

Carbon Dioxide–CO₂–R 744 (Carbonic Acid)

The History of an Interesting Substance

eurammon promotes all natural refrigerants which support the use of the refrigerant ammonia. Due to the problems with ODP and GWP, these substances have again become a focal point of scientists, users and politicians. Apart from ammonia, water, hydrocarbons–e.g. propane–and carbon dioxide belong to these natural refrigerants. The latter with the ISO code R 744 and the chemical formula CO₂ has in recent years witnessed a revival in research but also even as a refrigerant and a secondary refrigerant in real applications.

This eurammon information offers a view into the history of carbon dioxide, for which from now on the term CO₂ will be used.

We are surrounded by CO₂ in the atmosphere since primeval times, even though today in a lower concentration in comparison to nitrogen (N₂) and oxygen (O₂), but possibly with great impact on this atmosphere. The atmospheric CO₂ is released from very different deposits and processes, such as volcanoes, oceans (as storage), carbonic acid from natural springs, combustion of fossil fuels, forest fires, exhaust fumes from chemical production and processing of natural gas and crude oil and fermentation processes. Even human beings and animals emit CO₂ with their exhaled air, a human being e.g. about 1 kg per day varying due to constitution and workload. The fermentation process in the beer production results up to 3.5 kg CO₂ per hectolitre beer.

Under the trade name “carbonic acid” we encounter CO₂ in many non-alcoholic beverages and in other fields, e.g. drinking-water purification, wastewater treatment, fire-extinguishing technology, high-pressure extraction, pest control, food refrigeration, in deep-freezing and cold-milling, as inert gas and dry ice, in medical applications and again these days as refrigerant and secondary refrigerant in refrigeration systems. These versatile industrial applications result from the special properties of CO₂. As a gas, carbon dioxide is neutral, to name only some of the properties, in colour, smell, taste, and has a high density (standard

state about 2 kg/m³), roughly 1.5 times the density of air. On top of that, the chemical compound CO₂ is very stable.

The critical point is at	+31.0°C	and	73.83 bar
the triple point is at	-56.6°C	and	5.18 bar
the sublimation point is at	-78.9°C	and	0.981 bar

Often the name “carbonic acid” is used—not quite correctly—as a synonym for CO₂ (carbon dioxide). Only in a compound with water CO₂ becomes carbonic acid (H₂CO₃).

The CO₂ content in our atmosphere has risen from 280 ppm in 1800 via 295 ppm in 1900 to 368 ppm in 2000, which the majority of scientists blame on anthropogenic influences. The carbon/carbon dioxide cycle and the CO₂ equilibrium in nature and the greenhouse effect shall not be further discussed in this eurammon information. Below some highlights of the “history” of CO₂ shall be discussed without claiming to give a complete overview.

CO₂ has from time immemorial been known to emerge from geological sources. The Romans already knew the agreeable effect of bathes containing CO₂ from volcanic sources on the blood circulation. The hazardous effect (suffocation due to air displacement) was also known to them. Plinius calls it “spiritus letalis”, the “lethal spirit”, which kills its victims without leaving any traces. It used to be the custom to place candles in fermentation cellars to monitor the ambient air, their extinction indicating an excessive concentration of CO₂.

For centuries CO₂ has been known as a waste gas from fermentation and lime works. An older method to produce carbon dioxide was to pour water on marble pieces or limestones with hydrochloric acid or sulphuric acid, thus forming CO₂ gas. Paracelsus (1493–1541) already made a clear distinction between CO₂ and air and J. B. van Helmont (1577–1644) realized that the gases produced in different ways were in fact the same substance, which was a bit later also found as a component of air.

The French physicist Lavoisier (1780) coined the word "acide-carbonique" (translating into carbonic acid) after he had detected the composition of the gas of one part carbon and two parts oxygen.

In 1823 the physicist Faraday (1791–1867) was the first who managed to produce liquid CO₂ in small laboratory quantities. CO₂ in solid form as snow was first produced by Thilorier in 1834 by expansion of liquid CO₂ to atmospheric pressure. He reported "that the snow could be compressed easily, had a temperature of -78.5°C at atmospheric pressure and without melting first, transiting immediately from the solid into the vaporous state" (sublimation). This solid CO₂ is called "dry ice". Dry ice was first produced industrially in Montreal in 1924. After the Dry Ice Corporation New York propagated dry ice for the transport of ice cream and frozen food, the annual consumption in the USA rose from 135 t in 1925 to 120,000 t in 1935. A considerable dry ice production in Germany started at the beginning of the 1930s. The "Taschenbuch für Kälte-Techniker" (pocketbook for refrigeration mechanics) (1939) by W. Pohlmann mentions a production of 5,500 t in 1938 and 15 manufacturers. In the cities the price was about 0.30 to 0.40 reichsmark per kg. In the same reference, 75% of the world-wide production were attributed to the USA, which produced 150,000 t in 1937.

Even today dry ice is used in considerable quantities, chiefly for transportation refrigeration of food. The total European dry ice production was about 120,000 t in 2000. Liquid CO₂ was and is produced and used or consumed in even larger quantities. In Germany it was Dr. phil Wilhelm Carl Raydt a teacher at a grammar school for sciences in Hannover who started the liquefaction and industrial application of CO₂ (1877). He liquefied CO₂ via a reciprocating compressor at ambient temperature by hydrocooling. One of his first applications of CO₂ was the lifting and relocating of a 5 t anchor stone in the port of Kiel commissioned by the imperial navy. For this task Raydt had a diver fasten a rubber balloon on the anchor stone and had the balloon filled with CO₂ from a steel bottle. Thus the anchor stone could be floated to another place.

In 1880 Raydt took out a patent on "A Procedure and Apparatuses to Impregnate, Lift and Cast Water Aided by Droppable Carbonic Acid". This is the basis for the production of carbonated beverages and the use of CO₂ in the draught beer dispensation to pressurize and

transport the beer to the tap. This Dr. Raydt is mentioned, though with a different spelling, in the "Lebenserinnerungen" (memoirs) (1914) of Heinrich Dräger (founder of the Dräger-Werke, Lübeck). There he writes about a newspaper article, which he read a year ago or earlier:

"It dealt with liquid carbonic acid and how it could be used in commercial applications. The inventor Dr. Rhaidt intended to fill it into bottles and use it for beer dispensation. That is why he cooperated with a company in Hanover and their apparatuses would soon be on the market. The omniscient journalist had then used this news to criticize this intention very scholarly and disparagingly. Liquid carbonic acid had the incredible pressure of 35 atmospheres, which even increased significantly in warm temperatures. No landlord would accept such a bomb in his house and, by the way, the police would never give their permission for this. The railroad companies would hardly want to transport such explosives as furthermore there were no kegs which could withstand such a pressure. To confirm his analysis he had added a mathematic formula so that even the most simple-minded reader had to understand this man was right."

Heinrich Dräger realized that liquid carbonic acid was the ideal pressurizing agent for beer. He developed the then available beer pressurizing apparatuses (CO₂ pressure reducers) for the draught beer dispensation to perfection. Starting in 1902/03 H. Dräger, his son Bernhard and the Lübeck surgeon Dr. Otto Roth developed the first mechanical narcotic apparatus on the basis of this very beer pressurizing apparatus in order to achieve a controlled mixture of air or oxygen and the inhalation narcotic (award at the world exposition in St. Louis in 1904). A license agreement between Dr. Raydt and the Chemische Fabrik Kuhnheim & Co., Berlin-Niederschöneweide, in 1882 was the basis to start the first industrial production of liquid CO₂ in Germany there.

In 1883 it was transferred into the company "Actien-Gesellschaft für Kohlensäure-Industrie" (since 1931 Agefko), which in its first financial year (1884) produced 122,088 kg CO₂. Its first general manager, Hugo Baum, had a rather unconventional way to advertise his liquid CO₂ by asking the imperial shipyard in 1884 to be allowed "to supply the officers' mess hall on one of His Majesty's ships with two bottles of liquid carbonic acid free-of-charge as well as one complete beer pressure apparatus on loan". The "bottles" had a gross weight of about 60 kg, see below.

In 1886 the company Rommenhüller & Co., Rotterdam, managed to thwart the Raydt patents making room for further manufacturers. Six of these companies in competition to Agefko merged to a sales group (syndicate?) the "Kohlensäure-Verkaufs-Verein Ges. mbH" in 1892, which was joined by nine further companies. From October 1, 1895, to September 1, 1896, this group sold 8.5 million kg CO₂. Due to internal problems, further external competition and price wars it disintegrated as early as September 1, 1899 (status: 20 companies). But on January 1, 1901, a new union was founded in Berlin, the "Deutsche Kohlensäure-Gesellschaft mbH" (DGK). Except for the Buse company, all the meanwhile existing 30 carbonic acid factories – Agefko as well – joined the union.

The gas industry and the use of its liquefied gases received great impulses by the invention of light and safe compressed-gas bottles. In 1886 Howard Lane and Richard Taunton took out the English patent No. 12371 on the manufacture of weldless steel bottles made of one-inch-thick flat steel plates by forging, drawing, pushing, and pressing.

In the same year, the brothers Max and Reinhard Mannesmann in Germany presented their cold-rolling process for the manufacture of weldless pipes, which was soon introduced into the manufacture of thin-walled compressed-gas bottles. Before, an empty steel bottle forged out of one block weighed about 52 kg for a charge of 8 kg CO₂. Today an empty compressed-gas bottle for a content of 10 kg made of steel weighs about 16.5 kg and made of aluminium about 12 kg.

As a refrigerant, CO₂ was first proposed by Alexander Twinning in his British patent of 1850. In America Thaddeus S. C. Lowe experimented with CO₂ for military balloons in the 1860s and made the discovery to use CO₂ as a refrigerant. Lowe started to develop refrigeration systems and in 1867 took out the British patent No. 952. Around 1869 he erected a CO₂ machine in Jackson, Miss., and built another one on board a ship for the transportation of frozen meat from Texas to New York.

The first CO₂ compression refrigeration system in Europe was built by C. Linde in 1881 (Plank) (according to Göttsche in 1883), manufactured by the Maschinenfabrik in Augsburg and put into operation at Krupp in Essen in 1882. Linde was, however, not an advocate of the CO₂ machine and supplied it only on explicit request. He favoured ammonia. From 1893 to 1894 Linde tested such a CO₂ machine in Munich in order to prove the inferiority of the

CO₂ machines of his competitors Riedinger and Hall. He also wanted to prove that CO₂ machines could not reach the efficiency of NH₃ machines.

Since 1881 the above-mentioned W. Raydt in Hanover had also worked on the construction of CO₂ machines. In 1884 he took out the British patent 15475 for a "compression ice-making system using carbon dioxide".

An essential contribution to the breakthrough of CO₂ machines was the work of Franz Windhausen in Berlin (1886). The first CO₂ ship refrigeration systems in Germany were built according to his patent DRP 37214 by the companies Riedinger in Augsburg and Haubold in Chemnitz. In 1886 Windhausen took out the British patent 2864 for his CO₂ compressor. In accordance with this patent the company J. & E. Hall in England started to build ship refrigeration machines. The first was installed in the steamer "Highland Chief" in 1890 for the transportation of frozen meat.

At the same time, in 1887/90, the development and manufacture of CO₂ machines and plants in the USA started. The company "Kroeschell Bros. Ice Machine Company" propagated CO₂ as a "safety refrigerant" in contrast to sulphurous acid and ammonia, which were termed extremely "harmful". Kroeschell manufactured CO₂ refrigeration machines according to a patent (1898) by the Hungarian Julius Sedlacek and called his compressor series "North Pole compressors". In 1924 Kroeschell merged with the Brunswick Refrigeration Company of New Brunswick, N.J., which manufactured ammonia compressors.

Further U.S. companies, occupying themselves with CO₂ compressors and systems were among others a company founded in 1915 in Chicago by Fred Wittenmeier (former employee of Kroeschell's), the Carbondale Machine Company and the American Carbonic Machinery Company. The hitherto used cold air and ammonia machines in ships were more and more replaced by CO₂ machines. Ashore it was chiefly air-conditioning systems and the food industry, which were equipped with CO₂ refrigeration systems.

According to Bäckström 60% of the ship refrigeration plants and 10% of the land refrigeration plants were still operated with CO₂ in 1950. Göttsche (1912/15) names 29 factories in Europe building CO₂ refrigeration systems, 23 of them in Germany. Small refrigeration machines had a performance of between 2,300 and 16,000 kcal/h, (e.g. by the company Riedinger).

Conventional series had a capacity range of 2,000 to 140,000 kcal/h at a brine cooling from -2°C to -5°C. So-called plunger condensers or spray condensers served as liquefiers.

As a peculiarity Göttsche mentions a manual CO₂ ice-making machine, type "Kolibri" by Ths. Sabroe & Co. in Aarhus. The compressor was started via a manual crank. The machine could produce 1.5 to 2 kg ice per hour. According to Göttsche/Heinel almost 3,000 ammonia, 1,600 carbonic acid and 800 sulphurous acid machines were in use in Germany in 1908. 600 kg a year were regarded as a normal refrigerant loss due to leakages according to Pohlmann (1935), e.g. in a CO₂ brine system with a capacity of 80,000 kcal/h and a charge of 420 kg CO₂. The price for CO₂ was 0.75 RM (reichsmark)/kg (syndicate price) and 1.29 RM/kg in the small retail trade.

The development of CO₂ refrigeration systems in Europe was similar to that in the USA. CO₂ was used successfully in marine and industrial refrigeration systems in the early 1890s and for air-conditioning purposes since about 1900 to a peak in the mid-1920s in the USA. Due to their nontoxicity and nonflammability, CO₂ refrigeration systems were used in food markets, kitchens, hospitals, hotels, restaurants, theatres, passenger ships etc. Predominantly indirect refrigeration systems with a calcium chloride brine were used.

With the beginning of the 1930s, CO₂ in industrial refrigeration plants was more and more replaced by ammonia, which had indeed been used in parallel since the last quarter of the 19th century. In air-conditioning applications, the replacement of CO₂ started in the mid-thirties of the 20th century by the new "safety refrigerant" R 12 (e.g. Freon 12, Frigen 12).

The discussion about CO₂ as a refrigerant was revived essentially by a patent of Professor Gustav Lorentzen from 1990 "Trans-critical vapor compression cycle device", patent WO 90/07683. Other impulses came from the works about CO₂ as a refrigerant for automotive air-conditioning systems by G. Lorentzen and J. Pettersen in 1993/94.

Experts in many sectors realized that CO₂ had the potential to be an excellent refrigerant for our present energy awareness and environmental situation. Animated research activities started at institutes, companies, and universities in order to dig up more than 100-year-old research results and adapt them to our present abilities with regard to procedures, materials, lubrication and optimal energy consumption.

Various new CO₂ applications for refrigeration purposes have been developed recently and have been realized in practise in existing plants. So far, systems with CO₂ as the evaporating secondary refrigerant account for the highest percentage, preferably in the deep-freeze range (up to -50 °C), e.g. in freezers for bread, cakes and pastries as well as for other food products, in supermarkets (many in Sweden), frozen food storage facilities and artificial icerinks (e.g. in the southern, German-speaking region). As a rule, the cooling and recondensation of the secondary refrigerant in larger plants is done by one-stage or two-stage NH₃ refrigeration systems. Two-stage CO₂/NH₃ cascade plants with CO₂ compressors on the low pressure side and NH₃ compressors on the high pressure side have also been realized already, e.g. for freezer operations. Apart from that, systems for automotive air-conditioning systems and heat pumps with CO₂ as the refrigerant have been developed for the operation in the supercritical range.

Apart from the ecological benignity of these new CO₂ applications, there are also solid economic advantages, such as better product quality at lower temperatures, even secondary refrigerant temperatures (artificial ice-rinks), better heat transfer coefficients, smaller low pressure compressors, smaller pipe dimensioning, optimisation of the energy consumption.

The technical details and technological advantages of these new refrigeration systems as well as the physics, chemistry and the physiological properties of the refrigerant and the secondary refrigerant CO₂ will also be discussed in one of the eurammon information papers.

In case of doubt, the German-language original should be consulted as the authoritative text.

Published by eurammon
P. O. Box 71 08 64, D-60498 Frankfurt
Phone +49 69 6603 1277, Fax +49 69 6603 2276
e-mail: karin.jahn@eurammon.com
<http://www.eurammon.com>