CO_2 as a working fluid

Prof. Dr.-Ing. Armin Hafner
Professor Refrigeration Technology
NTNU, EPT
7491 Trondheim
Norway

Part A

1. CO_2 – A historic perspective
2. Properties of CO_2
3. The transcritical CO_2 cycle
4. Examples of CO_2 systems

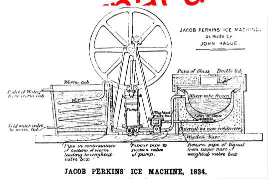
1. CO_2 – A historic perspective

Prof. Dr.-Ing. Armin Hafner
Professor Refrigeration Technology
NTNU, EPT
7491 Trondheim
Norway

Inventors and pioneers of mechanical refrigeration

Vapour compression cycle:

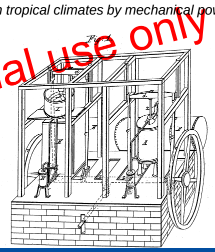
- ***Oliver Evans*** (1755-1819), USA
  "*The Abortion of the Young Steam Engineer's Guide*", 1805
- ***Jacob Perkins*** (1766-1849), American living in London
  British Patent No 6662, 14. August 1834
  Machine applying sulphur-ether, build by ***John Hague***.



Inventors and pioneers of mechanical refrigeration

Air cycle:

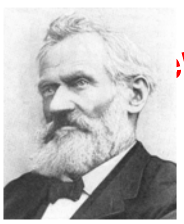
- ***John Gorrie*** (1802-1855), Florida, USA
  "An engine for ventilation and cooling air in tropical climates by mechanical power" 1842-1844



Inventors and pioneers of mechanical refrigeration

Absorption cycle:

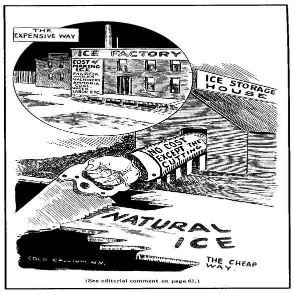
- ***Ferdinand Carré*** (1824-1900), France
  Patent NH_3/H_2O absorption system in 1859



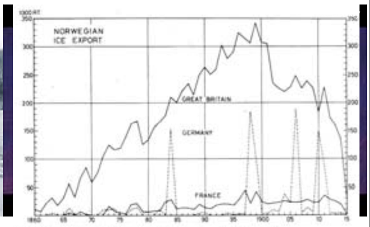
Three important 'drivers' in the late 19th century

Factors pushing the development of mechanical refrigeration technology from 1850 →

- "Artificial" ice production
- Brewing of beer (all year long)
- Transport of meat



150 years ago: ICE = refrigeration



Norwegian Ice Export from 1860 to 1915

Natural working fluids also common in the US:

Advertisement in ICE and REFRIGERATION, 1922, vol. 63

Three important 'drivers' in the late 19th century

Factors pushing the development of mechanical refrigeration technology from 1850 →

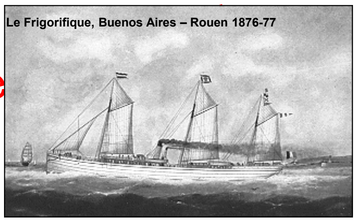
- "Artificial" ice production
- Brewing of beer (all year long)
- Transport of meat

Three important 'drivers' in the late 19th century

Factors pushing the development of mechanical refrigeration technology from 1850 →

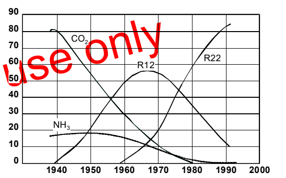
- "Artificial" ice production
- Brewing of beer (all year long)
- Transport of meat

Le Frigorifique, Buenos Aires – Rouen 1876-77



Why CO_2 disappeared in the early/mid 20th century?

- Leading within the industry (along with NH_3) until the 1940s
- Surpassed by synthetic CFCs and HCFCs (R-12, R-22) in the 1950-60s due to
  - Problems with leaks
  - Reduced cooling capacity at elevated heat rejection temperatures
  - Cold cooling water not available everywhere (especially USA)
  - Development and offensive marketing of CFC's ("Freon")
  - Opinion that high working pressures are a problem
  - Missing production- and material-technology
  - The safety standards and laws reduced the motivation to apply CO2 in the US more than in Europe.
  - 1. world war in Europe

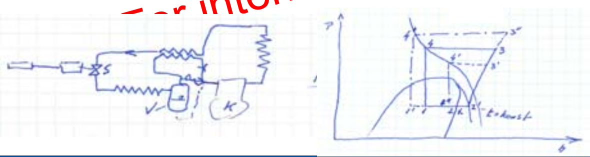


Percentage application of working fluids for ship refrigeration cold stores verified by Lloyd's from Stera (1992)

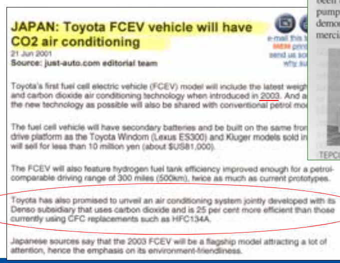
Rediscovered as a working fluid in the 1980s by professor Gustav Lorentzen (1915-1995)

First draft made for a patent application on how to operate and control transcritical CO_2- vapour compression systems

November 1988



CO_2 is back!



JAPAN: Toyota FCEV vehicle will have CO2 air conditioning

21 Jun 2001

Source: just-auto.com editorial team

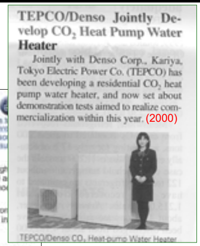
Toyota's first fuel cell electric vehicle (FCEV) model will include the latest weigh[…] and carbon dioxide air conditioning technology when introduced in 2003. And a[…] the new technology as possible will also be shared with conventional petrol mo[…]

The fuel cell vehicle will have secondary batteries and be built on the same fro[…] drive platform as the Toyota Windom (Lexus ES300) and Kluger models sold in[…] will sell for less than 10 million yen (about $US81,000).

The FCEV will also feature hydrogen fuel tank efficiency improved enough for a petrol-comparable driving range of 300 miles (500km), twice as much as current prototypes.

Toyota has also promised to unveil an air conditioning system jointly developed with its Denso subsidiary that uses carbon dioxide and is 25 per cent more efficient than those currently using CFC replacements such as HFC134A.

Japanese sources say that the 2003 FCEV will be a flagship model attracting a lot of attention, hence the emphasis on its environment-friendliness.



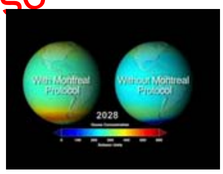
TEPCO/Denso Jointly Develop CO_2 Heat Pump Water Heater

Jointly with Denso Corp., Kariya, Tokyo Electric Power Co. (TEPCO) has been developing a residential CO_2 heat pump water heater, and now set about demonstration tests aimed to realize commercialization within this year. (2000)

TEPCO/Denso CO_2 Heat-pump Water Heater

Restricted use of synthetic working fluids

- CFC/HCFCs cause ozone depletion (Montreal protocol, 1987)
- HFCs induce green house effects (Kyoto protocol 1997, EU F-gas regulation 2006/2014)
- Strong position for natural working fluids



NTNU

2. Properties of CO_2

Prof. Dr.-Ing. Armin Hafner
Professor Refrigeration Technology
NTNU, EPT
7491 Trondheim
Norway

Content

- CO_2 in a HSE perspective
- Fundamental fluid properties
- Significance of low critical temperature
- Significance of high pressure in the triple point
- Consequences of high operational pressure
- Heat transfer properties of CO_2
- Volumetric expansion coefficient for CO_2 in liquid state

CO_2 in a HSE perspective

- CO_2 is **not acutely toxic** at low concentrations. Bodily reactions (difficulties breathing, increased pulse, headache, etc.) appear when the concentration exceeds 2-3 %. Concentrations above 10 % can be lethal.
- Similar to the traditional high GWP*-HFCs, **CO_2 has the ASHRAE safety classification A1** (non-flammable, non-toxic).
- High operational pressure (up to 130 bar).
- Dry ice formation can appear at pressures < 5.2 bar (triple point pressure), which can block valves and pipes. Important with sufficient routines regarding refilling and service of CO_2 systems.
- Dry ice at atmospheric pressure is very cold (~ -78 ℃) and can cause:
  - Brittle fractures in equipment
  - Frostbite injury

* GWP = global warming potential

CO_2 in a HSE perspective

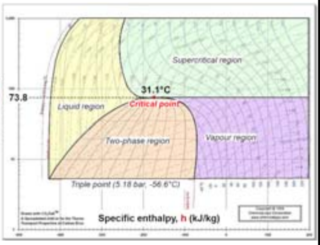
- CO_2 is a natural and environmentally friendly working fluid: GWP = 1 (0)*, ODP = 0

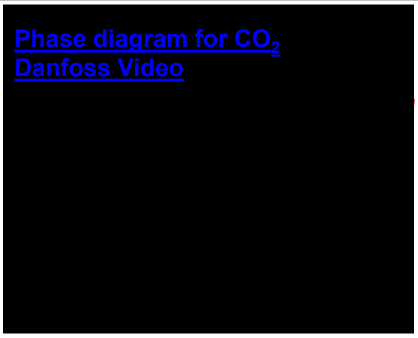
Refrigerant	Component(s)	Classification	Concentration limit kg/m³	GWP
R-744	Carbon dioxide	A1	0.1	1
R-22	Chlorodifluoromethane	A1	0.3	1810
R-23	Trifluoromethane	A1	0.68	14800
R-125	Pentafluoroethane	A1	0.37	3500
R-134a	Tetrafluoroethane	A1	0.21	1430
R-404A	R-125/R-143A/R-134a	A1	0.52	3920
R-407C	R-32/R-125/R-134a	A1	0.31	1770
R-407F	R-32/R-125/R-134a	A1	0.32	1820
R-408A	R-125/R-143a/R-22	A1	0.41	3150

*No formation of CO_2 when used as a working fluid

Fundamental fluid properties

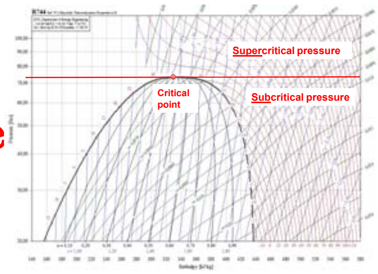
- Low critical temperature (T_C = 31.1℃)
  - 28℃: Practical upper limit for condensation
  - Heat rejection at supercritical pressures except at very low heat sink temperatures
- High critical pressure (73.8 bar)
- High pressures compared to other working fluids
  - Typically 5 to 10 times higher than for HFC
  - Relatively low pressure ratio (P_{gc}/P_E)
- Triple point pressure above atmospheric pressure (5.18 bar)
  - Equilibrium between 3 phases: Solid, liquid and vapour.
  - Sublimation: Dry ice does not melt but rather evaporates. Sublimation temperature at atmospheric pressures for solid CO_2 is -78.5 ℃





Fundamental fluid properties

- Superior heat transfer properties
  - Large volumetric heating capacity (VHC)
  - Steep pressure curve (Δt/Δp): low temperature loss per unit pressure loss
- Large volumetric expansion coefficient in liquid state

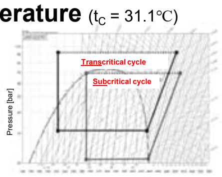


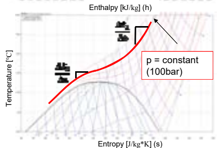
Significance of low critical temperature (t_C = 31.1℃)

CO_2 does not condensate above the critical pressure - Three possible operational modes:

- **Subcritical process**: Max condensation temperature of 28 ℃, but preferably much lower. Often necessary with a cascade system for heat rejections at higher temperature.
- **Transcritical process**: Heat rejection above the critical point. No condensation - CO_2 is cooled in the gas cooler at gliding temperatures. (Normal) evaporation of the fluid in subcritical region at constant temperature.

  Very efficient when heating a media over a large temperature range, i.e. domestic hot water (from 10-20 °C to 70-90 ℃).
- **Processes that alter between subcritical and transcritical:** Operation based on heat sink temperature. Subcritical operations if the heat sink allows it, as this would traditionally be most energy efficient when not utilizing access heat.

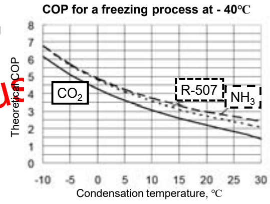




Significance of low critical temperature

- In comparison to other working fluids CO_2 has a slightly lower theoretical *Coefficient of Performance* (COP) during subcritical operation.
- Large throttling losses when the condensation temperature is close to the critical point. The same is true if the CO_2 temperature after the gas cooler in a transcritical cycle is high.
- Consequence: The theoretical COP is lower for CO_2 than for traditional working fluids.
- **However, CO_2 has proven more efficient than traditional working fluids in real life applications**.
  - **Low pressure ratio (P_C/P_E) → Less compression work**
  - **Low temperature losses (Δt/Δp): Heat exchanger can be designed for high pressure loss → enhances heat transfer**
  - **Small compression volume due to extremely high vapor density**

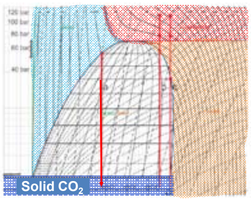
COP for a freezing process at - 40℃



Temperature [°C]	-40
NH_3 – Δt/Δp [K/bar]	26,1
CO_2 – Δt/Δp [K/bar]	2,7

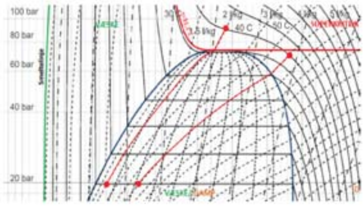
Significance of high pressure in the triple point

- Possible dry ice formations during system interventions (i.e. maintenance) as
  $P_{triple\text{-}point} > P_{atm}$.
- Generally formed if the pressure of liquid CO_2 is decreased during:
  - Filling/draining
  - Blowout of pressure regulative valves/ safety valve
- Possible formation of solid ice blockage
- Evaporation temperature limited to the theoretic triple point temperature (~ -56 ℃)
- Research within the area of CO_2 dry ice sublimation (These "evaporators" can achieve -78 ℃)



Consequences of high operational pressure

- CO_2 saturation pressure generally high compared to other working fluid.
- The pressure increases according to the specific volume curve during heating of a CO_2 liquid/vapour mixture.
- Specific volume (m³/kg) is the relationship between the container volume (m³) and the amount of media stored (kg).

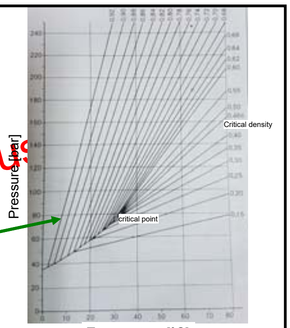


- Final pressure can be found in the interception between the specific volume curve and maximum temperature.

Consequences of charge

Isochoric lines:

equal density [kg/dm³]



Consequences of high operational pressure

LP=Low pressure, MP=mid-pressure, HP= high pressure

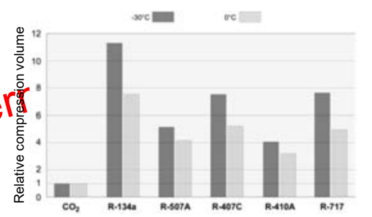
LP-side, frys [bar]	LP-side, kjøl [bar]	HP-side, underkritisk [bar]	MP-side, transkritisk [bar]	HP-side, transkritisk [bar]	Varmgass-avriming [bar]
26/41/61/(81)	41/61/(81)	41	80-90	80-120	53

- Dimensioning of equipment is done according to the specific pressures in CO_2 system
- Not economical to dimension all equipment in the system for maximum pressure
- Much smaller dimensions for pipelines and valves –mainly due to low viscosity and very low $\Delta t/\Delta p$
- 20-40 % lower weight of pipelines despite higher wall thickness

Type of system	Direct expansion (DX) system with R404A	Direct expansion (DX) with CO_2
Suction pipe line, return	76/102mm	42/68mm
Liquid line	35mm	22/48mm
Surface ratio	100 % (reference)	60 %

Consequences of high operational pressure

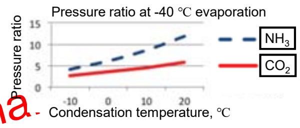
- High vapour density at high pressures
  - Smaller compression volume required
  - CO_2: 15-20 % volume compared to traditional working fluids
- → Smaller installations?
- → Less investment cost?



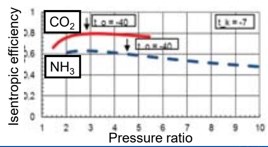
Relative required compression volume at -30/0 ℃ evaporation and 20 ℃ condensation

Consequences of high operational pressure

- Lower pressure ratio → lower required work input

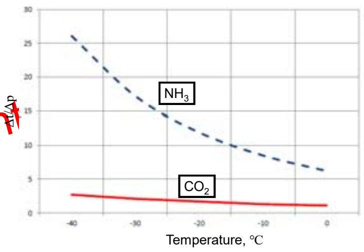


- Higher compressor efficiency



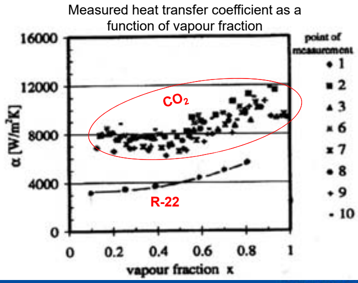
Consequences of high operational pressure

- Smaller change in temperature due to pressure loss
- Evaporator and condenser can be dimensioned for higher velocities



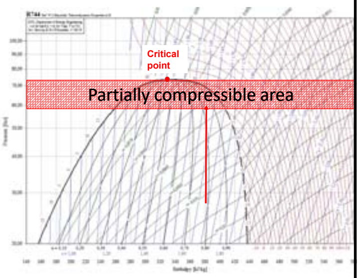
Heat transfer properties of CO_2

- High conductivity
- High specific heat capacity



Volumetric expansion coefficient for CO_2 in liquid state

- Liquid normally has a low compressibility. However, close to the critical point (20-30 °C) CO_2 is partially compressible.
- Due to the high thermal expansion coefficient, CO_2 will expand with 25 % when heated from -10 to 20 °C.
- 3.5 - 5 times higher compared to other working fluids.
- Increased danger of rupture when overfilling fluid in CO_2 system.



References

M. Bredesen, A. Hafner, J. Pettersen, P. Nekså, K. Aflekt: «Heat transfer and pressure drop for in-tube evaporation of CO2», IIR Proceedings 1997-5 «Heat Transfer in Natural Refrigerants», College Park (USA), November 6-7, 1997

Hrnjak, P., Young Park, C., 2006: «CO2 Evaporation at Low Temperature». C-Dig Meeting, March 16-17, 200

NTNU

3. The transcritical CO_2 cycle

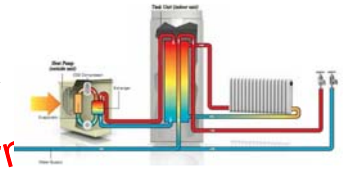
Prof. Dr.-Ing. Armin Hafner
Professor Refrigeration Technology
NTNU, EPT
7491 Trondheim
Norway

Content

- Background
- Transcritical process in the Pressure-enthalpy (P-h) diagram
- Temperature change in the gas cooler
- The influence of gas cooler pressure on COP
- Optimum high pressure control

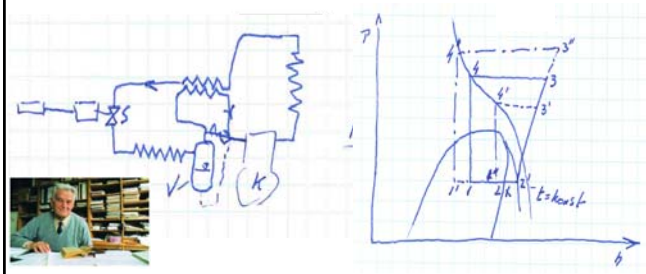
Background

- The transcritical CO_2 cycle is exceptional for domestic hot water heating (high temperature lift)
- 1980s: Research was done within the area of commercializing heat pumps for domestic hot water
- 2001: The 6 kW *EcoCute* heat pump was introduced to the Japanese market
- 2017: More than 5 million units installed in Japan

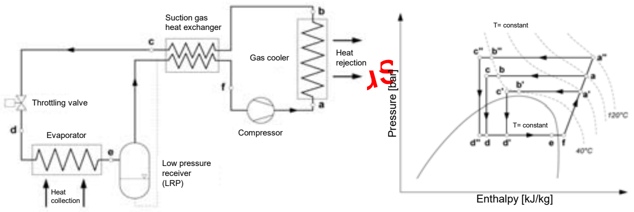


The Sanyo EcoCute System

Transcritical process in the Pressure-enthalpy (P-h) diagram

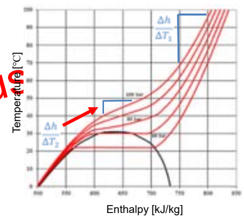


Transcritical process in the Pressure-enthalpy (P-h) diagram



Temperature change in the gas cooler

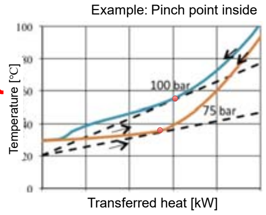
- Cooling of CO_2 in the gas cooler follows the constant pressure lines at gliding temperatures
- The specific heat ($c_p = \frac{\Delta h}{\Delta T}$) is not constant as ΔT is not proportional with Δh
- The shape of the temperature glide is essential in regards to gas cooler dimensioning



Temperature change in the gas cooler – pinch temperature

- Ideal heat transfer in HX: Completely parallel temperature curves
- For non-linear temperature curves, the temperature difference in the HX is limited by the *pinch point* (minimum temperature difference)
- Pinch point typically inside the gas cooler (low pressures) or at the outlet
- Important to consider when deciding the amount of fluid circulation (kg/s)

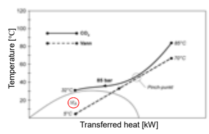
Example: Pinch point inside

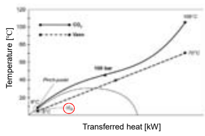


Temperature difference in the gas cooler – temperature approach

- *The temperature approach*, ΔT_a, is the temperature difference between the fluids at the gas cooler outlet
- ΔT_a expresses how adaptable the system is to transcritical operations
- Large ΔT_a
  - Large throttling losses
  - Low cooling capacity
  - Low COP
- ΔT_a should not be lager than 2-4 K

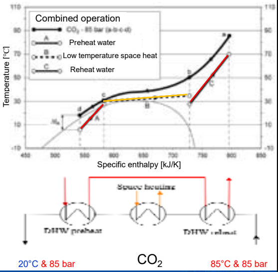
Good solution!





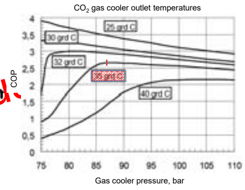
Temperature in the gas cooler – heating demand at different temperatures

- Transient operations are especially convenient when delivering heat at different temperatures, ie. domestic hot water, space heating, etc.
- Challenging to reach optimal efficiency if the different heating demands vary
- Perfect for modern flats / dwellings with 50%+ share of hot water demand / total heating demand (dependent on climate zone)



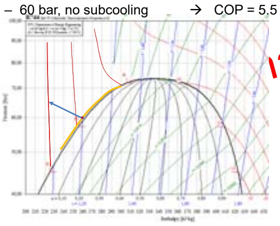
The influence of gas cooler pressure on COP

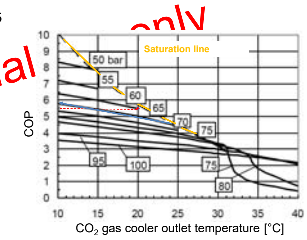
- Both cooling effect and COP increase in the transcritical region
- $COP = \frac{Qc}{Wc}$
- Optimal operational point is decided based on change in cooling capacity (Qc) relative to compression work (Wc)
- *35 grd C case:*
  - 75-87 bar: large increase in ΔQc relative to ΔWc
  - 87 + bar: small increase in ΔQc relative to ΔWc
  - Optimum operations at 87 bar



The influence of gas cooler pressure on COP

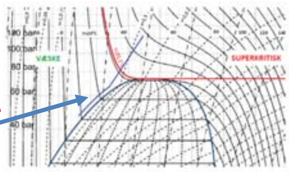
- High(er) pressure and subcooling is sometimes better than low pressure and no subcooling:
  - 65 bar, subcooling to 10 °C → COP = 5.8
  - 60 bar, no subcooling → COP = 5.5





The influence of gas cooler pressure on COP

- High pressure regulation
- Mechanical or electronic regulation of valves
- The pressure can be controlled according to the CO_2 temperature before throttling
  - For traditional cooling unit without heat recovery
  - Predetermined pressure/temperature curve
  - Necessary with electronic regulator and motor controlled throttling valve
- Selecting the best control strategy
  - Function of the system (ie. purely cooling vs. cooling and heat recovery)
  - Gas cooler pressure control and fan speed regulation



Regulation characteristics for optimal gas cooler pressure

References

G. Lorentzen: *Revival of carbon dioxide as a refrigerant.* Int. J. Refrig. Vol. 17, No. 5 1993

Jørn Stene: *Residential CO2 Heat Pump System for Combined Space Heating and Hot Water Heating,* Doctoral Thesis at NTNU 2004:53

K. B. Madsen: *Transcritical CO2 System in a Small Supermarked.* Danfoss-seminar om CO2 som kuldemedium, Oslo, 21.01.2009

Petter Nekså, Håvard Rekstad, G. Reza Zakeri and Per Arne Schiefloe: *CO2-heat pump water heater, characteristics, system design and experimental results,* Int. J. Refrig., Vol. 21, No. 3, pp 172-179, 1998

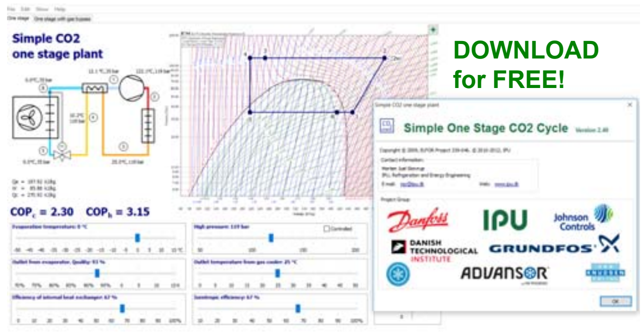
NTNU

4. Examples of CO_2 systems

Prof. Dr.-Ing. Armin Hafner
Professor Refrigeration Technology
NTNU, EPT
7491 Trondheim
Norway

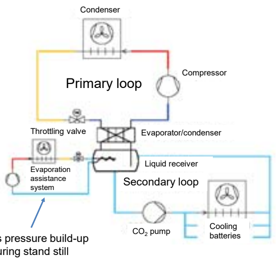
Content

- CO_2 as an evaporating secondary fluid
- CO_2 in a conventional cooling process (cascade system)
- Transcritical CO_2 process with low-pressure receiver
- Transcritical CO_2 process with mid-pressure receiver
- Transcritical CO_2 process with low and mid-pressure receivers
- Transcritical CO_2 booster system



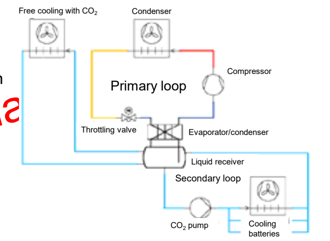
CO_2 as an evaporating secondary fluid

- Application:
  - Subcritical CO_2 system with NH_3 in the primary loop
  - Supermarkets, industrial freezers, ice rinks
- Advantages:
  - Flooded evaporator
  - Oil free CO_2 loop
  - High chiller efficiency
  - Smaller pipe dimensions and pump work compared to glycol circuits
- Disadvantages:
  - Complicated
  - Expensive



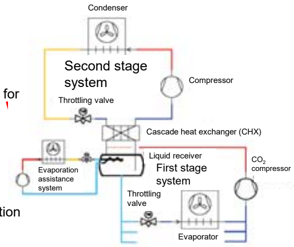
CO_2 as an evaporating secondary fluid

- Free cooling loop included
- System must be dimensioned for standstill pressure (→ No evaporation assistance system!)



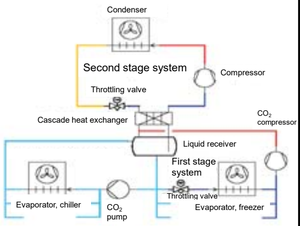
CO_2 in a conventional cooling process - cascade systems

- Application:
  - Two separate refrigeration units
  - First stage subcritical CO_2 system
  - Second stage system with a working fluid suitable for heat rejection (NH_3, propane (R290), etc.)
  - Utilized in supermarkets pre-transcritical cycle
- Advantages:
  - Energy efficient process
  - Small operational cost
  - The indirect system provides NH_3 leakage precaution
- Disadvantages:
  - Problematic if the second stage system is inactive
  - Challenging to regulate the CHX at small capacities without variable speed drive



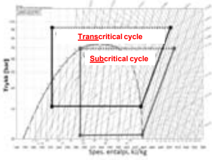
CO_2 in a conventional cooling process - cascade systems

- Application:
  - Large facilities with need for refrigeration at several temperature levels
- Advantages:
  - Flooded chiller evaporator
  - Compact
- Disadvantages:
  - Expensive
  - The CO_2 system fully relies on the second stage system for condensation



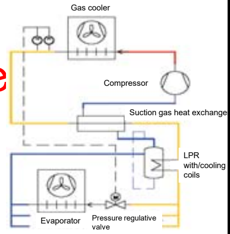
Transcritical CO_2 process: Important considerations

- Gas cooler pressure
- Placement of receivers
- Single vs. several throttling steps
- Mid pressure control
  - Dual throttling steps



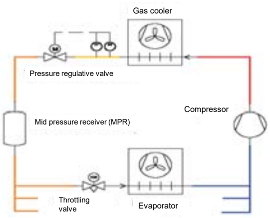
Transcritical CO_2 process with mid-pressure receiver

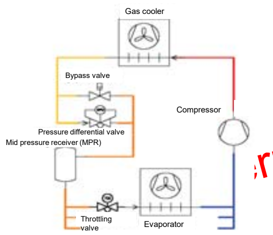
- Application:
  - Single throttling step
  - Smaller installations
  - Norild, Sonyo, Denso
- Advantages:
  - LRP enables flooded evaporation
  - High suction pressure than with TEV
  - Lower vapour quality before throttling due to the suction gas heat exchanger
- Disadvantages:
  - Single evaporator
  - Oil boil-off
  - Slow start-up due to liquid accumulation in LPR



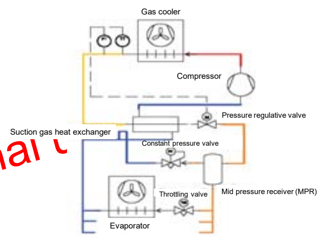
Transcritical CO_2 process with mid-pressure receiver

- Application:
  - Two throttling steps
  - Simple regulated systems
- Advantages:
  - Uncomplicated transcritical process
  - No connection between gas cooler pressure and feed to evaporator
- Disadvantages:
  - Superheat at evaporator outlet
  - Oil boil-off
  - Slow start-up due to liquid accumulation in MPR





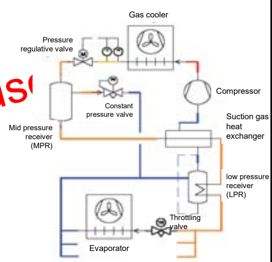
Regulation of gas cooler pressure by constant pressure difference – Passive mid pressure regulation



Active regulation of receiver pressure with flash gas bypass through constant pressure valve

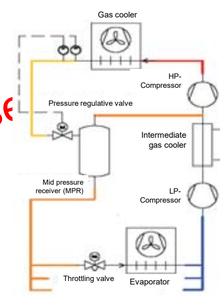
Transcritical CO_2 process with low and mid-pressure receivers

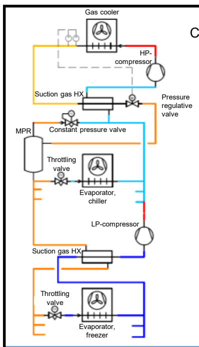
- Benefits from both LPR and MPR
  - Flooded evaporator
  - Enables higher suction pressure
  - No connection between gas cooler pressure control and feed to evaporator



Transcritical CO_2 booster system

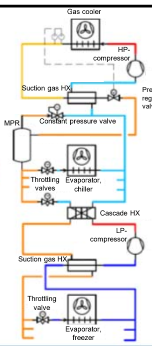
- Application:
  - Two stage compression and throttling
  - Leading solution in larger systems
- Advantages:
  - Robust and well developed
  - Standard components and regulation
  - Strong competitor to NH_3 systems in the industry
  - Well known and applicable all over the world
- Disadvantages:
  - Gas cooler outlet temperature in the range of 25-35℃





CO_2 booster system

- Smaller investment cost
- Higher efficiency



Cascade CO_2 booster system

- Avoid problems due to oil-return
- Possible to utilize oil of different viscosities for chiller and freezer evaporators

References

A. Hafner, T. S. Nordtvedt, E. Gukelberger, K. Banasiak, K. Widell: *Design of a R717/R744 Cascade System for the Pelagic Fish Industry.* 11th IIR Gustav Lorentzen Conference on Natural refrigerants, Hangzhou, China, 2014

Dr. A. B. Pearson (editor): *CO_2 as a Refrigerant*. IIR GUIDES. International Institute of Refrigeration, 2014. ISBN: 978-2-36215-005-0

Hillphoenix Refrigeration Systems: *Second Nature CO_2 Capable of Making a Difference.* http://www.hillphoenix.com/refrigeration-systems/second-nature/

Ole Christensen: *Typical ammonia/CO_2 Cascade System, Freezing and Cooling Application.* Technical Paper 1, 2006 IIAR Ammonia refrigeration Conference & Exhibition, Reno, Nevada, USA

S. Forbes Pearson, Ph.D.: *Using CO_2 To Reduce Refrigerant Charge.* ASHRAE Journal vol. 54, no. 3, October 2012

shecco guide: *Examples of NH_3 /CO_2 Secondary Systems for Cols store Operators.* https://issuu.com/shecco/docs/guide_nh3-final

Stene, J., 1988: *Guidelines for Design and Operation of Compression Heat Pump, Air Conditioning and Refrigerating systems with Natural Working Fluids.* IEA Heat Pump Programe, report no. HPP-AN22-4. ISBN 90-73-741-31-9.

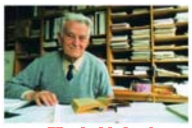
Y. Solemdal, T. M. Eikevik, I. Tolstorebrov, O.J. Veiby: *CO_2 as a Refrigerant for Cooling of Data-Center: A Case Study*. 11th IIR Gustav Lorentzen Conference on Natural Refrigerants, Hanszhou, China, 2014

Thank you for your attention

Contact:

armin.hafner@ntnu.no

A wise man said 22 years ago



Prof. Gustav Lorentzen (1915-1995)

We have heard a great deal lately of the **harmful effects to the environment when halocarbon refrigerants are lost to the atmosphere**. This should **not really** have come as **a surprise** since similar problems have happened over and over again. Numerous cases are on record where **new chemicals**, believed to be a benefit to man, **have turned out to be environmentally unacceptable**, sometimes even in quite small quantities (DDT, PCB, Pb etc.).

In the present situation, when the CFCs and in a little longer perspective the HCFCs are being banned by international agreement, it does not seem very logical to try to replace them by another family of related halocarbons**, the HFCs, equally foreign to nature**.

Int. Journal of Refrigeration 9. Vol. 18, No. 3, pp 190 197, **1995**