

## CO<sub>2</sub>-refrigeration in a historic perspective

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## CO<sub>2</sub> is back!

### JAPAN: Toyota FCEV vehicle will have CO<sub>2</sub> air conditioning

21 Jun 2001  
Source: just-auto.com editorial team  
Toyota's first fuel cell electric vehicle (FCEV) model will include the latest and carbon dioxide air conditioning technology when introduced in 2003. The new technology as possible will also be shared with conventional petrol cars.  
The fuel cell vehicle will have secondary batteries and be built on the air drive platform as the Toyota Windom (Lexus ES300) and Kluger models will sell for less than 10 million yen (about \$US\$1,000).  
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 HFC-134A.  
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<sub>2</sub> Heat Pump Water Heater

Jointly with Denso Corp., Kariya, Tokyo Electric Power Co. (TEPCO) has been developing a residential CO<sub>2</sub> heat pump water heater, and now set about demonstration tests aimed to realize commercialization within this year. (2000)



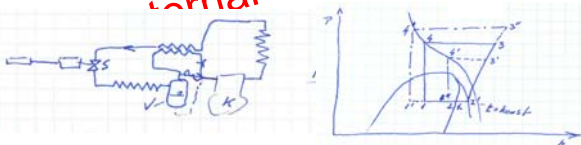
TEPCO/Denso CO<sub>2</sub> Heat Pump Water Heater  
Shecco TECHNOLOGY

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Professor  
Gustav Lorentzen  
1915-1995

First draft made for a patent application on how to operate and control transcritical CO<sub>2</sub>-vapour compression systems  
November 1988



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## CO<sub>2</sub>-refrigeration technology prior 1988?

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## Content

- How developed refrigeration technology?
- Factors which contributed to the development
- CO<sub>2</sub> i relation to other working fluids
- The people behind the innovations
- Synergies to today's situation
- CO<sub>2</sub> processes, system configurations and modifications
- Reasons why CO<sub>2</sub> refrigeration technology was absent between 1960 to 1990

**MOTIVATION:**  
Can we learn something when studying the historic CO<sub>2</sub> refrigeration systems?

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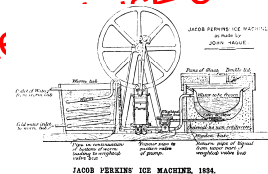
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## Inventors and pioneers of mechanical refrigeration

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 Hargreaves**



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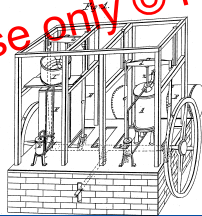
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## Inventors and pioneers of mechanical refrigeration

Air cycle:

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



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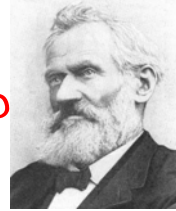
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## Inventors and pioneers of mechanical refrigeration

Absorption cycle:

- **Ferdinand Carré** (1824-1900), France  
Patent  $\text{NH}_3/\text{H}_2\text{O}$  absorption system in 1859



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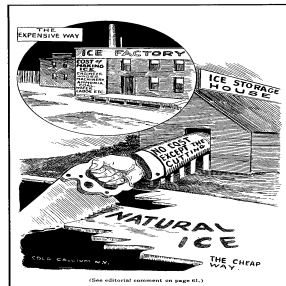
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## Three important 'drivers' in the late 19th century

Factors pushing the development of mechanical refrigeration technology from 1850 →

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

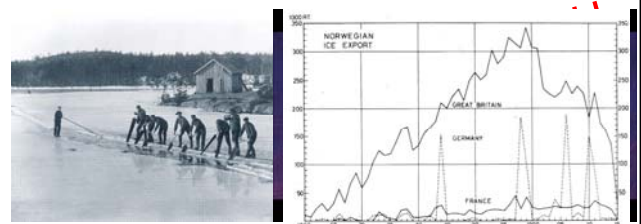


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## 150 years ago: ICE = refrigeration



Norwegian Ice Export from 1860 to 1915

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## Natural working fluids also common in the US:



Advertisement in ICE and REFRIGERATION, 1922, vol. 63

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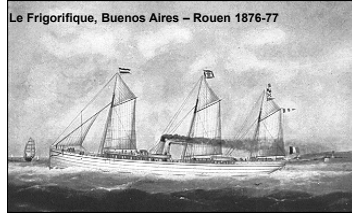
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### Three important 'drivers' in the late 19th century

Factors pushing the development of mechanical refrigeration technology from 1850 →

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



### Theory and Practice 1840-1870

- 2. law of thermodynamics: Carnot, 1824
- 1. law of thermodynamics: Clausius, Helmholtz, Joule, Mayer, Thomson (Lord Kelvin), 1842-1852
- Joule-Thomson expansion, 1862

- Perkins, 1834 (inventor, designer)
- Goettlieb, 1842 (medical doctor)
- Harrison, 1850-1860 (journalist, publisher)

"Perkins had little, if any, real understanding of the fundamental nature of his cycle" J. F. Sandfort, 1962

1870: Carl Linde established the fundamental thermodynamically base for mechanical refrigeration

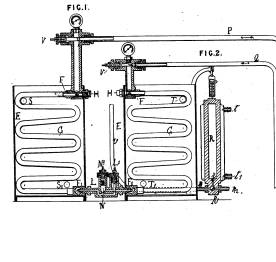
End of 19<sup>th</sup> century: Development moved from single pioneers/developers to companies with economic and technical resources

### CO<sub>2</sub>-refrigeration technology was born

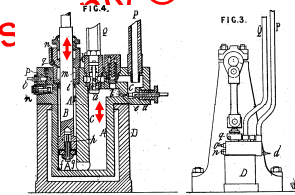
- 1850: CO<sub>2</sub> mentioned (?) as potential working fluid in patent application of Alexander C. Twining (1801-1884), USA  
"...a volatile liquid, as alcohol, ether, sulfuret of carbon, &c."
- 1866: First machine build (?) by Thaddeus Sobieski Carlincourt Lowe (1832-1913), USA.
  - Applied compressed CO<sub>2</sub> to inflate military balloons 1865-1866
  - British Patent No 952 on CO<sub>2</sub> system in 1867
  - Build ice machines in Dallas, Texas, and Jackson, Mississippi 1869
- 1882: Ca This Invention consists, first, in compressing carbonic acid or other gas into
- 1884: Br a liquid state, then bringing such liquid into contact or vicinity with water or CO<sub>2</sub> vapour
- 1886: Br other material to be refrigerated, and then relieving the pressure, so that the liquid carbonic acid or other gas may return to its gaseous state. The material in its gaseous state is then collected and returned to the pump or compressing apparatus, and again compressed and used as before.

### Franz Windhausen (1829-1904)

Britisk Patent No 2864, 1886

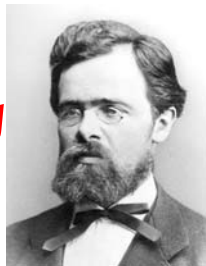


Mercury applied as "pressure fluid" (fluid piston), to transfer the movement of the plunger (B) to the compression of CO<sub>2</sub> in chamber C



### Carl von Linde (part1) (1842 – 1934)

Linde's articles on refrigeration technology had aroused the interest of brewers who had been looking for a reliable year round method of refrigeration for the fermentation and storage of their beer.



Carl Linde (1868)

### First industrial refrigeration machine: developed for a brewery

- Linde's first refrigeration system used Dimethyl ether as the refrigerant and was built by Maschinenfabrik Augsburg (now MAN AG) for the Spaten Brewery in 1873.
- He quickly moved on to develop more reliable ammonia (R717)-based cycles. These were early examples of vapor-compression refrigeration machines, and ammonia is still in wide use as a refrigerant in industrial applications.



The first Linde refrigeration machine. (1873)

## Spaten → Heineken → Carlsberg →

Rotterdam based Heineken Brewery ordered an ice machine in 1877 for ice production. In his collaboration with the Heineken Brewery, Linde developed "natural convection cooling" with a system of cooling pipes under the ceiling of the cellar.



Fermentation cellar of a brewery with natural convection cooling

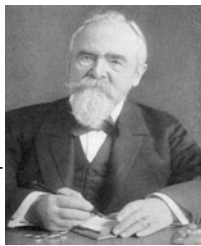
Linde came in contact with J.C. Jacobsen, head of the Carlsberg Brewery in Copenhagen, who ordered a large refrigeration unit in 1878.

## Linde: *godfather* of industrial refrigeration

- Linde's efficient new refrigeration technology offered big benefits to the breweries, and by 1890 Linde had sold 747 ammonia refrigeration machines. In addition to the breweries, other uses for the new technology were found in slaughterhouses and cold storage facilities all over Europe.

## Carl von Linde and "Refrigeration as a Science" (part 2)

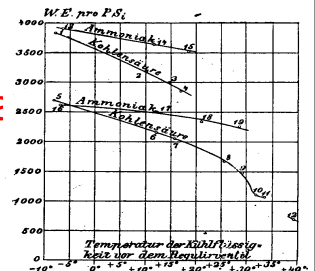
- Developed the fundamental thermodynamics for mechanical refrigeration in 1870-71 (Amanuensis, TH München)
- Experimental investigation funded by Spatenbrauerei 1872-73; (ether),  $\text{NH}_3$
- Consortium with Maschinenfabrik Augsburg-Nürnberg (MAN) 1873-79
- Established 'Gesellschaft für Linde's Eismaschinen', 1879-
- Test facility for refrigeration machines, Munich 1888-?



Carl von Linde, 1842-1934

## Linde's comparison of $\text{NH}_3$ and $\text{CO}_2$ systems

- Theory, 1894: "... $[\text{CO}_2]$  can never reach the efficient performance ratio of ammonia  $[\text{NH}_3]$  ..."
- Had to correct the existing thermodynamic (Zeuner) due to operation at supercritical high side pressure
- Results from experimental investigations performed at test facility in Munich published in Zeitschrift des VDI, 1895
- Published later "Ungleichwertigkeit von Ammoniak, Kohlensäure und schwefeliger Säure in Kompressions-Kaltdampfmaschinen" → non-equivalence of  $\text{NH}_3$ ,  $\text{CO}_2$ , and sulphurous acid in vapour compression machines



## Hans Lorenz (1865-?)

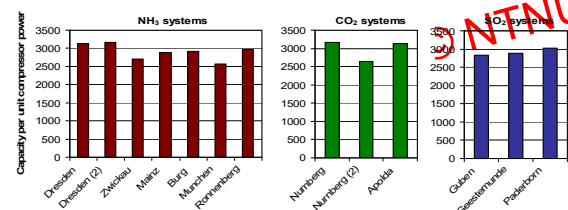


### 'Die praktische Gleichwertigkeit der drei Hauptsysteme von Kompressionskühlmaschinen.'

Von Professor Dr. H. Lorenz.

München und Berlin. Druck und Verlag von R. Oldenbourg, 1905.

## Results from field tests, Lorenz 1892-1901



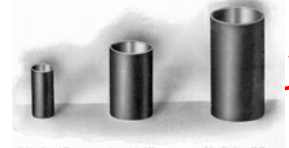
Similar results are shown by Stetefeld, 1904

# Applications and systems

## CO<sub>2</sub> as a working fluid

- High working pressures
- Small compressor displacements
- Low critical temperature

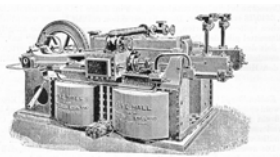
CO<sub>2</sub>: 31.1°C  
NH<sub>3</sub>: 132.1°C  
SO<sub>2</sub>: 157.5°C



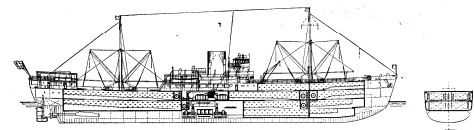
Vergleich der Spannungen der Kälteflüssigkeiten.  
Spannung in absoluten Atmosphären → kg pro qcm

Temperatur ° Cels.	Spannung in absoluten Atmosphären → kg pro qcm				
	Ammoniak NH <sub>3</sub>	Schwefel- säure SO <sub>2</sub>	Kohlensäure CO <sub>2</sub>	Chlormethyl Cl Hs Cl	Äthylchlorid C <sub>2</sub> H <sub>5</sub> Cl
-30	1,182	0,30	14,66	0,76	0,150
-20	1,069	0,65	20,03	1,15	0,235
-10	0,953	1,04	27,10	1,72	0,410
-5	0,879	1,29	31,00	2,07	0,522
0	0,817	1,58	35,40	2,48	0,633
+5	0,762	1,93	40,30	2,96	0,787
+10	0,711	2,34	45,70	3,51	0,981
+15	0,661	2,81	51,60	4,25	1,148
+20	0,612	3,35	58,10	5,22	1,385
+30	0,509	4,67	73,01	6,50	1,59
+40	0,401	6,35	100,03	8,50	2,61

## Marine Refrigeration



## Reefer, ca 1930



Skibskjølelægge for transport 175.000 cbl netto rumindhold for frosketst + 0,5° C, uanset for en snitlet ydelse av 320.000/kil time ved + 30° kjølevarm og + 10° fordamper.

## Freezing of fish (Ottesen, Nekolai Dahls method), 1915

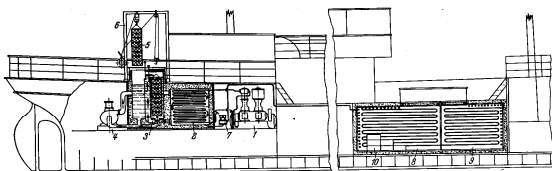


Abb. 102. Einbau einer OTTESEN-Fischgefrieranlage in den Dampfer „Karnøy“ (Thomas Th. Sabroe, Aarhus, Dänemark).  
1 Dampmaschine und CO<sub>2</sub>-Kompressor mit Kondensator, 2 Verdampfer, 3 Gefrierbehälter, 4 Sole-zirkulationspumpe, 5 isolierte Eisbehälter, 6 Hebevorrichtung für die Fischbehälter, 7 Solepumpe, 8, 9 Lagerräume, 10 gefrorene Fische versandfertig verpackt.

## Marine Refrigeration

Göttsche, 1915)

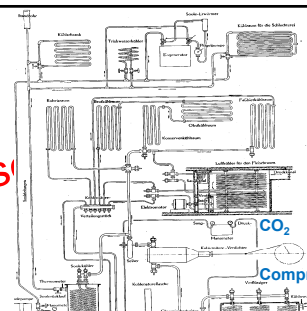
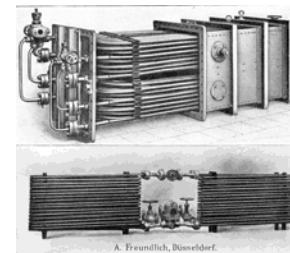


Fig. 62. Mariny von Luftkühlschlangen und Apparate für CO<sub>2</sub>-Verdampfung.



## Small capacity units

(Götsche, 1915) (Hubendick, 1921)

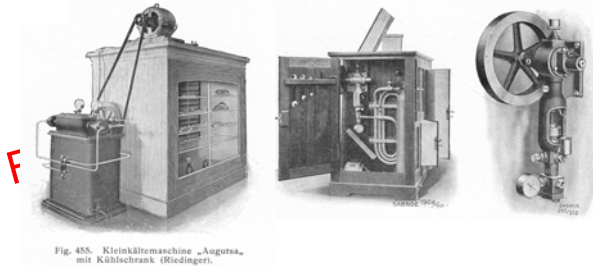


Fig. 455. Kleinkältemaschine „Augusta“, mit Kältebrank (Riedinger).

## AC system (USA)

For inte

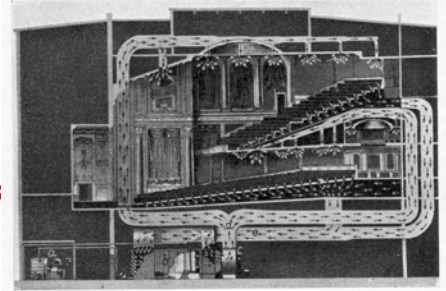
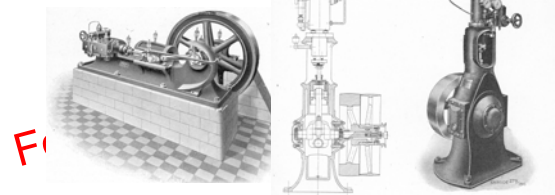


Abb. 114. Theater-Kühlanlage (nach L. L. Lewis).

## Components

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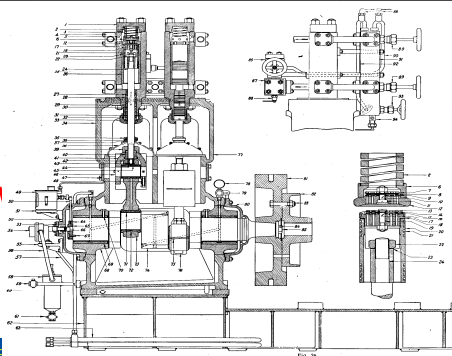
## Compressors



Slow rpm cross head compressors  
Stuffing box and piston rings / leather  
Lubricant: glycerine

## Compressor ca. 1930

**DRAVN**  
DUPLIX CO. KOMPRESSOR  
MED TRYKSKIBRØR  
**DRANNSJERN**  
STØBET OG HØJ VÆRNET



## Condenser concepts (1)

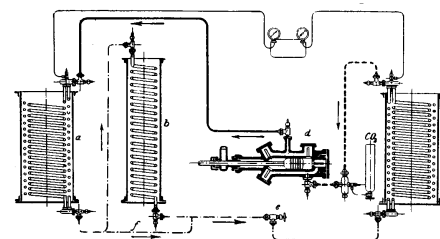


Fig. 448. CO<sub>2</sub>-Maschinenanlage mit Nachkühler.

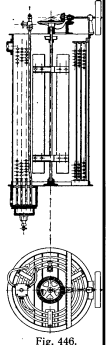
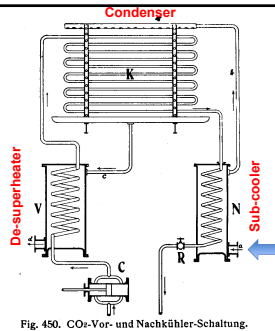
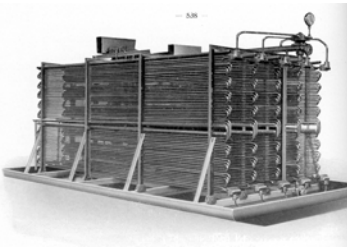


Fig. 446.

## Condenser concepts (2)



## "Tube and Shell heat exchangers"

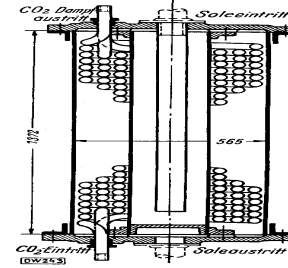
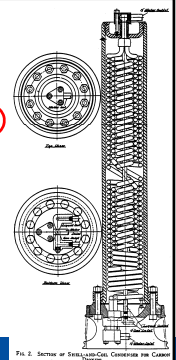


Abb. 63. Mantel- und Schlangen-Verdampfer (Shell and Coil) für Kohlensäure.



## Process- and system modifications

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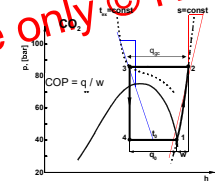
## R-744 (carbon dioxide) as Working Fluid

- specific refrigerant capacity and COP is reduced at high cooling water/ambient temperatures compared to other refrigerants.
- COP optimization in transcritical operation by operating the system at the optimum high side pressure:

$$\left( \frac{\partial h_3}{\partial p} \right)_\tau = -COP \left( \frac{\partial h_1}{\partial p} \right)_s$$

$$COP_{AC} = (h_1 - h_3) / (h_2 - h_1)$$

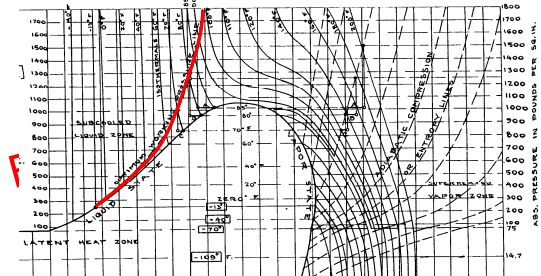
$$COP_{HP} = (h_2 - h_3) / (h_2 - h_1)$$



1928 H. Inokuty, (Mitsubishi Laboratory, Japan) developed the mathematical basis and a graphical method to find the optimum high side pressure, which maximizes the COP.

## Opt. high side pressure versus gascooler temperature

Goosmann, 1933



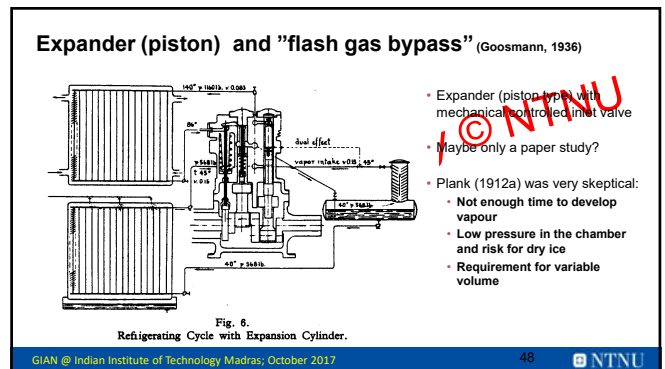
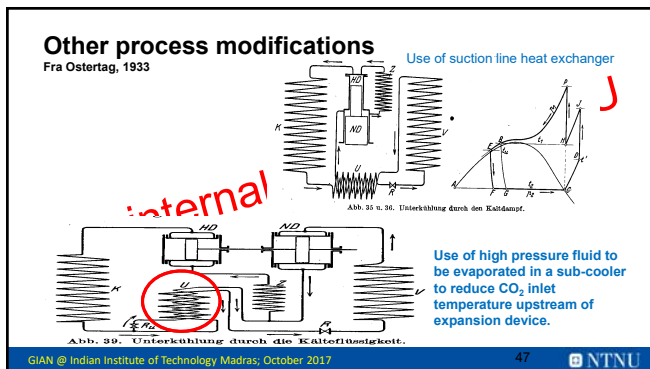
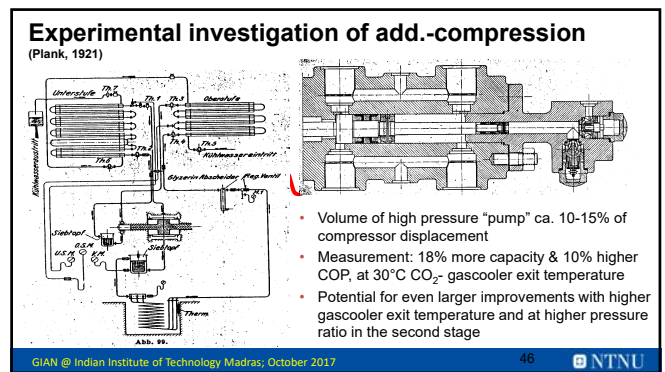
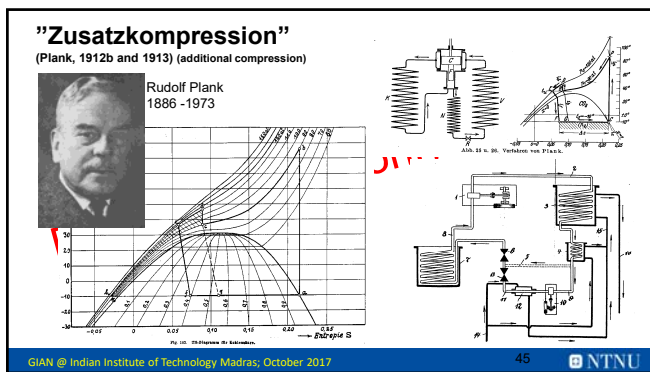
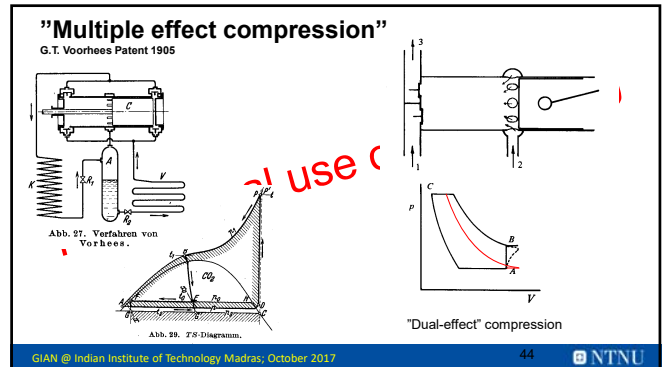
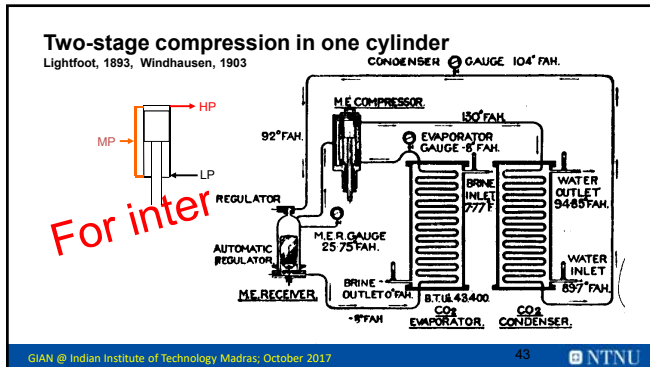
## Expansion losses

(Göttsche, 1915)

Das Regulierventil mit seiner drosselnden Wirkung bedeutet bei allen Kompressionsmaschinen einen Effektverlust, der aber bei den CO<sub>2</sub>-Maschinen besonders gross ist, zumal bei warmen Kühlwasserverhältnissen. Dieser Verlust beträgt theoretisch beispielsweise bei

+ 20 ° und - 10 ° Cels.		+ 30 ° und - 10 ° Cels.	
bei CO <sub>2</sub> .....	47,8 %	bei CO <sub>2</sub> .....	85,5 %
" NH <sub>3</sub> .....	9,8 %	" NH <sub>3</sub> .....	13,6 %
" SO <sub>2</sub> .....	13,0 %	" SO <sub>2</sub> .....	18,7 %

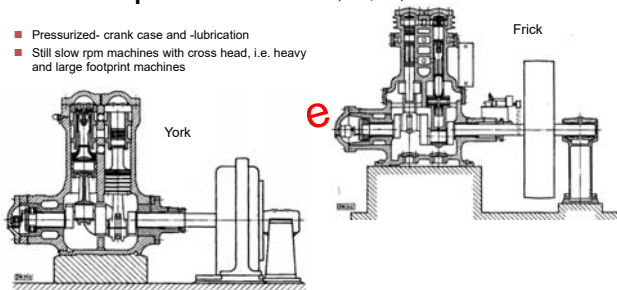
Modified processes can reduce these losses →





## Later compressor versions (Plank, 1929)

- Pressurized- crank case and -lubrication
- Still slow rpm machines with cross head, i.e. heavy and large footprint machines



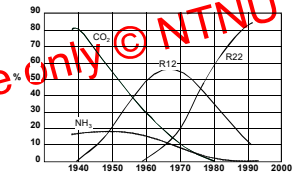
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## Why CO<sub>2</sub> disappeared in the early/mid 20<sup>th</sup> century?

- Problems with leaks
- Reduced cooling capacity at elevated heat rejection temperatures
- Cold cooling water not available everywhere (especially USA)
- Design of compressors with pressurized crank case<sup>3</sup> and high rpm (50/60Hz) not adapted for CO<sub>2</sub>
- 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 CO<sub>2</sub> in the US more than in Europe.
- 1. world war in Europe



Prosentvis andel av kuldemedier i eksisterende lastkulanlegg på skip klasset av Lloyd's Register Fra Stera (1992)

a: (Ballantine, 1877)

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