History and technological progress.

Cryogenic air separation.
Contents.

4 Refrigeration

5 Liquefaction of air

6 Air separation by rectification

7 The principles of air separation

8 Column design

9 Technological developments
   Structured packings
   Pure argon production by rectification
   Pure argon production by catalytic converter
   Internal compression
   External compression
   Advanced condenser/reboiler design

13 Supply chain

14 Typical cryogenic air separation process

16 Historical data

17 References

20 Contact
Design and construction of air separation plants is part of Linde’s traditional scope of activities, which led to the establishment of Linde’s Engineering Division at the turn of the 19th century. In 1902, the start-up of the world’s first air separation plant initiated the development of the cryogenic industry. Today, several hundred engineers and specialists work at Linde for the worldwide sale and contract execution of plants that recover the air constituents oxygen and nitrogen as well as various rare gases.

Over 3,000 air separation plants in 80 countries – 500 of them have been built in the last 15 years – bear witness to Linde’s pre-eminent market position in this field of technology.
Refrigeration.

In May 1895, Carl von Linde performed an experiment in his laboratory in Munich that led to his invention of the first continuous process for the liquefaction of air based on the Joule-Thomson refrigeration effect and the principle of countercurrent heat exchange. This marked the breakthrough for cryogenic air separation.

For his experiment, air was compressed from 20 bar to 60 bar in the compressor \(P\) and cooled in the water cooler \(K\) to ambient temperature \(t_1\). The pre-cooled air was fed into the countercurrent heat exchanger \(G\), further cooled down and expanded in the expansion valve \(E\) (Joule-Thomson valve) to liquefaction temperature. The gaseous content of the air was then warmed up again in the heat exchanger \(G\) and fed into the suction side of the compressor \(p_1\). The hourly yield from this experiment was approx. 3 liters of liquid air.

Linde based his experiment on findings discovered by J. P. Joule and W. Thomson (1853). They found that compressed gases expanded in a valve cool down by approx. 0.25 °C with each bar pressure drop. This proved that real gases do not follow the Boyle-Mariotte principle, according to which no temperature decrease is to be expected from expansion. An explanation for this effect was given by J. K. van der Waals (1873) who discovered that the molecules in compressed gases are no longer freely movable and the interaction among them leads to a temperature decrease after decompression.
Liquefaction of air.

To enable air to be separated into its constituents by means of rectification – the actual separation process – a large part of the air volume used must be liquefied. A gas can only be transformed into a liquid state at temperature and pressure conditions below those of its critical point.

The critical point of air is $T_{\text{crit}} = -140.7 \, ^\circ\text{C} (132.5 \, \text{K})$ and $P_{\text{crit}} = 37.7 \, \text{bar}$. In other words, air can be liquefied only at temperatures below $-140.7 \, ^\circ\text{C}$ (132.5 K).

The vapour pressure curve illustrates the allocation of temperatures and pressures at which a gas condenses or a liquid evaporates.

- Air below atmospheric pressure (1 bar) must be chilled to $-192 \, ^\circ\text{C} (81.5 \, \text{K})$ before condensation sets in.
- Air below a pressure of 6 bar must be chilled to $-172 \, ^\circ\text{C} (101 \, \text{K})$ before condensation begins.

The boiling point and condensation conditions of gas mixtures such as air are not identical. A condensation line and a boiling point line delineate the boiling point range.

Vapour pressure curves of atmospheric gases

- Critical point
- $N_2$
- Air
- $O_2$
- V Start of evaporation
- K Start of condensation

![Vapour pressure curves of atmospheric gases](image)
Rectification is synonymous with countercurrent distillation. This special distillation separation process enables the individual components of a mixture to be separated with a high purity combined with a good yield, even when their boiling points are relatively close to each other.

A result of the different vapour pressures of the individual components \((p_{N_2} > p_{O_2})\), the composition of the vapour differs from that of the liquid mixture. Correspondingly, a higher proportion of the component with the greater pressure vaporises during the evaporation process.

The vapour produced from a boiling liquid mixture of \(O_2/N_2\) will thus have a higher \(N_2\) concentration than the liquid mixture from which it originates.

Accordingly, the condensate produced when an \(O_2/N_2\) vapour mixture is liquefied will display a higher \(O_2\) concentration because the component with the lower partial pressure tends to transform into liquid.
The principles of air separation.

Air separation by rectification in a single/double column:

Using his air liquefaction principle as a basis, Carl von Linde constructed the first air separation plant for oxygen production in 1902 using a single column rectification system. In 1910, he set the basis for the cryogenic air separation principle with the development of a double-column rectification system. Now it was possible to produce pure oxygen and pure nitrogen simultaneously.

Below the low-pressure column a pressure column was installed. At the top of this column pure nitrogen was drawn off, liquefied in a condenser, and fed to the low-pressure column serving as reflux. At the top of this low-pressure column pure gaseous nitrogen was withdrawn as product while liquid oxygen evaporated at the bottom of this column to deliver the pure gaseous oxygen product. This principle of double-column rectification combining the condenser and evaporator to form a heat exchanger unit is still used today.

Condenser/reboiler

The principle of double-column rectification is characterized through the combination of condenser and evaporator to form a common heat exchanger unit. By this means the rectification is divided into two separate areas with different pressures.
Column design.

Any tray of the rectification column follows the same principle:

The \( \text{O}_2 \) concentration of the boiling \( \text{O}_2/\text{N}_2 \) liquid mixture \( F \) is greater than the \( \text{O}_2 \) concentration of the vapour \( D \). A certain volume of liquid corresponding to the same volume of reflux constantly flows from the tray above into the liquid mixture below with an equivalent volume flowing down over a weir onto the tray below.

The vapour \( D_u \) coming from the bottom tray penetrates the liquid mixture \( F \) and has a higher \( \text{O}_2 \) content than the vapour mixture \( D \). The \( \text{O}_2 \) concentration of the vapour \( D_o \) rising from the upper tray is in turn less than that of the vapour \( D \). Thus a product rich in nitrogen is obtained in the head of the column and a liquid rich in oxygen in the sump of the column.
Technological developments.

Structured packings

Significant progress in air separation technology was made in the mid-1980s. For the first time, structured packings were used in cryogenic rectification. Packed columns work according to a similar principle as sieve trays. The intensive contact between liquid and vapour required for the rectification takes place on the huge surface area of the packing material.

Liquid flowing down becomes increasingly richer in oxygen, whereby the ascending vapour is enriched with nitrogen. The main benefits of packed columns compared to tray sieves are a lower pressure drop and consequently a lower power consumption for the air separation process. This also set the basis for a new process for argon separation.
Pure argon production by rectification

Modern process
Within the so-called argon belly – the area in the low-pressure column where the argon concentration is at a maximum (approx. 10 %) – a gas stream is fed into the raw argon column for further rectification. The remaining oxygen in this gas stream is completely removed in the raw argon column, which is also a packed column. Due to the very low pressure drop in the packing, it is possible to install a sufficient number of ”theoretical trays” required for the rectification. In the adjoining pure argon column the remaining nitrogen is removed by rectification and the pure argon is liquefied.

Pure argon production by catalytic converter

Conventional process
Before the technological progress in the form of structured packings was applied, a significantly more complex, process for the production of pure argon had been used. At that time, it was not possible to remove the oxygen in the raw argon column completely by means of rectification. A percentage of 2.5 remained. This was due to a higher pressure loss through the trays, which consequently resulted in a lower oxygen concentration that was insufficient for complete rectification. An additional process step was required to remove the remaining oxygen by means of a catalytic converter using hydrogen.
Internal compression

The internal compression (or liquid pumping) process allows for oxygen, nitrogen as well as argon to be compressed within the cold box by means of liquid pumps, to be evaporated and warmed up in heat exchangers, and finally to be supplied to the end user at the required pressure.

In order to evaporate and warm up the compressed liquid, a countercurrent stream of nitrogen (or air) with a higher pressure than the required liquid is required for thermodynamic reasons.

For plants that produce pressurized nitrogen, the booster and/or recycle nitrogen compressor also provide the countercurrent stream for evaporation. With this method complex external oxygen compression is no longer required, thus plant operation and maintenance have become considerably easier and more reliable. Furthermore, the risk of dangerous hydrocarbon enrichment in the condenser is avoided because liquid oxygen is continuously withdrawn from the condenser and pumped into the heat exchanger where it evaporates. Compared with the external compression system a considerably higher level of safety has been achieved.

External compression

Conventional process

High-pressure gaseous oxygen is required for storage in pressure vessels or in high-pressure gas bottles, and for the application of oxygen in certain chemical processes. Pressures of up to 200 bar are used for oxygen storage. For chemical processes such as partial oxidation of residual oil, oxygen at a pressure of up to 100 bar is required.

A significant increase in applications in the chemical and petrochemical industries and the high requirement of plants with high capacities has led to alternative concepts with regard to the risks involved with high oxygen pressures.

In particular, the compression of oxygen in external compressors created problems due to the reduction of ignition temperature of organic and inorganic materials with increasing temperatures (e.g. the ignition temperature of iron/steel is reduced by more than 100 °C with a pressure increase from 50 to 100 bar). Furthermore, the required safety measures for external compression have an impact on overall investment costs.
Advanced condenser/reboiler design

Down flow condenser
- Used instead of two-storied or multi-storied bath condensers
- No-condenser vessel
- LOX recycle pump for reflux is necessary
- Oxygen pipework is necessary
- Suitable for ASUs with internal LOX compression
- Suitable for large ASUs
- Energy-saving solution

Combi condenser
- Combination of bath condenser plus down flow condenser
- No oxygen pipework
- No LOX recycle pump in connection with Kr/Xe production
- LOX recycle pump for reflux is necessary without Kr/Xe production
- Suitable for ASUs with internal LOX compression
- Suitable for large ASUs

Linde multi-stage bath condenser
This latest invention patented by Linde employs in principle a cascade of bath-type condensers. It combines a number of advantages such as low power requirements, improved wetting of the evaporator surface, further improved safety, and avoidance of an LOX recycle pump. The Linde Cascade Condenser package needs less space and it can be integrated into the LP column. The result is lower installation costs and an enhanced design for mega ASUs.
Supply chain.
Typical cryogenic air separation process.

Cryogenic air separation process for the production of gaseous pure oxygen and nitrogen with internal compression and the production of liquid oxygen, liquid nitrogen and liquid argon:

1. **Air compression**
   Compression of ambient air by a multi-stage turbo compressor with intercoolers at a supply pressure of approx. 6 bar. Removal of dust particles by a mechanical air filter at the inlet of the compressor.

2. **Air cooling and purification**
   Cooling of process air with water in a direct contact cooler and removal of soluble air impurities. Chilling of cooling water in an evaporation cooler against dry nitrogen waste gas from the rectification process. Removal of CO₂, water vapour and hydrocarbons from the process air in periodicaly loaded/regenerated molecular sieve adsorbers.

3. **Low-temperature heat exchange**
   Cooling of process air in heat exchangers down to nearly liquefaction temperature by means of countercurrent with nitrogen waste gas from the rectification process.

4. **Cold production & internal product compression**
   Further compression of a sidestream of process air by an air booster compressor. Expansion and cold production of the boosted air stream in an expansion turbine. Expansion and liquefaction of a sidestream of the boosted air in a liquid separator. Evaporation and warming to ambient temperature of the pumped oxygen and nitrogen product in high-pressure heat exchangers.
Cryogenic rectification of air
Pre-separation of the cooled and liquefied air within the pressure column into oxygen enriched liquid in the column sump and pure nitrogen gas at the column top. Liquefaction of the pure nitrogen gas in the condenser/reboiler against boiling oxygen in the sump of the low-pressure column. Liquefied nitrogen provides the reflux for the pressure column and (after sub-cooling) for the low-pressure column.

Further separation in the low-pressure column of the oxygen-enriched liquid within the low-pressure column into pure oxygen in the sump and nitrogen waste gas at the top.

Cryogenic rectification of argon
Argon-enriched gas from the low-pressure column is transformed into oxygen-free crude argon by means of separation within the crude argon column.

Pumping back liquid oxygen from the crude argon column sump into the low-pressure column. Removal of the remaining nitrogen in the pure argon column.
Historical data.

Linde Engineering milestones in air separation

<table>
<thead>
<tr>
<th>Year</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1902</td>
<td>World’s first air separation plant for the recovery of oxygen</td>
</tr>
<tr>
<td>1904</td>
<td>World’s first air separation plant for the recovery of nitrogen</td>
</tr>
<tr>
<td>1910</td>
<td>World’s first air separation plant using the double-column rectification process</td>
</tr>
<tr>
<td>1930</td>
<td>Development of the Linde-Fränkl process for air separation</td>
</tr>
<tr>
<td>1950</td>
<td>First Linde-Fränkl oxygen plant without pressure recycle and stone-filled reactors</td>
</tr>
<tr>
<td>1954</td>
<td>World’s first air separation plant with air purification by means of adsorbers</td>
</tr>
<tr>
<td>1968</td>
<td>Introduction of the molecular sieve technology for pre-purification of air</td>
</tr>
<tr>
<td>1978</td>
<td>Internal compression of oxygen applied to tonnage air separation plants</td>
</tr>
<tr>
<td>1981</td>
<td>Introduction of the elevated pressure process</td>
</tr>
<tr>
<td>1984</td>
<td>World’s largest VAROX® air separation plant with variable oxygen demand adjustment</td>
</tr>
<tr>
<td>1990</td>
<td>World’s first telecontrolled air separation plant with unmanned operation. Pure argon production by rectification</td>
</tr>
<tr>
<td>1991</td>
<td>World’s largest air separation plant with packed columns</td>
</tr>
<tr>
<td>1992</td>
<td>Megapure gases production in air separation plants</td>
</tr>
<tr>
<td>1997</td>
<td>Linde sets a new milestone in air separation history: four nitrogen generation trains are provided, each individually constituting the largest air separation plant ever built for nitrogen capacity of 40,000 t/d</td>
</tr>
<tr>
<td>2000</td>
<td>Development of the advanced multi-stage bath-type condenser</td>
</tr>
<tr>
<td>2006</td>
<td>Largest TKLS contract in the history of air separation with 30,000 MTPD capacity of oxygen for the Pearl GTL project in Qatar</td>
</tr>
<tr>
<td>2010</td>
<td>Advanced cryogenic process, high efficiency optimized for CCS application (Oxyfuel, IGCC)</td>
</tr>
</tbody>
</table>

Linde’s patent for the production of oxygen, dated 27.02.1902

1902 5 kg/h oxygen production
Air separation plants for the Pearl GTL project in RAS Laffan, Qatar

Customer
Qatar Shell GTL Ltd. (QSGTL Ltd.)

Design features
Cryogenic air separation, front-end air purification with MS, elevated process pressure, double-column system, internal compression of oxygen

Capacity
Total 30,000 MTD oxygen, ~860,000 Nm$^3$/h (eight trains)

Scope of work
Turnkey lump sum, basic and detail design, manufacture, delivery, construction, erection, commissioning and start-up

Contract signature
in 2006
One of the largest steelworks in China supplied with oxygen, nitrogen and argon from Linde air separation plants.

Customer
Wuhan Iron and Steel Company

<table>
<thead>
<tr>
<th>Plant</th>
<th>Status</th>
<th>Oxygen [tpd]</th>
<th>Nitrogen [tpd]</th>
<th>Other products</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/B</td>
<td>commissioned in 1975</td>
<td>690</td>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td>C/D</td>
<td>commissioned in 1982</td>
<td>690</td>
<td>605</td>
<td>argon</td>
</tr>
<tr>
<td>E/F</td>
<td>commissioned in 1992</td>
<td>2,100</td>
<td>1,860</td>
<td>argon, krypton, xenon</td>
</tr>
<tr>
<td>G/H</td>
<td>commissioned in 2004</td>
<td>4,190</td>
<td>4,860</td>
<td>argon, krypton, xenon, helium, neon</td>
</tr>
<tr>
<td>I/J</td>
<td>commissioned in 2006</td>
<td>4,190</td>
<td>4,860</td>
<td>argon, krypton, xenon, helium, neon</td>
</tr>
</tbody>
</table>
The largest multi-train air separation plant in the world supplying nitrogen for enhanced oil recovery in Mexico.

Customer
Pemex

- Turnkey project
- 5 trains in operation
- Product capacity of 63,000 t/d nitrogen (17,500 t/d oxygen equivalent)
- Commissioned in 2000
Engineering excellence – every step of the way.

Linde’s Engineering Division, a leading player in the international plant engineering business, covers every step in the design, project management and construction of turnkey industrial plants. Drawing on our extensive, proven process know-how, we set the standards for innovation, flexibility and reliability with ground-breaking concepts and a dedication to engineering excellence.

The success of our customers and partners around the globe is of primary importance. With a clear focus on efficiency, sustainability and growth, we develop customised solutions for projects of all sizes and degrees of complexity. We have already delivered more than 4,000 plants worldwide and always aim to find the best technical and economic solution for our customers.

Core competencies in plant engineering:
→ Air separation plants
→ LNG and natural gas processing plants
→ Petrochemical plants
→ Hydrogen and synthesis gas plants
→ Chemical plants
→ Adsorption plants
→ Cryogenic plants
→ Biotechnology plants
→ Carbon capture and utilisation plants
→ Furnaces, fired heaters, incinerators

Core competencies in component manufacturing:
→ Packaged units and coldboxes
→ Coil-wound heat exchangers
→ Plate-fin heat exchangers
→ Cryogenic columns
→ Cryogenic tanks
→ Air-heated vaporisers
→ Water bath vaporisers
→ Spiral-welded aluminium pipes

Get in touch – find the best solution.

Air separation plants
Phone +49.89.7445-2612
airseparation@linde-le.com