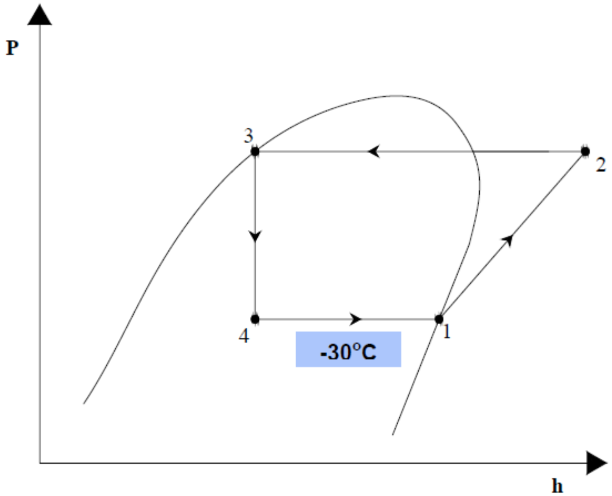
$$w_{in} = w_{compI} + w_{compII} = (1 - x_6)(h_2 - h_1) + (1)(h_4 - h_9) \quad \text{(kJ/kg)}$$

The coefficient of performance: $COP_R = q_L / w_{in}$

Variations of Refrigeration Systems with a Single Compressor (Muti-evaporators)

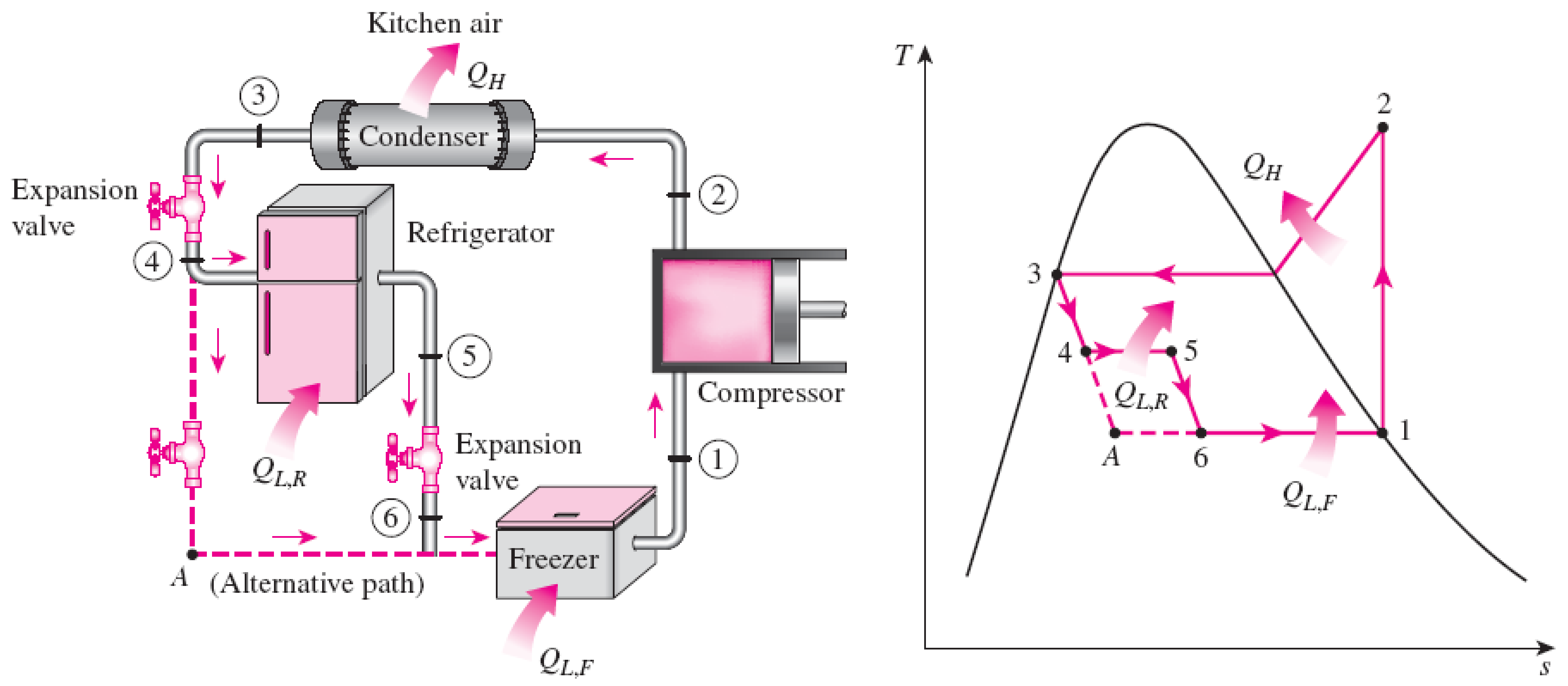
There may not be any improvement in system COP due to this arrangement. It is easy to see that this modification does not result in significant improvement in performance due to the fact that the refrigerant vapor at the intermediate pressure is reduced first using the PRV and again increased using compressor.



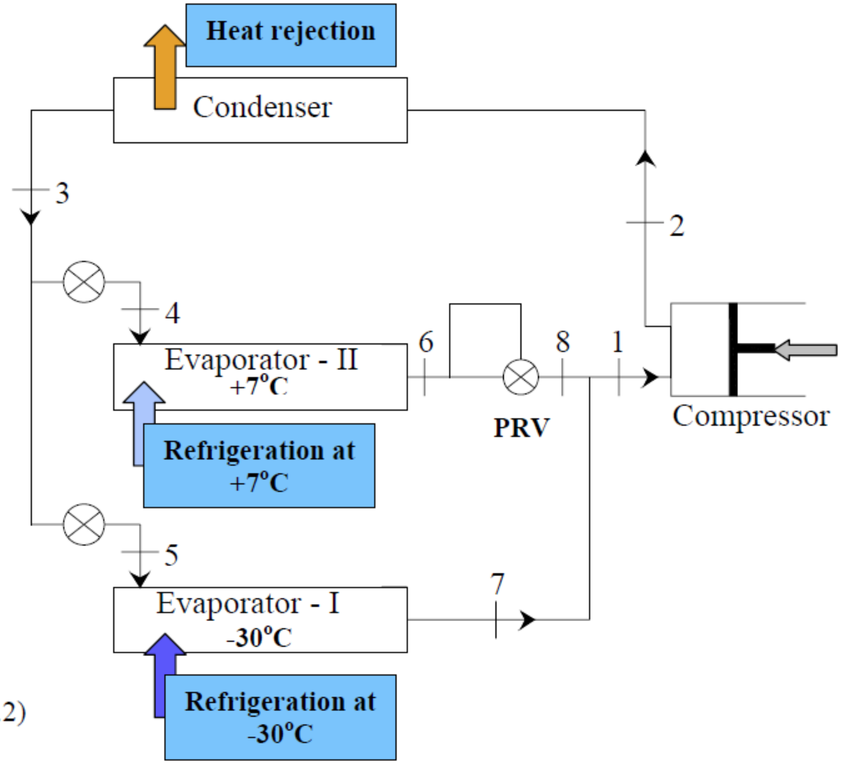


Multipurpose Refrigeration Systems with a Single Compressor (Muti-evaporators)

Some applications require refrigeration at more than one temperature. A practical and economical approach is to route all the exit streams from the evaporators to a single compressor and let it handle the compression process for the entire system.



Schematic and *T*-*s* diagram for a refrigerator–freezer unit with one compressor.



The COP of the above system is given by:

$$COP = \frac{Q_{e,I} + Q_{e,II}}{W_c} = \frac{\dot{m}_I(h_7 - h_5) + \dot{m}_{II}(h_6 - h_4)}{(\dot{m}_I + \dot{m}_{II})(h_2 - h_1)} \quad (13.2)$$

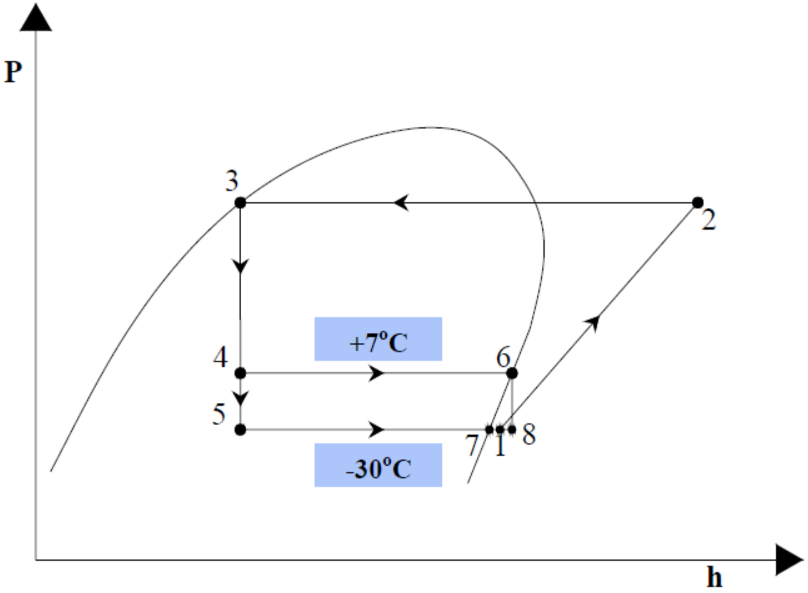
where $\dot{m}_I$ and $\dot{m}_{II}$ are the refrigerant mass flow rates through evaporator I and II respectively. They are given by:

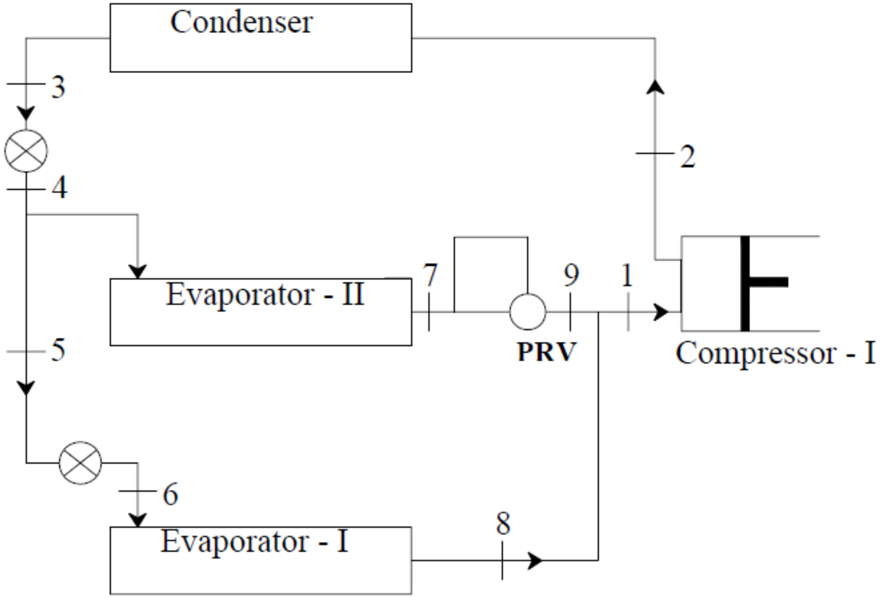
$$\dot{m}_I = \frac{Q_{e,I}}{(h_7 - h_5)} \quad (13.3)$$

$$\dot{m}_{II} = \frac{Q_{e,II}}{(h_6 - h_4)} \quad (13.4)$$

Enthalpy at point 2 (inlet to compressor) is obtained by applying mass and energy balance to the mixing of two refrigerant streams, i.e.,

$$h_2 = \frac{\dot{m}_I h_7 + \dot{m}_{II} h_8}{\dot{m}_I + \dot{m}_{II}} \quad (13.5)$$





The COP of this system is given by:

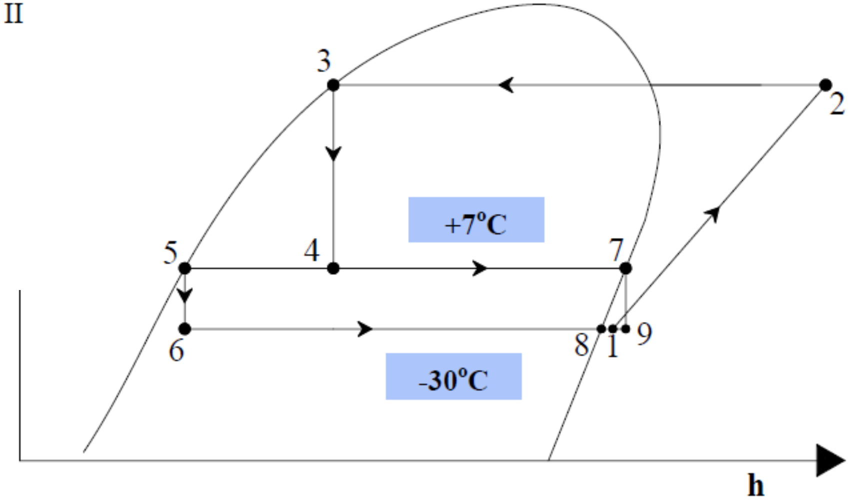
$$COP = \frac{Q_{e,I} + Q_{e,II}}{W_c} = \frac{\dot{m}_I (h_8 - h_6) + \dot{m}_{II} (h_7 - h_4)}{(\dot{m}_I + \dot{m}_{II})(h_2 - h_1)} \qquad (13.6)$$

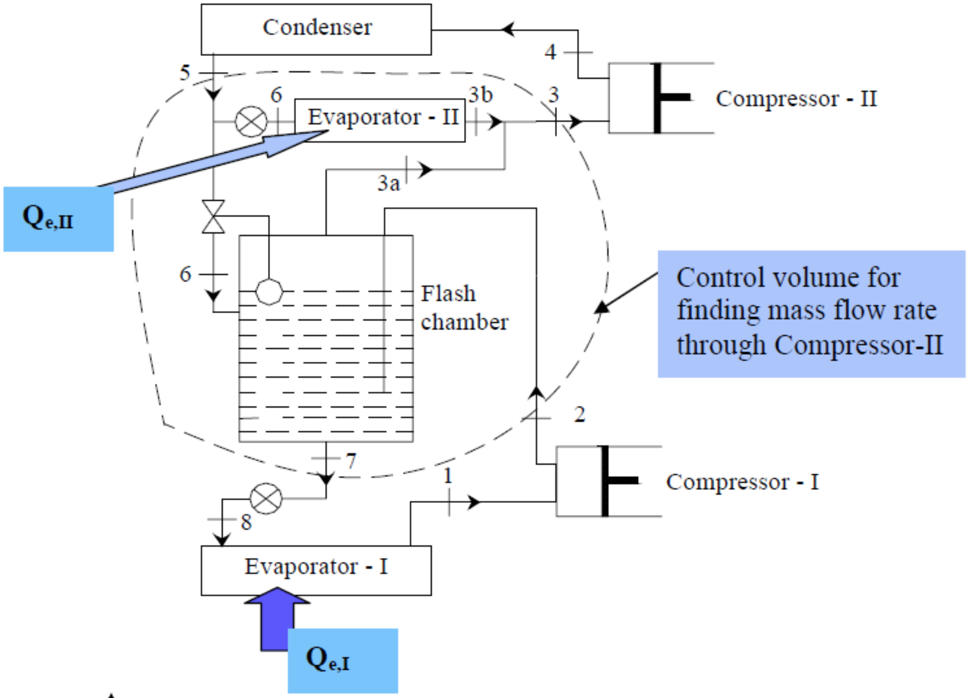
where $\dot{m}_I$ and $\dot{m}_{II}$ are the refrigerant mass flow rates through evaporator I and II respectively. They are given by:

$$\dot{m}_I = \frac{Q_{e,I}}{(h_8 - h_6)} \qquad (13.7)$$

$$\dot{m}_{II} = \frac{Q_{e,II}}{(h_7 - h_4)} \qquad (13.8)$$

$$h_2 = \frac{\dot{m}_I h_8 + \dot{m}_{II} h_9}{\dot{m}_I + \dot{m}_{II}} \qquad (13.9)$$





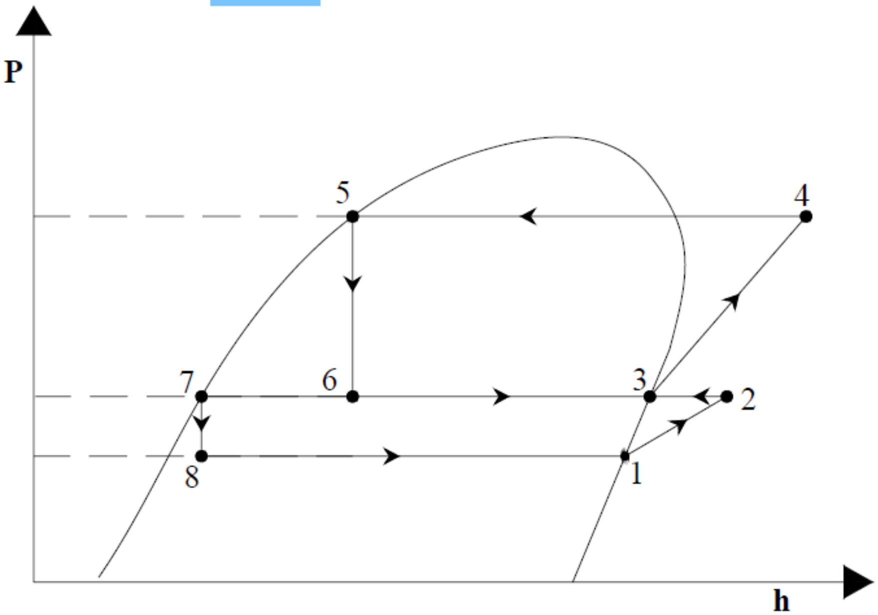
The COP of this system is given by:

$$COP = \frac{Q_{e,I} + Q_{e,II}}{W_{c,I} + W_{c,II}} = \frac{\dot{m}_I(h_1 - h_8) + \dot{m}_{e,II}(h_3 - h_6)}{\dot{m}_I(h_2 - h_1) + \dot{m}_{II}(h_4 - h_3)} \qquad (13.10)$$

where $\dot{m}_I$ and $\dot{m}_{e,II}$ are the refrigerant mass flow rates through evaporator I and II respectively. They are given by:

$$\dot{m}_I = \frac{Q_{e,I}}{(h_8 - h_6)} \qquad (13.11)$$

$$\dot{m}_{e,II} = \frac{Q_{e,II}}{(h \quad - h \quad)} \qquad (13.12)$$



mass balance:

$$\dot{m}_5 + \dot{m}_2 = \dot{m}_7 + \dot{m}_3; \ \dot{m}_5 = \dot{m}_{II} = \dot{m}_3 \ \ \& \ \dot{m}_2 = \dot{m}_I = \dot{m}_7 \qquad (13.13)$$

energy balance:

$$\dot{m}_5 h_5 + \dot{m}_2 h_2 + Q_{e,II} = \dot{m}_7 h_7 + \dot{m}_3 h_3 \qquad (13.14)$$

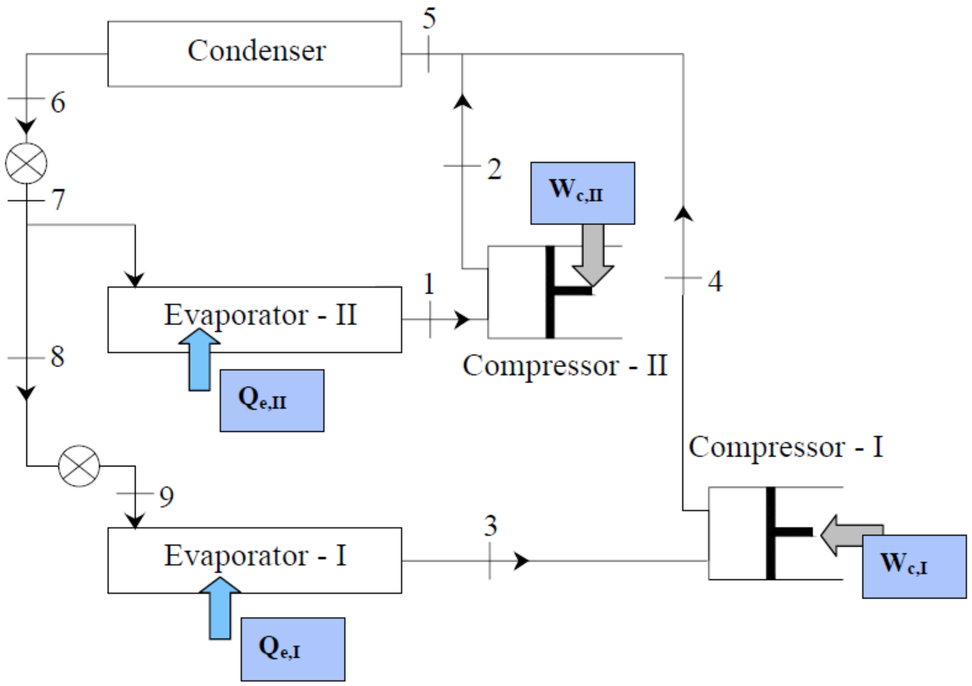
The COP of this combined system is given by:

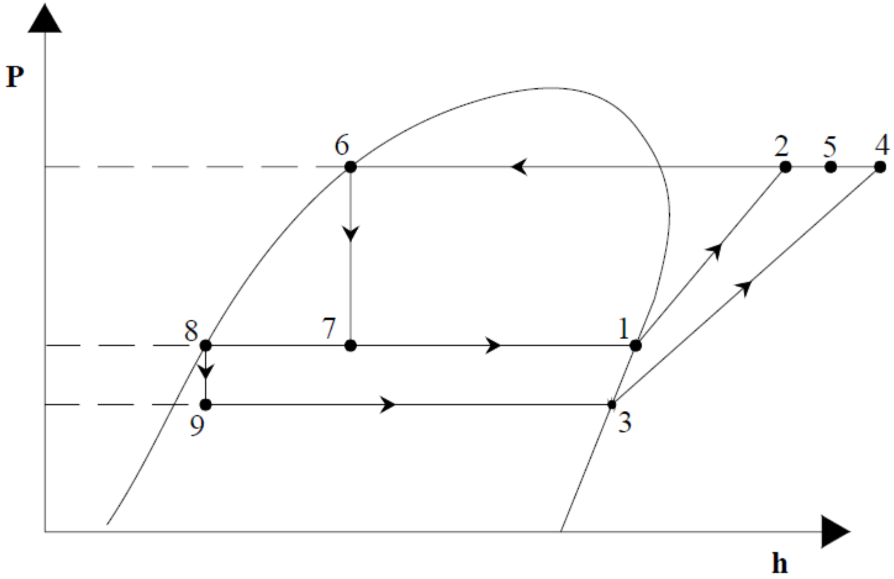
$$COP = \frac{Q_{e,I} + Q_{e,II}}{W_{c,I} + W_{c,II}} = \frac{\dot{m}_I(h_3 - h_9) + \dot{m}_{II}(h_1 - h_7)}{\dot{m}_I(h_4 - h_3) + \dot{m}_{II}(h_2 - h_1)} \tag{13.15}$$

where $\dot{m}_I$ and $\dot{m}_{II}$ are the refrigerant mass flow rates through evaporator I and II respectively. They are given by:

$$\dot{m}_I = \frac{Q_{e,I}}{(h_3 - h_9)} \tag{13.16}$$

$$\dot{m}_{II} = \frac{Q_{e,II}}{(h_1 - h_7)} \tag{13.17}$$

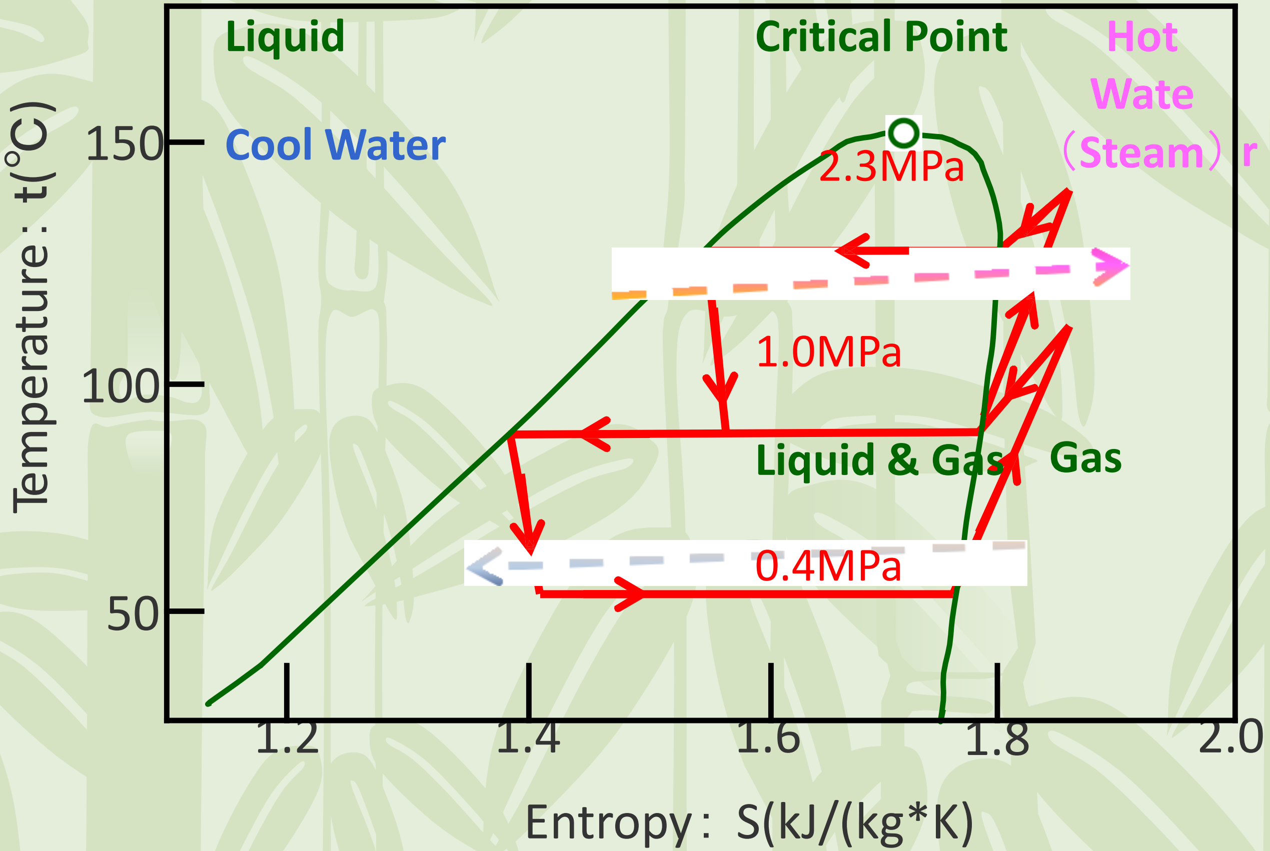




Limitations of multi-stage systems

- Since only one refrigerant is used throughout the system, the refrigerant used should have high critical temperature and low freezing point.
- The operating pressures with a single refrigerant may become too high or too low. Generally only R12, R22 and NH_3 systems have been used in multi-stage systems as other conventional working fluids may operate in vacuum at very low evaporator temperatures. Operation in vacuum leads to leakages into the system and large compressor displacement due to high specific volume.
- Possibility of migration of lubricating oil from one compressor to other leading to compressor break-down.
- The above limitations can be overcome by using cascade systems.

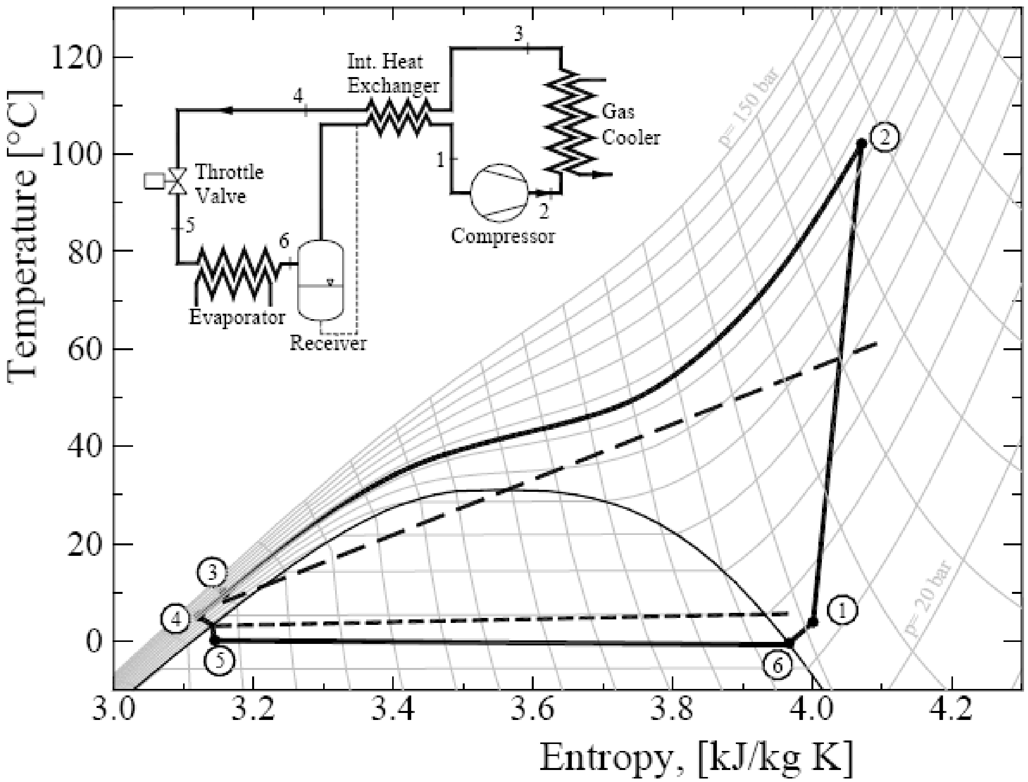
Two- stage compression reverse Rankine cycle (HFC-245fa)

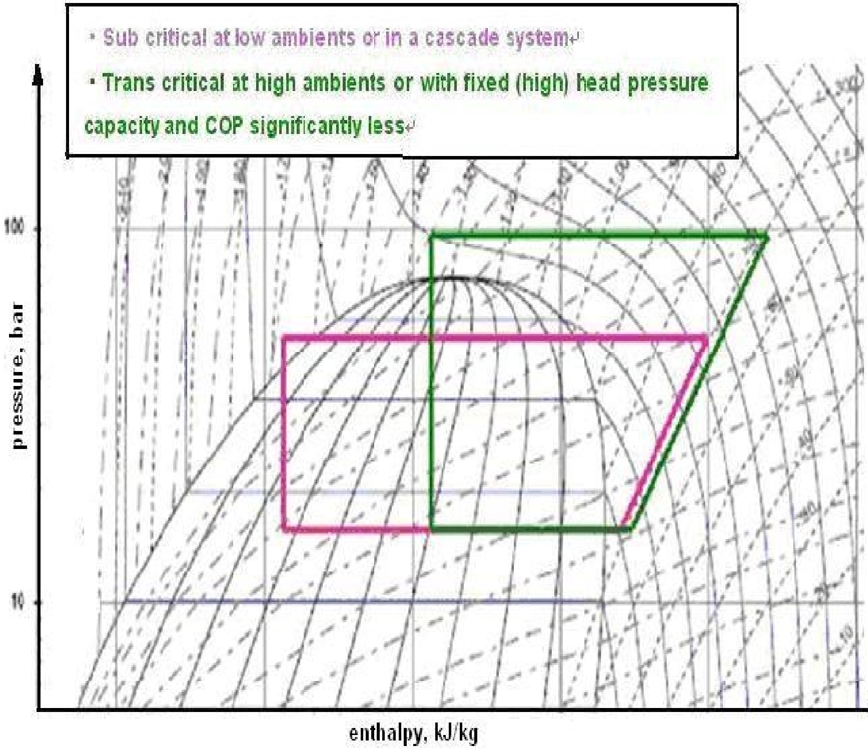


Transcritical Carbon Dioxide (R744) Refrigeration Cycles

- Compared to conventional refrigerants, CO_2 has many advantages as a refrigerant.
- It is a stable substance with a minimal environmental impact (ODP=0, GWP=1) and higher cooling capacity (up to 6 times the capacity of R404A).
- Its good heat transfer performance makes smaller evaporators and condensers possible and its lower viscosity makes less pipe work pressure drop.
- But CO_2 also has some disadvantages, such as its low critical temperature, high pressures in refrigeration cycle and high coefficient of expansion.
- So CO_2 refrigeration cycle is always in trans-critical operation in high ambient with air cooled condensers, which cause the capacity and COP reduction.

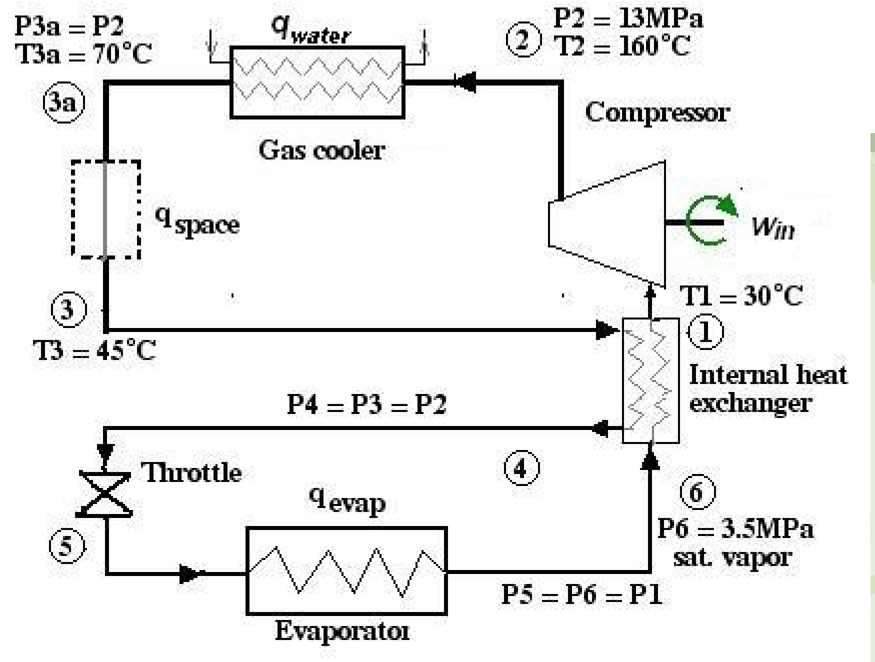
- Due to the critical point of CO_2 (73.77 bar and 30.85°C) the refrigeration cycle has to be operated transcritically when the ambient temperature is near or higher than the critical temperature.
- In this case the evaporation takes place at subcritical pressure and temperature and the heat rejection at supercritical state.




- Sub critical at low ambients or in a cascade system
- Trans critical at high ambients or with fixed (high) head pressure capacity and COP significantly less

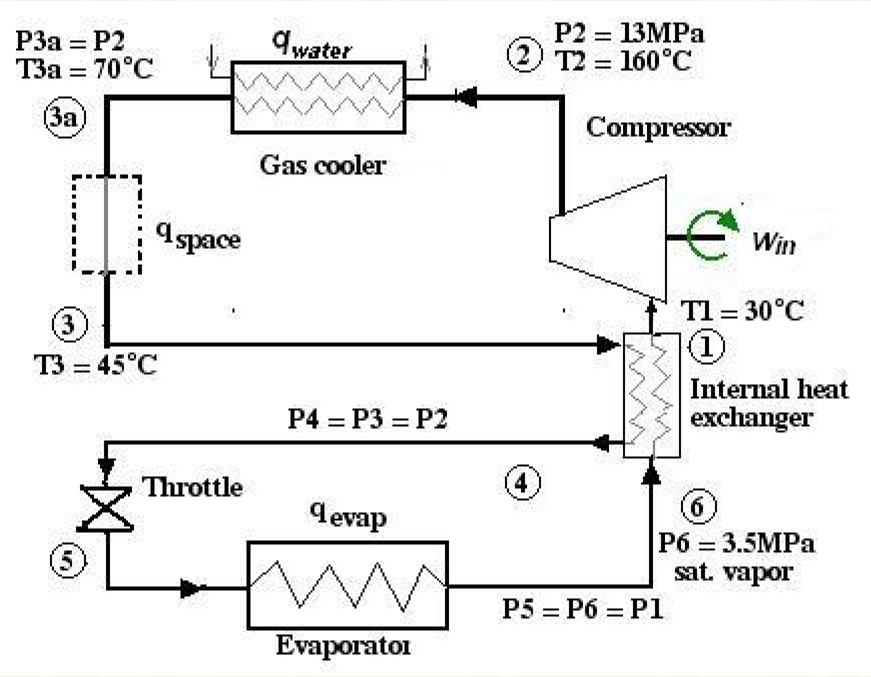
cycles of subcritical and transcritical operation of CO_2

- The main components of a CO_2 refrigeration cycle are compressor, gas cooler (instead of a condenser because of the supercritical heat rejection, which occurs sometimes), internal heat exchanger, expansion valve, evaporator and low-pressure receiver.
- At the transcritical cycle the compressor sucks refrigerant as superheated vapor and compresses to high pressure.



Schematic diagram of a CO_2 refrigeration cycle (heat pump cycle)

- At the supercritical pressure, the CO_2 is cooled in the gas cooler by transferring a heat flux to the ambient climate.
- The CO_2 is cooled down near to the ambient temperature.
- In the internal heat exchanger the high-pressure CO_2 is cooled and the low-pressure CO_2, as saturated vapor from the receiver, is superheated. Then the refrigerant is throttled to low pressure.

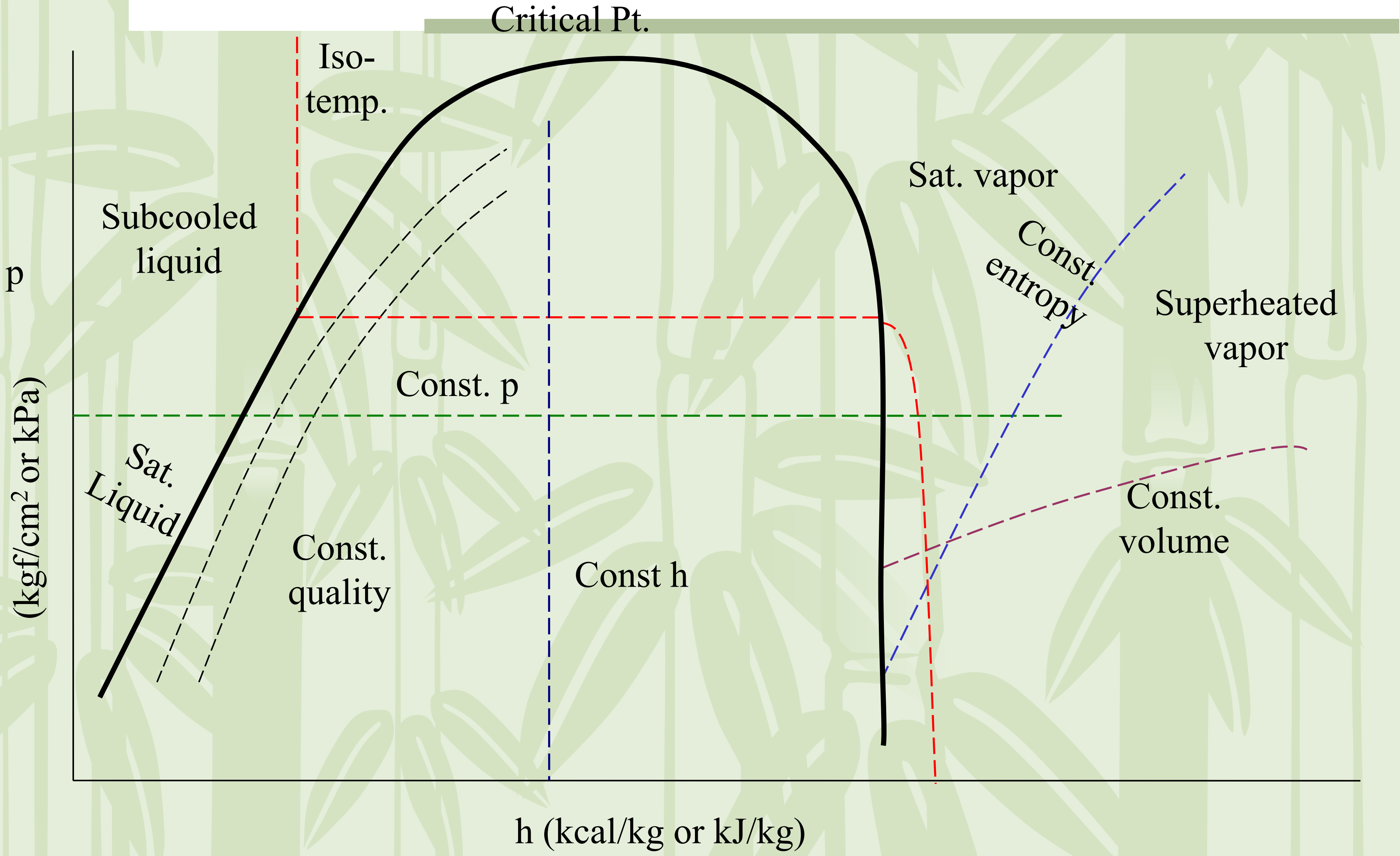


Schematic diagram of a CO_2 refrigeration cycle (heat pump cycle)

Types of refrigerants

- **Refrigerants can be divided in two main groups:**
  - **synthetic** (basically halocarbon fluids: CFCs, HCFCs and HFCs) and **non-synthetic** (hydrocarbons, carbon dioxide, ammonia, water, air – so-called natural refrigerants).
  - **Natural,** such as hydrocarbons, carbon dioxide, ammonia, water, air and the like.

The Mollier Diagram



How are refrigerants named?

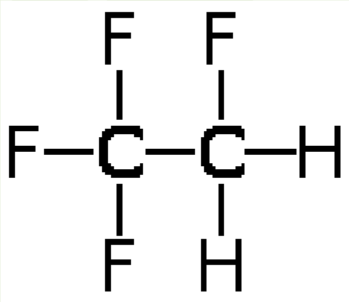
R – 134a

refrigerant

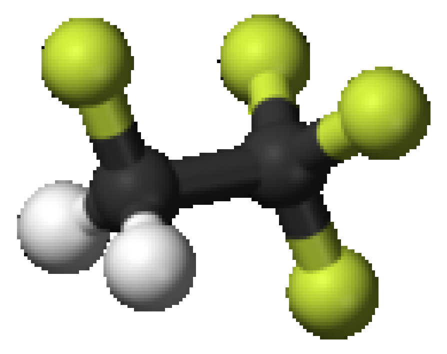
one less than the # of carbon atoms

one plus the # of hydrogen atoms

# of fluorine atoms



$$\mathrm{F-\underset{F}{\overset{F}{C}}-\underset{H}{\overset{F}{C}}-H}$$



structure of 134 molecule

ASHRAE Numbering System

From ASHRAE Standard 34

- Single Component Fluorocarbons
  - 000 Series - Methane Based Molecules
  - 100 Series - Ethane Based
  - 200 Series - Propane Based Fluids
  - 300 Series - Butane Based
- Mixtures
  - 400 Series - Zeotropic Blends (or “Non-Azeotropic”)
  - 500 Series - Azeotropes
- Others
  - 600 Series - Miscellaneous Organic Compounds
  - 700 Series - Inorganic Compounds

Types of Refrigerants

Prefix	Stands for	Atoms in Molecule	Example
CFC	chlorofluorcarbon	Cl, F, C	CFC-11 (R-11)
HCFC	hydrochlorofluorocarbon	H, Cl, F, C	HCFC-22 (R-22)
HFC	hyrofluorocarbon	H, F, C	HFC-134a (R-134a)

Applications vary

- refrigerators / freezers R-11, R-12, R-134a
- air conditioners / heat pumps R-22, R-410A
- chillers R-11, R-12, R-123, R-22, R-134a
- commercial refrigeration R-12, R-22, R-502, R-404A
- industrial refrigeration R-12, R-22, R-502, R-134a, NH_3

Desirable Refrigerant Characteristics

Physical	Thermodynamic	Safety
high heat transfer	high latent heat	nonflammable
low water solubility	low freezing temperature	non toxic
stability	positive evaporator pressure	non irritability
	low condensing pressure	

SELECTING THE RIGHT REFRIGERANT

- Several refrigerants may be used in refrigeration systems such as chlorofluorocarbons (CFCs), ammonia, hydrocarbons (propane, ethane, ethylene, etc.), carbon dioxide, air (in the air-conditioning of aircraft), and even water (in applications above the freezing point).
- R-11 (R-123), R-12, R-22, R-134a, and R-502 account for over 90 percent of the market.
- The industrial and heavy-commercial sectors use *ammonia* (it is toxic).
- R-11 is used in large-capacity water chillers serving A-C systems in buildings. (currently replaced by R-123)
- R-134a (replaced R-12, which damages ozone layer) is used in domestic refrigerators and freezers, as well as automotive air conditioners.
- R-22 is used in window air conditioners, heat pumps, air conditioners of commercial buildings, and large industrial refrigeration systems, and offers strong competition to ammonia.
- R-502 (a blend of R-115 and R-22) is the dominant refrigerant used in commercial refrigeration systems such as those in supermarkets.
- CFCs allow more ultraviolet radiation into the earth's atmosphere by destroying the protective ozone layer and thus contributing to the greenhouse effect that causes global warming. Fully halogenated CFCs (such as R-11, R-12, and R-115) do the most damage to the ozone layer. Refrigerants that are friendly to the ozone layer have been developed.
- Two important parameters that need to be considered in the selection of a refrigerant are the temperatures of the two media (the refrigerated space and the environment) with which the refrigerant exchanges heat.

The choice of refrigerant

- Dependence?
  - The efficiency of a Carnot heat engine is independent of the working medium of the engine.
  - The coefficient of performance of a Carnot refrigerator is independent of the refrigerant.
  - Vapor-compression cycle cause the coefficient of performance to dependent to some extent on the refrigerant.
- Other factors:
  - toxicity, flammability, cost, corrosion properties, vapor pressure in relation to temperature, etc.

- Safety, risk & regulation
  - Environmental impacts
  - Likelihood of future availability
- Refrigerant properties
  - Toxicity & flammability
  - Thermodynamic & Transport
  - Other
- Economics
  - Operating efficiency
  - Capital costs (refrigerant & equipment)
- Staff capabilities

- Two requirement:
  - **The vapor pressure of the refrigerant at the evaporator temperature should be greater than atmospheric pressure to avoid air leaking.**
  - **The vapor pressure at the condenser temperature should not be unduly high, because of the initial cost and operating expense of high-pressure equipment.**
- Refrigerants
  - Ammonia, methyl chloride, carbon dioxide, propane and other hydrocarbons
  - Halogenated hydrocarbons
    - common in 1930s (e.g. CCl_3F, CCl_2F_2) and now mostly end
    - stable molecules causing severe ozone depletion
    - replacements are certain hydrochlorofluorocarbons, less than fully halogenated hydrocarbons, and hydrofluorocarbons which contains no chlorine (e.g., $CHCl_2CF_3$, CF_3CH_2F).

Synthetic refrigerants

- Refrigerators from the late 1800s until 1929 used the higher ***toxicity gases - ammonia, methyl chloride, and sulphur dioxide***. Fatal accidents occurred from time to time because of leakage from refrigerators.
- In 1928, CFCs and HCFCs were invented ***as substitutes for the higher toxicity and flammable refrigerants***. CFCs and HCFCs are a group of aliphatic organic compounds ***containing the elements carbon and fluorine,*** and, in many cases, other halogens (especially chlorine) and ***hydrogen***.
- Most CFCs and HCFCs tend to be ***colorless, odorless, non-flammable, non-corrosive substances***. Because CFCs and HCFCs have low toxicity, their use eliminated the danger posed by refrigerator leaks.

Chlorofluorocarbons (CFC)

Inert, non-toxic, non-flammable compounds with low boiling points that once is called the perfect refrigerants.

- CFCs consist of ***chlorine, fluorine, and carbon***. The most common refrigerants in this group are R-11, R-12 and R-115 (within the blend R-502).
- Widespread use since the 1930s, in nearly all applications.
- Contain no hydrogen, CFCs are very ***chemically stable***, and tend to have ***good compatibility*** with most materials and traditional lubricants such as mineral oils
- Generally ***good thermodynamic and transport properties***, thereby offering the potential for good efficiency.
- However, because they ***contain chlorine***, CFCs are damaging to the ozone layer, and due to their long atmospheric life, ***the CFCs have a high ODP***.
- Similarly, they are ***strong greenhouse gases with high GWP***.

Hydrochlorofluorocarbons (HCFCs)

- HCFCs consist of ***hydrogen, chlorine, fluorine, and carbon***. The most common refrigerants in this group are R-22, R-123 and R-124 (within various blends).
- Widespread use since the 1930s, in nearly all applications, including commercial refrigeration, cold storage, transport refrigeration, stationary air conditioning and chillers.
- ***HCFCs Contain hydrogen, HCFCs are theoretically less chemically stable than CFCs,*** but nevertheless tend to have ***good compatibility with most materials*** and traditional lubricants such as mineral oils.
- Good ***thermodynamic and transport properties***, thereby offering the potential for very good efficiency.
- As with CFCs, because of the chlorine content, they are ***damaging to the ozone layer*** , although ***with a relatively low ODP***.
- Similarly, they are ***strong greenhouse gases with high GWP.***

Hydrofluorocarbons (HFCs)

- HFCs consist ***of hydrogen, fluorine, and carbon***. The most common refrigerants in this group are R-134a, R-32, R-125 and R-143a (mostly within blends, such as R-404A, R-407C and R-410A).
- ***Large scale use since the 1990s***, in nearly all applications that have traditionally used CFCs and HCFCs, including domestic and commercial refrigeration, cold storage, vehicle air conditioning, transport refrigeration, stationary air conditioning and chillers.
- ***HFCs are generally chemically very stable, and tend to have good compatibility with most materials***.
- ***Not miscible*** with traditional lubricants, ***synthetic oils are needed***.
- Their ***thermodynamic and transport properties range from fairly to very good***, thereby offering the potential for good efficiency.
- ***HFCs contain no chlorine, do not damage the ozone layer***.
- However, due to their long atmospheric lifetime, they are typically ***strong greenhouse gases with high GWP***.

Environmental Effects of Refrigerants

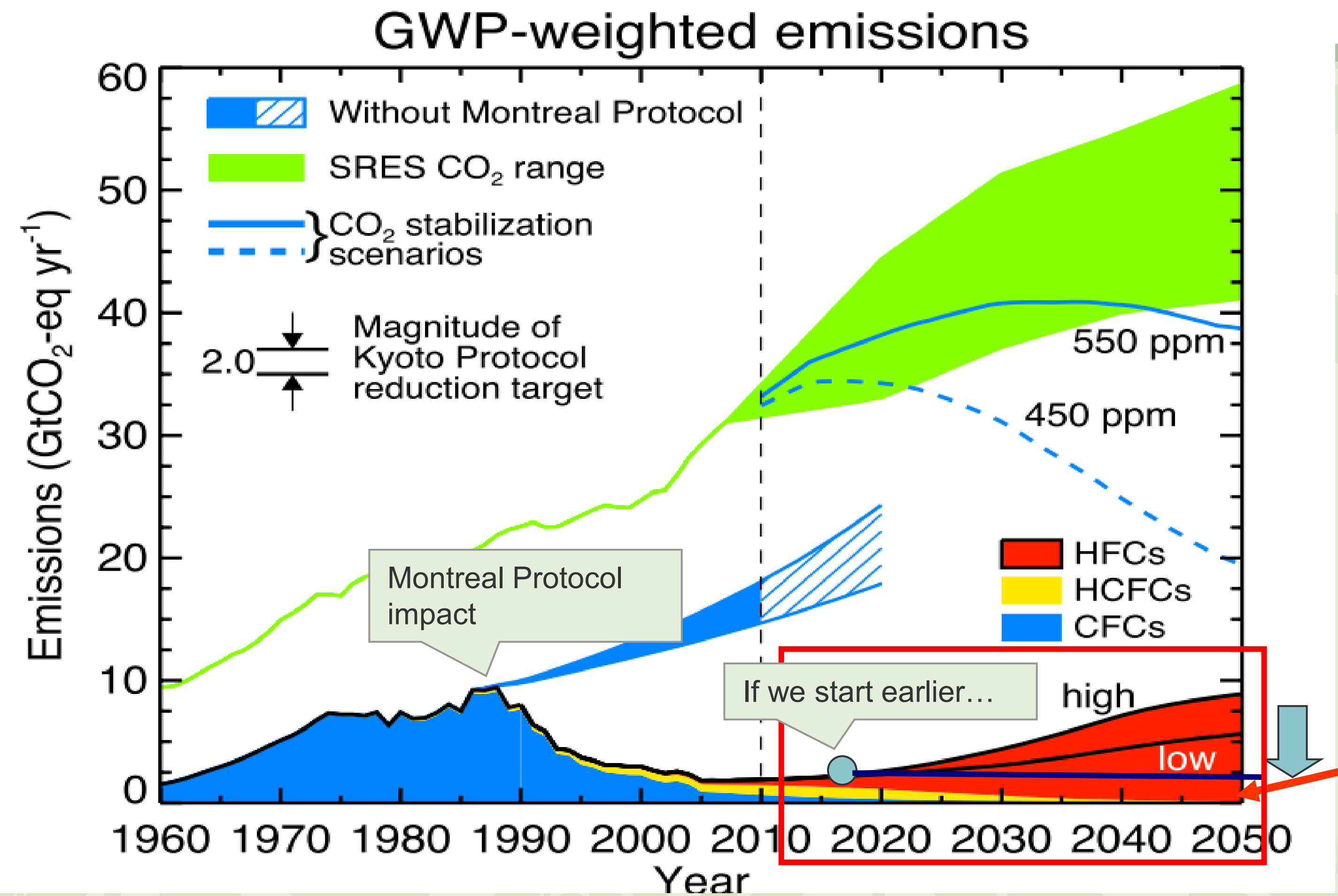
- Depletion of the ozone layer in the stratosphere (CFC/HCFC)

- Global warming : (CFC/HCFC/HFC)

  Refrigerants directly contributing to global warming when released to the atmosphere

  Indirect contribution based on the energy consumption (CO_2 produced by power stations)

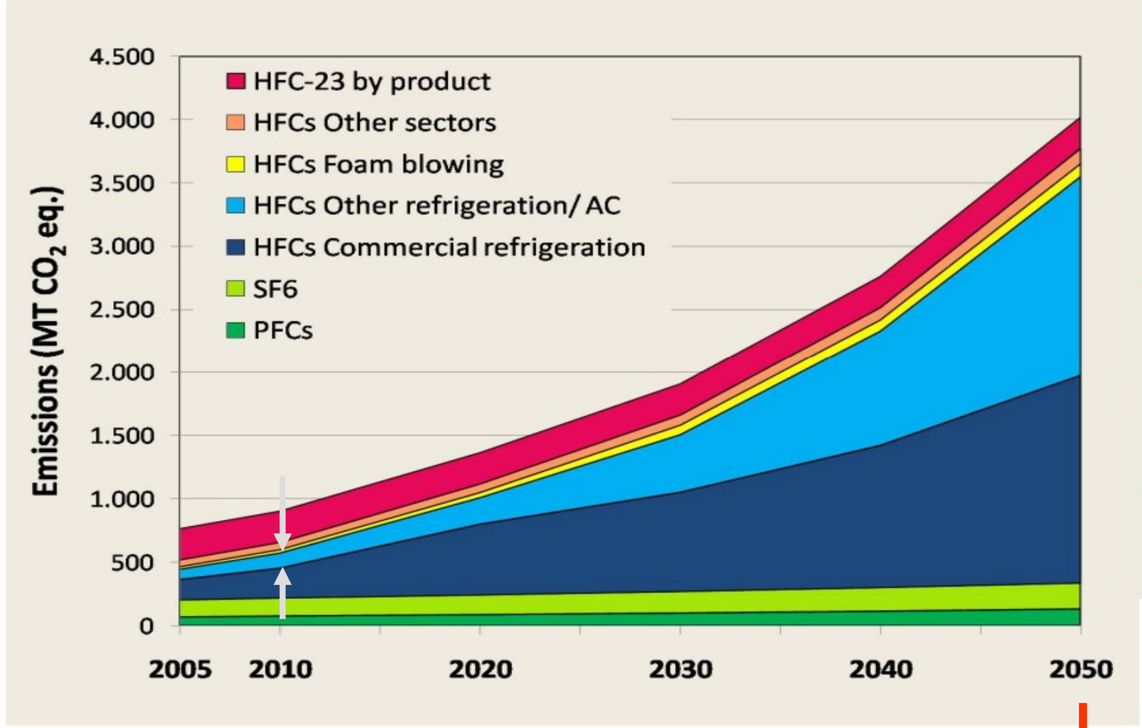
Background The sooner the lesser



The sooner we introduce alternatives for todays HFCs, the lesser the impact would be

Source:
"The large contribution of projected HFC emissions to future climate forcing" by Guus J.M.Velders et.al.

Background HFC Growth (BAU)and Impact of Developing Countries

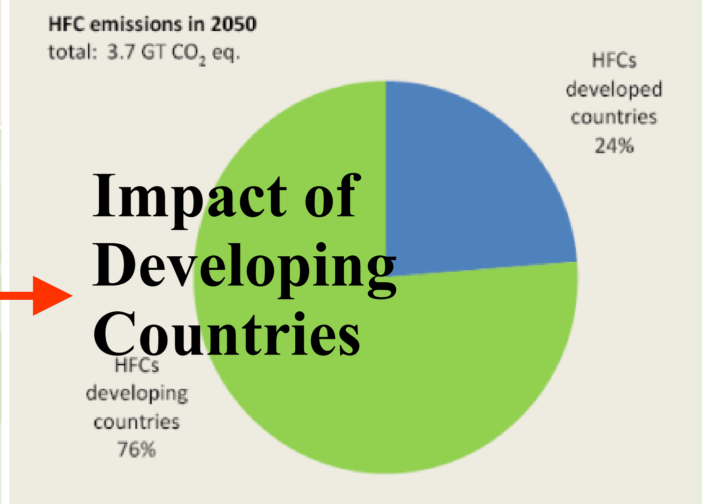


Impact of Refrigeration/AC

Note: includes stationary and mobile AC

Impact of Commercial Refrigeratio

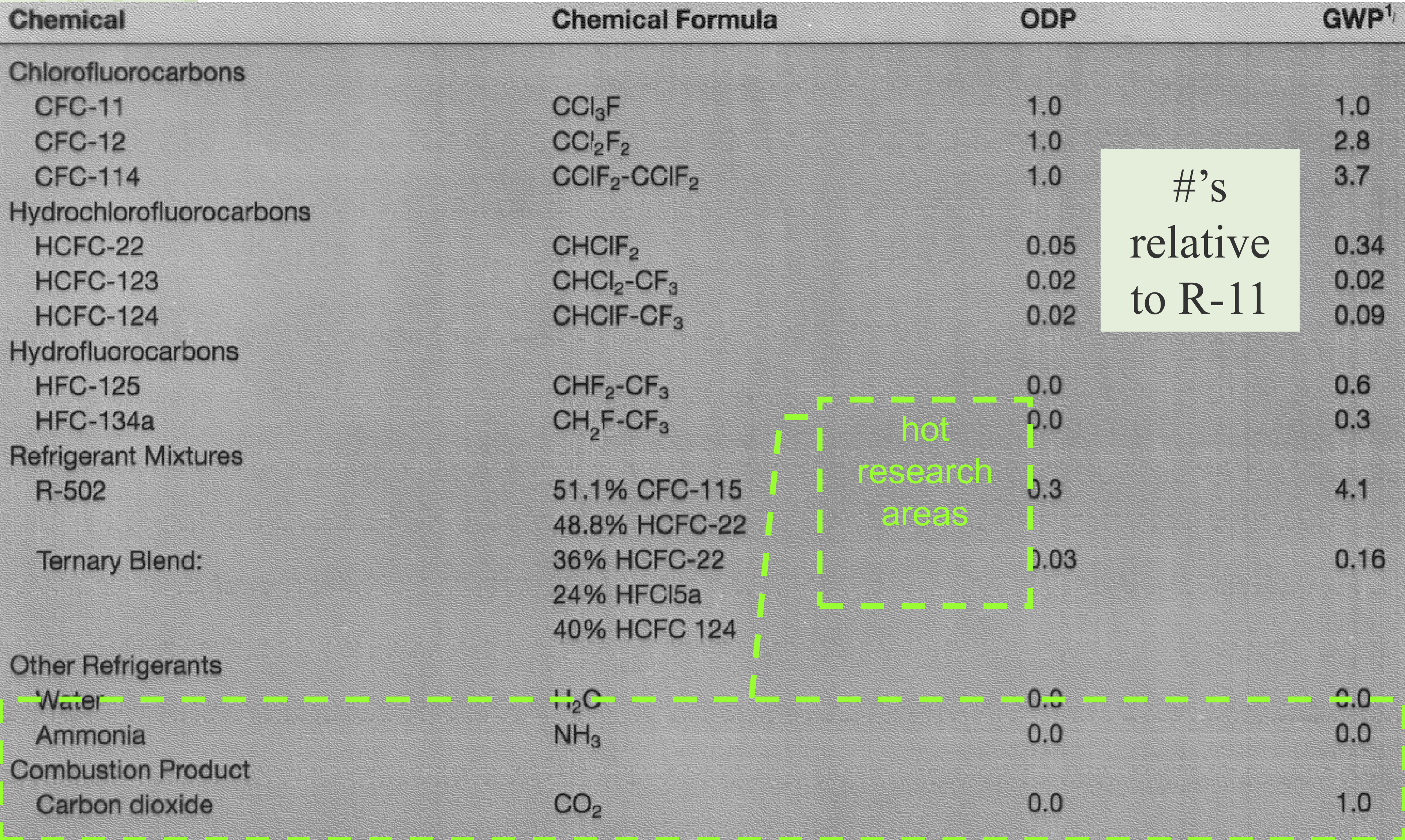
Source:
"Projections of global emissions of fluorinated green house gases in 2050" by Öko Recherche



Impact of Developing Countries

Quick Gain is important

Refrigerants & Climate Change

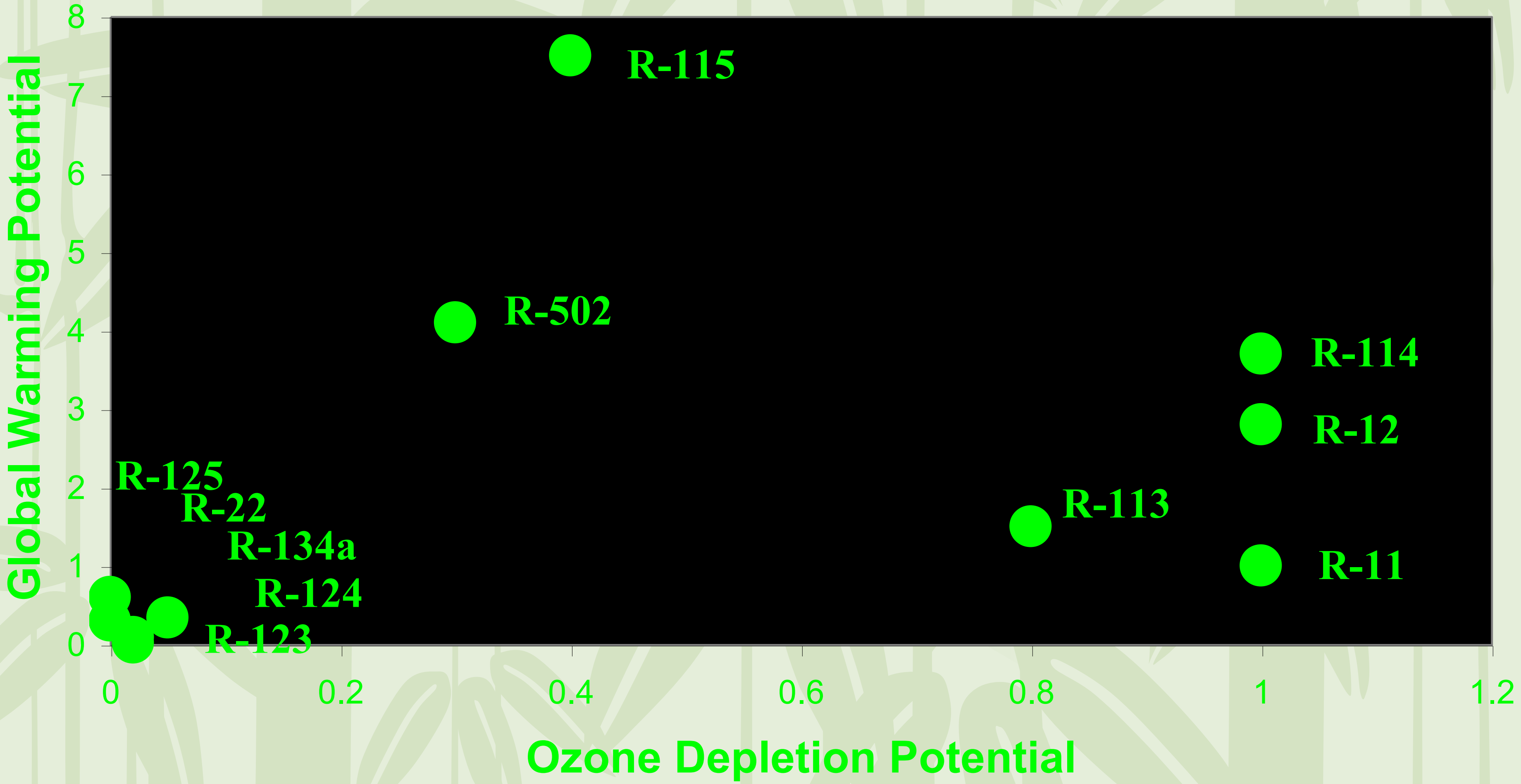


Chemical	Chemical Formula	ODP	GWP[1]
Chlorofluorocarbons			
CFC-11	CCl_3F	1.0	1.0
CFC-12	CCl_2F_2	1.0	2.8
CFC-114	$CClF_2$-$CClF_2$	1.0	3.7
Hydrochlorofluorocarbons			
HCFC-22	$CHClF_2$	0.05	0.34
HCFC-123	$CHCl_2$-CF_3	0.02	0.02
HCFC-124	$CHClF$-CF_3	0.02	0.09
Hydrofluorocarbons			
HFC-125	CHF_2-CF_3	0.0	0.6
HFC-134a	CH_2F-CF_3	0.0	0.3
Refrigerant Mixtures			
R-502	51.1% CFC-115 48.8% HCFC-22	0.3	4.1
Ternary Blend:	36% HCFC-22 24% HFCl5a 40% HCFC 124	0.03	0.16
Other Refrigerants			
Water	H_2O	0.0	0.0
Ammonia	NH_3	0.0	0.0
Combustion Product			
Carbon dioxide	CO_2	0.0	1.0

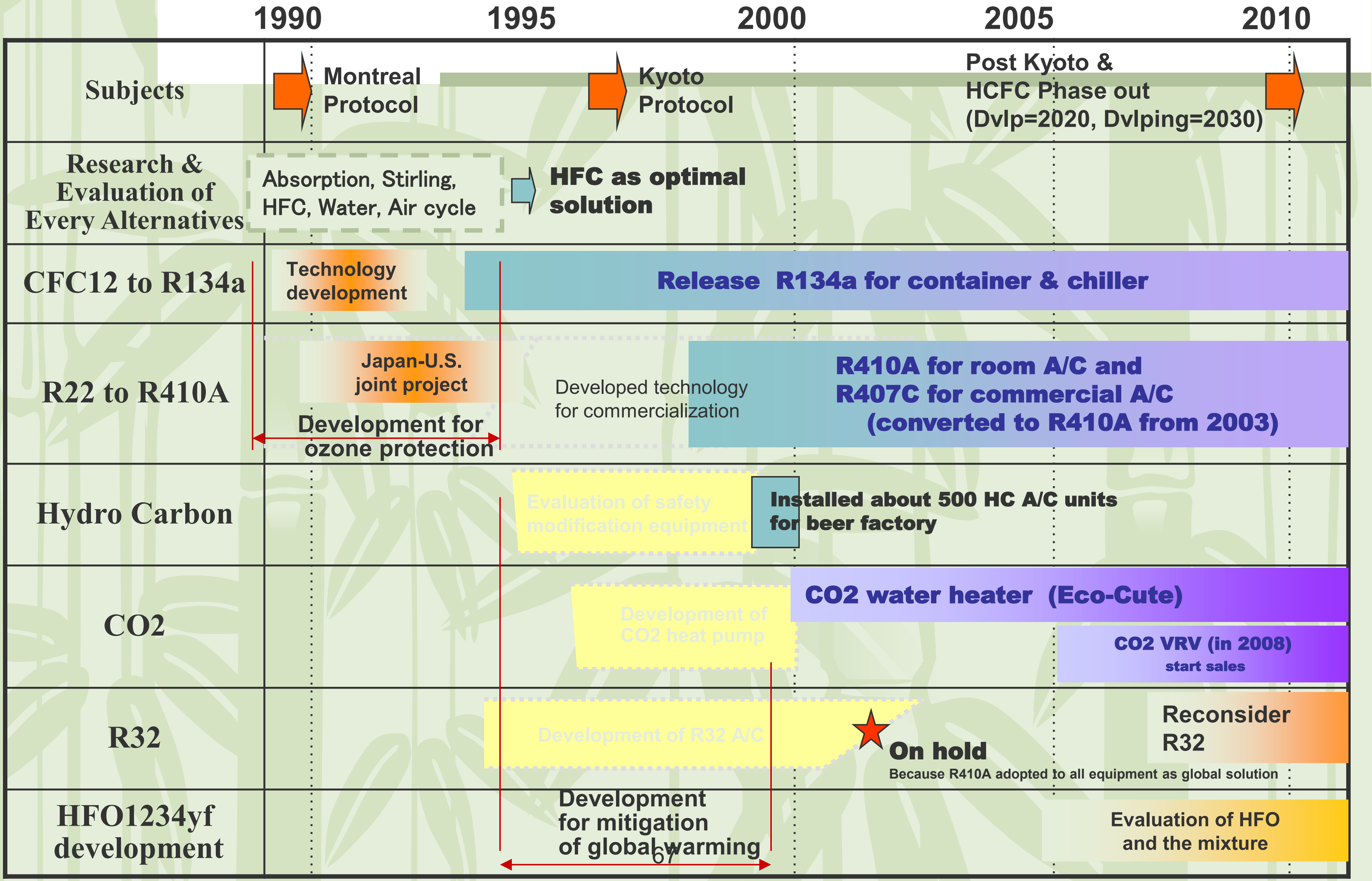
#'s relative to R-11

hot research areas

Contributions to Climate Change



What are the Possible Options?



Subjects	Montreal Protocol Kyoto Protocol Post Kyoto & HCFC Phase out (Dvlp=2020, Dvlping=2030)
Research & Evaluation of Every Alternatives	Absorption, Stirling, HFC, Water, Air cycle HFC as optimal solution
CFC12 to R134a	Technology development Release R134a for container & chiller
R22 to R410A	Japan-U.S. joint project Development for ozone protection Developed technology for commercialization R410A for room A/C and R407C for commercial A/C (converted to R410A from 2003)
Hydro Carbon	Evaluation of safety modification equipment Installed about 500 HC A/C units for beer factory
CO2	Development of CO2 heat pump CO2 water heater (Eco-Cute) CO2 VRV (in 2008) start sales
R32	Development of R32 A/C On hold Because R410A adopted to all equipment as global solution Reconsider R32
HFO1234yf development	Development for mitigation of global warming Evaluation of HFO and the mixture

Refrigerants with zero ozone depleting potential (other than HFCs)

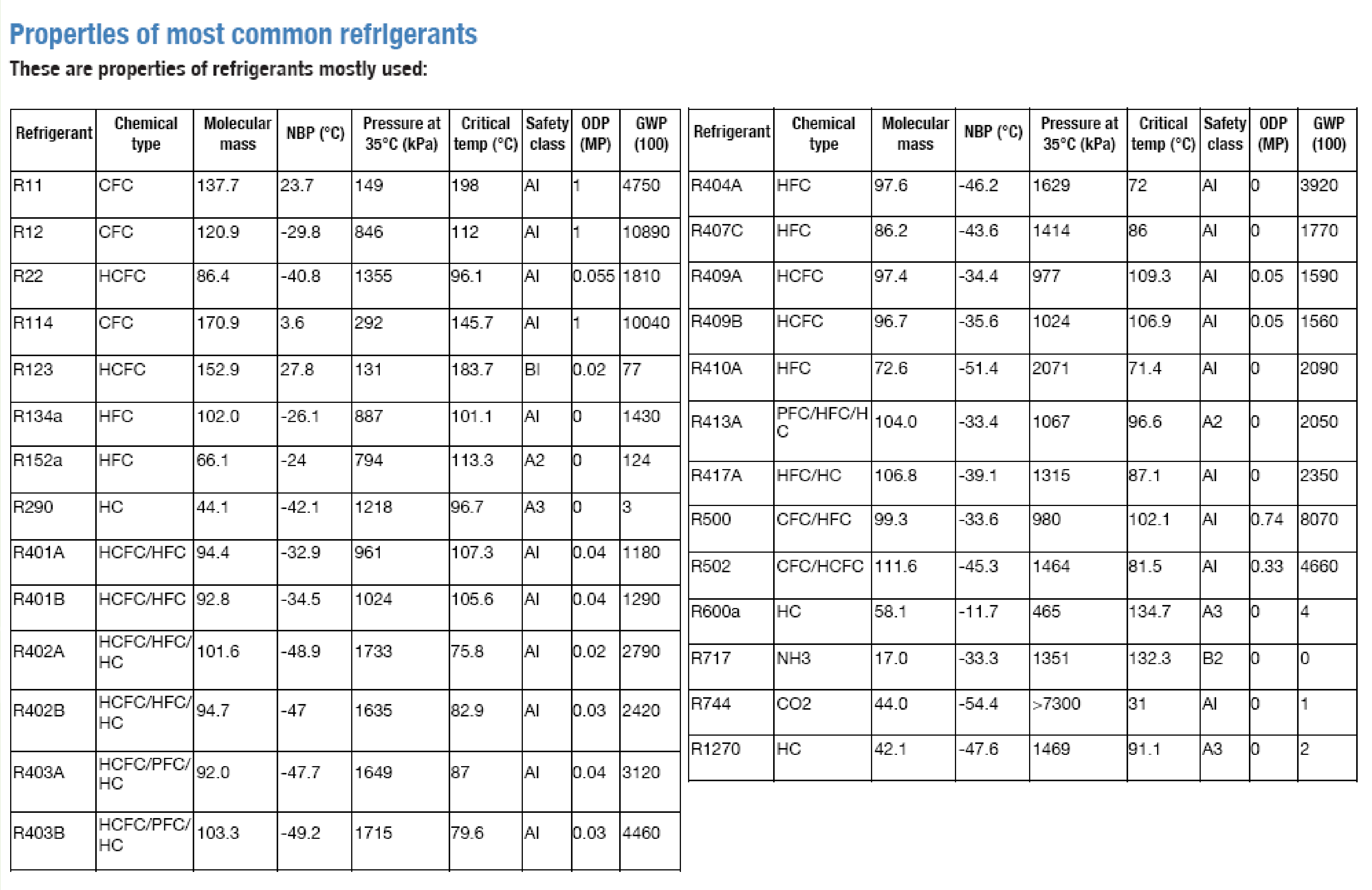
- **Perfluorocarbons**
  - They represent another group of fluorocarbons which contains five different fluids. One of these (R218) is occasionally used in refrigerant blends. Generally ***PFCs are very stable***, but as a result ***have very high GWP***.
- **Unsaturated HFCs**
  - Whilst conventional HFCs are saturated, there are a small number of ***unsaturated HFCs, known as olefins***. ***Generally, there are highly unstable***, but recently ***a small number have been identified which are sufficiently stable*** to be used as refrigerants, and have ***low-toxicity and low flammability and low GWP***. The two receiving most interest are ***R-1234yf and R-1234ze***; the former is being considered for use in MVAC systems, ***but it is unlikely that they will be applied as refrigerant in other sectors*** for several years.

- **Hydrofluoroethers (mainly for solvent)**
  - This group of fluorinated chemicals tends to be ***fairly stable*** and amongst them have a fairly wide range of boiling points, although they tend to be lower pressure fluids. They have been considered as use as refrigerants, but to date have not achieved market acceptance for various reasons.
- **Natural refrigerants**
  - Various hydrocarbons, ammonia and carbon dioxide belong to a group named "natural refrigerants". All natural refrigerants exist in material cycles present in the nature even without human interference. They have zero ODP and zero or negligible GWP.
  - **Some natural refrigerants: Ammonia (NH_3, R-717) , Carbon dioxide (CO_2, R-744) , Hydrocarbon…**

Ammonia as Refrigerant

- Advantages
  - ODP = 0, GWP = 0
  - Excellent thermodynamic characteristics: small molecular mass, large latent heat, large vapor density and excellent heat transfer characteristics
  - High critical temperature (132 °C) : highly efficient cycles at high condensing temperatures
  - Its smell causes leaks to be detected and fixed before reaching dangerous concentration
  - Relatively Low price
- Drawbacks:
  - Toxic
  - Flammable (16 – 28% concentration)
  - Not compatible with copper
  - Temperature on discharge side of compressor is higher compared to other refrigerants

Source: Manual for Refrigeration Servicing Technicians



Properties of most common refrigerants

These are properties of refrigerants mostly used:

Refrigerant	Chemical type	Molecular mass	NBP (°C)	Pressure at 35°C (kPa)	Critical temp (°C)	Safety class	ODP (MP)	GWP (100)
R11	CFC	137.7	23.7	149	198	AI	1	4750
R12	CFC	120.9	-29.8	846	112	AI	1	10890
R22	HCFC	86.4	-40.8	1355	96.1	AI	0.055	1810
R114	CFC	170.9	3.6	292	145.7	AI	1	10040
R123	HCFC	152.9	27.8	131	183.7	BI	0.02	77
R134a	HFC	102.0	-26.1	887	101.1	AI	0	1430
R152a	HFC	66.1	-24	794	113.3	A2	0	124
R290	HC	44.1	-42.1	1218	96.7	A3	0	3
R401A	HCFC/HFC	94.4	-32.9	961	107.3	AI	0.04	1180
R401B	HCFC/HFC	92.8	-34.5	1024	105.6	AI	0.04	1290
R402A	HCFC/HFC/HC	101.6	-48.9	1733	75.8	AI	0.02	2790
R402B	HCFC/HFC/HC	94.7	-47	1635	82.9	AI	0.03	2420
R403A	HCFC/PFC/HC	92.0	-47.7	1649	87	AI	0.04	3120
R403B	HCFC/PFC/HC	103.3	-49.2	1715	79.6	AI	0.03	4460
R404A	HFC	97.6	-46.2	1629	72	AI	0	3920
R407C	HFC	86.2	-43.6	1414	86	AI	0	1770
R409A	HCFC	97.4	-34.4	977	109.3	AI	0.05	1590
R409B	HCFC	96.7	-35.6	1024	106.9	AI	0.05	1560
R410A	HFC	72.6	-51.4	2071	71.4	AI	0	2090
R413A	PFC/HFC/HC	104.0	-33.4	1067	96.6	A2	0	2050
R417A	HFC/HC	106.8	-39.1	1315	87.1	AI	0	2350
R500	CFC/HFC	99.3	-33.6	980	102.1	AI	0.74	8070
R502	CFC/HCFC	111.6	-45.3	1464	81.5	AI	0.33	4660
R600a	HC	58.1	-11.7	465	134.7	A3	0	4
R717	NH3	17.0	-33.3	1351	132.3	B2	0	0
R744	CO2	44.0	-54.4	>7300	31	AI	0	1
R1270	HC	42.1	-47.6	1469	91.1	A3	0	2

Following table shows properties of alternative refrigerants compared to R22.

			Refrigerant physical properties					
			Cond.Press. MPa	ODP	GWP (IPCC4)	Life Year	Flamm -ability	Toxicity
R22		Single	**1.73**	**0.05**	**1810**	**11.9**	**No**	**Low**
HFC	R410A	Azeotrope	**2.72**	**0**	**2090**	**5-29**	**No**	**Low**
	R407C	Zeotrope	**1.86**	**0**	**1770**	**5-29**	**No**	**Low**
	R32	Single	**2.80**	**0**	**675**	**5**	**Low*1**	**Low**
	HFO1234ze	Single	**0.88**	**0**	**6**	**11 days**	**Low*1**	**Low*3**
	HFO1234yf	Single	**1.16**	**0**	**4**	**7 days**	**Low*1**	**Low*3**
	HFO mixture	**Under investigation**						**Low**
Non-HFC	Propane (R290)	Single	**1.53**	**0**	**<3**	**Some days**	**High**	**Low**
	CO2(R744)	Single	**10.0**	**0**	**1**	**120**	**No**	**Low*2**
	Ammonia (R717)	Single	**1.78**	**0**	**0**	**0**	**Low**	**High**

*1 According to ISO817 draft
*2 Practical limit is 0.1 kg/m^3 according to EN378
*3 Based on latest data proposed for ASHRAE34

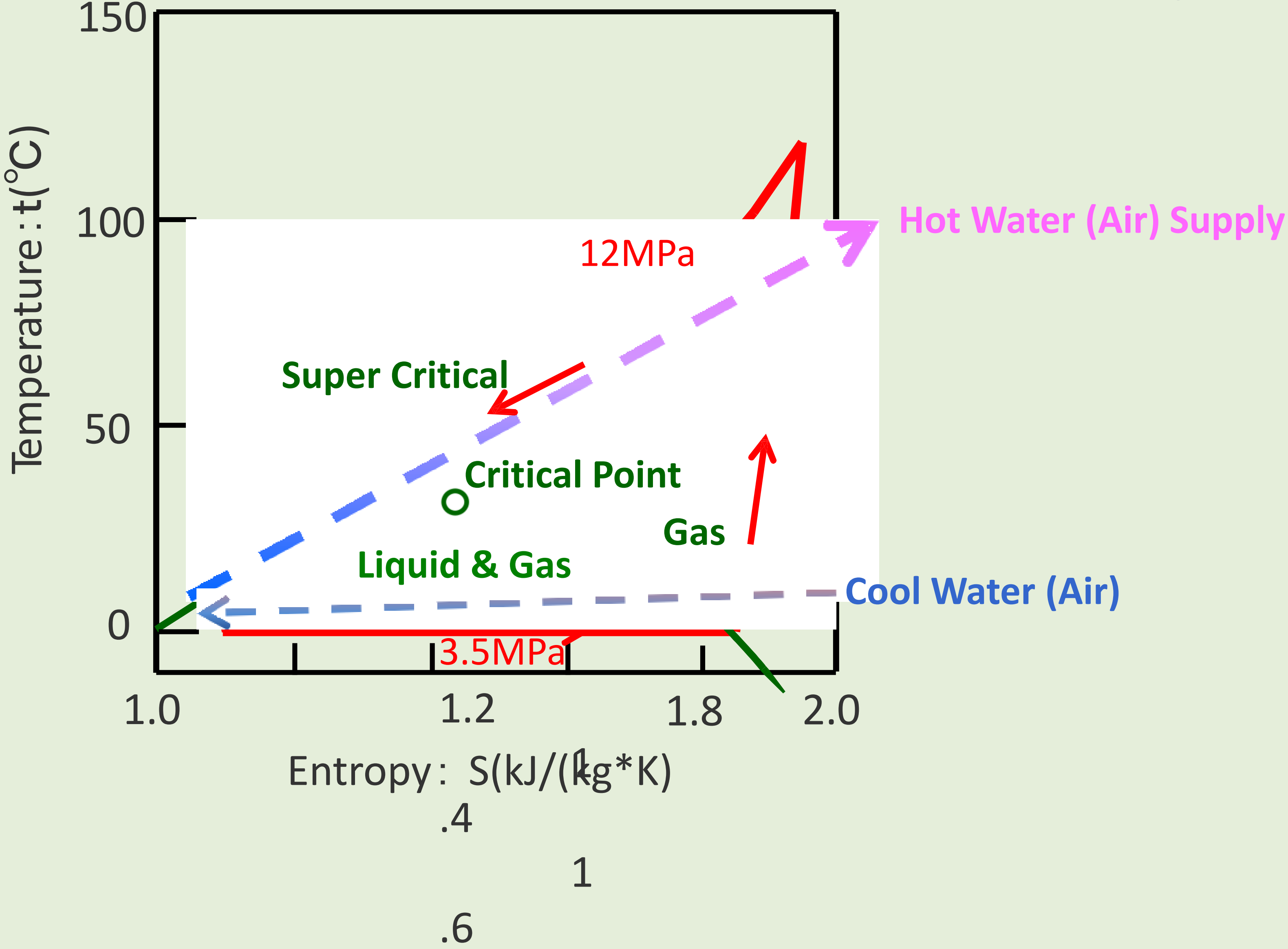
Carbon Dioxide as Refrigerant

- Non Flammable
- Non toxic
- Inexpensive and widely available
- Its high operating pressure provides potential for system size and weight reducing potential.

Drawbacks:

- Operating pressure (high side) : Above 80 bars
- Low efficiency

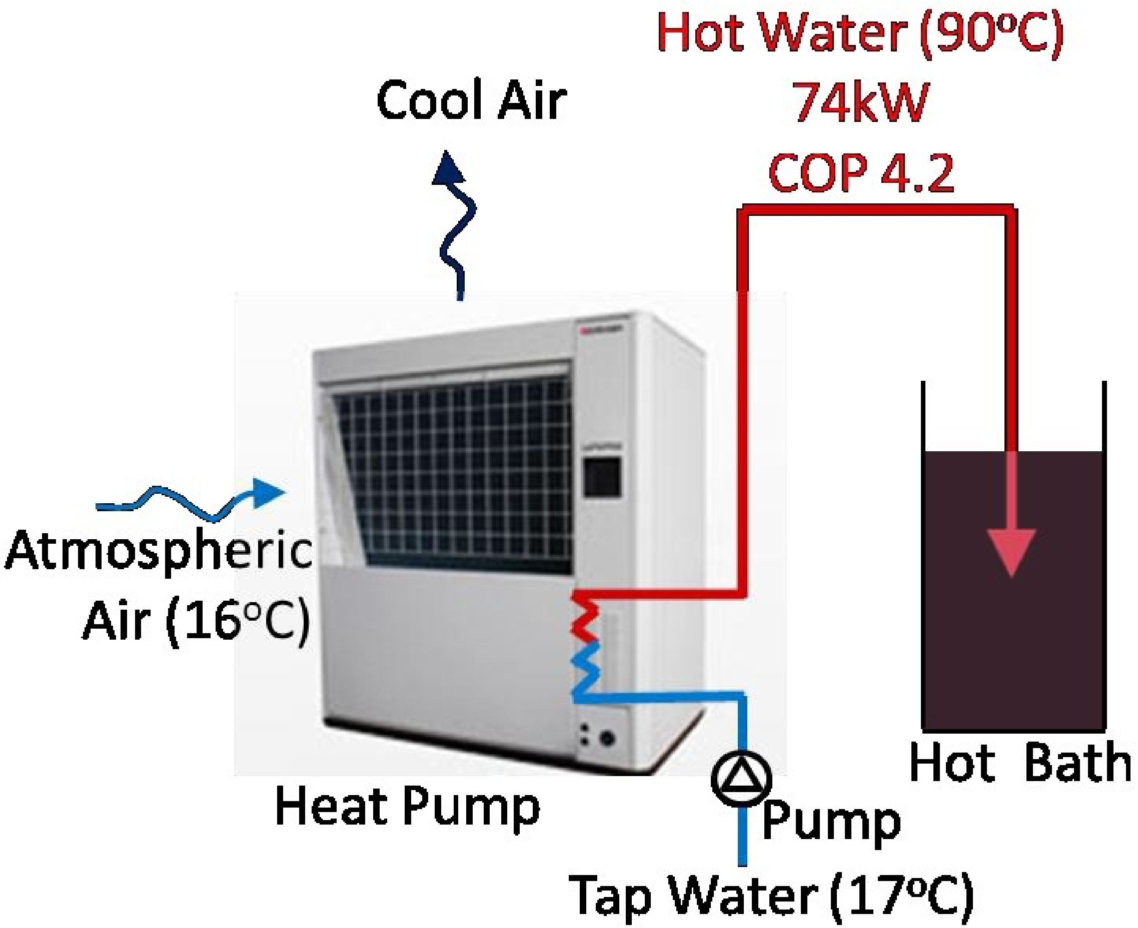
CO_2 transcritical Heat Pump Cycle



Air-source CO_2 transcritical heat pump

Mayekawa Mfg. Co., Ltd.

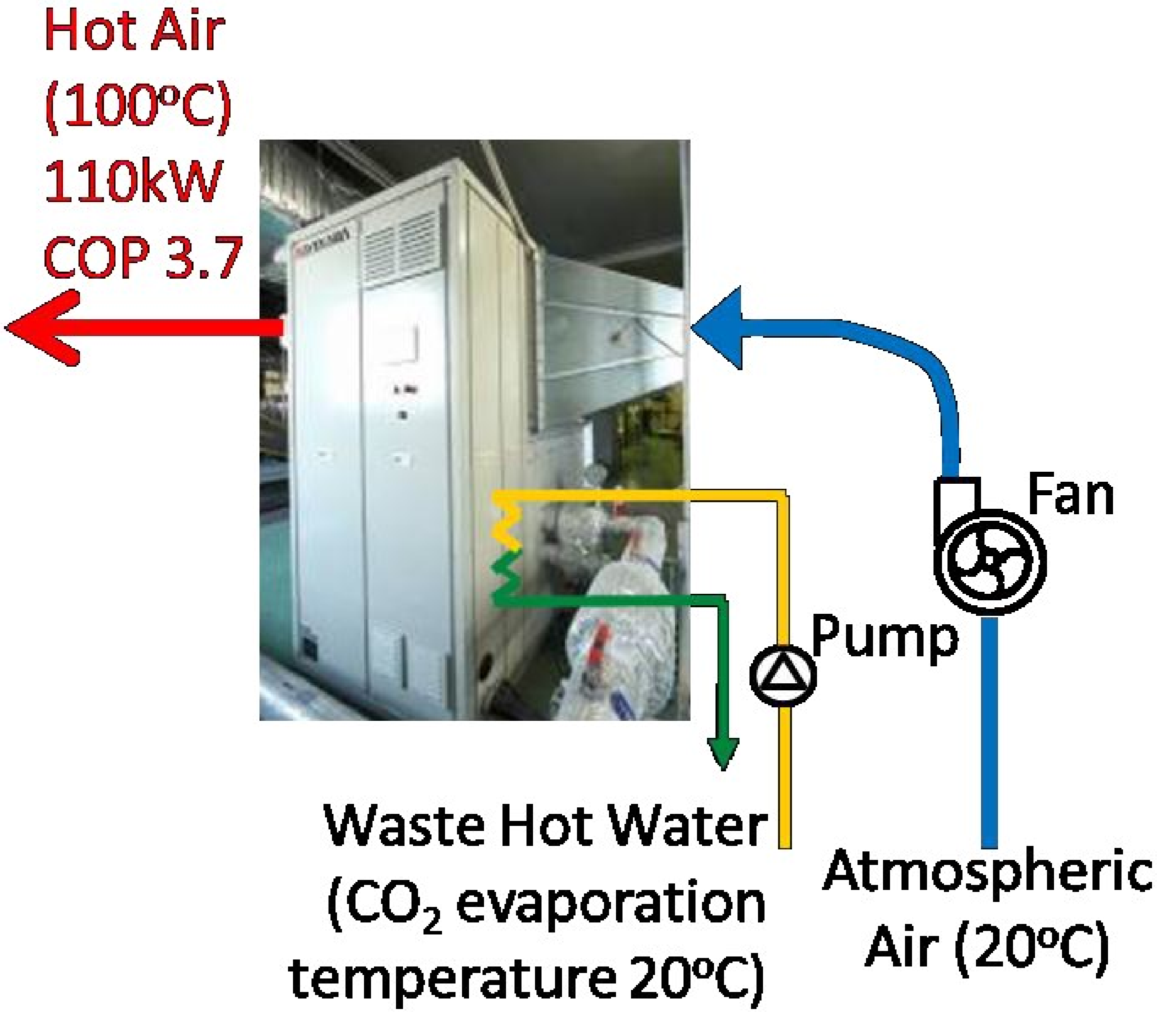
- delivering hot water, with screw type compressor
- supplied to Japan, South Korea, Taiwan, Indonesia



Water-source CO_2 transcritical heat pump

Mayekawa Mfg. Co., Ltd.

- delivering hot air, with screw type compressor



Hydrocarbon Refrigerants

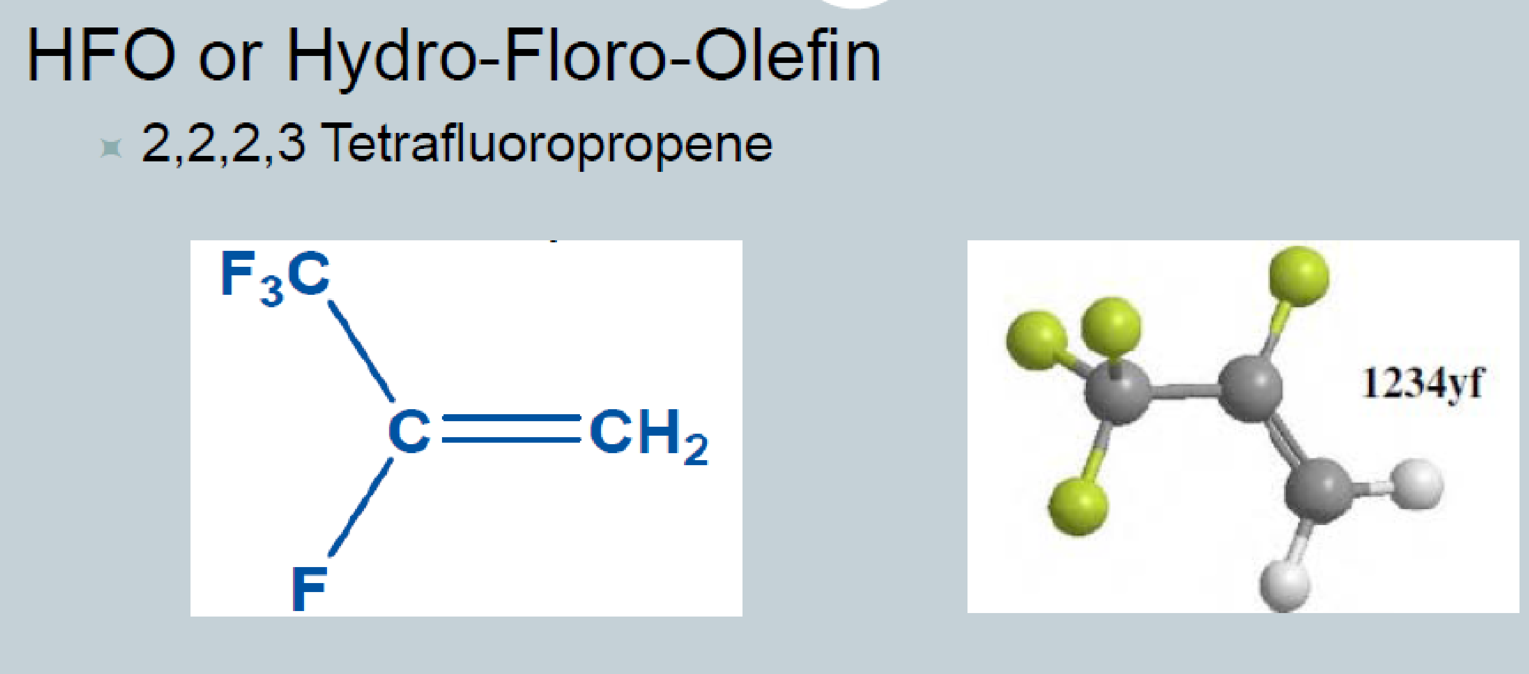
- Used since the 1880's
- Zero ODP and negligible GWP
- Good substitutes for CFC's, HCFC's, and HFC's.
- Drop in solution
- Compatible with copper
- Miscible with mineral oil
- A third of original charge only is required when replacing halocarbons refrigerant in existing equipment
- Energy saving : up to 20% due to lower molecular mass and vapor pressure

Drawback :

- Flammable

Why R-1234yf?

- GWP = 4
- Similar to R-134a (property & production)
- Drop-in replacement of R-134a



HFO or Hydro-Floro-Olefin

- 2,2,2,3 Tetrafluoropropene

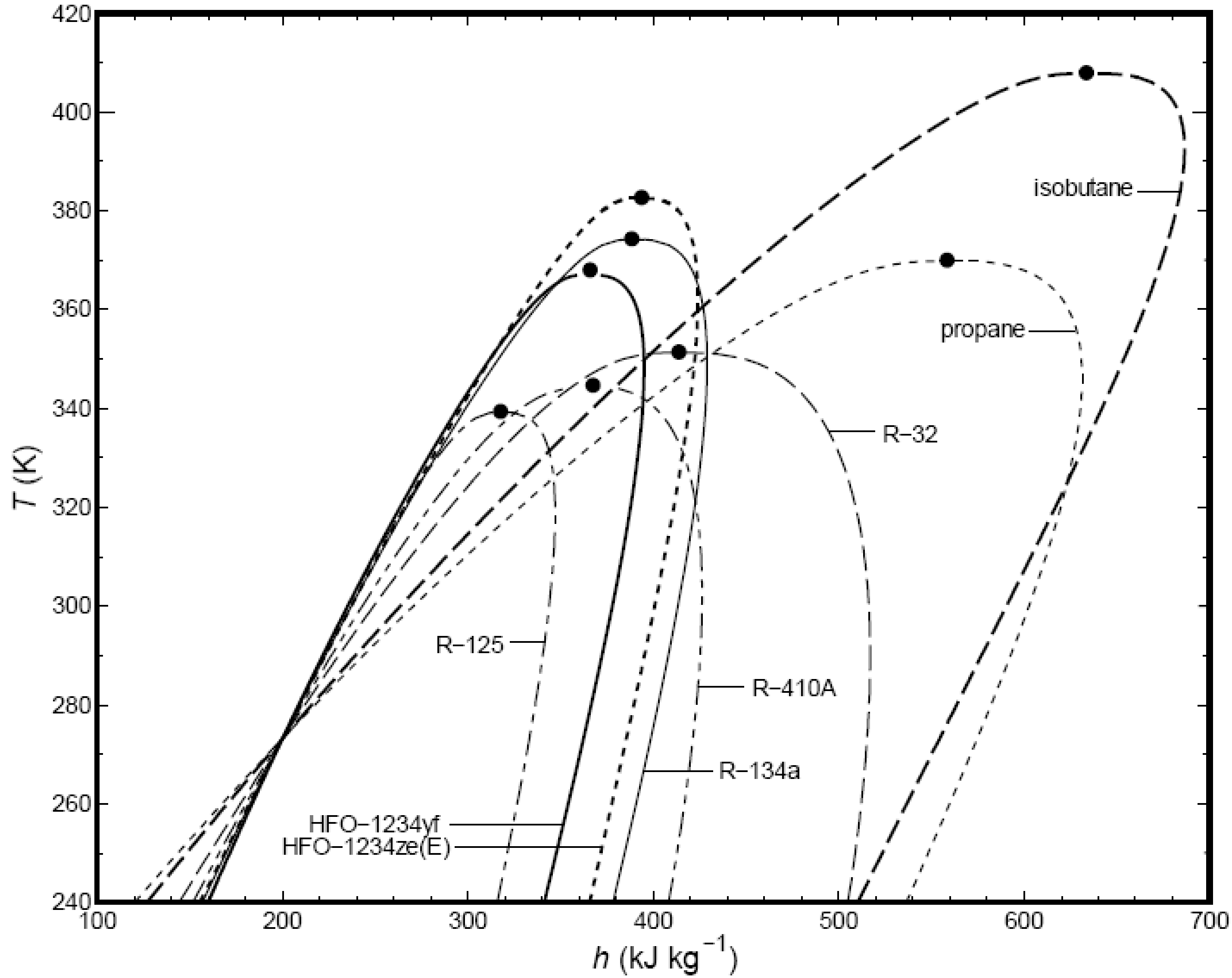
Table 1a – Fundamental constants of HFO-1234yf.

	molecular weight	critical temperature	Critical pressure
R-134a	102 g mol^{-1}	374.13 K	4.07 MPa
R-1234yf	114.042 g mol^{-1}	367.85 K	3.382 MPa

Table 1b – Thermodynamic and transport properties of HFC-1234yf.

T °C	Fluid	P kPa	ρ_L kg/m^3	ρ_G kg/m^3	μ_L μPa s	μ_G μPa s	k_L W/m K	k_G W/m K	i_{LG} kJ/kg	σ N/m	Cp_L kJ/kg K	Cp_G kJ kg K
0	R-134a	292.8	1295	14.43	271.1	10.73	0.092	0.01151	198.6	0.01156	1.341	0.0897
	R-1234yf	315	1175	17.17	220	11.44	0.0746	0.0091	162.3	0.0093	1.259	0.933
5	**R-134a**	**350**	**1278**	**17.14**	**254.4**	**10.94**	**0.0898**	**0.01195**	**194.8**	**0.01085**	**1.355**	**0.921**
	R-1234yf	**372**	**1160**	**20.8**	**206**	**11.67**	**0.073**	**0.0094**	**159**	**0.00868**	**1.275**	**0.957**
10	R-134a	414.6	1261	20.23	238.8	11.15	0.0876	0.0124	190.7	0.01014	1.37	0.946
	R-1234yf	436	1144	24.4	194	11.9	0.0713	0.0098	155.6	0.0081	1.293	0.983
20	R-134a	571.7	1225	27.78	210.7	11.58	0.0833	0.01333	182.2	0.00876	1.405	1.001
	R-1234yf	590	1111	33	171	12.36	0.0672	0.0106	148.3	0.0067	1.332	1.041
30	R-134a	770.2	1187	37.54	185.8	12.04	0.079	0.01433	173.1	0.00742	1.446	1.065
	R-1234yf	782	1075	44	152	12.86	0.0631	0.01143	140.1	0.00563	1.379	1.11
40	R-134a	1017	1147	50.09	163.4	12.55	0.0747	0.01544	163	0.0061	1.498	1.145
	R-1234yf	1017	1037	58.3	134	13.49	0.0586	0.0123	131.1	0.00462	1.437	1.196
50	**R-134a**	**1318**	**1102**	**66.27**	**143.1**	**13.12**	**0.0704**	**0.01672**	**151.8**	**0.0048**	**1.566**	**1.246**
	R-1234yf	**1301**	**993.3**	**76.7**	**118**	**14.12**	**0.054**	**0.01326**	**120.9**	**0.0035**	**1.515**	**1.31**

2010 International Symposium on Next-generation Air Conditioning and Refrigeration Technology, , Tokyo, Japan; *Yukihiro Higashi*



Experimental analysis of the low-GWP refrigerant R1234yf as a drop-in replacement for R134a in a typical mobile air conditioning system, Proc IMechE Part C: J Mechanical Engineering Science, 2012

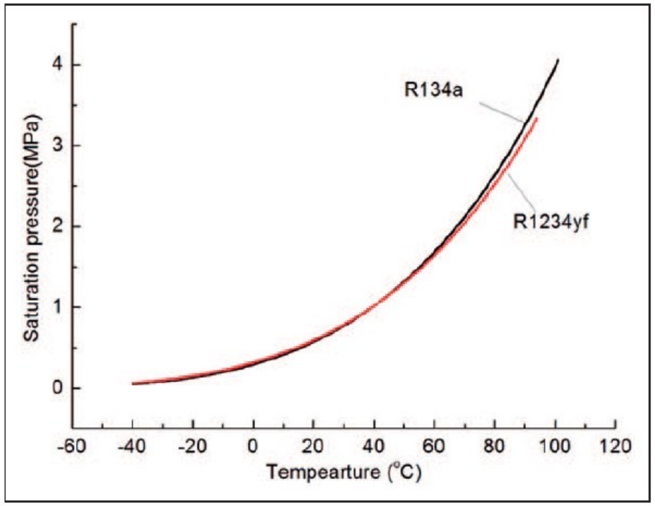
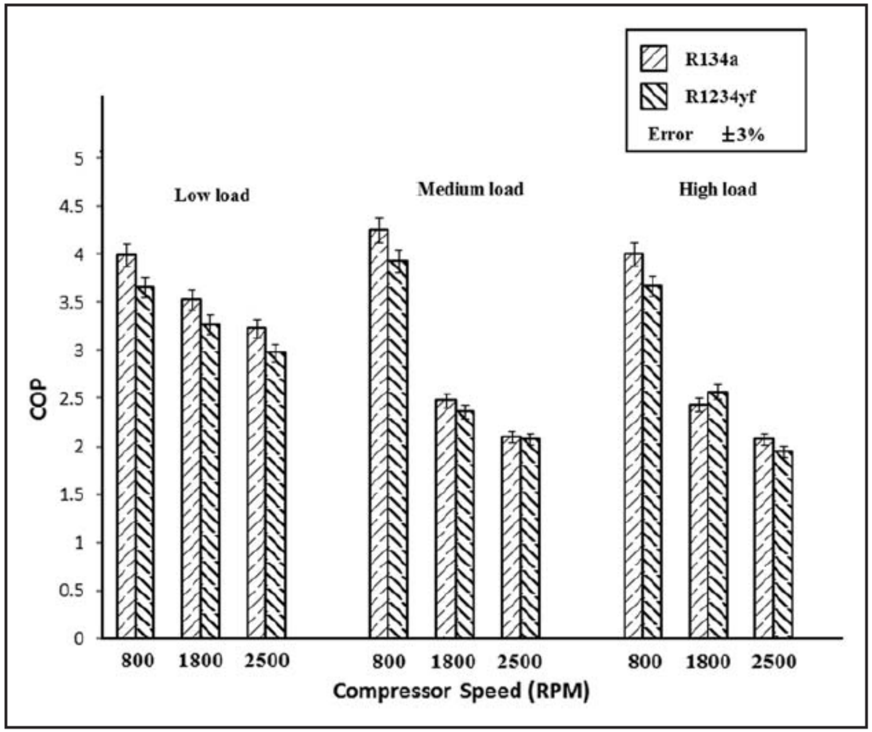


Table 1. Main physical properties of R134a and R1234yf.

Parameter	R134a	R1234yf
ODP	0	0
GWP	1300	4
Molar mass (g/mol)	102	114
Critical temperature (°C)	101	95
Critical pressure (kPa)	4059	3382
Critical density (kg/m^{3})	512	478
Normal boiling point (°C)	−26	−29

ODP: ozone depletion potential; GWP: global warming potential.



Comparison of COP between R134a and R1234yf systems.

Study of refrigeration system with HFO-1234yf as a working Fluid, Int. J. of Refrigeration

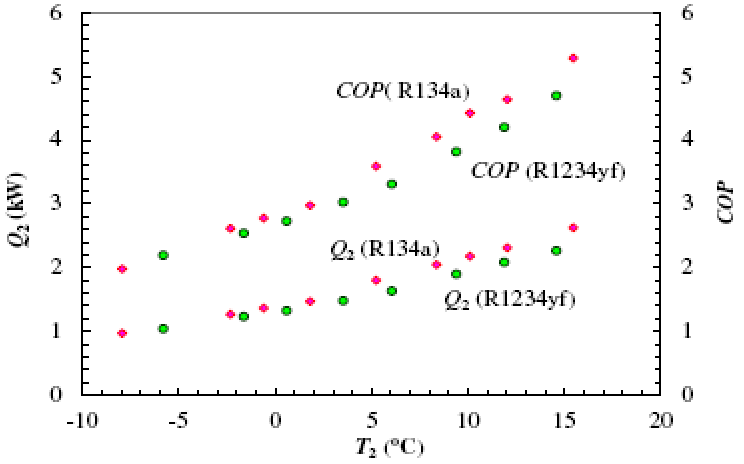


Fig. 6 – Cooling capacity and COP vs. T_2 at condenser temperature = 40 °C.

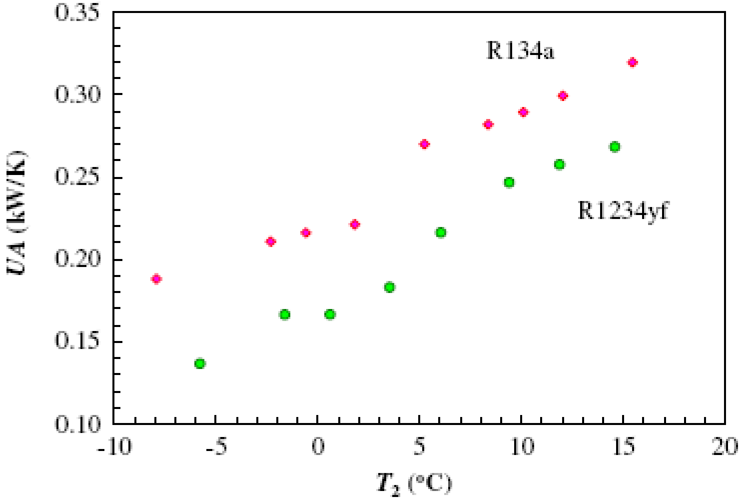


Fig. 8 – Heat transfer per unit temperature vs. T_2 at condenser temperature = 40 °C.

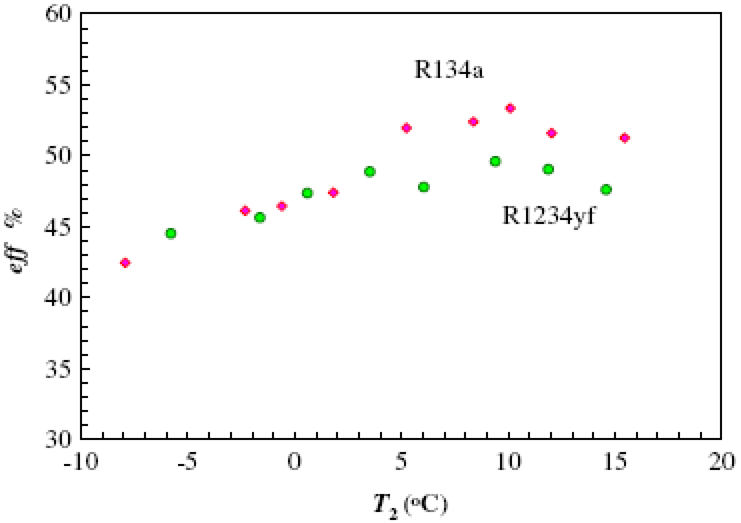


Fig. 7 – Efficiency vs. T_2 at condenser temperature = 40 °C.

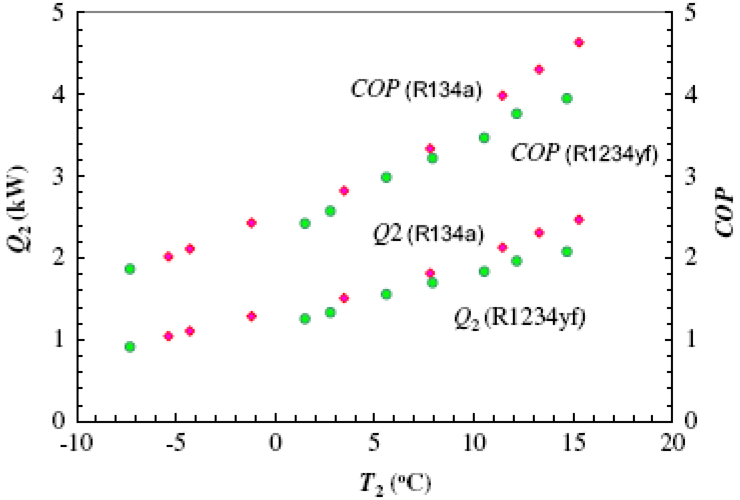


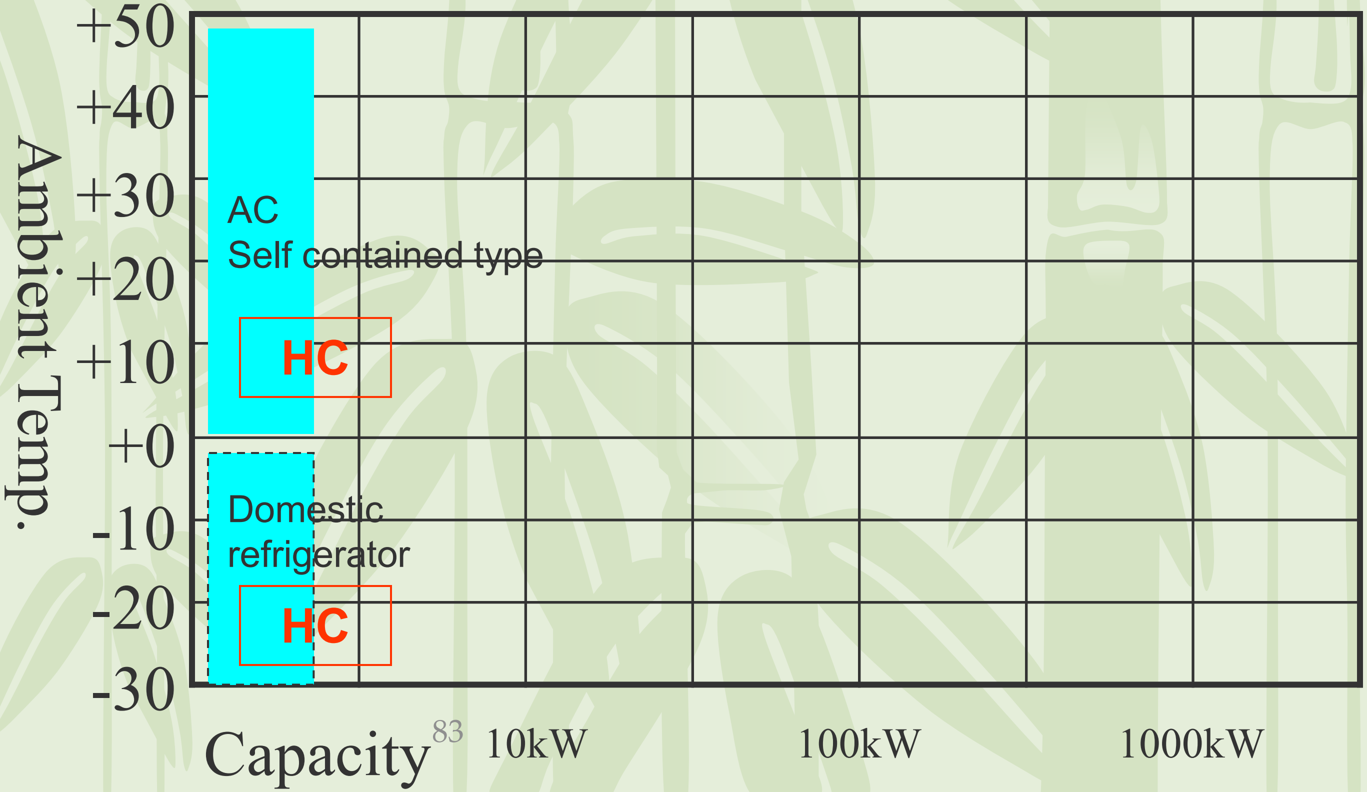
Fig. 9 – Cooling capacity and COP vs. T_2 at condenser temperature = 45 °C.

Candidates

HC

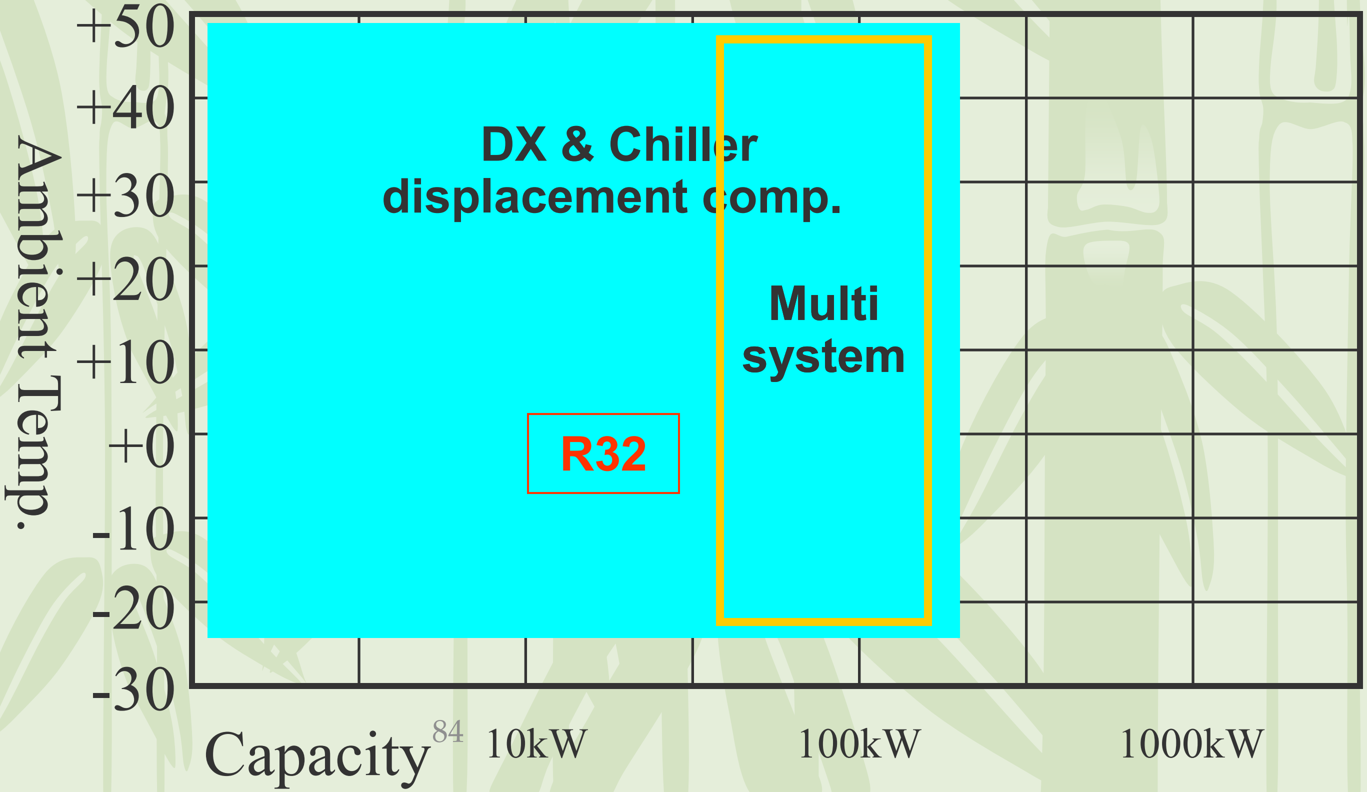
GWP

- Natural refrigerant
- Usable for only small capacity due to limited refrigerant volume



R32

- Better performance than R410A in cooling and heating
- Better performance for high ambient temp. than R410A
- Classified as Mildly Flammable (A2L) by ASHRAE 34 and ISO817
- Refrigerant charge volume can be reduced
- Use of A2L refrigerants should be discussed for wider application
- Upper charge volume should be decided by taking into consideration safe use of multi system
- Continuous refrigerant containment measures are necessary.

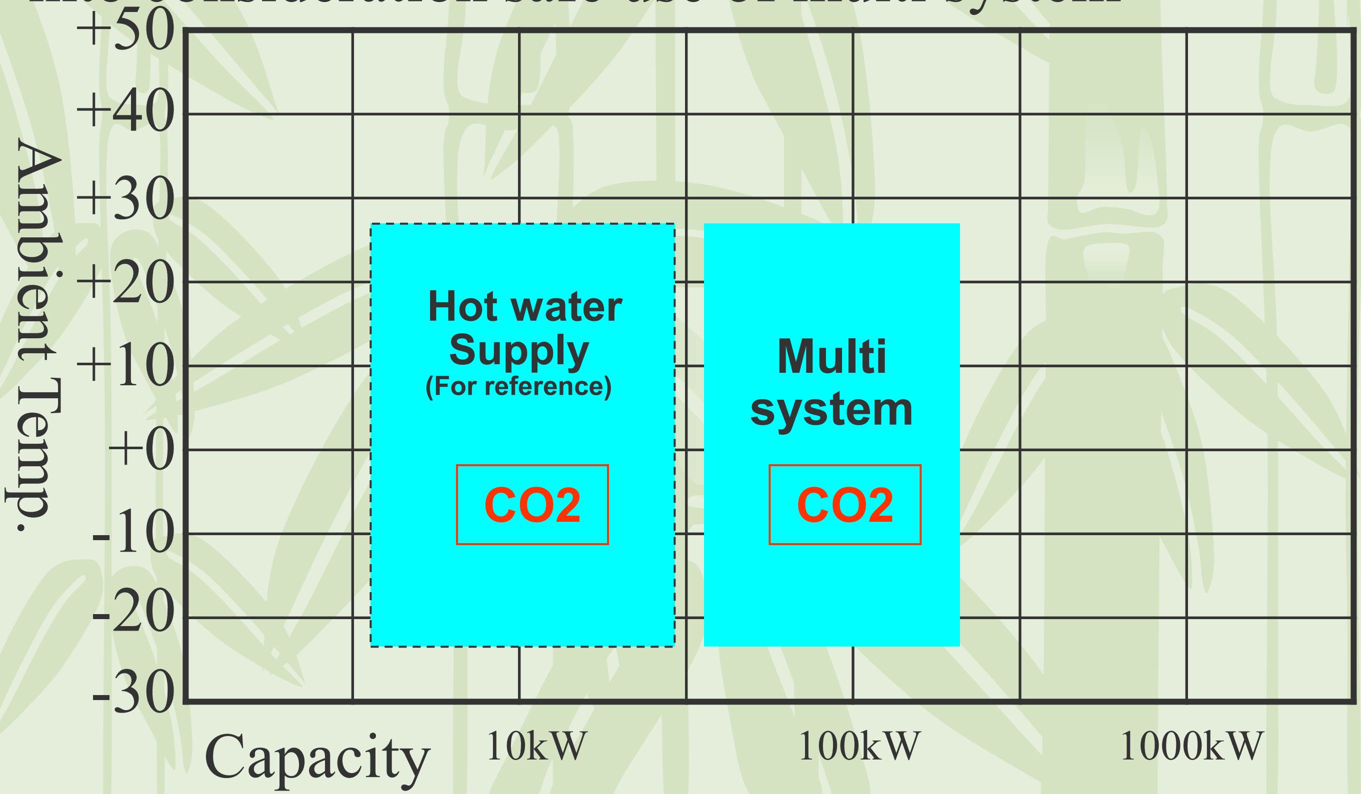


Candidates

CO2

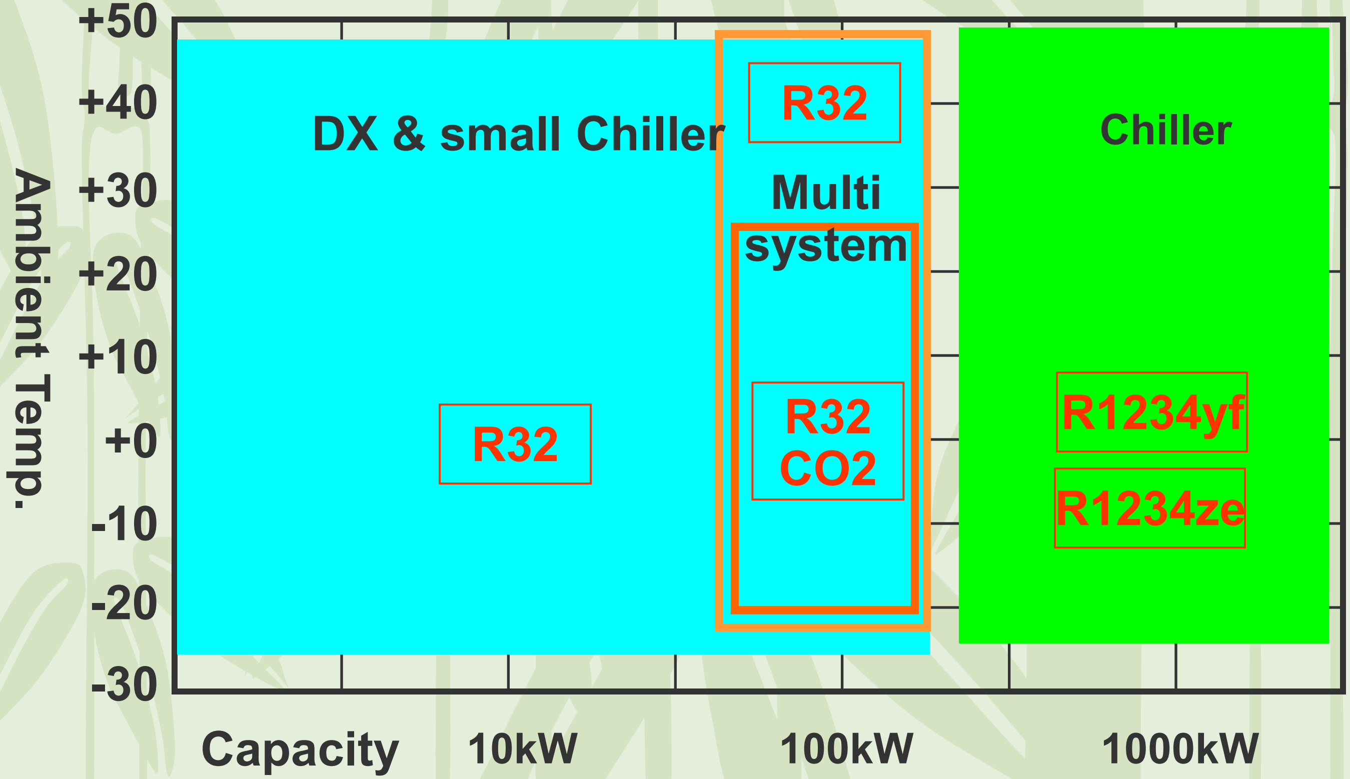
GWP

- Natural refrigerant
- Usable in limited ambient temp. (below 25 deg Celsius)
- Upper charge volume should be decided by taking into consideration safe use of multi system



Candidates for Lower GWP refrigerants

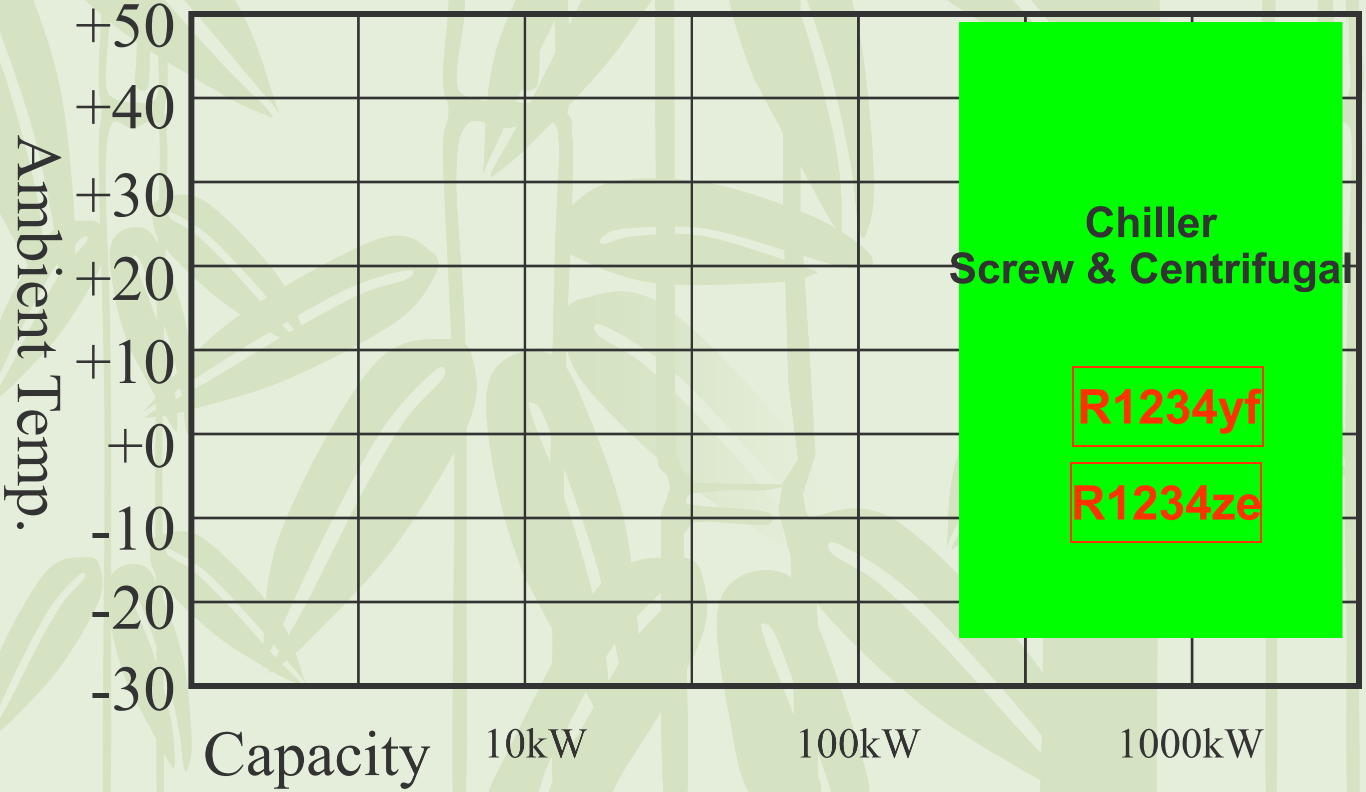
- R32 and HFOs should be added as alternatives for high GWP refrigerants.
- Use of Mildly flammable (A2L) refrigerants should be discussed for wider application
- CO2/multi system is optional solution where there is a wish for ultra low GWP



Candidates

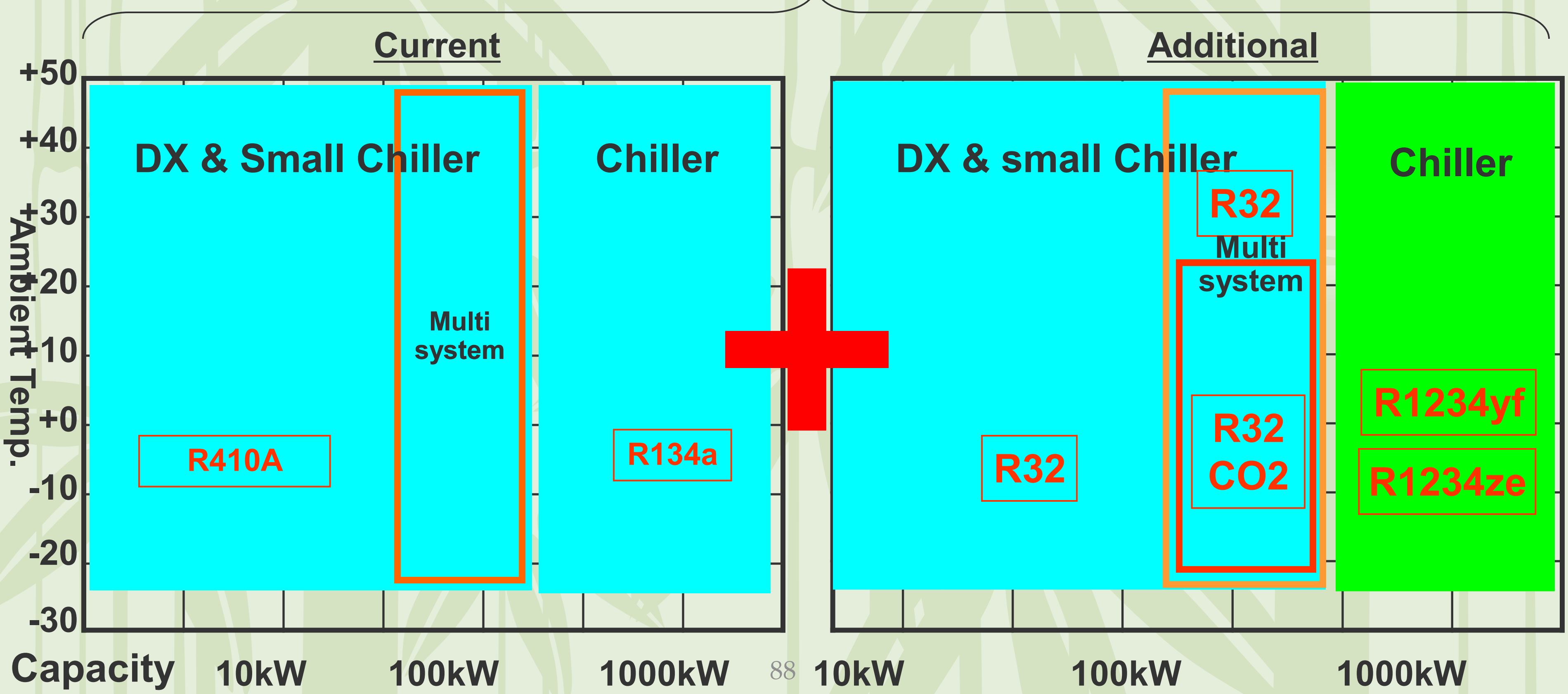
R1234yf, ze

- Suitable for middle to larger system
- Classified as Mildly Flammable (A2L) by ASHRAE 34 and ISO817
- Use of A2L refrigerants should be discussed for wider application

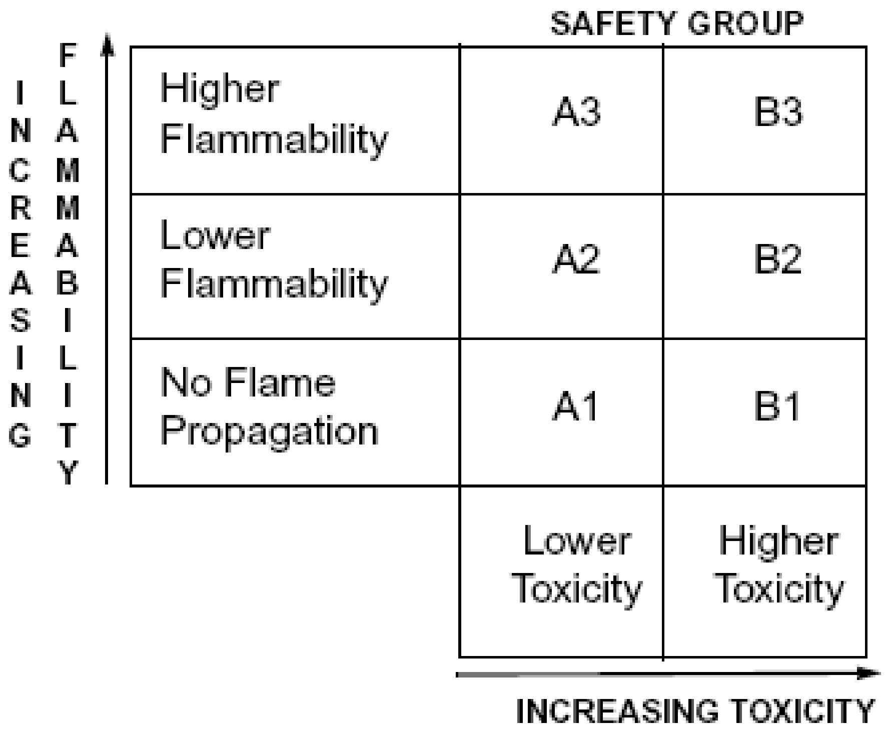


Refrigerants Daikin Recommends for Sustainable Future

Best mix of refrigerant for next generation



ASHRAE STD 34



INCREASING FLAMMABILITY

	SAFETY GROUP	
Higher Flammability	A3	B3
Lower Flammability	A2	B2
No Flame Propagation	A1	B1
	Lower Toxicity	Higher Toxicity

INCREASING TOXICITY

Figure 1 Refrigerant safety group classification.

Table 1
Refrigerant Data and Safety Classifications

Refrigerant Number	Chemical Name[a,b]	Chemical Formula[a]	Molecular Mass[a]	Normal Boiling Point[a] (°C)	Normal Boiling Point[a] (°F)	Safety Group
	Methane Series					
11	trichlorofluoromethane	CCl_3F	137.4	24	75	A1
12	dichlorodifluoromethane	CCl_2F_2	120.9	–30	–22	A1
12B1	bromochlorodifluoromethane	$CBrClF_2$	165.4	-4	25	
13	chlorotrifluoromethane	$CClF_3$	104.5	-81	-115	A1
13B1	bromotrifluoromethane	$CBrF_3$	148.9	-58	-72	A1
14	tetrafluoromethane (carbon tetrafluoride)	CF_4	88.0	-128	-198	A1
21	dichlorofluoromethane	$CHCl_2F$	102.9	9	48	B1
22	chlorodifluoromethane	$CHClF_2$	86.5	-41	-41	A1
23	trifluoromethane	CHF_3	70.0	-82	-116	A1
30	dichloromethane (methylene chloride)	CH_2Cl_2	84.9	40	104	B2
31	chlorofluoromethane	CH_2ClF	68.5	-9	16	
32	difluoromethane (methylene fluoride)	CH_2F_2	52.0	-52	-62	A2
40	chloromethane (methyl chloride)	CH_3Cl	50.5	-24	-12	B2
41	fluoromethane (methyl fluoride)	CH_3F	34.0	-78	-108	
50	methane	CH_4	16.0	-161	-259	A3
	Ethane Series					
113	1,1,2-trichloro-1,2,2-trifluoroethane	CCl_2FCClF_2	187.4	48	118	A1
114	1,2-dichloro-1,1,2,2-tetrafluoroethane	$CClF_2CClF_2$	170.9	4	38	A1
115	chloropentafluoroethane	$CClF_2CF_3$	154.5	-39	-38	A1
116	hexafluoroethane	CF_3CF_3	138.0	-78	-109	A1
123	2,2-dichloro-1,1,1-trifluoroethane	$CHCl_2CF_3$	153.0	27	81	B1
124	2-chloro-1,1,1,2-tetrafluoroethane	$CHClFCF_3$	136.5	-12	10	A1
125	pentafluoroethane	CHF_2CF_3	120.0	-49	-56	A1
134a	1,1,1,2-tetrafluoroethane	CH_2FCF_3	102.0	-26	-15	A1
141b	1,1-dichloro-1-fluoroethane	CH_3CCl_2F	117.0	32	90	
142b	1-chloro-1,1-difluoroethane	CH_3CClF_2	100.5	-10	14	A2
143a	1,1,1-trifluoroethane	CH_3CF_3	84.0	-47	-53	A2
152a	1,1-difluoroethane	CH_3CHF_2	66.0	-25	-13	A2
170	ethane	CH_3CH_3	30.0	-89	-128	A3
	Propane Series					
218	octafluoropropane	$CF_3CF_2CF_3$	188.0	-37	-35	A1
236fa	1,1,1,3,3,3-hexafluoropropane	$CF_3CH_2CF_3$	152.0	–1	29	A1
245fa	1,1,1,3,3-pentafluoropropane	$CHF_2CH_2CF_3$	134.0	15	59	B1
290	propane	$CH_3CH_2CH_3$	44.0	-42	-44	A3
	Cyclic Organic Compounds					
C318	octafluorocyclobutane	$-(CF_2)_4-$	200.0	-6	21	
	See Table 2 for Blends					
	Miscellaneous Organic Compounds					
	hydrocarbons					
600	butane	$CH_3CH_2CH_2CH_3$	58.1	0	31	A3
600a	isobutane	$CH(CH_3)_2CH_3$	58.1	-12	11	A3
	oxygen compounds					
610	ethyl ether	$CH_3CH_2OCH_2CH_3$	74.1	35	94	
611	methyl formate	$HCOOCH_3$	60.0	32	89	B2
	sulfur compounds					
620	*(Reserved for future assignment)*					
	Nitrogen Compounds					
630	methyl amine	CH_3NH_2	31.1	-7	20	
631	ethyl amine	$CH_3CH_2(NH_2)$	45.1	17	62	

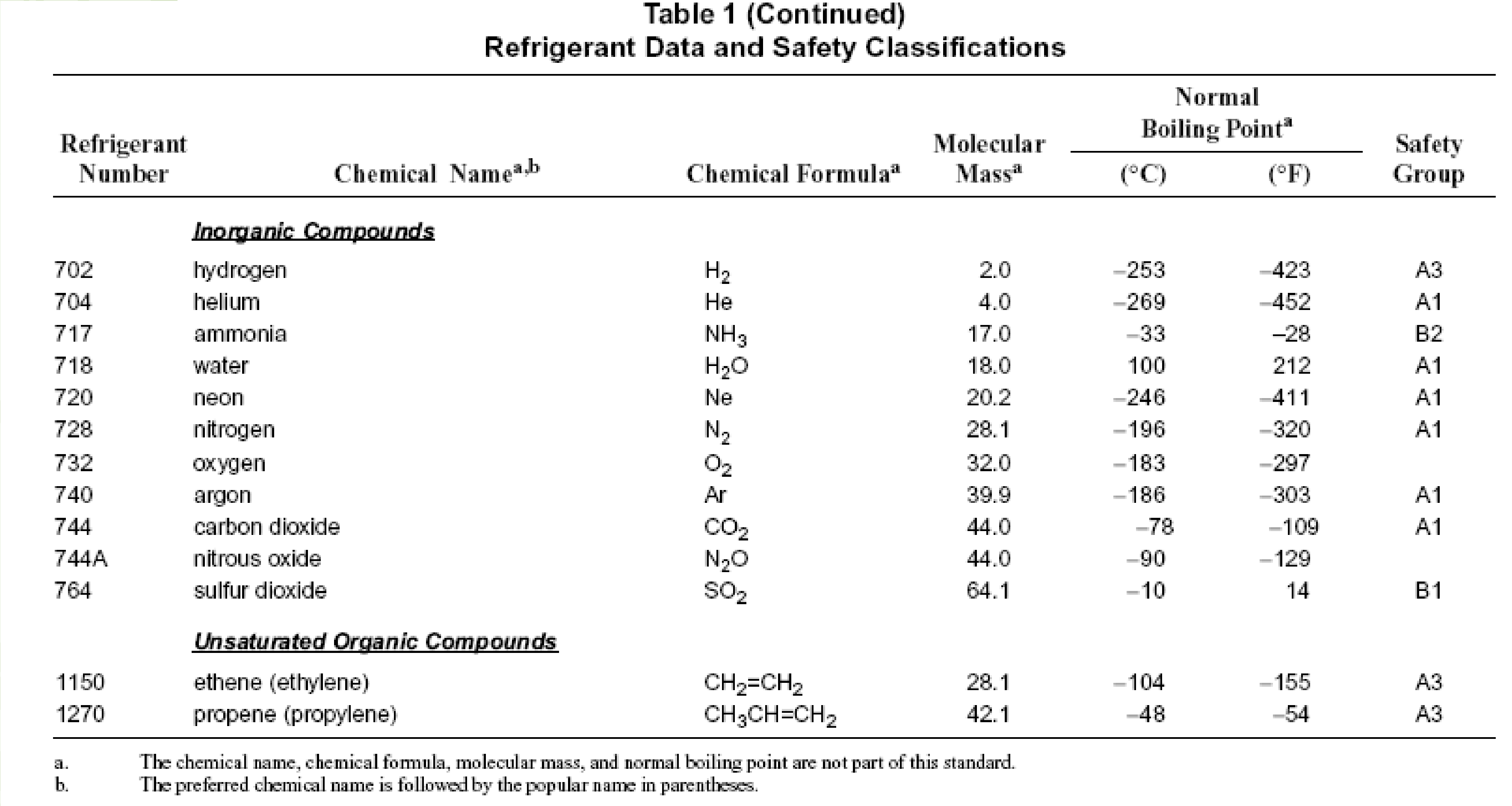


Table 1 (Continued)
Refrigerant Data and Safety Classifications

Refrigerant Number	Chemical Name[a,b]	Chemical Formula[a]	Molecular Mass[a]	Normal Boiling Point[a] (°C)	Normal Boiling Point[a] (°F)	Safety Group
	Inorganic Compounds					
702	hydrogen	H_2	2.0	–253	–423	A3
704	helium	He	4.0	–269	–452	A1
717	ammonia	NH_3	17.0	–33	–28	B2
718	water	H_2O	18.0	100	212	A1
720	neon	Ne	20.2	–246	–411	A1
728	nitrogen	N_2	28.1	–196	–320	A1
732	oxygen	O_2	32.0	–183	–297	
740	argon	Ar	39.9	–186	–303	A1
744	carbon dioxide	CO_2	44.0	–78	–109	A1
744A	nitrous oxide	N_2O	44.0	–90	–129	
764	sulfur dioxide	SO_2	64.1	–10	14	B1
	Unsaturated Organic Compounds					
1150	ethene (ethylene)	$CH_2{=}CH_2$	28.1	–104	–155	A3
1270	propene (propylene)	$CH_3CH{=}CH_2$	42.1	–48	–54	A3

a. The chemical name, chemical formula, molecular mass, and normal boiling point are not part of this standard.

b. The preferred chemical name is followed by the popular name in parentheses.

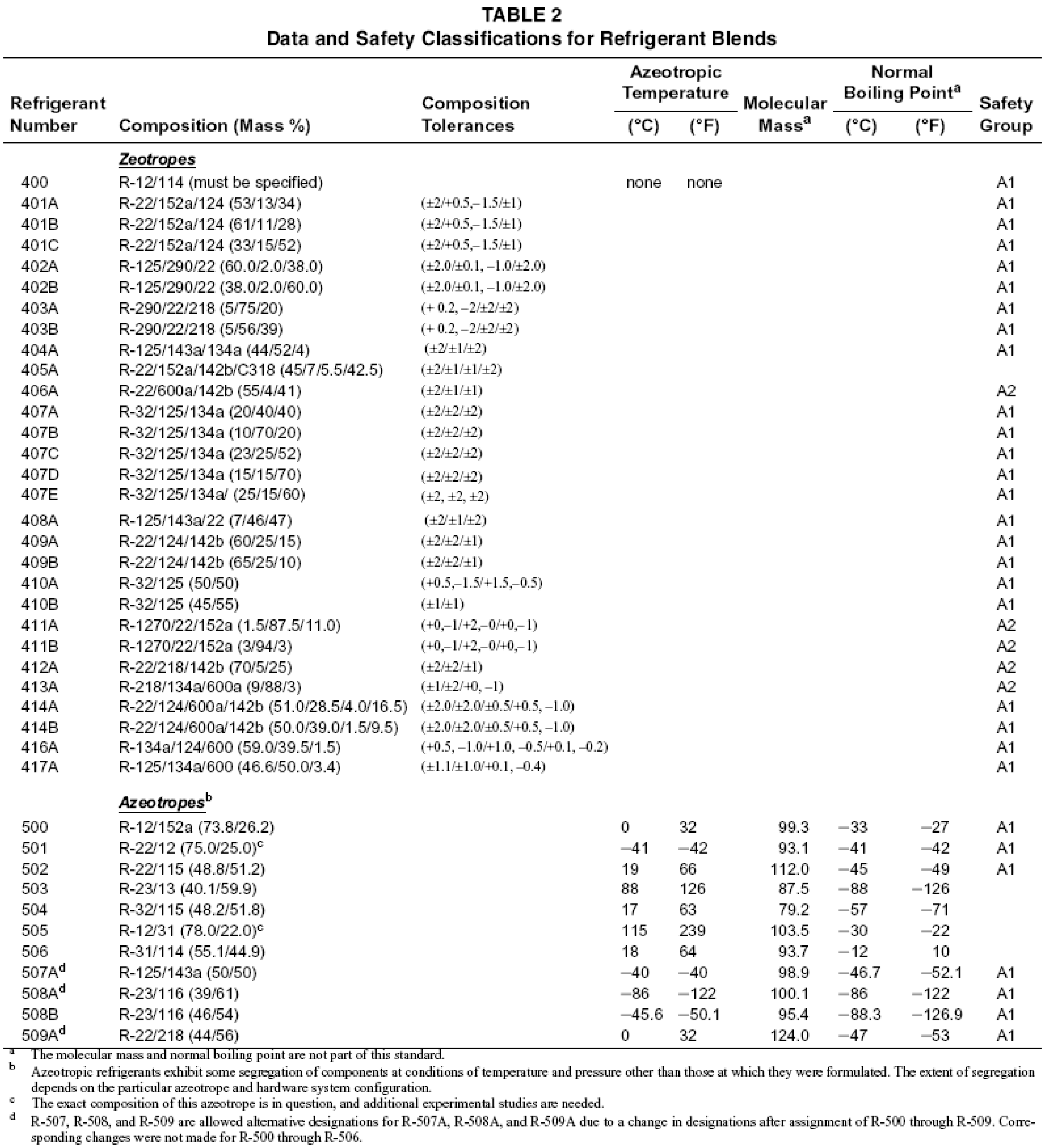


TABLE 2
Data and Safety Classifications for Refrigerant Blends

Refrigerant Number	Composition (Mass %)	Composition Tolerances	Azeotropic Temperature (°C)	Azeotropic Temperature (°F)	Molecular Mass[a]	Normal Boiling Point[a] (°C)	Normal Boiling Point[a] (°F)	Safety Group
	Zeotropes							
400	R-12/114 (must be specified)		none	none				A1
401A	R-22/152a/124 (53/13/34)	(±2/+0.5,–1.5/±1)						A1
401B	R-22/152a/124 (61/11/28)	(±2/+0.5,–1.5/±1)						A1
401C	R-22/152a/124 (33/15/52)	(±2/+0.5,–1.5/±1)						A1
402A	R-125/290/22 (60.0/2.0/38.0)	(±2.0/±0.1, –1.0/±2.0)						A1
402B	R-125/290/22 (38.0/2.0/60.0)	(±2.0/±0.1, –1.0/±2.0)						A1
403A	R-290/22/218 (5/75/20)	(+ 0.2, –2/±2/±2)						A1
403B	R-290/22/218 (5/56/39)	(+ 0.2, –2/±2/±2)						A1
404A	R-125/143a/134a (44/52/4)	(±2/±1/±2)						A1
405A	R-22/152a/142b/C318 (45/7/5.5/42.5)	(±2/±1/±1/±2)						
406A	R-22/600a/142b (55/4/41)	(±2/±1/±1)						A2
407A	R-32/125/134a (20/40/40)	(±2/±2/±2)						A1
407B	R-32/125/134a (10/70/20)	(±2/±2/±2)						A1
407C	R-32/125/134a (23/25/52)	(±2/±2/±2)						A1
407D	R-32/125/134a (15/15/70)	(±2/±2/±2)						A1
407E	R-32/125/134a/ (25/15/60)	(±2, ±2, ±2)						A1
408A	R-125/143a/22 (7/46/47)	(±2/±1/±2)						A1
409A	R-22/124/142b (60/25/15)	(±2/±2/±1)						A1
409B	R-22/124/142b (65/25/10)	(±2/±2/±1)						A1
410A	R-32/125 (50/50)	(+0.5,–1.5/+1.5,–0.5)						A1
410B	R-32/125 (45/55)	(±1/±1)						A1
411A	R-1270/22/152a (1.5/87.5/11.0)	(+0,–1/+2,–0/+0,–1)						A2
411B	R-1270/22/152a (3/94/3)	(+0,–1/+2,–0/+0,–1)						A2
412A	R-22/218/142b (70/5/25)	(±2/±2/±1)						A2
413A	R-218/134a/600a (9/88/3)	(±1/±2/+0, –1)						A2
414A	R-22/124/600a/142b (51.0/28.5/4.0/16.5)	(±2.0/±2.0/±0.5/+0.5, –1.0)						A1
414B	R-22/124/600a/142b (50.0/39.0/1.5/9.5)	(±2.0/±2.0/±0.5/+0.5, –1.0)						A1
416A	R-134a/124/600 (59.0/39.5/1.5)	(+0.5, –1.0/+1.0, –0.5/+0.1, –0.2)						A1
417A	R-125/134a/600 (46.6/50.0/3.4)	(±1.1/±1.0/+0.1, –0.4)						A1
	Azeotropes[b]							
500	R-12/152a (73.8/26.2)		0	32	99.3	−33	−27	A1
501	R-22/12 (75.0/25.0)[c]		−41	−42	93.1	−41	−42	A1
502	R-22/115 (48.8/51.2)		19	66	112.0	−45	−49	A1
503	R-23/13 (40.1/59.9)		88	126	87.5	−88	−126	
504	R-32/115 (48.2/51.8)		17	63	79.2	−57	−71	
505	R-12/31 (78.0/22.0)[c]		115	239	103.5	−30	−22	
506	R-31/114 (55.1/44.9)		18	64	93.7	−12	10	
507A[d]	R-125/143a (50/50)		−40	−40	98.9	−46.7	−52.1	A1
508A[d]	R-23/116 (39/61)		−86	−122	100.1	−86	−122	A1
508B	R-23/116 (46/54)		−45.6	−50.1	95.4	−88.3	−126.9	A1
509A[d]	R-22/218 (44/56)		0	32	124.0	−47	−53	A1

---

[a] The molecular mass and normal boiling point are not part of this standard.

[b] Azeotropic refrigerants exhibit some segregation of components at conditions of temperature and pressure other than those at which they were formulated. The extent of segregation depends on the particular azeotrope and hardware system configuration.

[c] The exact composition of this azeotrope is in question, and additional experimental studies are needed.

[d] R-507, R-508, and R-509 are allowed alternative designations for R-507A, R-508A, and R-509A due to a change in designations after assignment of R-500 through R-509. Corresponding changes were not made for R-500 through R-506.

International treaties targeting global climate change

- Ozone Depletion
  - Montreal Accord, 1987
  - phase out of R-12 and others
  - U.S. participates
- Global Warming
  - Kyoto Protocol, 1998
  - refrigerants have both a direct and indirect impact
  - U.S. will not ratify

Heat Operated Vapor Compression Refrigeration Cycle

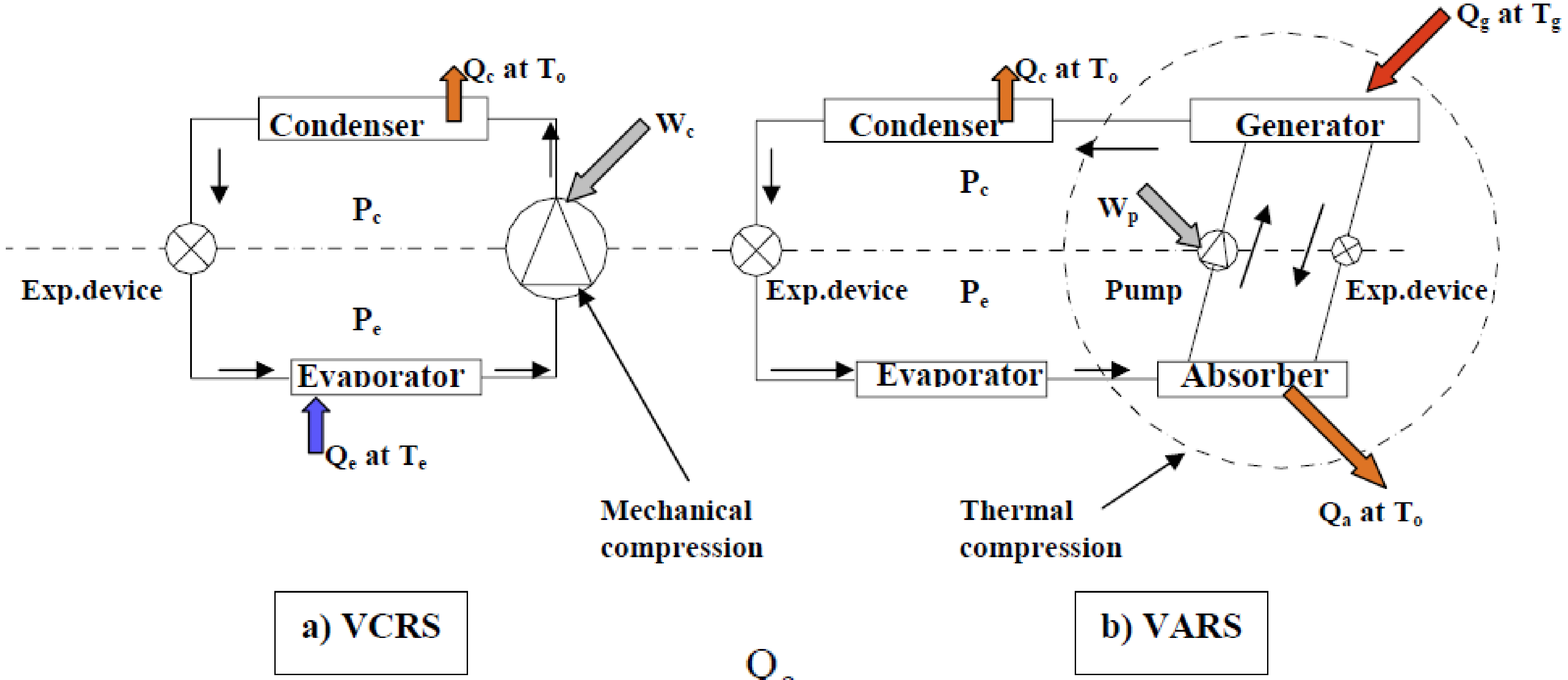
- Conventional cooling systems utilize ***mechanical compressors that are driven by electricity***.
- However, the wide-spread application of cooling, and air-conditioning systems in summer could overload electricity supplies and use of the ***electricity generated from fossil fuels has a serious impact on the environment***.
- These problems could be eased by utilization of alternative energy sources for refrigeration and air-conditioning systems.
- ***Thermal energy is one that looks promising***. There is abundant thermal energy appeared in different forms in the world, such as solar thermal, geothermal, various wasted heats and biomass energy etc.
- These energies can be used to drive refrigeration and air-conditioning systems.

- There are three kinds of vapor compression refrigeration cycles that can be driven by thermal energy.
- They are:
  - the absorption refrigeration cycle
  - the adsorption refrigeration cycle
  - the vapor jet refrigeration cycle

Absorption refrigeration systems (ARS) involve the absorption of a *refrigerant* by a *transport medium*.

- The most widely used system is the ammonia–water system, where ammonia (NH_3) serves as the refrigerant and water (H_2O) as the transport medium.
- Other systems include ***water–lithium bromide*** and ***water–lithium chloride*** systems, where water serves as the refrigerant. These systems are limited to applications such as A-C where the minimum temperature is above the freezing point of water.
- Compared with vapor-compression systems, ARS have one major advantage: ***A liquid is compressed instead of a vapor and as a result the work input is very small*** (on the order of one percent of the heat supplied to the generator) and often neglected in the cycle analysis.
- ARS are often classified as ***heat-driven systems***.
- ARS are *much more expensive than the vapor-compression refrigeration systems. They are more complex and occupy more space, they are much less efficient thus requiring much larger cooling towers to reject the waste heat, and they are more difficult to service since they are less common*.
- Therefore, ARS should be considered only ***when the unit cost of thermal energy is low and is projected to remain low relative to electricity***.
- ARS are primarily used in **large commercial and industrial installations**.

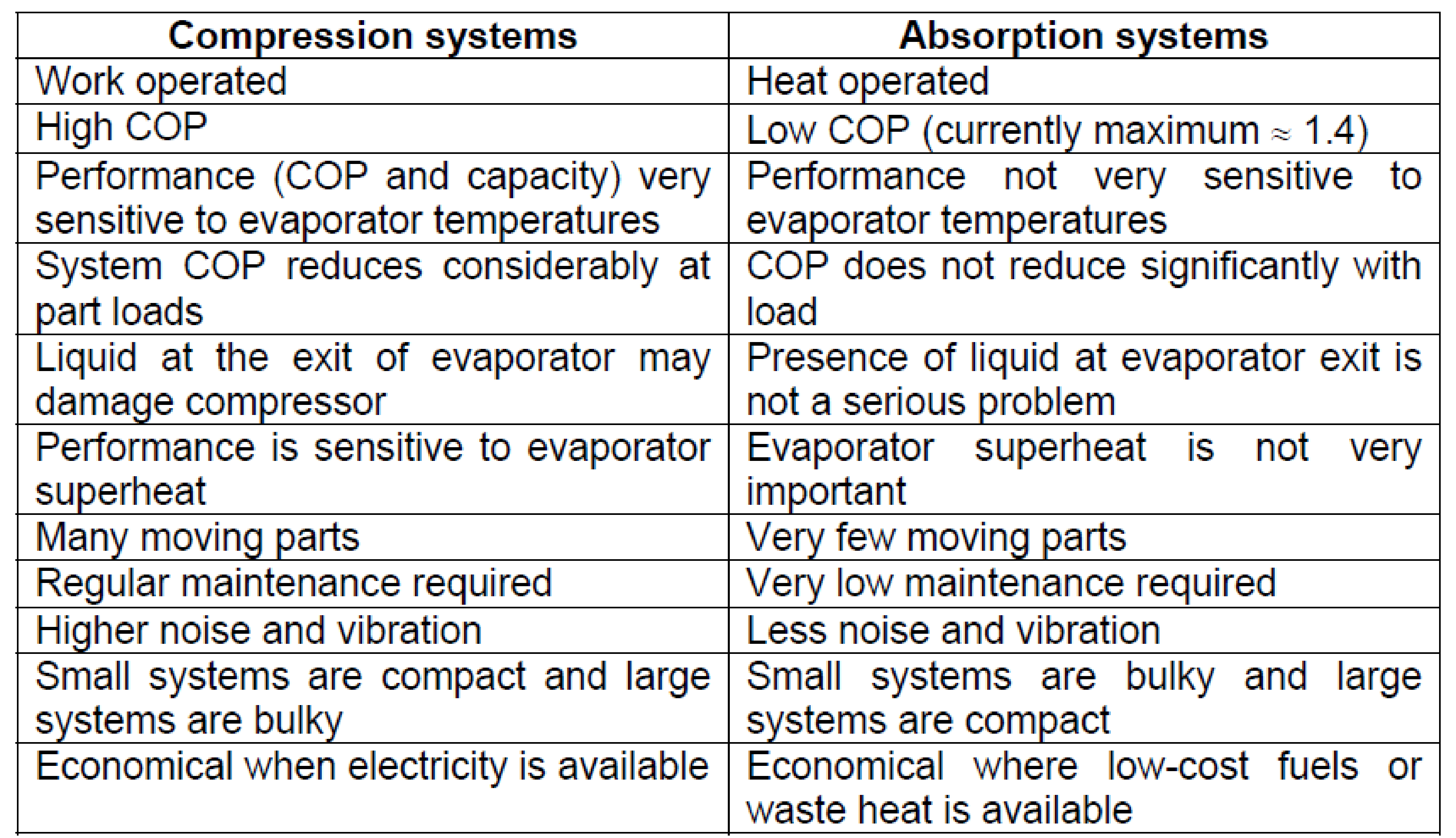
Comparison between Vapor compression (VCR) and Vapor absorption Refrigeration (VAR)



$$COP_{VCRS} = \frac{Q_e}{W_c}$$

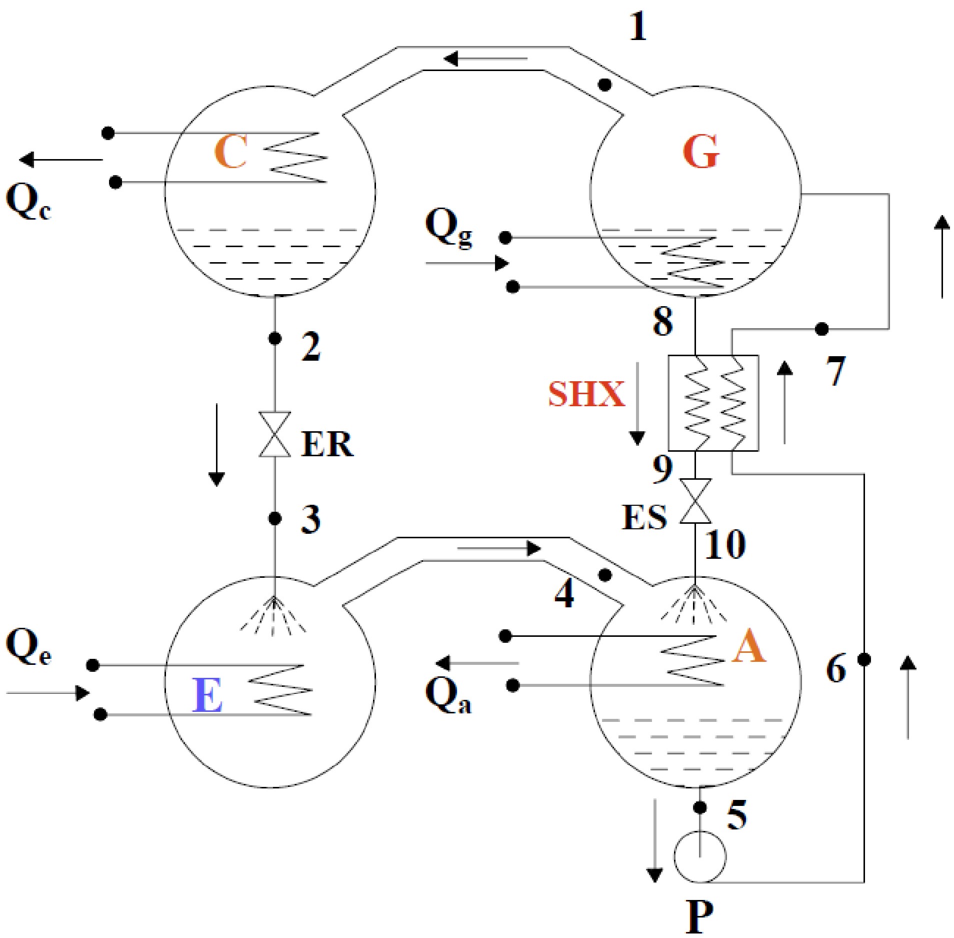
$$COP_{VARS} = \frac{Q_e}{Q_g + W_p} \approx \frac{Q_e}{Q_g}$$

Comparison between compression and absorption systems

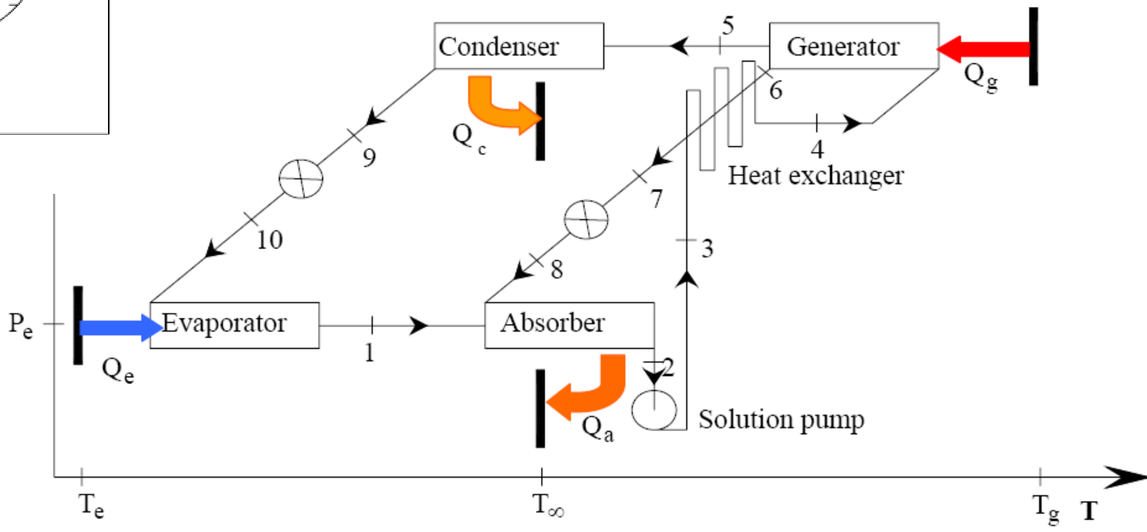


Compression systems	Absorption systems
Work operated	Heat operated
High COP	Low COP (currently maximum ≈ 1.4)
Performance (COP and capacity) very sensitive to evaporator temperatures	Performance not very sensitive to evaporator temperatures
System COP reduces considerably at part loads	COP does not reduce significantly with load
Liquid at the exit of evaporator may damage compressor	Presence of liquid at evaporator exit is not a serious problem
Performance is sensitive to evaporator superheat	Evaporator superheat is not very important
Many moving parts	Very few moving parts
Regular maintenance required	Very low maintenance required
Higher noise and vibration	Less noise and vibration
Small systems are compact and large systems are bulky	Small systems are bulky and large systems are compact
Economical when electricity is available	Economical where low-cost fuels or waste heat is available

A: Absorber; C: Condenser; E: Evaporator; G: Generator; P: Solution Pump
SHX: Solution HX; ER: Refrigerant Expansion valve; ES: Solution Expansion valve



Schematic of a H2O-LiBr system



The desirable properties of refrigerant-absorbent mixtures

- The refrigerant should exhibit high solubility with solution in the absorber.
- There should be large difference in the boiling points of refrigerant and absorbent (greater than 200 ^{o}C), so that only refrigerant is boiled-off in the generator.
- It should exhibit small heat of mixing so that a high COP can be achieved.
- The refrigerant-absorbent mixture should have high thermal conductivity and low viscosity for high performance.
- It should not undergo crystallization or solidification inside the system.
- The mixture should be safe, chemically stable, non-corrosive, inexpensive and should be available easily.

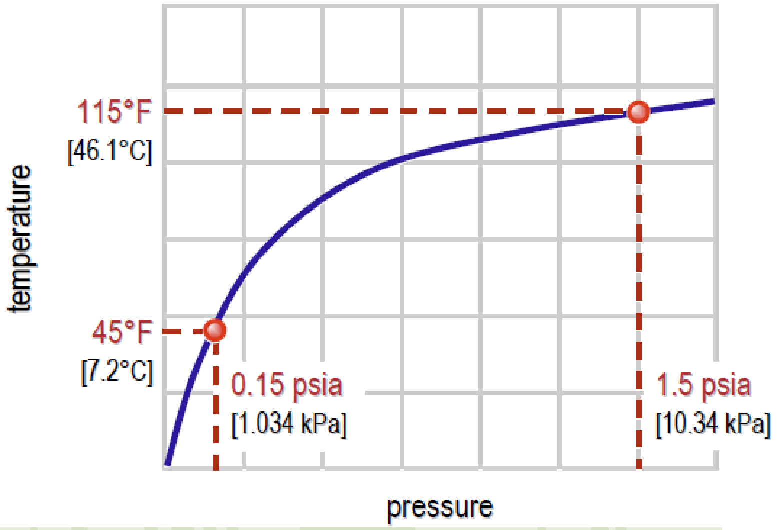
The most commonly used refrigerant-absorbent pairs:

- Water-Lithium Bromide (H_2O-LiBr) system for above 0 ^oC applications such as air conditioning. Here water is the refrigerant and lithium bromide is the absorbent. (Normally for AC system)
  - Practical problems in water-lithium bromide systems
    - Crystallization
    - Air leakage, and
    - Pressure drops
- Ammonia-Water (NH_3 -H_2O) system for refrigeration applications with ammonia as refrigerant and water as absorbent. (Normally for Refrigeration System)

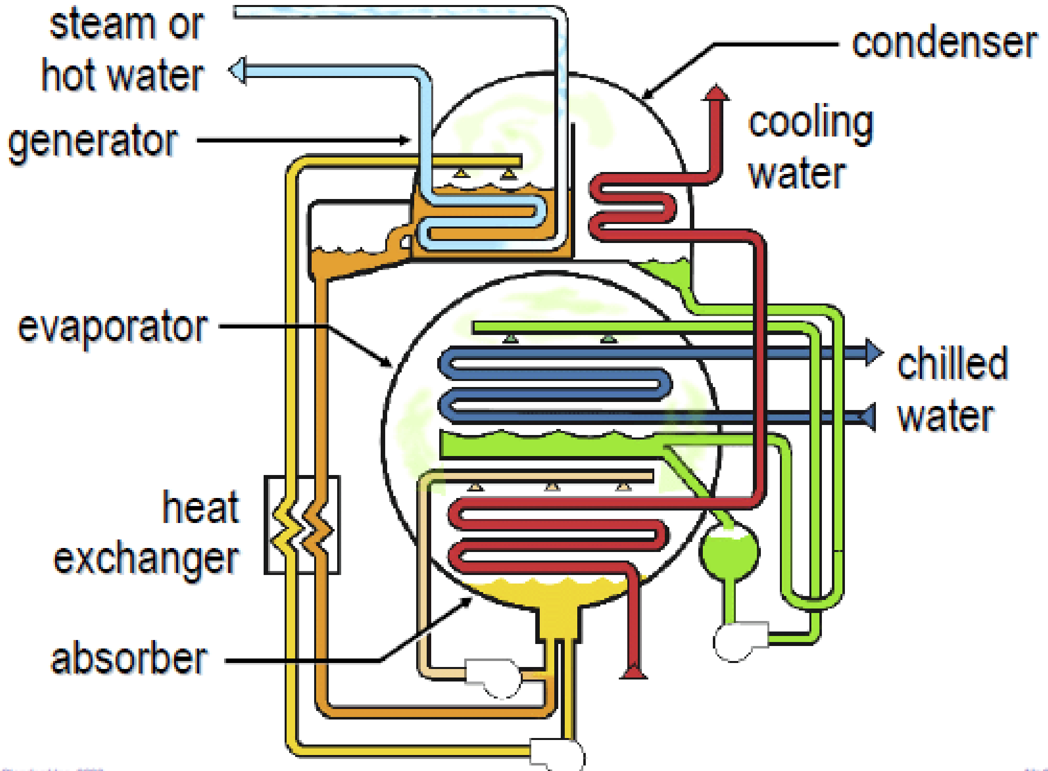
Components of the Absorption Cycle

- The four basic components of the absorption refrigeration cycle are *the generator and condenser on the high-pressure side*, and the *evaporator and absorber on the low-pressure side*. The pressure on the high-pressure side of the system is approximately ten times greater than that on the low-pressure side.

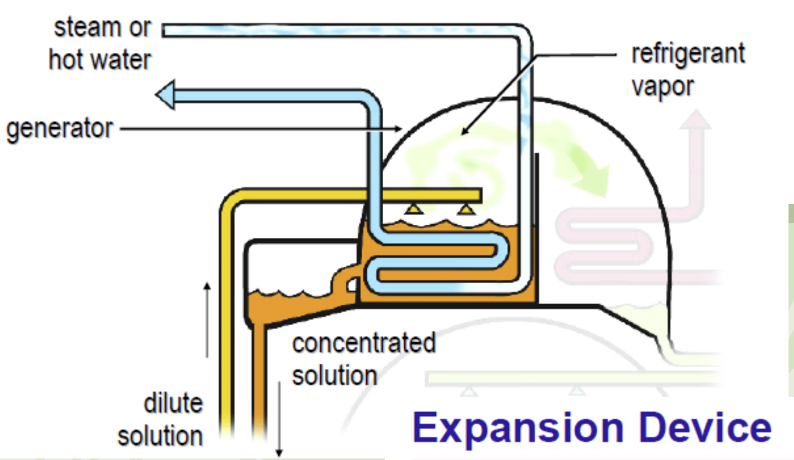
Boiling Point of Water



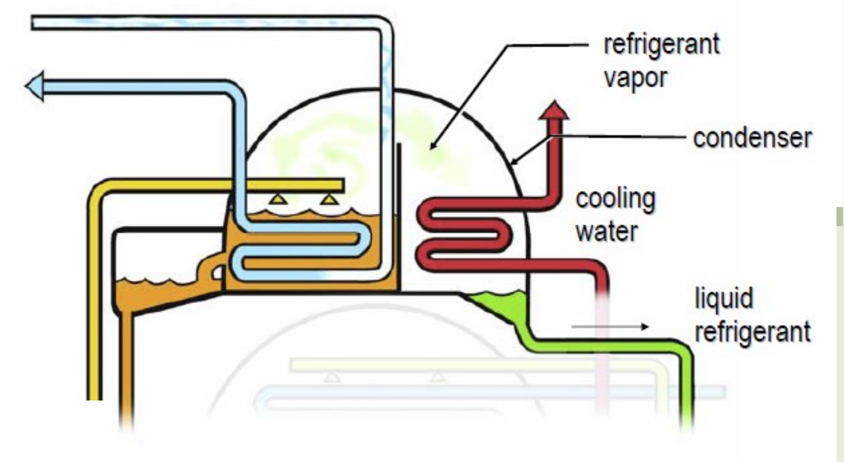
Absorption Refrigeration Cycle



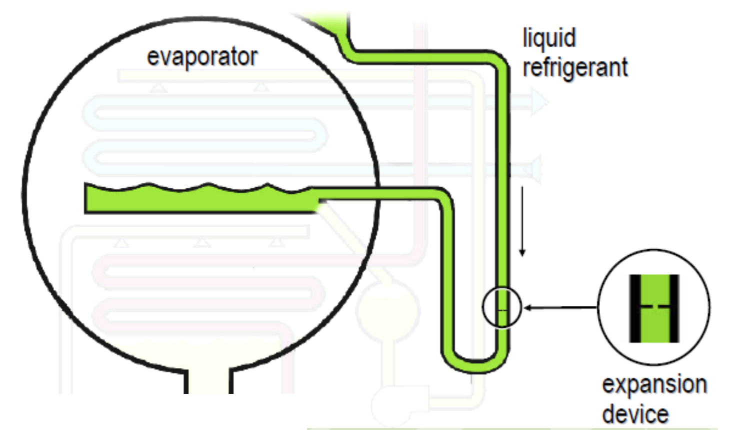
Generator



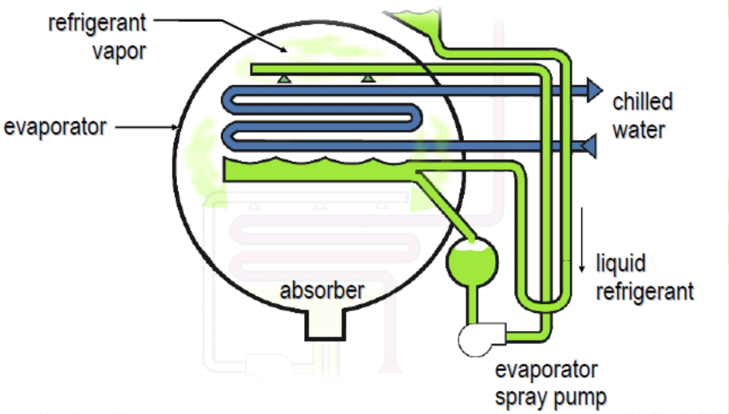
Condenser



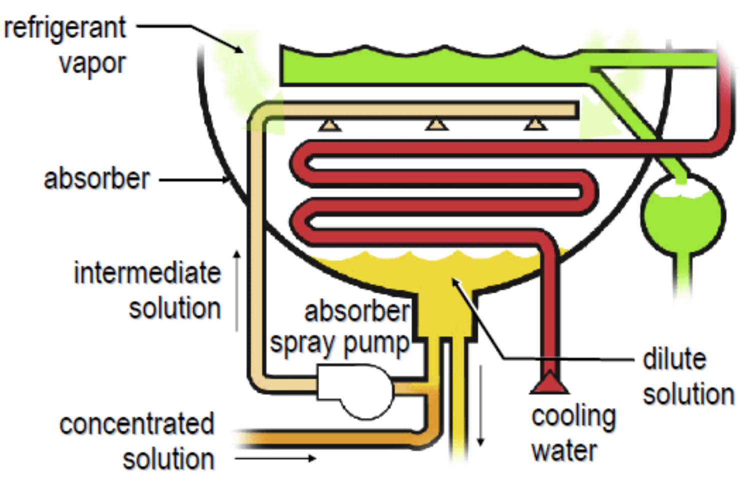
Expansion Device



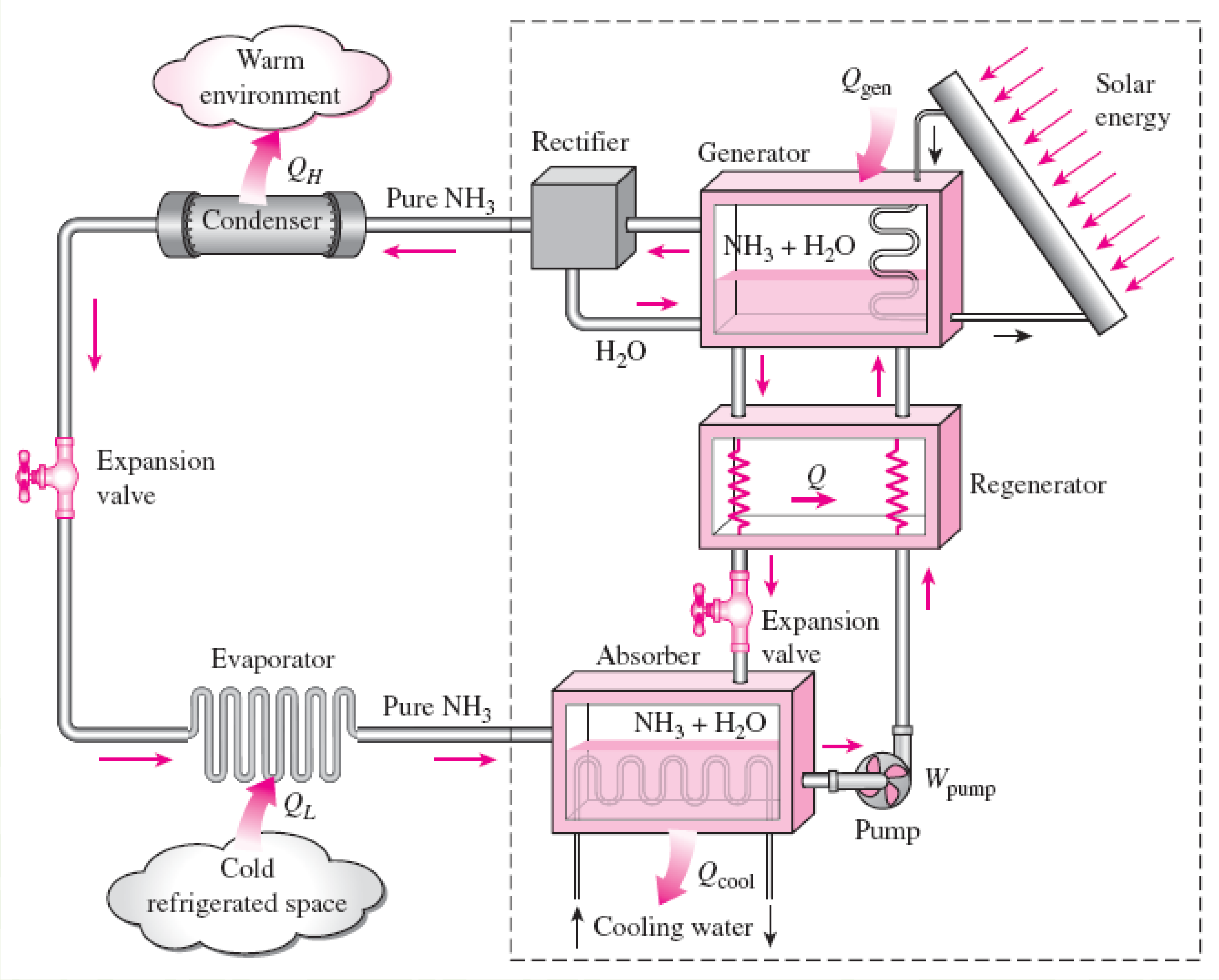
Evaporator



Absorber



ABSORPTION REFRIGERATION SYSTEMS

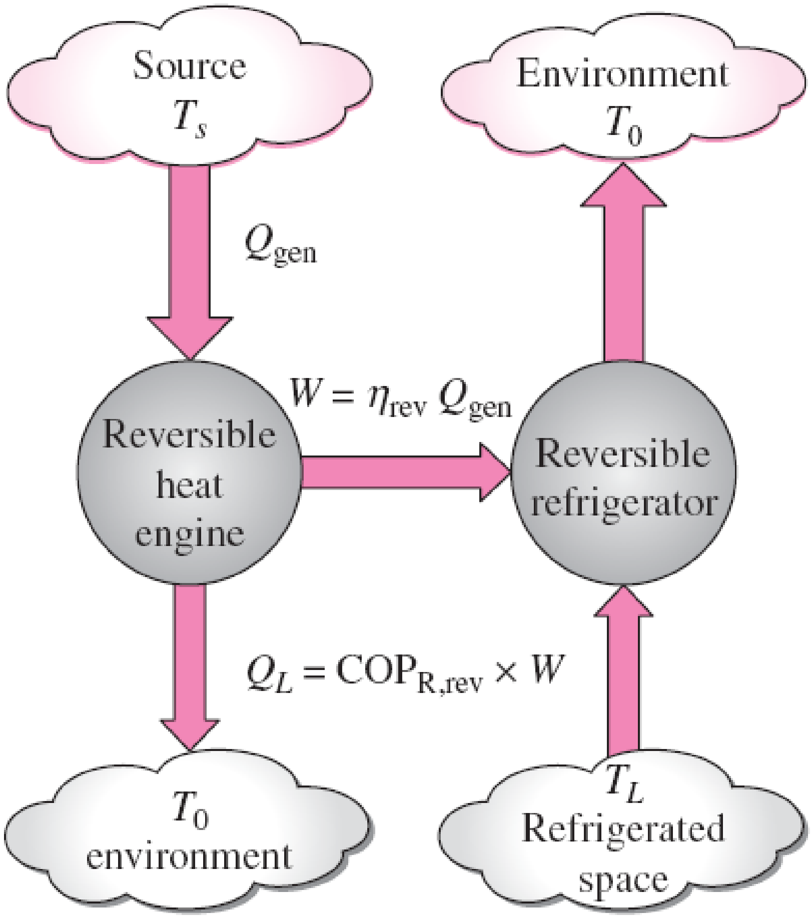


Ammonia absorption refrigeration cycle.

Absorption refrigeration is economical when there is a source of inexpensive thermal energy at a temperature of 100 to 200°C.

Some examples include geothermal energy, solar energy, and waste heat from cogeneration or process steam plants, and even natural gas when it is at a relatively low price.

$$\mathrm{COP}_{\text{absorption}} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{Q_{\text{gen}} + W_{\text{pump,in}}} \cong \frac{Q_L}{Q_{\text{gen}}}$$



$$W = \eta_{\text{rev}}\, Q_{\text{gen}} = \left(1 - \frac{T_0}{T_s}\right) Q_{\text{gen}}$$

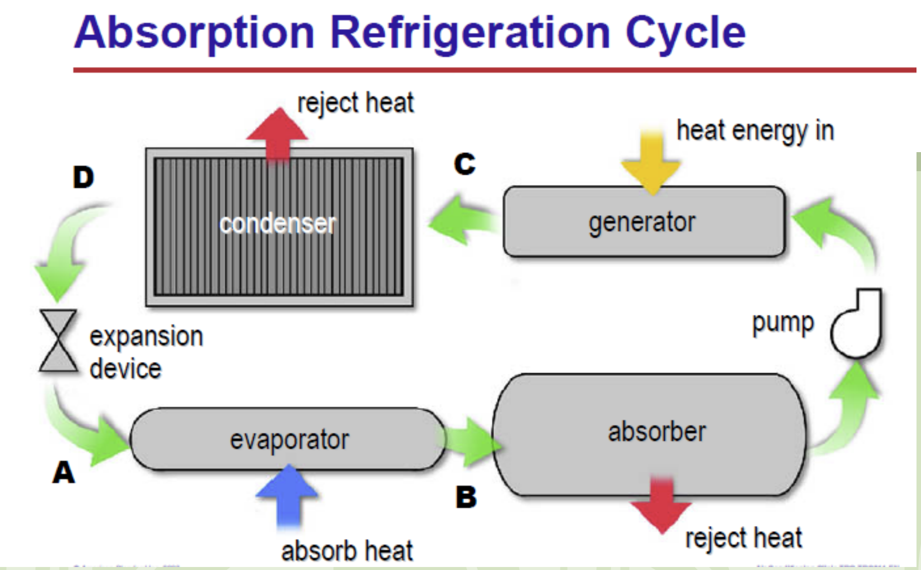
$$Q_L = \mathrm{COP}_{\mathrm{R,rev}}\, W = \left(\frac{T_L}{T_0 - T_L}\right) W$$

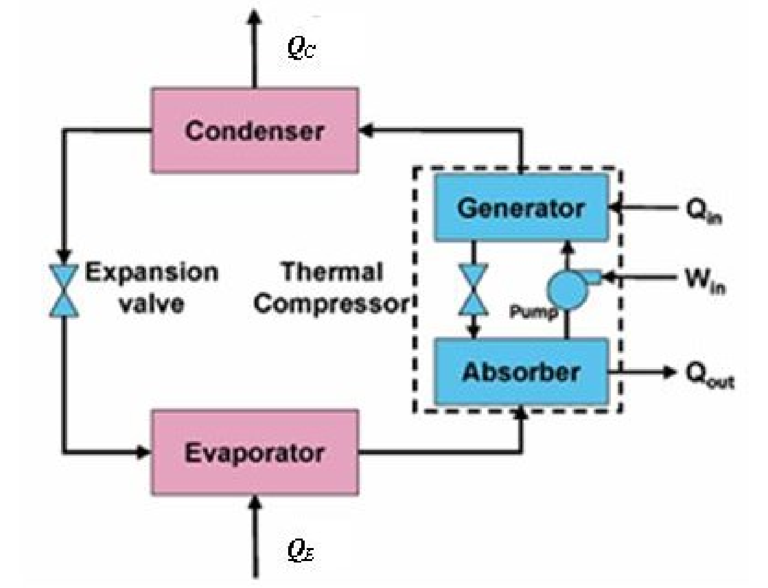
$$\mathrm{COP}_{\text{rev,absorption}} = \frac{Q_L}{Q_{\text{gen}}} = \left(1 - \frac{T_0}{T_s}\right)\left(\frac{T_L}{T_0 - T_L}\right)$$

The COP of actual absorption refrigeration systems is usually less than 1.

Air-conditioning systems based on absorption refrigeration, called ***absorption chillers***, perform best when the heat source can supply heat at a high temperature with little temperature drop.

Determining the maximum COP of an absorption refrigeration system.



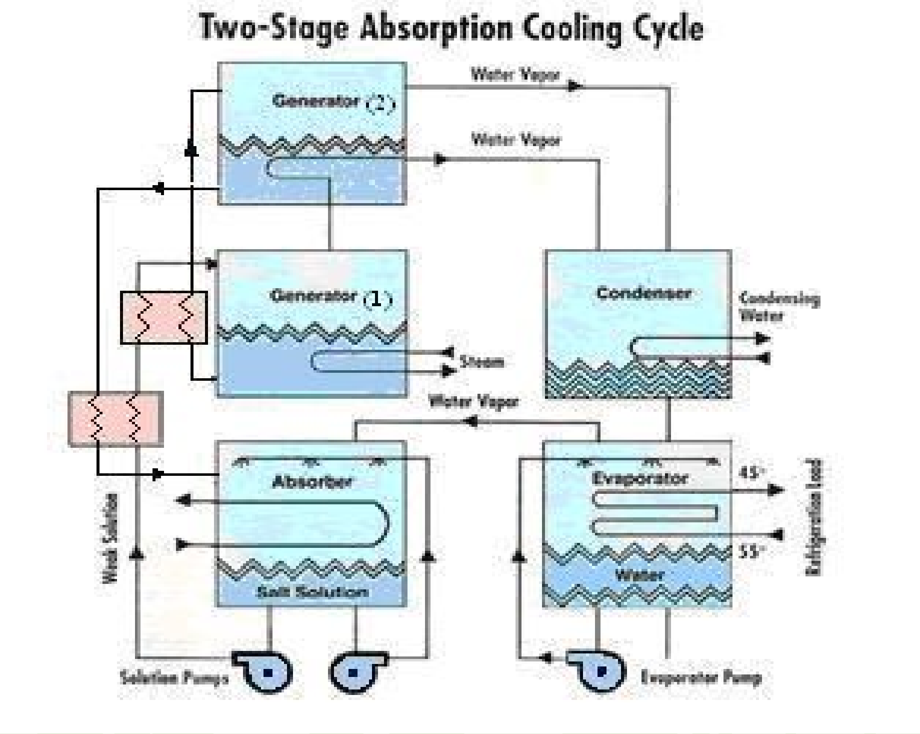


1. Principles of absorption refrigeration

- There are two fundamental differences between the absorption refrigeration cycle and the vapor-compression refrigeration cycle.
- The first is that the compressor is replaced by an absorber, pump, and generator.
- The second is that, in addition to the refrigerant, the absorption refrigeration cycle uses a secondary fluid, called the absorbent. The condenser, expansion device, and evaporator sections, however, are the same.

Multiple-Effect and direct- or indirect-fired Absorption Chillers

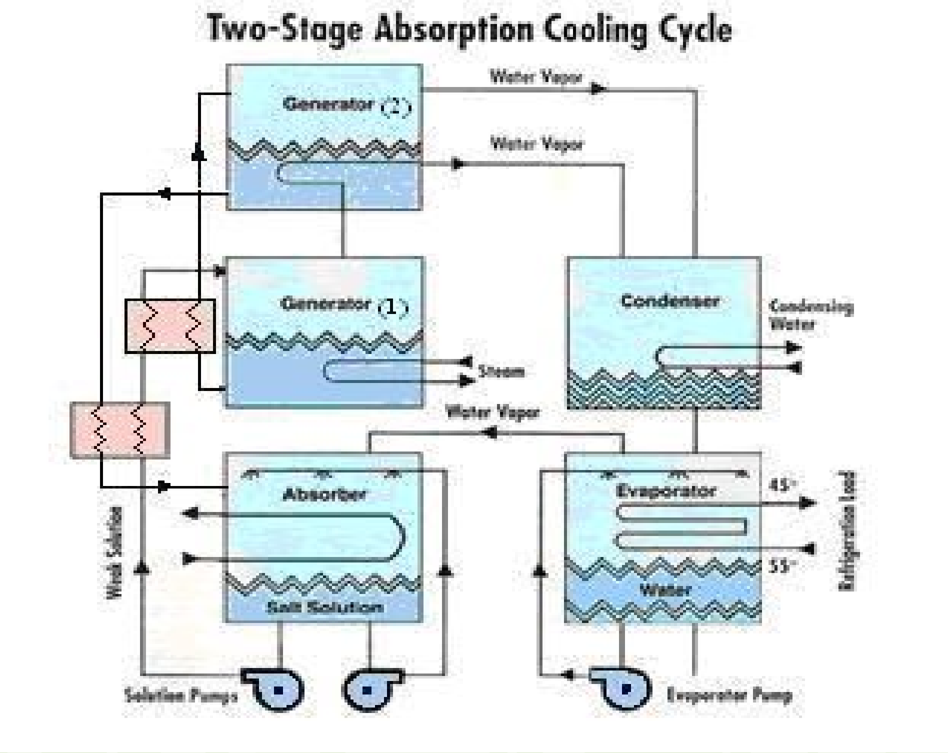
- Absorption chillers can be direct- or indirect-fired and single- or multiple-effect.
- Double-effect absorption machines uses two generators paired with a single condenser, absorber, and evaporator.
- The higher-temperature generator (1) is called the first stage-generator.
- The refrigerant vapor produced in the generator (1) is then used to desorb additional refrigerant (water) from a lower-temperature, the second-stage generator (2).



a double-effect absorption cycle

- So heat energy from the first stage is recovered and is utilized in the second stage. Consequently, a double-effect absorption cycle is more efficient than a single-effect one.

- For example of a LiBr absorption system used for air conditioning, the heat ratio of absorption chillers ranges from 0.60 to 0.70 for indirect-fired single-effect systems, to about 1.20 for indirect-fired double-effect units.



a double-effect absorption cycle

Heat Operated vapor Compression Refrigeration Cycle (2)

Vapor Adsorption Refrigeration

1. Adsorption and desorption

(1) Adsorption

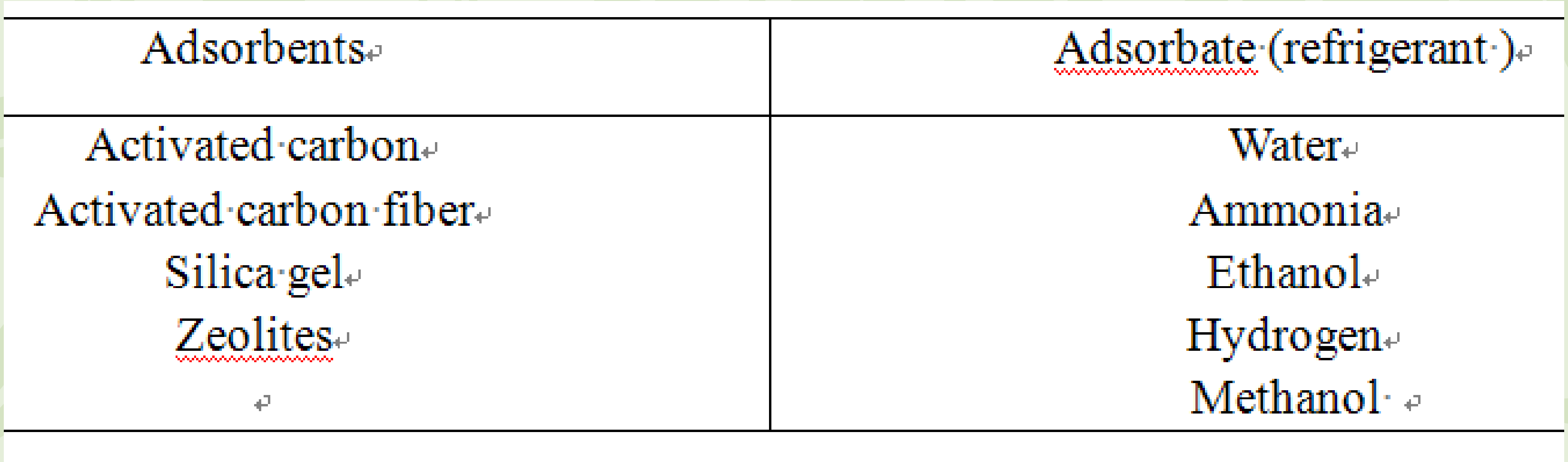
- Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate).
- The term sorption encompasses both processes, while desorption is the reverse process of adsorption.

(2) Desorption

- Desorption is a phenomenon whereby a substance is released from or through a surface.
- The process is the opposite of sorption (that is, adsorption and absorption).
- As the temperature rises, so does the likelihood of desorption occurring.

2. The working pairs in adsorption refrigeration

Main working substances in adsorption refrigeration

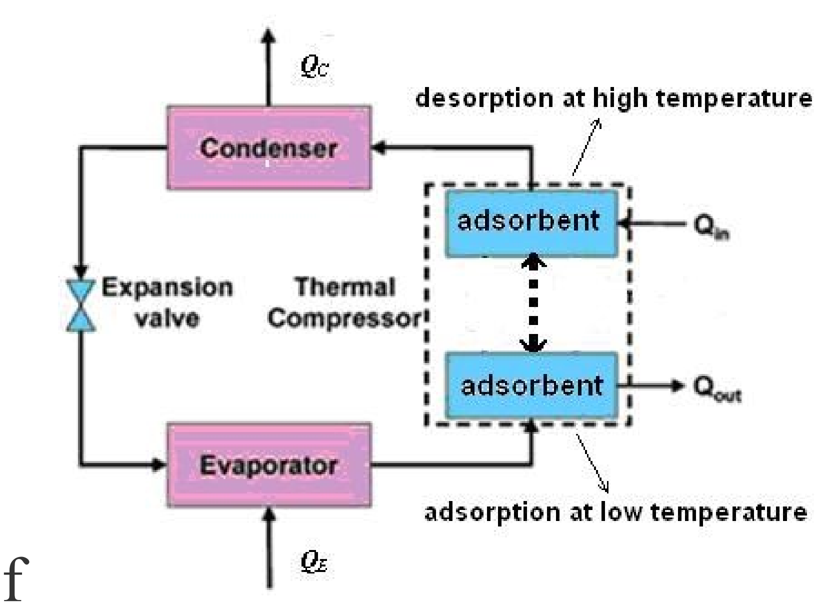


Adsorbents	Adsorbate (refrigerant)
Activated carbon	Water
Activated carbon fiber	Ammonia
Silica gel	Ethanol
Zeolites	Hydrogen
	Methanol

- Most industrial adsorbents fall into one of three classes:
  - ***Oxygen-containing compounds – Are typically hydrophilic and polar, including materials such as silica gel and zeolites***.
  - ***Carbon-based compounds – Are typically hydrophobic and non-polar, including materials such as activated carbon***.
  - ***Polymer-based compounds - Are polar or non-polar functional groups in a porous polymer matrix***.

3. Principles of adsorption refrigeration

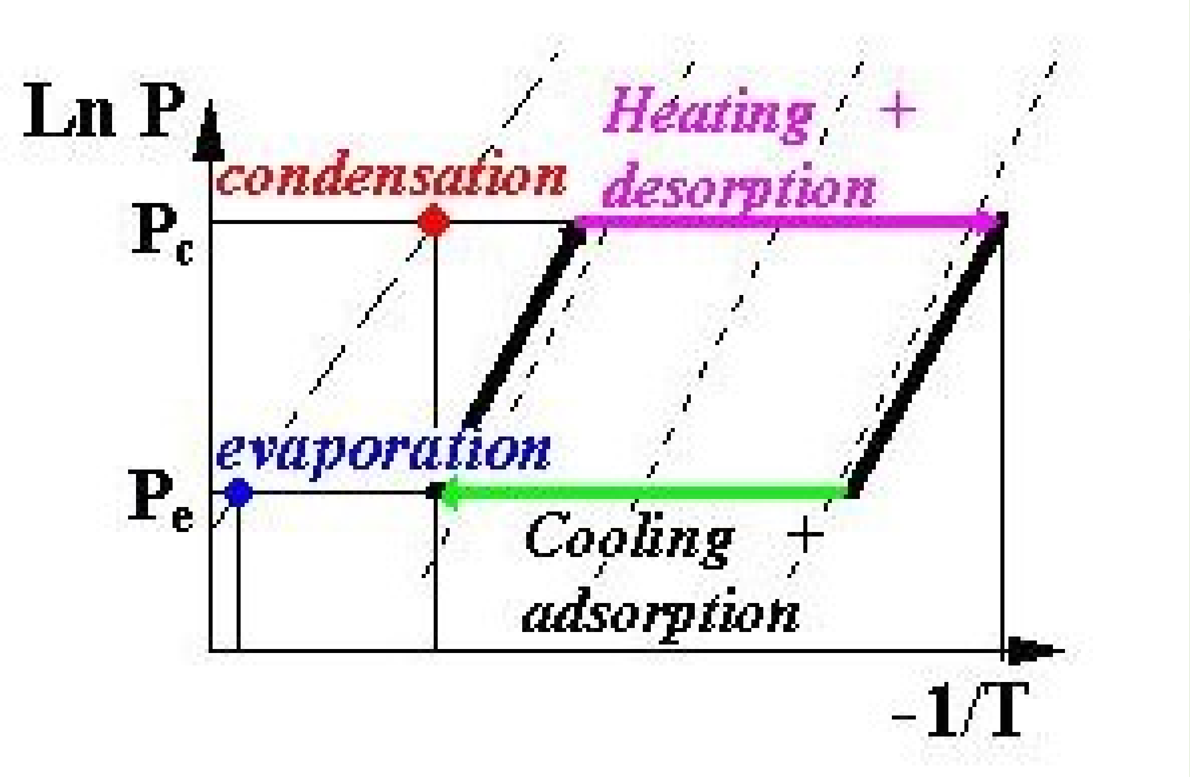
- Like the mechanical vapor compression refrigeration cycle and the absorption refrigeration cycle, the adsorption refrigeration cycle can accomplish the removal of heat through the evaporation of a refrigerant at a low pressure and the rejection of heat through the condensation of the refrigerant at a higher pressure.
- The pressure difference in the adsorption refrigeration system is created by adsorption and desorption of refrigerant vapor by adsorbent at low temperature and at high temperature respectively, as shown in Figure.



essential components of the vapor absorption cycle

- In comparison with mechanical vapor compression systems, adsorption systems have the benefits of **energy saving if powered by waste heat or solar energy, simpler control, no vibration and lower operation costs**.
- In comparison with liquid absorption systems, adsorption ones present the ***advantage of being able to be powered by a large range of heat source temperatures***, starting at 50℃ and going up to 500℃.
- Moreover, the adsorption system ***does not need a liquid pump*** or rectifier for the refrigerant, ***does not present corrosion problems*** due to the working pairs normally used, and it is also less sensitive to shocks and to the installation position.

- ***An adsorption cycle for refrigeration (or heat pumping) does not use any mechanical energy, but only heat energy***.
- Moreover, ***this type of cycle basically is a four temperature discontinuous cycle***. The cycle consists of four periods as shown.



Heating and desorption + condensation

(1) Heating and pressurization

- During this period, the adsorber receives heat while being closed.
- The adsorbent (refrigerant) temperature increases, which induces a pressure increase, from the evaporation pressure up to the condensation pressure.

(2) Heating and desorption + condensation

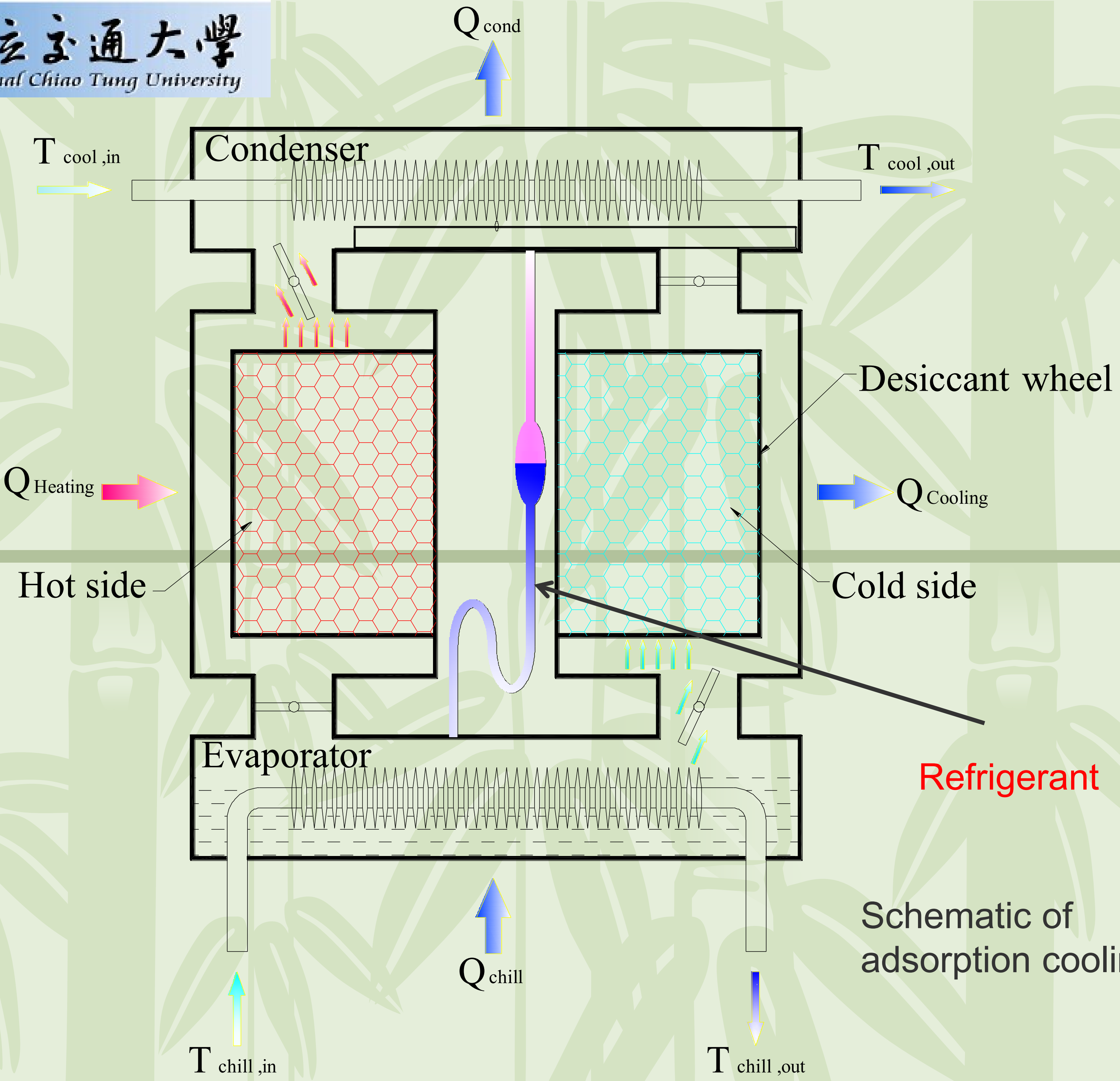
- During this period, the adsorber continues receiving heat while being connected to the condenser, which now superimposes its pressure.
- The adsorbent temperature continues increasing, which induces desorption of vapor. This desorbed vapor is liquefied in the condenser.

(3) Cooling and depressurization

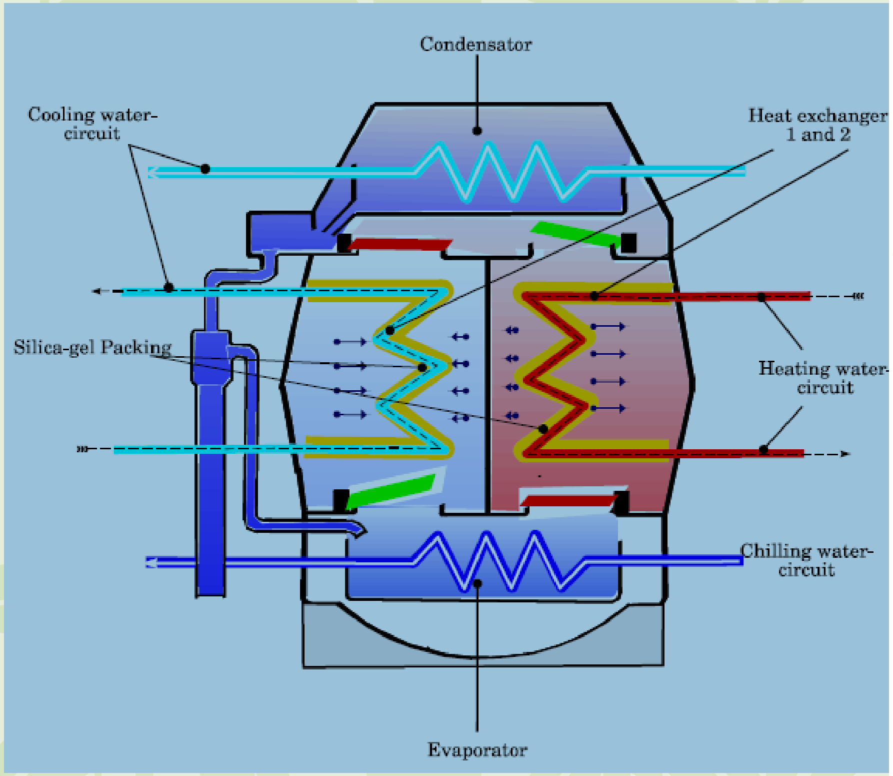
- During this period, the adsorber releases heat while being closed.
- The adsorbent temperature decreases, which induces the pressure decrease from the condensation pressure down to the evaporation pressure.

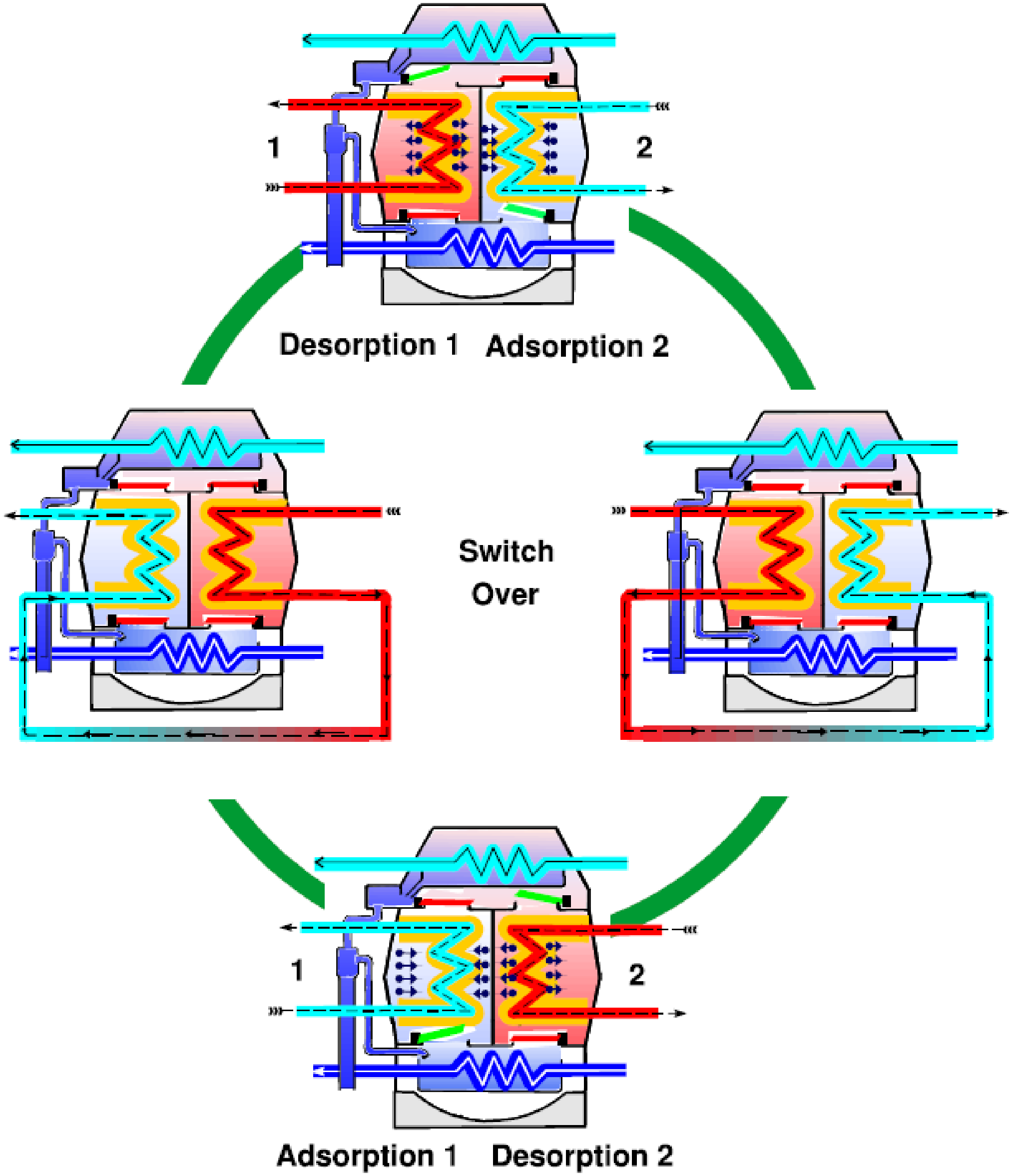
(4) Cooling and adsorption + evaporation

- During this period, the adsorber continues releasing heat while being connected to the evaporator, which now superimposes its pressure.
- The adsorbent temperature continues decreasing, which induces adsorption of vapor.
- This adsorbed vapor is vaporized in the evaporator.
- The evaporation heat is supplied by the heat source at low temperature.
- For a single absorber system, the cycle is intermittent because cold production is not continuous: cold production proceeds only during part of the cycle.
- When there are two adsorbers in the unit, they can be operated out of phase and the cold production is quasi-continuous.

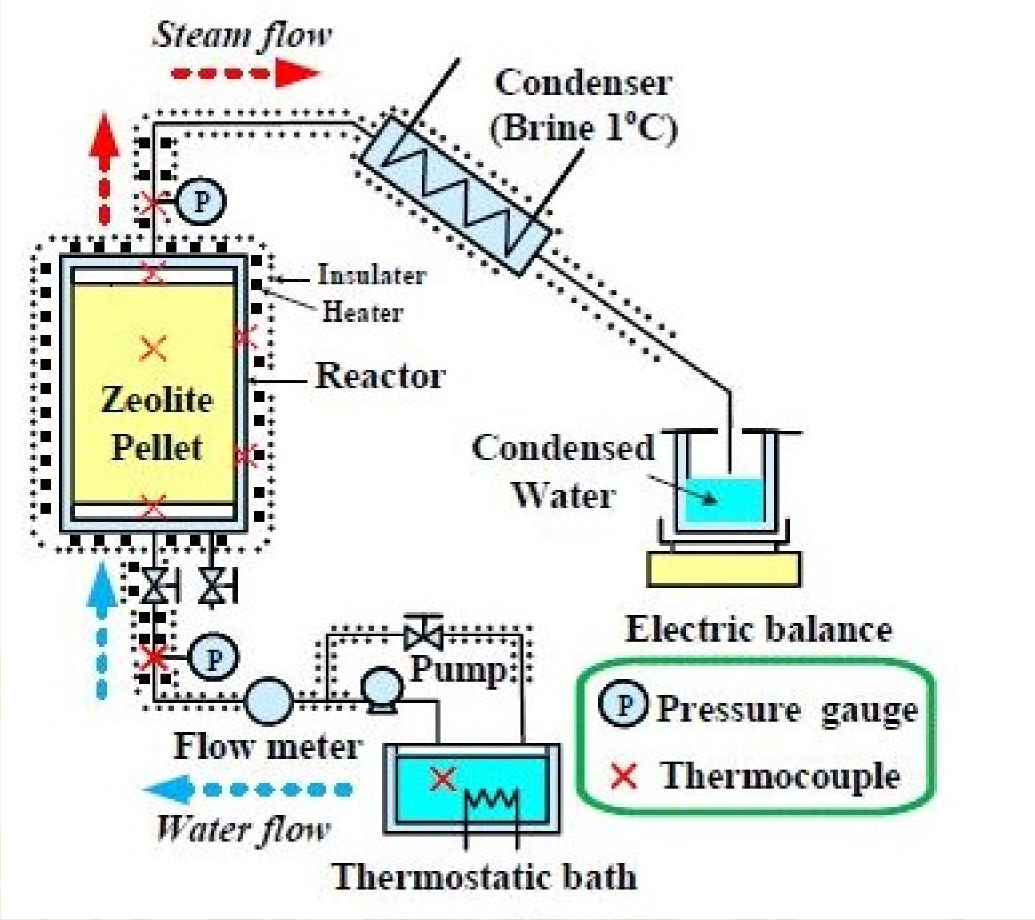


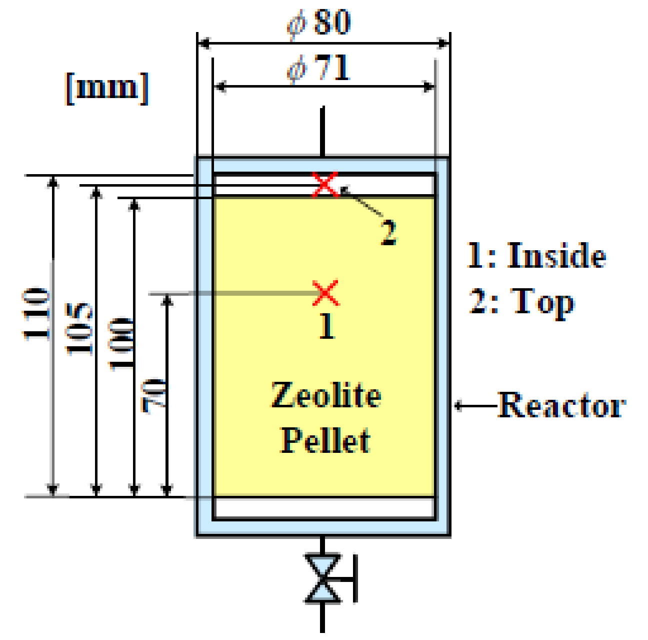
Schematic of adsorption cooling


Condensator
Cooling water-circuit
Heat exchanger 1 and 2
Silica-gel Packing
Heating water-circuit
Chilling water-circuit
Evaporator


1
2
Desorption 1
Adsorption 2
Switch Over
1
2
Adsorption 1
Desorption 2

The inlet water is adsorbed on zeolite surface sequentially from the bottom. While the generated steam moves upwards, some amount of steam is adsorbed on the other zeolite surfaces until the zeolite locally reaches equilibrium state. Steam which is not adsorbed there advances to the next particles and is adsorbed. As a result, steam is expected to leave from the top of the packed bed after the whole regions reach equilibrium state.



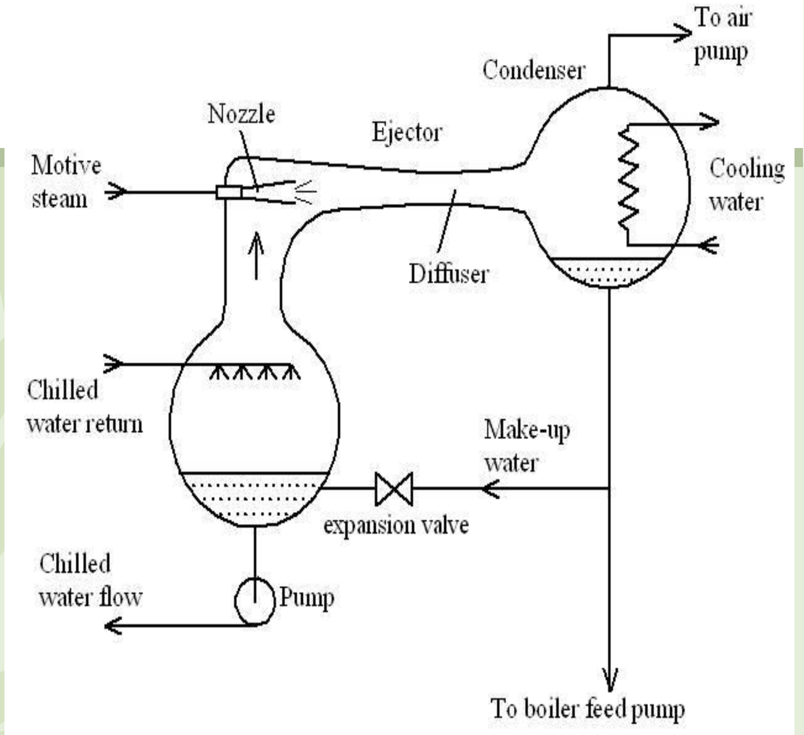


Heat Operated vapor Compression Refrigeration Cycle (3)

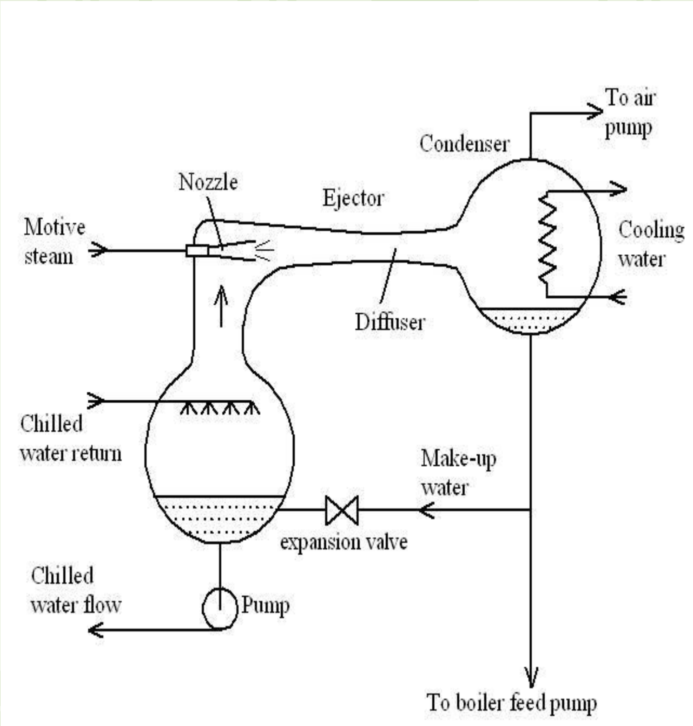
------Vapor Jet Refrigeration

1. Principles of vapor jet refrigeration systems

- Vapor jet refrigeration is other type of vapor compression refrigeration cycle driven by heat source of high temperature.
- As the same as the mechanical vapor compression refrigeration cycle, the vapor jet refrigeration cycle can accomplish the removal of heat through the evaporation of a refrigerant at a low pressure and the rejection of heat through the condensation of the refrigerant at a higher pressure.
- The pressure difference in the system is created by a high pressure vapor or steam ejector. The refrigerant sown in Fig. is water.
- A supply of high-pressure vapor, usually steam, passes through a nozzle in which it acquires a high velocity and some vacuum whilst expanding down to evaporator pressure.



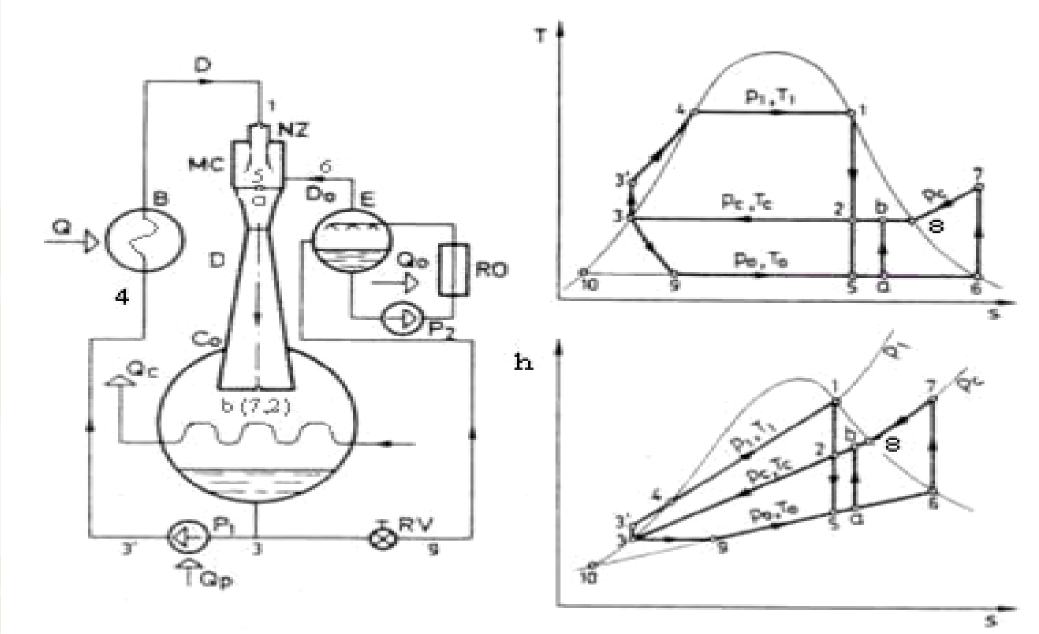
refrigeration system using a steam ejector or thermo-compressor



refrigeration system using a steam ejector or thermo-compressor

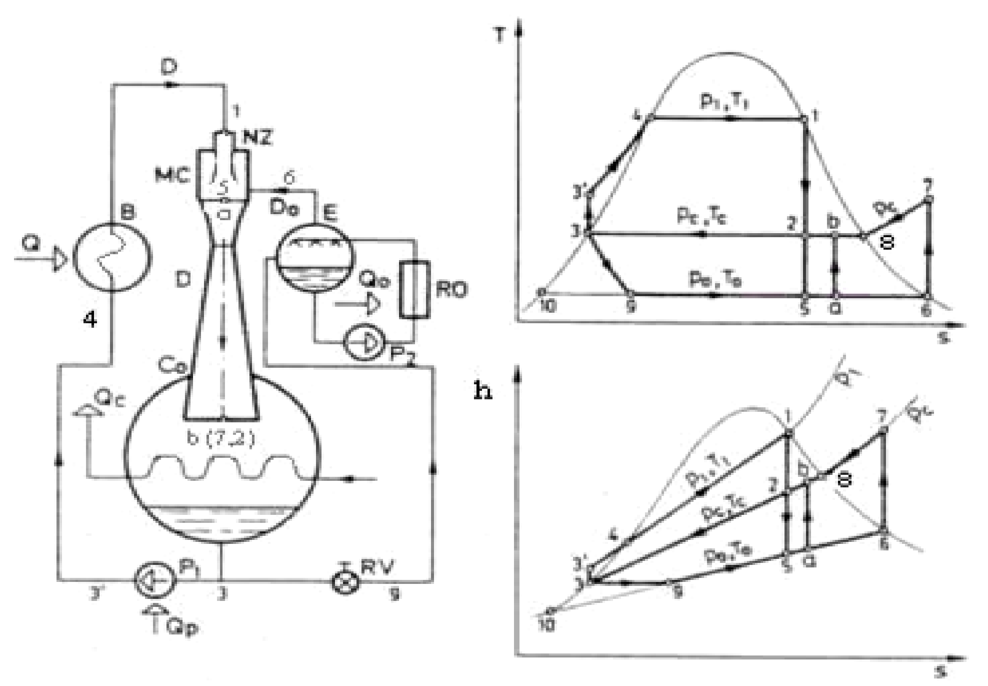
- This steam, known as the motive steam, shares its momentum with vapor from the evaporator so that the resulting mixture has sufficient velocity to move against the pressure gradient up to the condenser pressure in a diffuser, in which the mixture is decelerated and compressed.
- Both the motive vapor and the vapor drawn from the evaporator are condensed, and the condensate is then divided into two flows, one to pass an expansion valve and feed the evaporator and the other to supply the boiler of motive steam through a feed pump.

2. An analysis for a basic steam jet



a scheme of a steam jet refrigeration system and T-s and h-s diagrams of its cycle (B –boiler; E –evaporator; NZ –nozzle; MC –mixing chamber; Df –diffuser; Co –condenser; RV –expansion valve; P –pump; RO –refrigeration object)

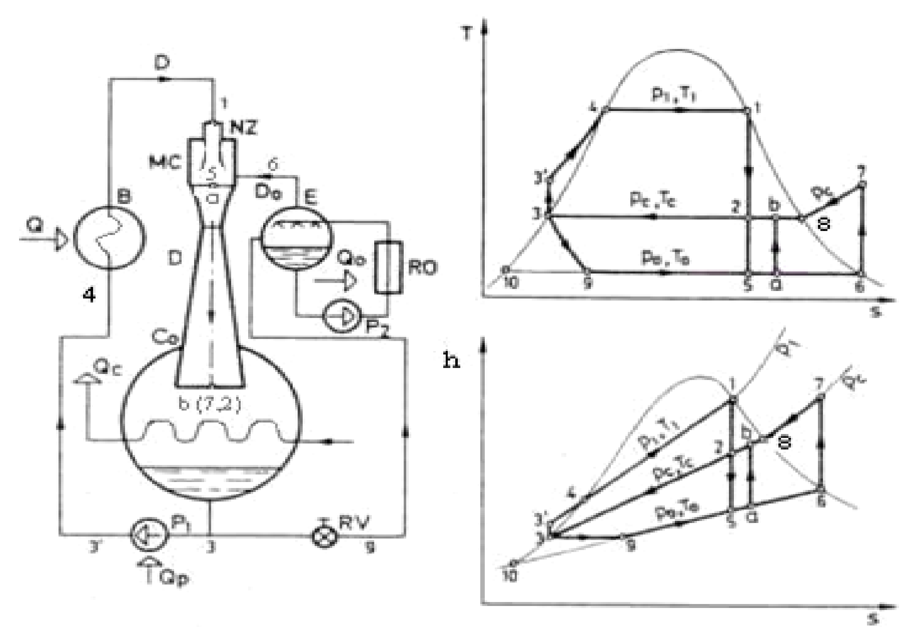
- The basic steam jet refrigeration system, seen in Figure, consists of the following components:
  - an evaporator;
  - a refrigerated object;
  - a boiler;
  - a nozzle, a mixing chamber;
  - a diffuser;
  - a condenser;
  - an expansion valve;
  - pumps.



a scheme of a steam jet refrigeration system and T-s and h-s diagrams of its cycle (B –boiler; E –evaporator; NZ –nozzle; MC –mixing chamber; Df – diffuser; Co –condenser; RV –expansion valve; P –pump; RO –refrigeration object)

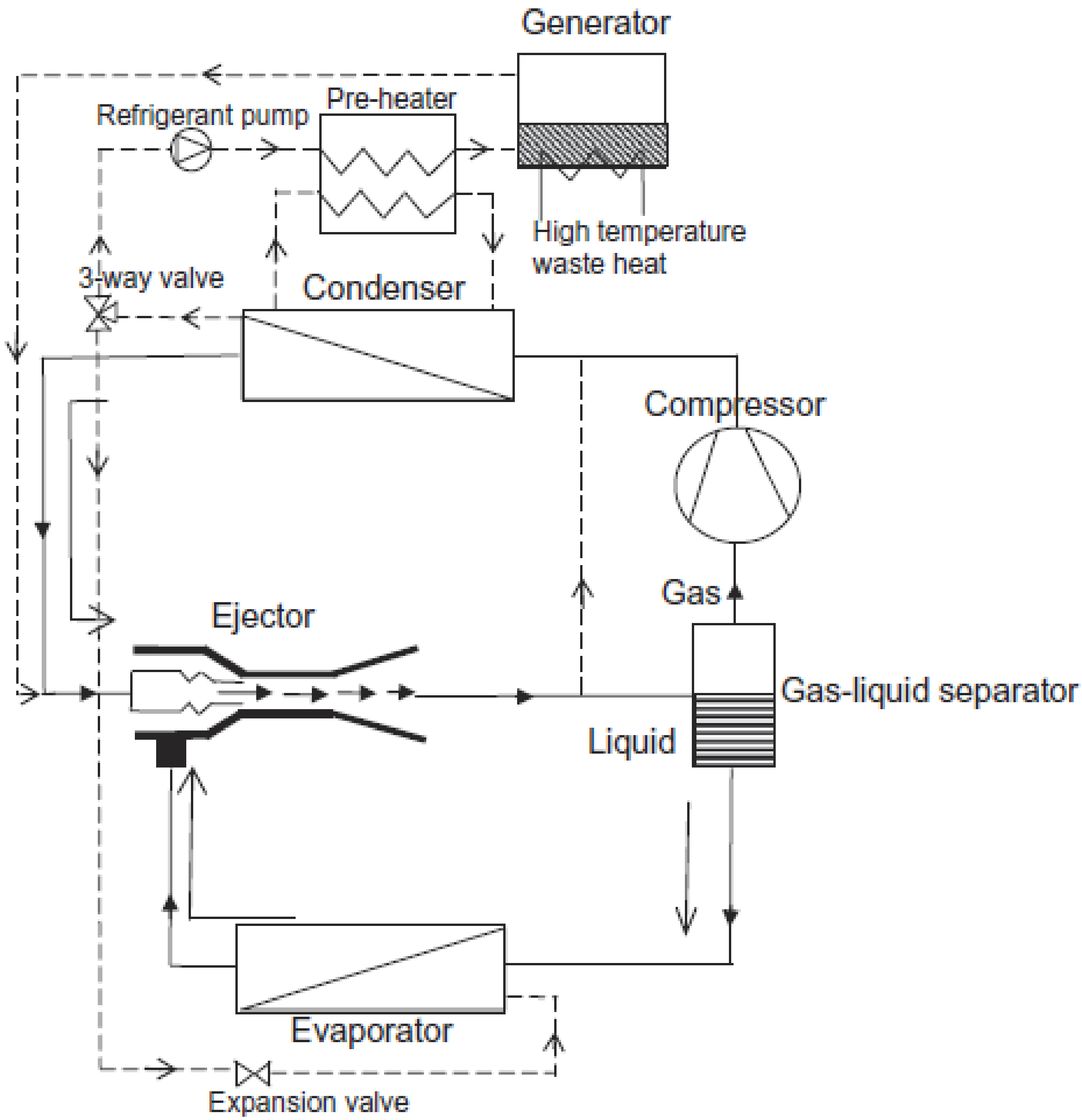
- In the steam jet system the vapor power cycle (1-2-3-3'-4-1) and the refrigeration cycle (6-7-8-3-9-6) are realized simultaneously.
- This can be explained by the progressive, independent observation that the state of the motive steam and refrigerant vapor changes.
- Motive steam is expanded in the nozzle from point 1 to point 5, but after mixing with refrigerant vapor it is compressed from 5 to 2, or in the mixture from *a* to *b*.

- The motive steam in the cycle's expansion process generates work $i = h1 - h2$ converted from the part of the heat q added to the working body.
- This work is transmitted in the mixing chamber to the refrigerant vapor, which is compressed from 6 to 7 in the diffuser, so $i = h = h7\text{-}h6$.
- The resulting change of the mixture in the diffuser for both stream of motive steam and refrigerant vapor is from point a to point *b*.
- The specific absorbed heat in the evaporator is $qe = h6 – h9 = h6 - h3$.



a scheme of a steam jet efrigeration system and T-s and h-s diagrams of its cycle (B –boiler; E –evaporator; NZ –nozzle; MC –mixing chamber; Df –diffuser; Co –condenser; RV –expansion valve; P –pump; RO –refrigeration object)

- The limitations of the **water steam jet-pump cycle are that cooling temperatures can only be above the freezing point** of water and utilize high grade heat energy to power the jet-pump cycle.
- These limitations can be solved by choosing some proper fluids as refrigerants.
- In some cases the steam jet refrigeration system can utilize low grade heat energy to power the jet-pump cycle, at temperatures ranging upwards from 60° C.
- This energy is available from a plate solar collector, waste steam, exhaust from automobiles and flue gases.
- In these cases the cost of the heat supply is negligible and, therefore, the operating costs can be significantly lower than for conventional vapor compression systems.


Generator
Refrigerant pump
Pre-heater
High temperature waste heat
3-way valve
Condenser
Compressor
Gas
Ejector
Gas-liquid separator
Liquid
Evaporator
Expansion valve

Short Summary

- Heat pumps are machines able to absorb thermal energy at a low temperature level (heat source), and transfer it to a higher temperature level (heat sink) for further utilization (heating, hot water or process heat).
- Working fluids in the process plays the essential role for the required temperature.
- Large scale high temperature heat pumps allow waste heat recovery from low temperature waste heat. Various kinds of heat pumps, absorption and adsorption can also be implmented.

Thank You