NTNU – Trondheim
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High temperature heat pumps applying natural fluids

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Master's Thesis

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MASTER THESIS

for

student Merisa Brčić

Fall 2013

High temperature heat pumps applying natural fluids

Høytemperatur varmepumper for naturlige kuldemedier

Background and objective

The heat pump market has so far mainly focused on residential heat pumps for space heating and domestic hot water production. Less focus has been on heat pumps for higher temperature applications and industrial use due to high initial investment costs, competition with alternative investments, and non-mature or non-existing technologies for the applications to be served. New developments in compact high pressure components, e.g. compressors, ejectors and heat exchangers for CO_2 – ammonia and hydrocarbon heat pump systems , are important drivers for change of this situation.

The project work will concentrate on the design of a high temperature heat pump for production of hot water (~105°C) from surplus heat. Which working fluid should be chosen to achieve high energy efficiency? There is a wide range of application area for such systems.

The following tasks are to be considered:

1. Literature review of high temperature heat pumps and application areas
2. Evaluate different refrigerants for high temperature
3. Design of new concepts
4. Analysis of the different systems

5. Write a scientific paper with the main results from the thesis
6. Make proposal for further work not covered in this thesis

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Within 14 days of receiving the written text on the master thesis, the candidate shall submit a research plan for his project to the department.

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The thesis should be formulated as a research report with summary both in English and Norwegian, conclusion, literature references, table of contents etc. During the preparation of the text, the candidate should make an effort to produce a well-structured and easily readable report. In order to ease the evaluation of the thesis, it is important that the cross-references are correct. In the making of the report, strong emphasis should be placed on both a thorough discussion of the results and an orderly presentation.

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☐ Work to be done in lab (Water power lab, Fluids engineering lab, Thermal engineering lab)

☐ Field work

Department of Energy and Process Engineering, September9th2013

______________________ _________________________

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Abstract

The heat pump market has so far mainly focused on residential heat pumps for space heating and domestic hot water production. That means that industrial heat pumps are successfully integrated as low temperature heat recovery systems but rarely employed in processes with heat requirements above 100°C, due to very high investment costs, or non-existing technologies for the applications to be served.

The project work will concentrate on the design of a high temperature heat pump for production of hot water (~105°C) from surplus heat. There were considered working fluids with accent on natural working fluids and after that it is calculated which working fluid should be chosen to achieve high energy efficiency.

There is a wide range of application area for such systems. Successful application depends on the working principles of the heat pumps applied, the utilized working fluid and chosen components. All of those components and principles are briefly descriebed and the results indicate that mechanical compression heat pumps are most(suitable for heat recovery in those systems.

Preface

This thesis is written to conclude one semester I attend at the Department of Energy and Process Engineering at NTNU on the Fall of 2013.

I would like to thank my supervisor professor Trygve Magne Eikevik for providing me with an interesting issue, and for his guidance during the course of this thesis and for his contact and support.

During this thesis I have learned a great deal; I have been challenged in a practical and theoretical manner so, I also want to thank to SWEEB Programme (esspecially to professor Vojislav Novakovic) who gives me a an opportunity to visit NTNU and attend one great semester there.

Trondheim (Norway), 18.11.2013. Merisa Brčić

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Nomenclature

COP	coefficient of performance
Cp	specific heat (kJ/(kg K))
CRPR	ratio of COP to PR
h5	enthalpy at the evaporator inlet (kJ/kg)
h6	enthalpy at the evaporator outlet (kJ/kg)
h7s	enthalpy at the compressor outlet based on an isentropic process (kJ/kg
mh	mass flow rate (kg/s)
mic	mass flow rate of the working fluid (kg/s)
P6	pressure at the compressor inlet (kPa)
P7	pressure at the compressor outlet (kPa)
PR	pressure ratio between the compressor inlet and outlet
Qeva	evaporator power (kW)
Tc	condensation temperature (°C)
Tcrit	critical temperature (°C)

1. Background

1.1. Industrial Heat Pumps Definition

Industrial heat pumps are defined as heat pumps in the medium and high power range (in each case > 50 kW) which can be used for heat recovery and heat upgrading in industrial processes, but also for heating, cooling and air-conditioning in industrial, commercial and multi-family residential buildings as well as district heating [27].

1.2. Possibilities of Heat Pumps Applications

The heat pump market in many countries is presently focused on residental application and heat pumps for industrial applications have on many markets been neglected due to the payback period. As energy costs are growing, industrial payback period values are more easy attainable. Industrial heat pumps potential for energy conservation and reduction of CO_2 emissions is enormus and at this moment not naturally a part of policy papers.

The Industrial Sector includes manufacturing (defined as all establishments engaged in the mechanical or chemical transformation of materials or substances into new products) and nonmanufacturing (agriculture, construction, mining, and resource extraction) industries, and consumes more energy than any other end-use sector, about half of the world’s delivered energy. Long-term projections made by the EIA estimate its average energy consumption to increase on average 1.5% per year through 2035 [1].

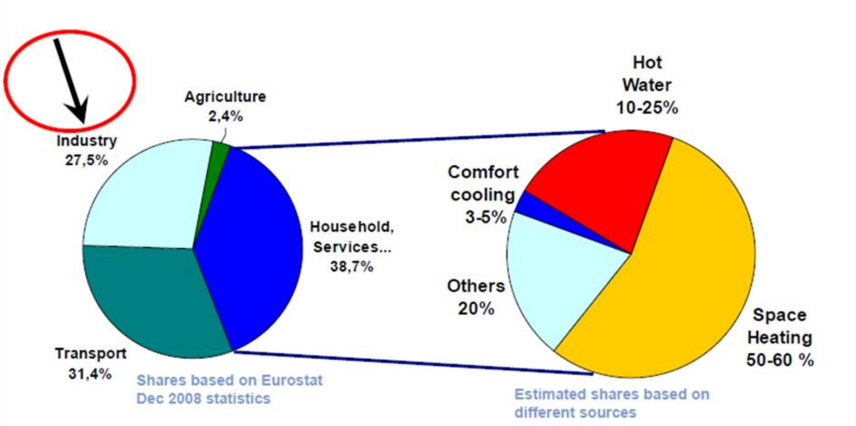

Figure 1.: *Final Energy consumption – EU 27 by Sector (Chart produced by IZWe, 2009.)*

The industrial sector contributed to a third of the total energy consumption, and 85% of its demand was related to heating purposes .

The energy consumption in the sector is dominated by five industries, accounting for more than 60% of the energy consumed in the sector put together. These five industries are Chemicals, Iron and steel, Non-metallic minerals, Pulp and paper and Nonferrous metals, which can all be defined as manufacturing industries. Their respective contribution to the energy consumption is represented in Figure 2. [1].

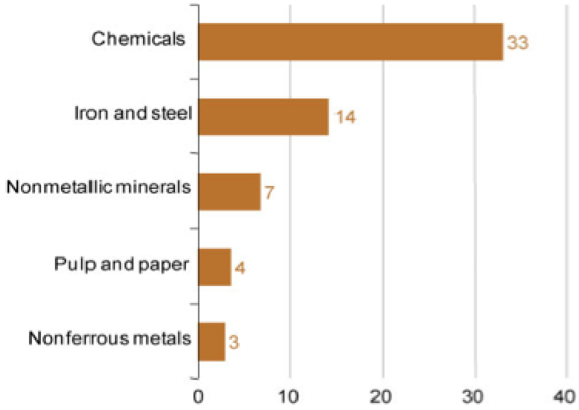

Figure 2: *World industrial sector energy consumption by major energy-intensive industry shares, 2009*

As we can see the industries still hold a large potential for increased energy efficiency.

Current publications from the International Energy Agency (IEA) estimates that manufacturing industries based in OECD countries can improve their energy efficiency by 18-26% compared to 2004 levels, alongside a reduction of CO2-emissions between 19% and 32%, in terms of primary energy sources alone (energy sources as found in nature). [3]

Excess energy (heat) from industry can be recovered passively or actively. Passive heat recovery implies direct energy transfer between two energy levels within a working system. Active heat recovery requires energy transfer from an external source to elevate low-grade energy to a higher level, and facilitates energy savings when conventional passive recovery is not possible[22].

Energy consumption in industry in some of the biggest European countries is given in Figure 3.

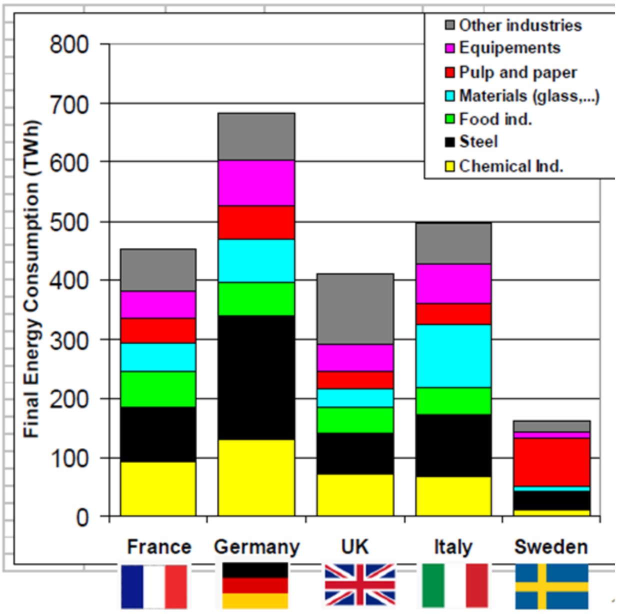

Figure 3: *Energy consumption in the industries (Source EDF)*

As we can see from Figure 3. The biggest energy consumption has Germany with huge technical potential (shown in Figure 4 an Figure 5)in surplus heat.

Heat pump systems are able to reverse this surplus heat, and transfer energy from lower temperature sources to higher temperature heat.

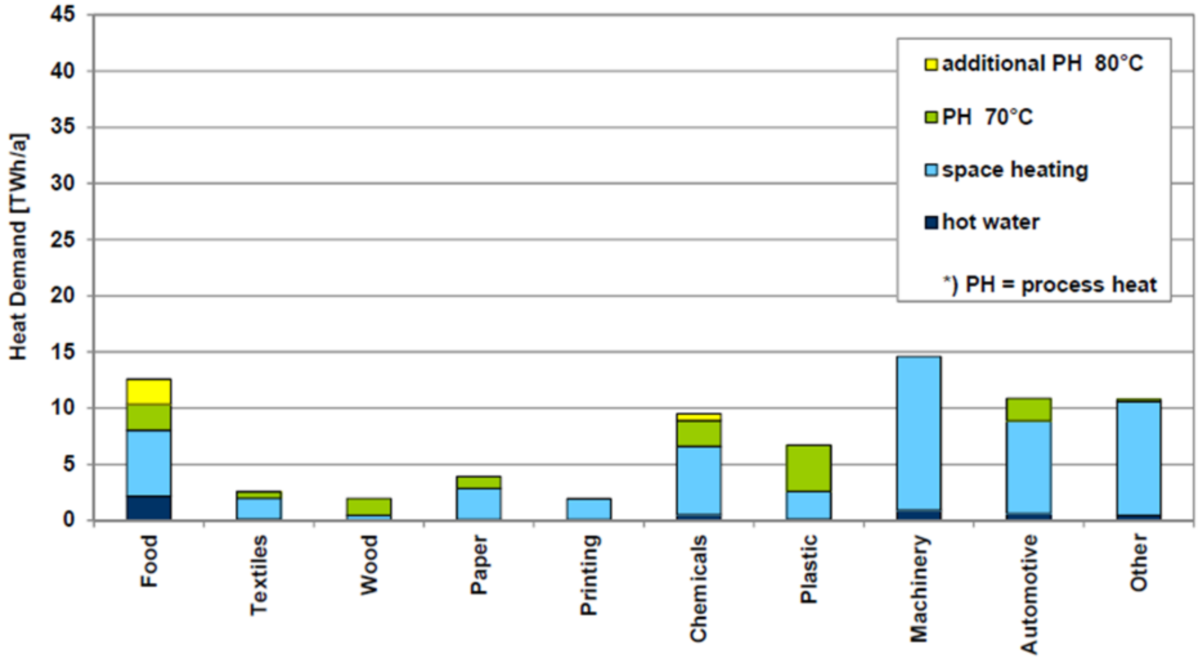

Figure 4. *Technical potential for industrial heat pumps in Germany for lower temperatures*

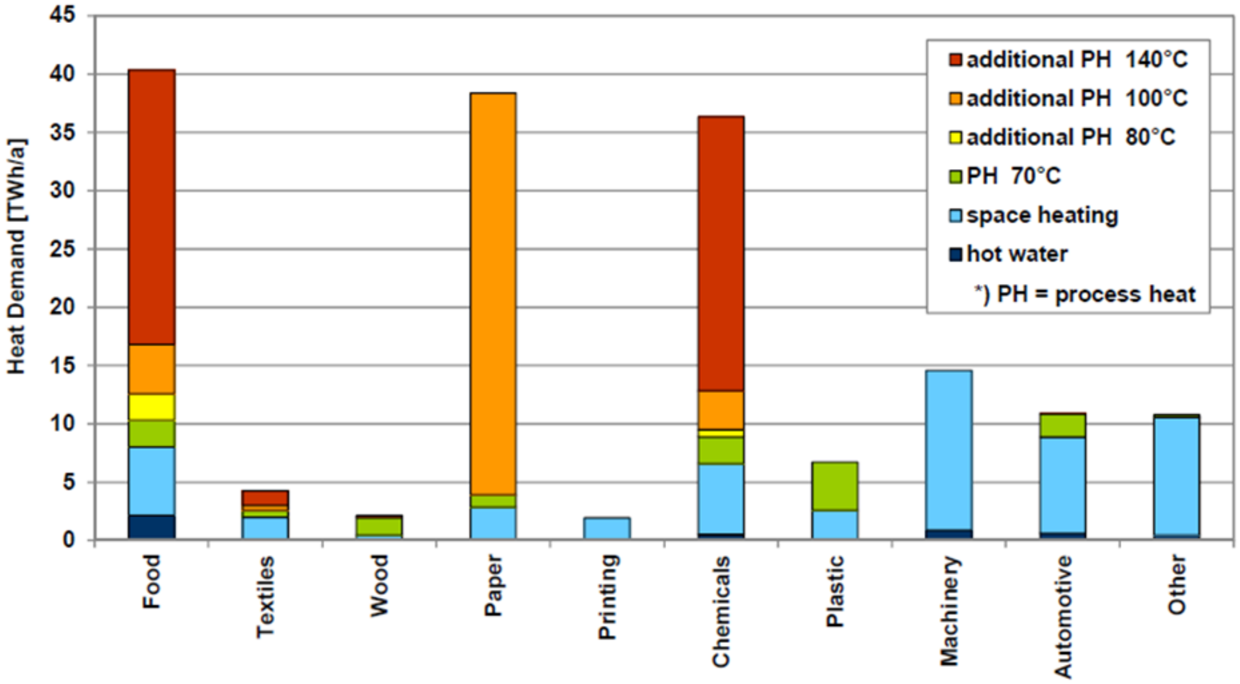

Figure 5. *Technical potential for industrial heat pumps in Germany for higher temperatures*

As we can see technical potential is as it follows:

- Temperature level 70 °C: 73 TWh
- Temperature level 80 °C: 75 TWh
- Temperature level 140 °C: 166 TWh

166 TWh correspond to 33 % of the industrial heat demand and to 16 % of the entire final energy demand of the German industry[6].

There are major differences between the markets for residential heat pumps and those for industrial heat pumps. While standardised products are generally to satisfactory for the residential market, the majority of heat pump applications for industry involve special conditions to which products must be adapted. Moreover, a high level of expertise is crucial.

Many barriers to be overcome. Some of them are:

- Relatively high investment costs
- Lack of knowledge among planers and customers
- Lack of knowledge about energy demands and possible heat sources in industrial plants etc.

However, the possible applications of the heat pumps are numerous. It is worth examining some typical examples well described in the literature, not only to give an idea of the achieved performances, but also of the problems encountered and, above all, of the plant lay-outs.

Some of the typical examples of using heat pumps are shown in Figure 6.

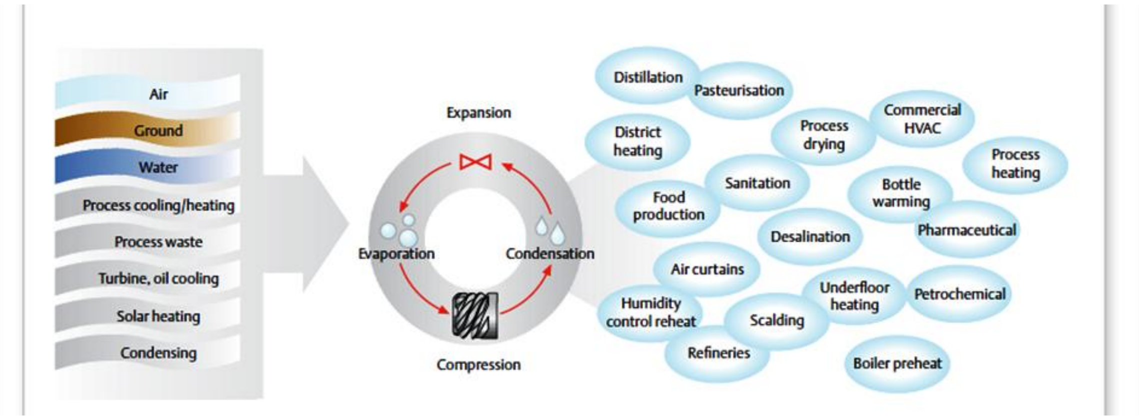

***Figure 6.** Different heat sources for a wide range of applications*

As we can see numerous solutions have been employed to take advantage of the energy saving potential, related to both energy recovery and recycling of materials and fuel. Industrial application of heat pumps addresses the first challenge.

Beside that, there is a lot of promissing processes where heat pumps can be integrated. Some of them are shown in Table 1a and Table 1b .

Table 1a : *Promissing Processes for heat pump integration*

Sector	Process	Technological status	Temperature (°C)
General	Process heat networks	high temp.HP	110 to 120
	Preheating	high temp.HP	>100
	Washing	common/high temp.HP	30 to 90
Chemicals	Biochemical reactions	common HP	20 to 60
	Distillation	high temp.HP	>100
	Cooking	high temp.HP	80 to 110
	Thickening	very high temp.HP	130 to 140
Paper	Bleaching	very high temp.HP	40 to 150
	De-inking	common HP	50 to 70
	Cooking	very high temp.HP	110 to 180
	Drying	high temp.HP	>90

As we can see the biggest potential for applying high temperature heat pumps is in Industry (temperatures in range of 20 °C up to 180°C and for higher temperature applications the biggest potential is ih paper industry).

Table 1b : *Promissing Processes for heat pump integration*

Sector	**Process**	**Technological status**	**Temperature (°C)**
Food	Blanching	common/high temp.HP	60 to 90
	Scalding	common/high temp.HP	50 to 90
	Evaporating	high temp.HP	40 to 130
	Cooking	high temp.HP	70 to 120
	Pasteurization	very high temp.HP	60 to 150
	Smoking	common HP	20 to 80
	Cleaning	common/high temp.HP	60 to 90
	Sterilization	high temp.HP	100 to 140
	Tempering	common HP	40 to 80
	Drying	common/high temp.HP	<40

Sector of food is separeted from other fields of industry, and it also consist a lot of promissing processes for heat pump integration.

2. Heat Pump Basics

2.1. Heat Pump Components

The basic components of the heat pump systems suitable for industrial applications are:

- Mechanical Compressors
- Solution Pumps.
- Expansion Valves and
- Heat Exchangers.

It is very important to understand each of those components in order to understand working principle of high temperature heat pumps.

2.1.1. Mechanical Compressors

Compressor systems are used to increase the pressure (and accordingly the temperature) of the working fluid vapor exiting the evaporation stage in a heat pump. Industrial application requires relatively large compressor systems, with high initial costs, due to increased heat load requirements accompanied by larger working fluid flow rates. Open systems (separate compressor and engine) are therefore in preference of closed systems (compressor and engine in the same shell) to simplify maintenance work. Compression is either dry (pure gas) or wet (liquid entrained in the inlet gas). Dry compression is preferable; as it minimizes wear

and tear during compression, reduce the system's operational and maintenance costs. Compressors are generally oil-lubricated (to cool, seal and/or lubricate the internal parts), as most working fluids fail to self-lubricate the system during compression. Oil-free systems are available, but costly compared to oil-lubricated compressors. High temperatures tend to affect the pressurized oil negatively, and diminish its lubricating effects. The pressurized oil consequently restricts a compressor’s operational temperature range, and must be chosen to complement system pressures and temperature ranges. Oil recovery systems are also a requirement, to reduce operational costs.[22]

2.1.1.1. Compressors design

Compressors are broadly classified by their operating principle, based on dynamic compression or positive displacement of the compressed medium. Both categories have include several different subsystems, all applicable in industrial processes.[8]

- **Positive displacement compressors** increase working fluid pressure by confinementand reduction of its gas volume. Pressure ratios across the compressionstages are accordingly determined by the compressors physical design, rather than by fluid velocity. Current research on compression systems requiring high-pressure ratios typically accordingly focus on reciprocating and screw compressors. Their operational principles are sketched and illustrated by Figure 7a and Figure 7b,c, respectively.[8]

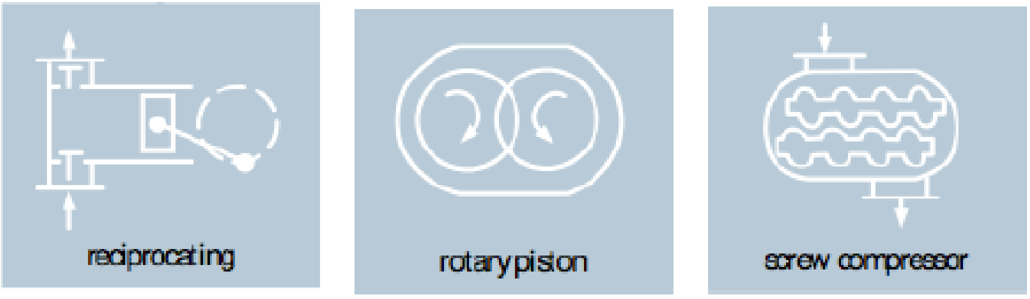

Figure 7.: *(a) Reciprocating compressor (b) Screw compressor –front view (c)Screw compressor- side view*

Screw compressors are therefore chosen over dynamical compression and reciprocating compressors, supported by three beneficial characteristics.

Screw compressors raise gas pressure by trapping a fixed gas volume on its suctionside, and progressively decreasing the volume through the compressor. Screw compressors do not require internal lubrication by pressurized oil. Steamwater compression can use the working fluid for lubrication, and are operable with mechanically loaded pressure differences up to 12 bar. Screw compressors handle20 bar when oil lubricated. Current systems limit the output gas temperature to 250°C, which restricts system applicability in high temperature industrial application. Screw compressors are also capable of compressing practically all gases.

- **Dynamic compression systems** convert a working fluid's kinetic energy into apressure increase. Dynamic compressors operate with axial, mixed or centrifugal flow. All present an affinity to high volumetric flow rate compression, but cannot produce large pressure ratios.

This feature reduces their application in high temperature industrial processes, where an often significant temperature elevation (and accordingly large pressure ratios across the compression stage(s) is the most pressing design condition.

2.1.2. Solution Pumps

The pumps are used to increase the pressure (and temperature) of liquid working fluids in heat pump application. They are operable as positive displacement pumps and dynamical systems (typically centrifugal operation). Pumps are estimated to use 20% of the world's electrical power.

They are, accordingly, found in system utilizing gas-liquid reactions in heat transfer, which requires both liquid and gas at high temperature levels. Current pump technologies are capable of compressing pure liquids, and liquid solutions with entrained solids and/or gas bubbles.

2.1.3. Expansion Valves

Expansion valves experience phase change from gas to liquid or liquid to gas, depending on the thermodynamic state of the working fluid exiting the heat exchanger (the former when gas exits after transcritical heat transfer, the latter when saturated liquid exits a condensing system).

Expansion valves and restrictors are components used to decrease the working fluid pressure after heat release to the designated heat sink. Its mechanical configuration is greatly simplified compared to the other components in heat pump systems, as its sole purpose is to restrict the working fluid's flow rate as it enters the evaporation stage.

2.1.4. Heat Exchangers

Heat exchangers are used for transfer heat between the working fluid and the available thermal reservoirs. Heat exchangers are typically chosen as one of two types: shell-and-tube heat exchangers and plate-and-fin heat exchangers. Both systems have prominent features and disadvantages in application, and operate as condensers as well as evaporators. The ensuing section gives a brief introduction to heat exchanger design [22]

2.1.4.1 Heat Exchangers Design

- Shell-and-tube use is problematic as the working fluid condenses/evaporates within tubes, which affect its heat transfer abilities. A gas-liquid mixture forms during heat exchange, and complicates control of the heat transfer effects and optimize performance. Superheating the evaporating working fluid (to ensure dry compression) is also problematic, and require some margin in operation. Pressure losses in fluid transport through the thin, long tubes may also be significant, and affect overall system performance.

  Shell-and-tube heat exchangers typically operate with counter-current flow, to facilitate heat transfer with the aforementioned favorable temperature glides. Anothercommon design solution employs tube-side inflow and outflow on only one side of the heat exchanger. But as it prevents counter-current flow, these are often dismissed from heat pump design.

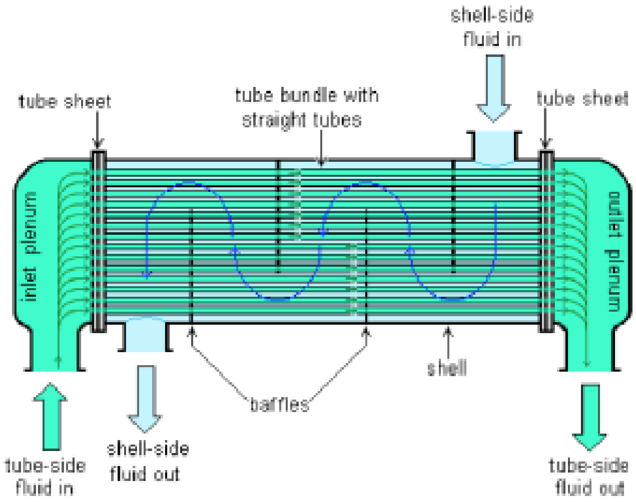

Figure 8: *Shell- and –tube exchanger design*

- Plate-and-fin systems have a compact design and are easily adapted to support the heat pump’s designed performance. Large surface areas between the two sides of the heat exchanger ensure low temperature driving force requirements. They do, however, experience large pressure losses, which affect their overall efficiency during heat transfer. Superheating is, again, problematic to control, and require a certain margin in operation.

  One of the typical example of plate- and- fin heat exchangers is shown on Figure 9.

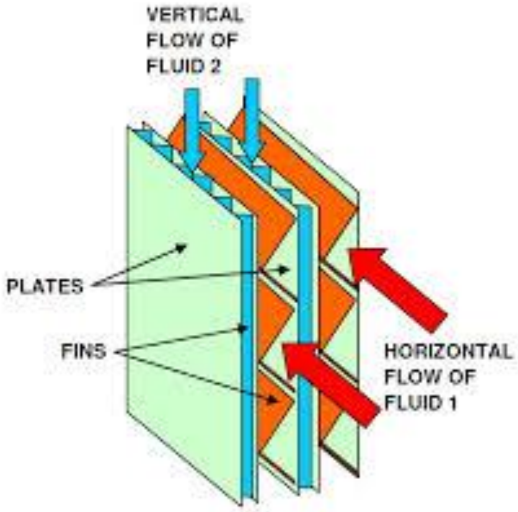

Figure 9.: *Plate- and –fin exchanger design*

Both systems are in theory applicable in heat transfer with air flow as the thermal reservoirs.

2.2. Working Principle

Several types of heat pumps exist, but all heat pumps perform the same three basic functions:

- Receipt of heat from the waste-heat source
- Increase of the waste-heat temperature
- Delivery of the useful heat at the elevated temperature.

One of the more common heat pump types, the mechanical heat pump, will be used to show how these functions work.

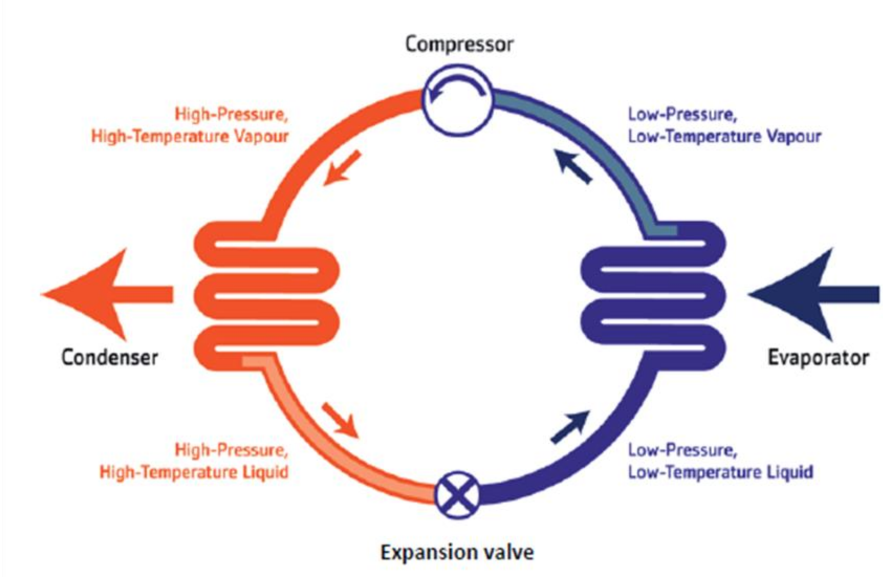

Figure 10. *Working principle of the mechanical heat pump*

As we can see from Figure 10, waste heat is delivered to the heat-pump evaporator in which the heat-pump working fluid is vaporized. The compressor increases the pressure of the working fluid, which in turn increases the condensing temperature. The working fluid condenses in the condenser, delivering high-temperature heat to the process stream that is being heated. A key parameter influencing the savings that a heat pump achieves is the temperature lift realized in the heat pump. Temperature lift is the difference between the evaporator and condenser temperatures [29].

A number of different types of heat pump cycle can be used in industrial applications, the most important being:

- Closed-Cycle Mechanical Heat Pumps
- Open-Cycle Mechanical Vapor Compression (MVC) Heat Pumps
- Open-Cycle Thermocompression Heat Pumps
- Closed-Cycle Absorption Heat

2.2.1. Closed-Cycle Mechanical Heat Pumps

Closed-Cycle Mechanical Heat Pumps use mechanical compression of a working fluid to achieve temperature lift. The working fluid is typically a common refrigerant. Most common mechanical drives are suitable for heat-pump use; examples include electric motors, steam turbines, combustion engines, and combustion turbines.

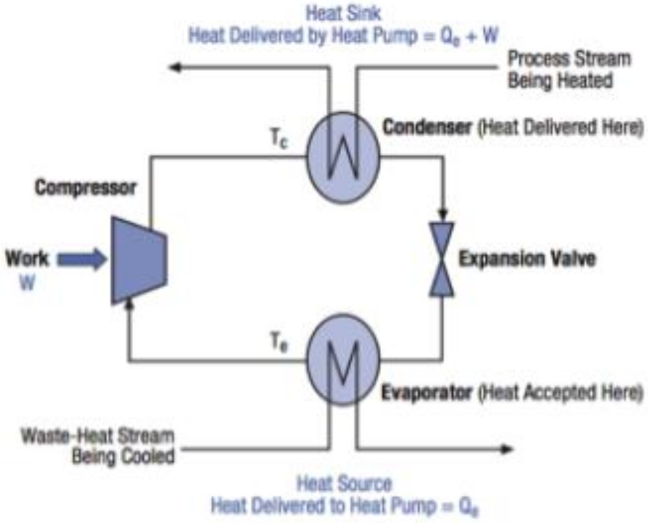

Figure 11: *Closed-Cycle Mechanical Heat Pumps*

The simplest closed-cycle mechanical heat pumps consist of four basic elements: an evaporator, a compressor, a condenser and an expansion valve; as well as a working fluid transferring the heat from the cold to the warm reservoir. Closed-cycle operation refers to recycling of the working fluid, which is a pure component. [29]

As we can see from Figure 11, excess heat is absorbed (isothermally, due to the pure working fluid) from a heat source to vaporize the working fluid in the evaporator, at a low temperature and pressure. A mechanical compressor increases the working fluid’s pressure before it enters the condenser, elevating the vapor’s condensing temperature. Vapor is condensed to deliver useful heat at the heat sink, fulfilling the purpose of the heat pump. Heat release is either isothermal or with a temperature glide, depending on the working fluid’s critical temperature and the condenser temperature. The high-pressure working fluid is finally expanded to the low pressure and temperature required in the evaporator, and the working fluid restart its heat transfer cycle.

2.2.2. Open-Cycle Mechanical Vapor Compression (MVC) Heat Pumps

Open-Cycle Mechanical Vapor Compression (MVC) Heat Pumps use a mechanical compressor to increase the pressure of waste vapor. Typically used in evaporators, the working fluid is water vapor. MVC heat pumps are considered to be open cycle because the working fluid is a process stream. Most common mechanical drives are suitable for heat-pump use; examples include electric motors, steam turbines, combustion engines, and combustion turbines.[29]

2.2.3. Open-Cycle Thermocompression Heat Pumps

Open-Cycle Thermocompression Heat Pumps use energy in high-pressure motive steam toincrease the pressure of waste vapor using a jet-ejector device. Typically used in evaporators, the working fluid is steam. As with the MVC Heat Pump, thermocompression heat pumps are open cycle.

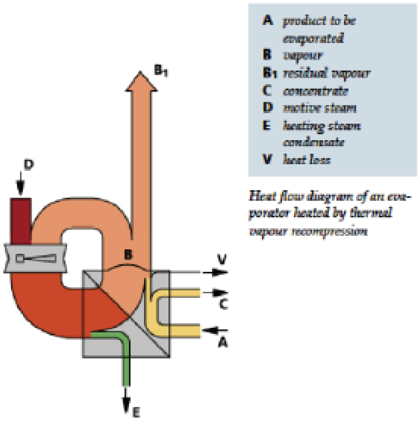

Figure 12: *Operating principle of the open – cycle thermocompression heat pump*

The motive stream and excess vapor process stream mix, and the jet ejector compress the resulting stream to a higher pressure and temperature. The warmer mixture stream is sent to a condenser to recover the useful heat created by this system. Surplus energy extracted in the evaporator corresponds to the energy supplied by the motive stream. Heat transfer is considered to be isothermal, as the mixed stream is close to a pure fluid.[22]

2.2.4. Closed-Cycle Absorption Heat Pumps

Closed-Cycle Absorption Heat Pumps use a two-component working fluid and the principles of boiling-point elevation and heat of absorption to achieve temperature lift and to deliver heat at higher temperatures. The operating principle is the same as that used in steam-heated absorption chillers that use a Lithium Bromide/water mixture as their working fluid. Key features of absorption systems are that they can deliver a much higher temperature lift than the other systems, their energy performance does not decline steeply at higher temperature lift, and they can be customized for combined heating and cooling applications. Four heat exchangers—an evaporator, condenser, generator, and absorber—are found in a typical absorption heat pump. High-temperature prime energy (steam or fuel) is supplied to the desorber, where vapor is boiled out of the working fluid at high pressure. The high-pressure vapor is condensed in the condenser, where the heat is recovered into a process stream. High-pressure condensate from the condenser is throttled to a lower pressure in the evaporator, where the waste heat is recovered to vaporize the low-pressure condensate. In the absorber, concentrated working fluid from the desorber contacts low-pressure vapor from the evaporator, creating heat that is recovered into a process stream. The working fluid returns to the desorber to complete the cycle.

In a typical absorption heat-pumping application, waste heat at low temperature is delivered to the evaporator, and prime heat at high temperature is delivered to the generator. An amount of heat equivalent to the sum of the high- and low-temperature heat inputs can be recovered at an intermediate temperature via the condenser and absorber. This is analogous to the thermocompression heat pump, in which high-pressure steam is used to increase or lift low-pressure waste vapor to a higher pressure and temperature. However, in the case of the high-lift absorption heat pump, the temperature lift can be 200 to 300° F, rather than the 20 to 50° F of the thermocompression system.[29]

An important variation of the Type-1 Absorption Heat Pump is obtained by selecting operating parameters so that the device effects chilling at the 'cold-end' of the cycle while delivering hot water. The ability to provide simultaneous cooling and heating provides additional benefits over a 'heatingonly' heat pump and improves the economics of an installation. An alternate configuration for an absorption heat pump allows a medium-temperature waste-heat stream to split into one higher-temperature stream and one lower-temperature stream. Adjusting the operating pressures and working-fluid concentrations accomplishes this reconfiguration.

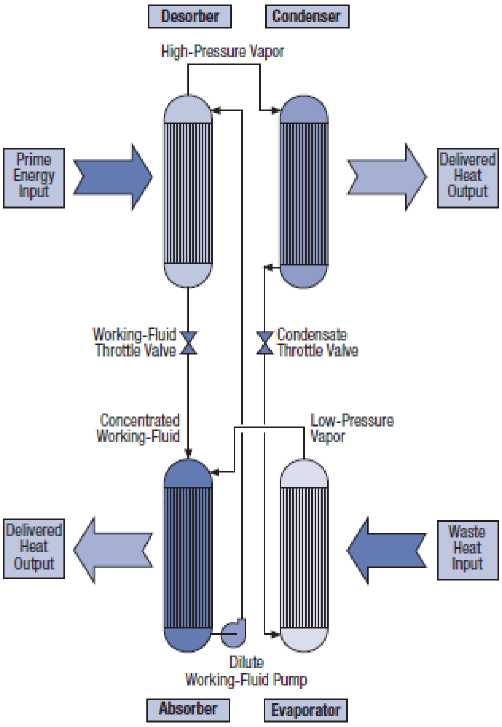

Figure 13.: *Simplified Schematic of an Absorption Heat Pump*

2.3. Aplications and Heat Pump Types

Table 2 provides a representative overview of heat-pump applications in industrial processes. The table is not comprehensive, but highlights the most common industrial applications and heatpump types.[22]

Table 2: *Representative Overview of Heat-Pump Applications in Industrial Manufacturin Activities*

Industry	Manufacturing Activity	Process	Heat-Pump Type
Petroleum Refining and Petrochemicals	Distillation of petreleum and petrochemical products	Seperation of propane/propylene,butane/butylene and ethane/ethylene	Mechanical Vapor Compression,Open cycle
Chemicals	Inorganic salt manufacture including salt sodum carbonate,boric acld	Concentration of product salt solutions	Mechanical Vapor Compression,Open cycle
	Treatment of process efiuent	Concentration of waste streams to reduce hydraulic load on waste treatment facitlles	Mechanical Vapor Compression,Open cycle
	Heat recovery	Compression of low-pressure waste steam or vapor for use as a heating medium	Mechanical Vapor Compression,Open cycle
	Pharmaceuticals	Process water heating	Mechanical Compression,Open cycle
Wood Products	Pulp manufacturing	Concentration of black liquor	Mechanical Vapor Compression,Open cycle
	Paper manufacturing	Process water heating	Mechanical Vapor Compression,Open cycle
	Paper manufacturing	Flash-steam recovery	Thermocompression,Open cycle
	Lumber manufacturing	Product drying	Mechanical Vapor Compression,Open cycle
Food and Beverage	Manufacturing of alcohol	Concentration of waste liqulds	Mechanical Vapor Compression,Open cycle
	Beer breving	Concentration of waste beer	Mechanical Vapor Compression,Open cycle
	Wet com milling/corn syrup manufacturing	Concentration of steep water and syrup	Mechanical Vapor Compression,Open cycle Thermocompression,O

			pen cycle
	Sugar refining	Concentration of sugar solution	Mechanical Vapor Compression,Open cycle Thermocompression,Open cycle
	Dairy products	Concentration of milk and of whey	Mechanical Vapor Compression,Open cycle Thermocompression,Open cycle
	Juice manufacturing	Juice concentration	Mechanical Vapor Compression,Open cycle
	General food-product manafacturing	Heating of process and cleaning water	Mechanical Compression,Closed cycle
	Soft drink manafacturing	Concentration of effluent	Mechanical Compression,Closed cycle
Utitles	Nuclear power	Concentration of radioactive waste	Mechanical Vapor Compression,Open cycle
		Concentration of cooling tower blowdown	Mechanical Vapor Compression,Open cycle
Miscellaneous	Manufacturing of drinking water	Desalination of sea water	Mechanical Vapor Compression,Open cycle
	Steam-stripping of waste water or process streams	Flash steam recovery	Thermocompression,Open cycle
	Electroplating Industries	Heating of process solutions	Mechanical Compression,Open cycle
		Concentration of effluent	Mechanical Vapor Compression,Open cycle
	Textiles	Process and wash-water heating	Mechanical Compression,Closed cycle
		Space heating	Mechanical Compression,Closed cycle
		Concentration of dllute	Mechanical

		dope stream	Compression,Closed cycle
	General manufacturing	Process and wash-water heating	Mechanical Compression,Closed cycle
		Space heating	Mechanical Compression,Closed cycle
	District heating	Large-scale apace heating	Mechanical Compression,Absorption Closed cycle
	Solvent recovery	Removal of solvent from air streams	Mechanical Compression,Open cycle

3. Working Fluids in Industrial Heat Pump Systems

3.1. Refrigerant definition

A refrigerant is a substance, usually a fluid, used in a heat pump and refrigeration cycle. In most cycles it undergoes phase transitions from a liquid to a gas and back again. Many working fluids have been used for such purposes. Fluorocarbons, especially chlorofluorocarbons, became commonplace in the 20th century, but they are being phased out because of their ozone depletion effects. Other common refrigerants used in various applications are ammonia, sulfur dioxide, and non-halogenated hydrocarbons such as propane.

The choice of the working fluid for this high temperature heat pump should takes into account several considerations like environmental, economical, safety, efficiency, thermodynamic properties. In general, synthetic refrigerants (R134a, R245fa, R1234yf …) dominate vapor compression refrigeration systems.

Table 3 presents the selection of working fluids for industrial heat pumps.

Table 3: *Selection of most common working fluids for industrial heat pumps*

Refrigerant	Maximum Sink temperature	Minimum Source temperature	GWP	Toxicity	Flamability
R245fa	140°C	15°	950	yes	no
R600a(Isobutane)	140°C	0°C	>1	no	high
R717(Ammonia)	110°C	-30°C	0	yes	medium
DR-2	160°C	35°C	9,4	no	no
SES36	160°C	35°C	low	n/a	n/a
R744 (CO_2)	130°C	About – 10 °C	1	no	no

Table 3 shows some of the most important refrigerant properties as GWP, toxicity, flamability etc. Other important working fluid requirements are:

- High critical temperature
- Low pressure range
- no ozone depletion potential (ODP)
- low global warming potential (GWP)
- not flamable
- not toxic etc.

3.2. Working fluid types

Traditionally, the most common working fluids for heat pumps have been:

- CFC-12 Low- and medium temperature (max. 80°C);
- CFC-114 High temperature (max. 120°C);
- R-500 Medium temperature (max. 80°C);
- R-502 Low-medium temperature (max. 55°C);
- HCFC-22 Virtually all reversible and low-temperature heat pumps (max. 55°C).

Due to their chlorine content and chemical stability, CFCs (Chlorofluorocarbons) are harmful to the global environment. They have both a high ozone depletion potential (ODP) and a global warming potential (GWP). Environmental effects can also be represented with the Total Equivalent Warming Impact (TEWI) concept to determine the overall contribution of CFC alternatives to global warming. TEWI is the sum of the direct contribution of greenhouse gases used tomake or operate the systems and the indirect contribution of the carbon dioxide emissions resulting from the energy required to run the systems over their normal lifetime.

3.2.1. CFCs

CFCs belong to the group of prohibited refrigerants. Due to their high ozone depletion potential the manufacture of these refrigerants, and their use in new plants, is now banned although they are still permitted in existing plants. However, only purified (recycled) refrigerants from decommissioned and retrofitted plants are available. It is therefore expected that these refrigerants will become more and more expensive, and at some point will no longer be available. This group includes the following refrigerants: R-11, R-12, R-13, R-113, R-114, R-115, R-500, R-502, R-13B1.

As a general requirement, heat pumps using alternative working fluids should have at least the same reliability and cost effectiveness as (H) CFC systems. Moreover, the energy efficiency of the systems should be maintained or be even higher, in order to make heat pumps an interesting energy-saving alternative. In addition to finding new and environmentally acceptable working fluids, it is also important to modify or redesign the heat pumps. Generally speaking, the energy efficiency of a heat pump system depends more on the heat pump and system design than on the working fluid.

3.2.2. HCFCs

HCFC (hydrochlorofluorocarbons) working fluids also contain chlorine, but they have much lower ODP (ozone depletion potential) than CFCs, typically 2-5% of CFC-12, due to a lower atmospheric chemical stability. The GWP (global warming potential) is typically 20% of that of CFC-12. H-CFCs are so-called transitional refrigerants. They should only be used for retrofit applications. H-CFCs include R-22, R-401, R-402, R-403, R-408 and R-409. Table 4 shows the phase-out schedule of CFCs and HCFCs for industrialised countries, which was agreed under the Montreal Protocol and its amendments and adjustments. HCFCs should be phased out for industrialised countries by the year 2020, and should be phased out entirely by 2040. The European Union has adopted an accelerated phase-out schedule for these substances, which requires them to be phased out by January 2015.

Table 4. *Phase – out schedule for HCFCs and CFCs for developed countries*

Date	Control Measure
1 January 1996	CFCs phased out (1) HCFCs frozen at 1989 levels of HCFC + 2.8% of 1989 consumption of CFCs (base level)
1 January 2004	HCFCs reduced by 35% below base levels
1 January 2010	HCFCs reduced by 65%
1 January 2015	HCFCs reduced by 90%

3.2.3. HFCs

HFCs (hydrofluorocarbons) can be considered long-term alternative refrigerants. This means that they are chlorine-free refrigerants such as R-134a, R-152a, R-32, R-125and R-507. Since they do not contribute to ozone depletion, these are long-term alternatives to R-12, R-22 and R-502. However, they do still contribute to global warming. Special attention must be given to the use of lubricants. Mineral oils are non-miscible with these refrigerants. Normally only ester-based lubricant oils recommended by the refrigerant manufacturer should be used. Mineral oil residues must be completely removed during retrofitting.

- **HFC-134a** is quite similar to CFC-12 in thermophysical properties. The coefficient of performance (COP) of a heat pump with HFC-134a will be practically the same as for CFC-12. At low evaporating temperatures (below -1°C) and/or high temperature lifts the COP will be slightly lower.
- **HFC-152a** has mainly been used as a part of R-500, but it has also been successfully applied in a number of small heat pump systems and domestic refrigerators. HFC-152a is currently applied as a component in blends. Because of its flammability, it should only be used as a pure working fluid in small systems with low working fluid charge (see also Hydrocarbons).
- **HFC-32** is moderately flammable and has a GWP close to zero. It is considered as a suitable long-term replacement for HCFC-22 in space-conditioning, heat pump and industrial refrigeration applications. Due to its flammability, HFC-32 is usually applied as a main component in non-flammable mixtures replacing R-502 and HCFC-22.

- **HFC-125 and HFC-143a** have properties fairly similar to R-502 and HCFC-22. They are mainly applied as components in ternary mixtures replacing R-502 and HCFC-22. The GWPs are, however, about three times as high as that of HFC-134a.

3.2.4. Blends

Blends or mixtures represent an important possibility for replacement of CFCs, both for retrofit and new applications. A blend consists of two or more pure working fluids, and can be zeotropic, azeotropic or near-azeotropic. Azeotropic mixtures evaporate and condense at a constant temperature, the others over a certain temperature range (temperature glide). The temperature glide can be utilised to enhance performance, but this requires equipment modification. The advantage of blends is that they can be custom-made to fit particular needs.

Early blends for replacement of CFC-12 and R-502 all contained HCFC-22 and/or other HCFC working fluids, such as HCFC-124 and HCFC-142b, and are therefore considered as transitional or medium-term working fluids.

The new generation of blends for replacement of R-502 and HCFC-22 are chlorine-free, and will mainly be made from HFCs (HFC-32, HFC-125, HFC-134a, HFC143a) and hydrocarbons (e.g. propane). Two of the most promising alternative working fluids for eventually replacing R-22 in heat pumping applications are the blends R-410A and R407-C, that are discussed below in more detail. The main difference between the two is the chemical composition: R-410A is a mixture of R-32 and R-125 with minimal temperature glide, while R-407C consists of R-32, R-125 and R-134A and has a large temperature glide.

Annex 18 of the IEA Heat Pump Programme has performed a detailed study on thermophysical properties of blends.

- **R-407C** is the only refrigerant available for immediate use in existing R-22 plants Ð thermal properties and operating conditions are close to those of R-22. However, because of its temperature glide it is only suitable for certain systems. The use of this refrigerant is increasing, although there are still some engineering difficulties for service companies and manufacturers.
- Research has shown that the use of **R-410A** can result in an improved COP compared to R-22. Using R-410A means that overall cost reductions can be achieved, because the system components, particularly the compressor, can be significantly downsized since it has a higher volumetric capacity. The main disadvantage is the higher operating pressure compared to R-22, which indicates that the pressure-proof design of most components should be reviewed. R-410A is very popular, mainly in the US and Japan, for packaged heat pumps and air-conditioning units. Commercial R-410A components for small- and medium-sized refrigeration systems are either already available or under development.

3.2.5. Natural working fluids

New heat pump developments have focused on implementing natural working fluids (molecular structures existing in the biosphere), to eliminate and/or minimize system ODP and GWP to near-zero levels.[53]

Natural working fluids are substances, naturally existing in the biosphere. They generally have negligible global environmental drawbacks (zero or near-zero ODP and GWP). They are therefore long-term alternatives to the CFCs. Examples of natural working fluids are ammonia (NH3), hydrocarbons (e.g. propane), carbon dioxide (CO2), air and water. Some of the natural working fluids are flammable or toxic. The safety implications of using such fluids may require specific system design and suitable operating and maintenance routines.

- **Ammonia** (NH3) is in many countries the leading working fluid in medium- and large refrigeration and cold storage plants. Codes, regulations and legislation have been developed mainly to deal with the toxic and to some extent, the flammable characteristics of ammonia. Thermodynamically and economically ammonia is an excellent alternative to CFCs and HCFC-22 in new heat pump equipment. It has so far only been used in large heat pump systems, and high-pressure compressors have raised the maximum achievable condensing temperature from 58°C to 78°C . Ammonia can also be considered in small systems, the largest part of the heat pump market. In small systems the safety aspects can be handled by using equipment with low working fluid charge and measures such as indirect distribution systems (brine systems), gas-tight rooms or casing, and fail-safe ventilation. Copper is not compatible with ammonia, so that all components must be made of steel. Ammonia is not yet used in high-temperature industrial heat pumps because there are currently no suitable high-pressure compressors available (40 bar maximum). If efficient high-pressure compressors are developed, ammonia will be an excellent high-temperature working fluid.

- **Hydrocarbons** (HCs) are well known flammable working fluids with favourable thermodynamic properties and material compatibility. Presently, propane, propylene and blends of propane, butane, iso-butane and ethane are regarded as the most promising hydrocarbon working fluids in heat pumping systems. HCs are widely used in the petroleum industry, sporadically applied in transport refrigeration, domestic refrigerators/freezers and residential heat pumps (notably in Europe). Due to the high flammability, hydrocarbons should only be retrofitted and applied in systems with low working fluid charge. To ensure necessary safety during operation and service, precautions should be taken such as proper placing and/or enclosure of the heat pump, fail-safe ventilation systems, addition of tracer gas to the working fluid, use of gas detectors etc.

Hydrocarbon working fluids are based on the short-chained HC molecules, which have favorable thermodynamic properties for high temperature application in heat pump systems. Butane and isobutane are particularly interesting, with critical temperatures of 136 °C and 151°C, respectively. This enables high operational temperatures with the traditional mechanical compression systems. System pressures are tolerable at these temperatures, rendering the heat pump components readily available.However, the chosen components must be designed and implemented with care.

- **Water** is an excellent working fluid for high-temperature industrial heat pumps due to its favourable thermodynamic properties and the fact that it is neither flammable nor toxic. Water has mainly been used as a working fluid in open and semi-open MVR systems, but there are also a few closed-cycle compression heat pumps with water as working fluid. Typical operating temperatures are in the range from 80°C to 150°C. 300°C has been achieved in a test plant in Japan, and there is a growing interest in utilising water as a working fluid, especially for high-temperature applications. The major disadvantage with water as a working fluid is that the low volumetric heat capacity (kJ/m3) of water. This requires large and expensive compressors, especially at low temperatures.

- **CO2** is a potentially strong refrigerant that is attracting growing attention from all over the world. CO2 is non-toxic, non-flammable and is compatible to normal lubricants and common construction materials. The volumetric refrigeration capacity is high and the pressure ratio is greatly reduced. However, the theoretical COP of a conventional heat pumping cycle with CO2 is rather poor, and effective application of this fluid depends on the development of suitable methods to achieve a competitively low power consumption during operation near and above the critical point. CO2 products are still under development, and research continues to improve systems and components. CO2 is now being used as a secondary refrigerant in cascade systems for commercial refrigeration.

4. Working fluid selection and energy efficiency

4.1. Methods

In this work six working fluids, R123, R134a, R245fa, R600a, R600 and R290, were selected and compared in order to identify suitable working fluids which may yield high system efficiencies.

4.2. Results

The calculated results show that because of high system pressure for R290 and R134a, R600a is the more suitable working fluid in terms of expander size parameter, system efficiency and system pressure. R600a is also the most appropriate working fluid in terms of pressure ratio and coefficient of performance. R600 and R600a are more suitable working in terms of overall coefficient of performance and refrigerating capacity per unit mass flow rate.

4.3. Conclusions:

In sum, R600a is the most suitable working fluid for those systems, through comprehensive comparison of efficiency, expander size parameter, pressure ratio, coefficient of performance and system pressure for six different working fluids. However, the flammability of R600a should attract enough attention.

4.4. System design and working fluid selection

As we already said there are several different solutions to heat pump technology, but all are based on the three basic steps of operation described below:

1. Recovery of (excess/waste) heat from a heat source; *QC*

2. Increase of temperature by work input; *Wnet*
3. Delivery of (useful) heat at elevated temperature to a heat sink; *QH*[7]

as shown in Figure 14.

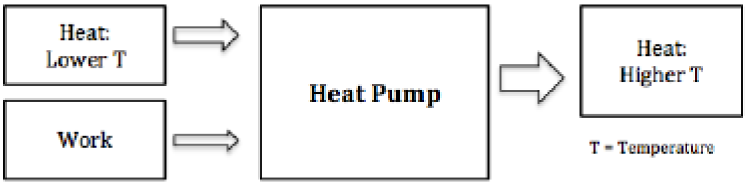

Figure 14: *Operating principle of the heat pump*

Here we are considering mechanical heat pumps shown on Figure 14.
Working principle of this system is as follows: As we can see , excess heat is absorbed (isothermally, due to the pure working fluid) from a heat source to vaporize the working fluid in the evaporator, at a low temperature and pressure. A mechanical compressor increases the working fluid's pressure before it enters the condenser, elevating the vapor's condensing temperature. Vapor is condensed to deliver useful heat at the heat sink, fulfilling the purpose of the heat pump. Heat release is either isothermal or with a temperature glide, depending on the working fluid's critical temperature and the condenser temperature. The high-pressure working fluid is finally expanded to the low pressure and temperature required in the evaporator, and the working fluid restart its heat transfer cycle.

To adapt the instability of heat source and coolant, the radial and axial flow expander is employed. To improve the drive efficiency, the compressor and the expander are directly coupled on the same shaft without gear and coupling.

The common refrigerants HCFC (R123) and HFCs (R134a and R245fa) are selected as the working fluids for the system. However, this work is rectricted only on natural fluids and with increased environmental awareness, these refrigerants are now being regulated. It is well known that the HCs are environmentally friendly, non-toxic, chemically stable and highly soluble in conventional mineral oil. The only real argument against the application of HCs is flammability. So, the HCs, such as butane (R600), isobutene (R600a) and propane (R290) are also selected as the working fluids.

Properties of six selected working fluids are shown in Table 5.

Table 5: *Properties of Working fluids*

Substance	**Molecular mass [g/mol]**	**T_{cr} [° C]**	**ODP**	**GWP [100 years]**
R290	44.10	96.68	0	3
R600	58.13	151.98	0	20
R600a	58.13	134.67	0	20
R123	152.93	183.68	0.012	76
R245fa	134	154.05	0	820
R135a	102.03	101.1	0	1,320

4.5. Thermodynamic model

To develop the thermodynamic model, the following assumptions are made:

1. Friction and heat losses in the heat pump cycle are negligible.
2. The power consumed by condensers is negligible.

$$W_{com} = W_{exp} \tag{1}$$

$$Q_{eva} = m_{ic}\,(h_6 - h_5) \tag{2}$$

$$W_{com} = m_{ic}\,\frac{(h_{7s} - h_6)}{\eta_{com}} \tag{3}$$

$$COP = \frac{Q_{eva}}{W_{com}} \tag{4}$$

$$PR = \frac{P_7}{P_6} \tag{5}$$

$$CRPR = \frac{COP}{PR} \tag{6}$$

The overal performance of system is defined as follows:

$$COP_s = \eta_p\, COP_c \tag{7}$$

$$\mathrm{m_N} = \frac{\mathrm{Q_{eva}}}{\mathrm{C_P(T_{N1} - T_{N2})}} \tag{8}$$

$$N = \frac{m_N}{m_h}\ x\ 1000 \tag{9}$$

$$CPRm_h = \frac{\mathrm{Q_{eva}}}{\mathrm{m_p + m_i c}} \tag{10}$$

4.6. Results and discussions

The temperature of surplus heat at the generator inlet, Th, is in the range of 70°C to 95°C, and the condensation temperature is respectively equal to 35°C, 40°C and 45°C. For the sake of simplification, the mass flow rate of the working fluid is 1 kg/s. The evaporation temperature is 5°C and remains invariable, The isentropic efficiencies for the expander, compressor and working fluid pump are 0.85, 0.8 and 0.9,respectively.

4.6.1. Effect of working fluid types

The condensation temperature varies with ambient. Table 6 shows the effects of Tc and working fluid types on COPc, PR and CRPR. In Table 6, Th equals 85°C. As shown in Table 2, COPc, PR and CRPR depend largely on Tc, COPc and CRPR decrease with Tc, and PR increases with Tc. This is due to the fact that when the pressure and temperature remain invariable at the compressor inlet, the increasing Tc leads to the increase of pressure and enthalpy at the compressor outlet and thus the increase of PR and the decrease of COPc as well as CRPR according to Equations 2 to 6.

Table 6: *Performance of cyclus with different* T_C

Fluid Type	T_{cr} [° C]	COP	PR	CRPR	N[kg /t]
R123	35	6,41	3,20	2,oo	1.366,7
R123	40	5,36	3,78	1,42	893,32
R123	45	4,56	4,45	1,02	575,81
R134a	35	5,30	2,54	2,09	1.475,9
R134a	40	4,46	2,91	1,53	1.005,8

R134a	45	3,58	3,32	1,08	618,99
R245fa	35	6,10	3,20	1,91	1.364,8
R245fa	40	5.05	3,78	1,43	887,59
R245fa	45	4,27	4,45	0,96	568,8
R600a	35	5,77	2,49	2,32	1.402,9
R600a	40	4,76	2,85	1,67	911,84
R600a	45	3,99	3,24	1,23	583,79
R600	35	6,03	2,64	2,28	1.385,8
R600	40	5,00	3,05	1.64	902,63
R600	45	4,22	3,49	1,21	579,49
R290	35	3,41	3,00	1,14	1.020,2
R290	40	2,87	3,37	0,85	689,69
R290	45	2,43	3,78	0,64	455.06

It is obvious from Table 6 that R123 has the maximum COPc while R290 has the minimum COPc. PR for R123 and R245fa are almost the same and they are greater than those for the four other working fluids. PR for R600a is the lowest among the six selected working fluids. It is well known that working fluids with high COPc and low PR are suitable refrigerants. To evaluate working fluid refrigeration performance and the relationships between COPc and PR, CRPR is hence defined as the ratio of COPc to PR, which is an indicator of working fluid refrigeration performance. Higher CRPR indicates better refrigeration performance for working fluids. R600a has the maximum CRPR compared with the five other working fluids, followed by R600, as shown in Table 6.

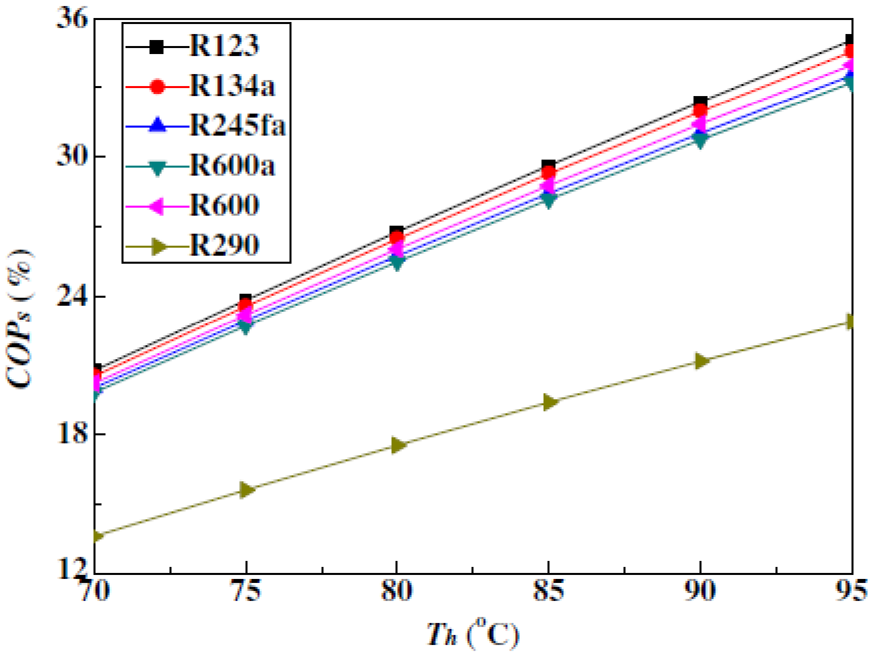

Figure 15.: *Effect of T_h on COP_s*

Figure 15 illustrates the variation of COPs as a function of Th. In Figure 15, with the increase of Th, COPs increases for all working fluids. COPs equals the product of ηp and COPc. ηp for R123 is the lowest among the six working fluids, as shown in Figure 2, and COPc is however highest for R123 among the six working fluids in Table 6; as a result, the product of ηp and COPc is highest. As evident in Figure 15, R123 has the highest COPs and R290 has the lowest COPs for all heat source temperatures. Except R290, the differences between COPs for the five other working fluids are very small.

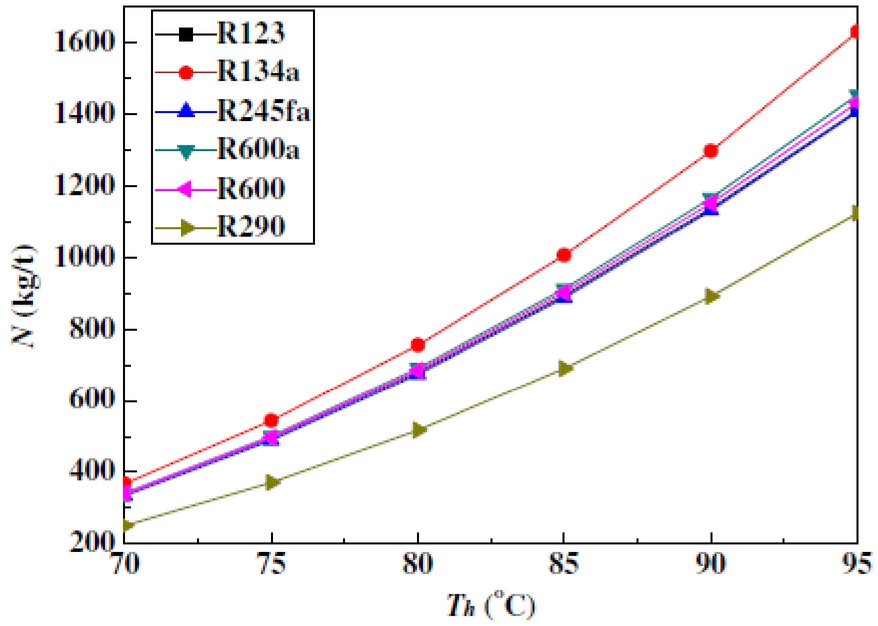

Figure 16.: *Effect of T_h on N*

According to the comprehensive comparison of COPc, PR and CRPR for the six different working fluids, it is clear that R600a is the most suitable working fluid for such systems.

To prove this we can make one more check. This time we are going to consider only R600 and R600a. Cycle characteristics of those fluids are shown in following figures.

Evaporation temperatures are in range from 35°C to 60°C. Effect of evaporation temperature on COP is shown in Figure 17.

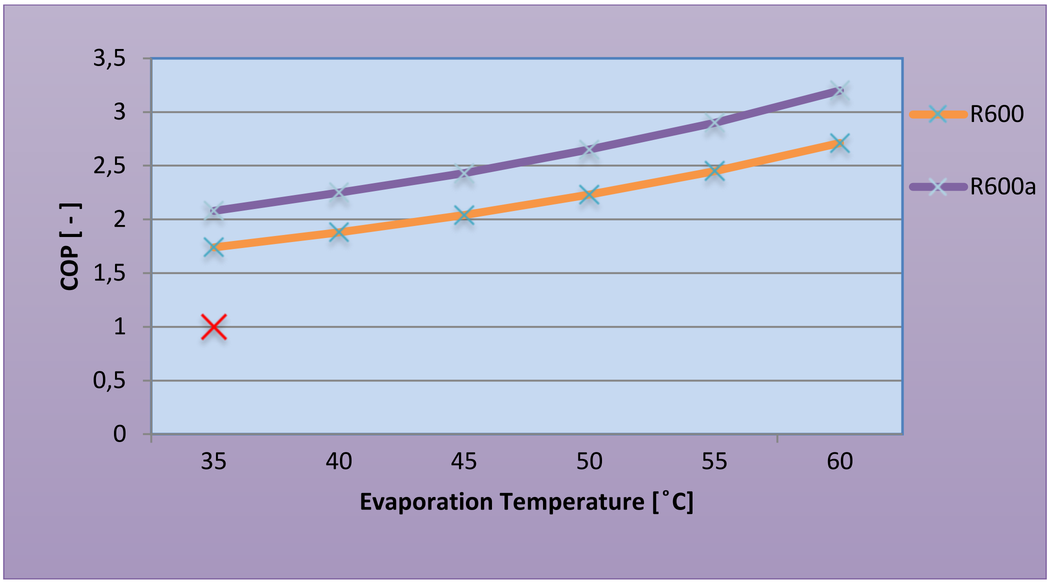

Figure 17.: *Effect of evaporation temperature on COP*

From the other side we can consider effect of condensing temperature on COP . The result is shown on Figure 18.

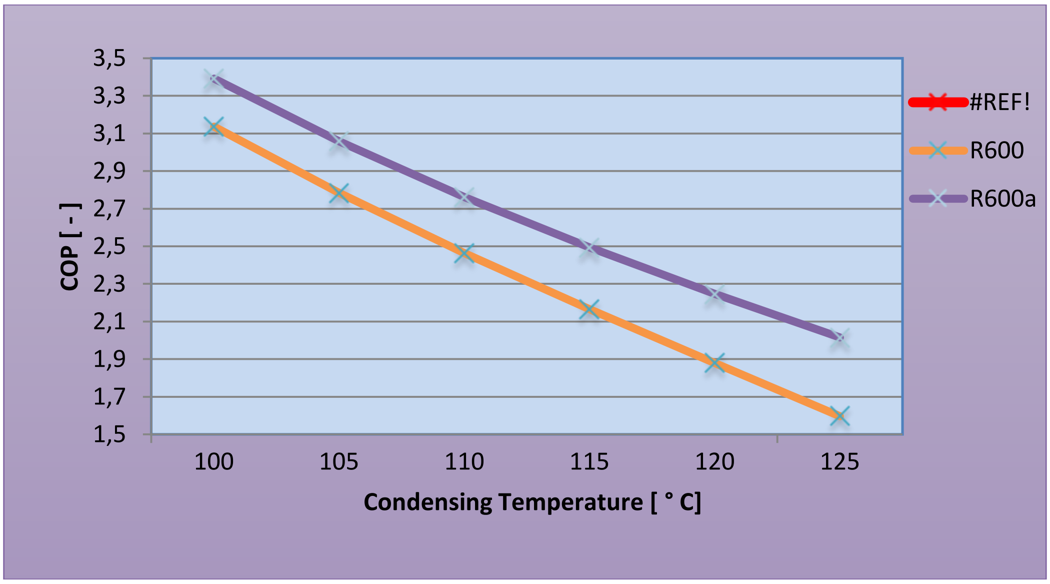

Figure 18.: *Effect of condensing temperature on COP*

As we can see from figures 17 and 18, COP is higher for R600a then for R600 in both cases .

5. Conclusion

This thesis has shown that High temperature heat pumps are very close to be integrated in every industrial process where the surplus heat exist.

Like every other process components, high energy heat pumps has some presents advantages and disadvantages.

Present disadvantages are:

- Lack of the refrigerants in the interesting temperature rang
- Lack of experimental and demonstration plants
- Lack of necessary knowledge of heat pump technology and aplication of designers and consulting engineers.

On the other hand in comparison to heat pump for space heating there is a lot of advantages:

- Long annual operating time
- Waste heat production and heat demand occur at the same time
- Relatively low investment costs, due to large units ona small distance between heat source and heat sink
- High coefficient of performance (COP) due to low temperature lift and /or high temperature levels.

Further work should be focused on refrigerants.

Natural refrigerants are a focal point in heat pump development, to accommodateemission restrictions and increased environmental awareness.Application of industrial heat pumps for high temperature heat recovery is a highly complex task, which requires extensive analytical work, experimental work andmarket research to be completed successfully. This thesis aims at identifying themost prominent restrictions, and appoints available heat pumps which challengethese restrictions. Suitable working fluids must be appointed to pursue further examination.

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