Citric Acid

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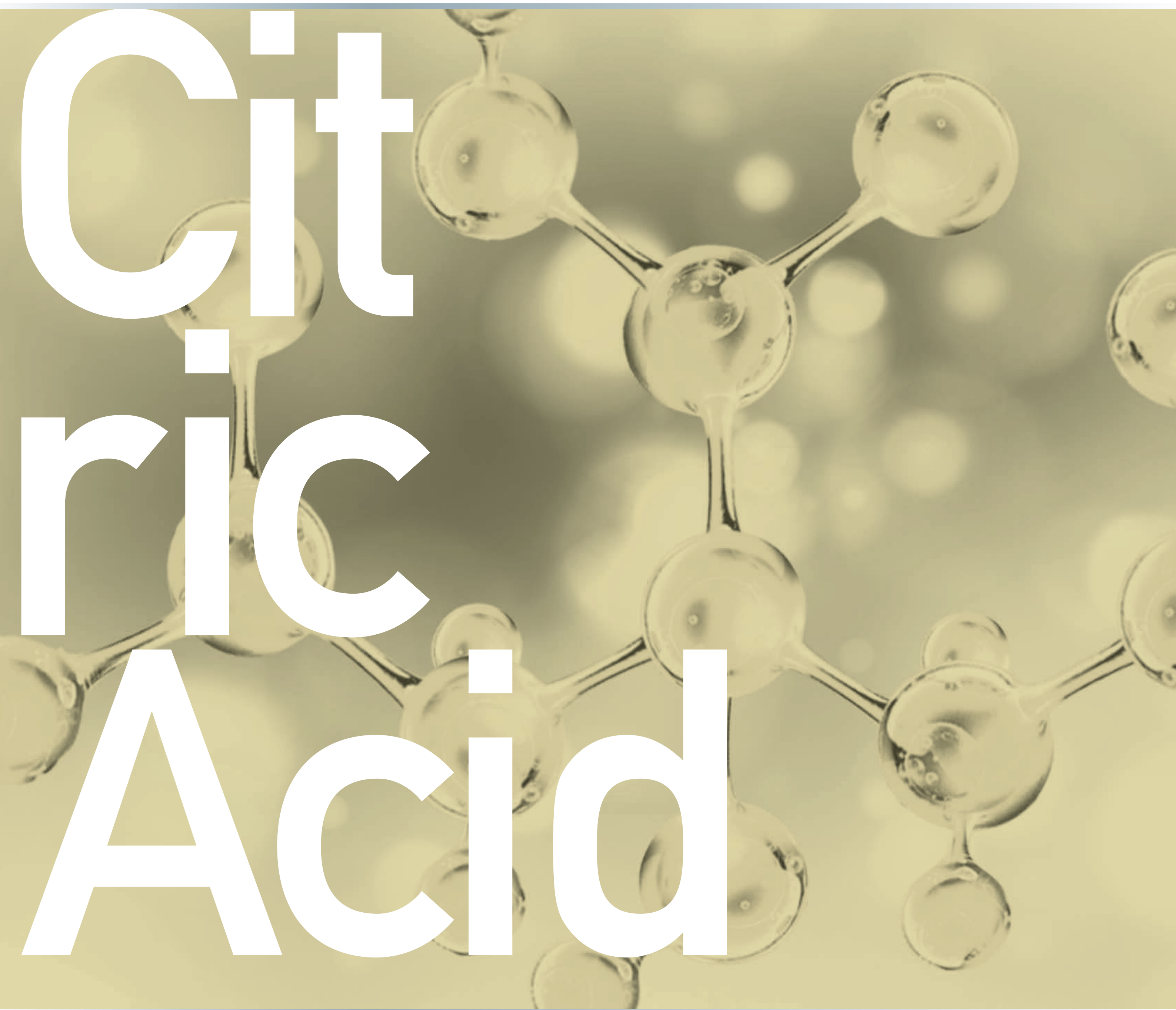
Biocommodities



Citric Acid

Process Technology

VOGELBUSCH CITRIC ACID PLANTS
Know-how and technology licensing

Well-known for the development and industrial application of cutting-edge citric acid processes, Vogelbusch is the world's leading supplier of citric acid plants – and not just because we deliver advanced technology that is tailored to customer and market requirements. Customers also benefit from the fact that we are the only producer-independent engineering company with proprietary process and engineering know-how.

With our decades of experience in international plant construction activities and many years of work when it comes to building citric acid plants, Vogelbusch is equipped with both the expertise and the ability to carry out all project work associated with the construction of a citric acid plant, from start to finish.

HOW YOU BENEFIT FROM OUR EXPERTISE

We are able to offer high-performance production technology by harnessing synergies available with other bioprocesses at our disposal. In particular, our customers benefit from:

- Proprietary technology and engineering know-how
- Proprietary microorganism strains (*Aspergillus niger*) that have been adapted for industrial citric acid fermentation
- Proprietary apparatus for spore propagation and pilot fermentation
- Feedstock-adapted plant designs, individually tested in our in-house laboratories
- Selected, tried-and-tested upstream and downstream processes ensuring optimum product quality
- Reference projects spread across four continents

APPLICATIONS

Given its impeccable organoleptic, physiological, and chemical properties, citric acid is one of the most indispensable and frequently used organic acids. It is of particular importance for various applications in the consumer industries such as:

- **Food and beverages** use as an acidifier, pH buffer and ingredient of preservatives
- **Pharmaceuticals and cosmetics** use as a stabilizer
- **Detergents** use as a substitute for phosphate in the composition of cleaning and washing agents for its sequestration characteristics and biodegradability

Worldwide production currently stands at 1.5 to 2 million metric tons per year.

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OUR SERVICES FOR CITRIC ACID PLANTS

Vogelbusch provides engineering, consultancy and contracting services, and licenses technology. Our service packages for developing citric acid facilities include:

- Conceptual Design
- License, process know-how and basic engineering for the process plant
- Detail engineering or review of customer's detail engineering
- Supplying proprietary technical components and standard equipment and/or providing procurement assistance
- Supplying automation systems including field instruments together with DCS hardware and software
- Supplying our *Aspergillus niger* strains as citric acid-producing organism
- Supervising plant installation and start up
- Technical support for plant upgrades, etc.

PRODUCTIVITY AND PROCESS ECONOMICS

Here is a summary of process parameters achieved in the fermentation process, taking pure substrates and high-quality molasses as an example.

	STARCH HYDROLYSATE	RAW SUGAR	MOLASSES
Yield [1]	82% CAM / MS	85% CAM / DS	slightly lower
Volumetric production / total cycle time	1.1 CAM g/l/h	0.8 CAM g/l/h	related to quality
Biomass	appx. 15 g/l cell d.s.		
Byproducts:			
Gluconic acid	negligible		up to several g/l
Oxalic acid	negligible		low
Temperature	30 - 32°C		
Cycle time [2]	140 h	180 h	related to quality
Final titre	145 – 160 g/l CAM		related to quality

[1]) fermentable sugar as mono- (MS) or disaccharides (DS)
[2]) depending on final titre

Fermentation section

Filtration section

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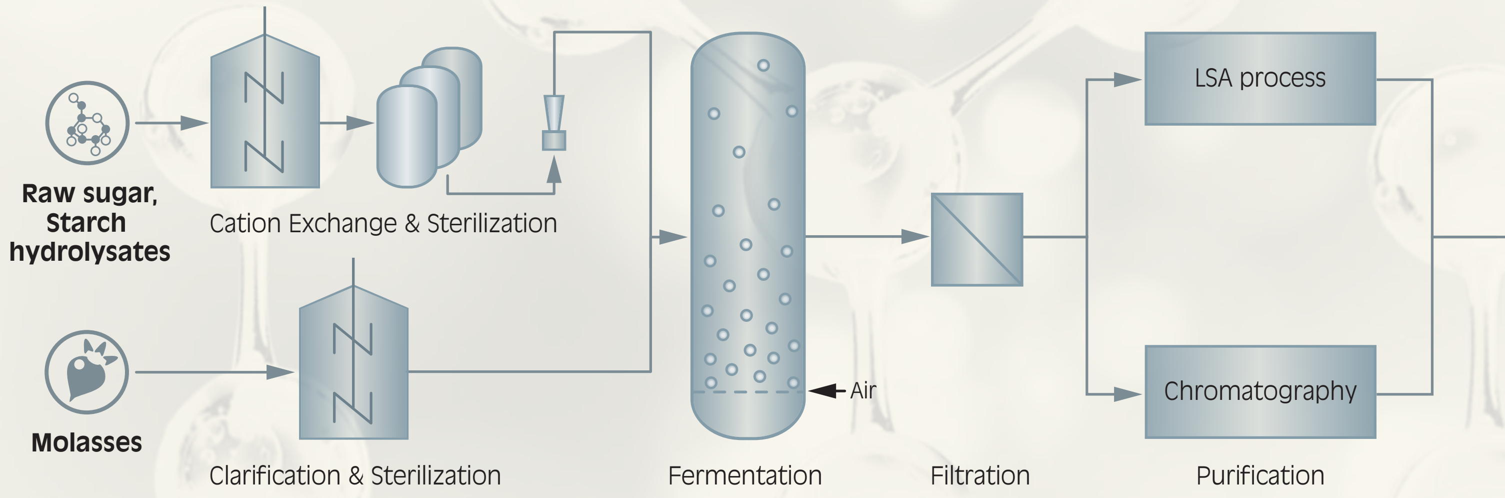

RAW MATERIAL PREPARATION

The raw materials used for the industrial production of citric acid typically are (by-) products from the sugar and starch processing industry. Pure substrates such as starch hydrolysates, glucose and raw sugar are particularly suitable, while beet or cane molasses may be used under certain conditions. Specially developed technologies are used to process these raw materials, which are adapted to the needs of the individual case.

Starch-containing feedstocks have to go through a saccharification process in order to convert the starch into glucose, which can then be utilized by the microorganism. The resulting starch hydrolysates, just as raw sugar solutions, are often very pure, only needing be decationized and then sterilized. Substrates with a high degree of impurity, such as molasses in particular, are subject to hexacyanoferrate clarification, with simultaneous boiling and sterilization processes. Notwithstanding the efficiency of this method, availability and handling of hexacyanoferrate are often considered as problematic so that molasses are rarely used in modern plants.

SPORE CULTIVATION AND TESTING

A precondition for an efficient microbial production process is the availability of high-quality inoculation material. Vogelbusch licenses its own strains of *Aspergillus niger*, which have been selected and enhanced for use in industrial citric acid fermentation.

Sporebox

Pilot fermentation racks

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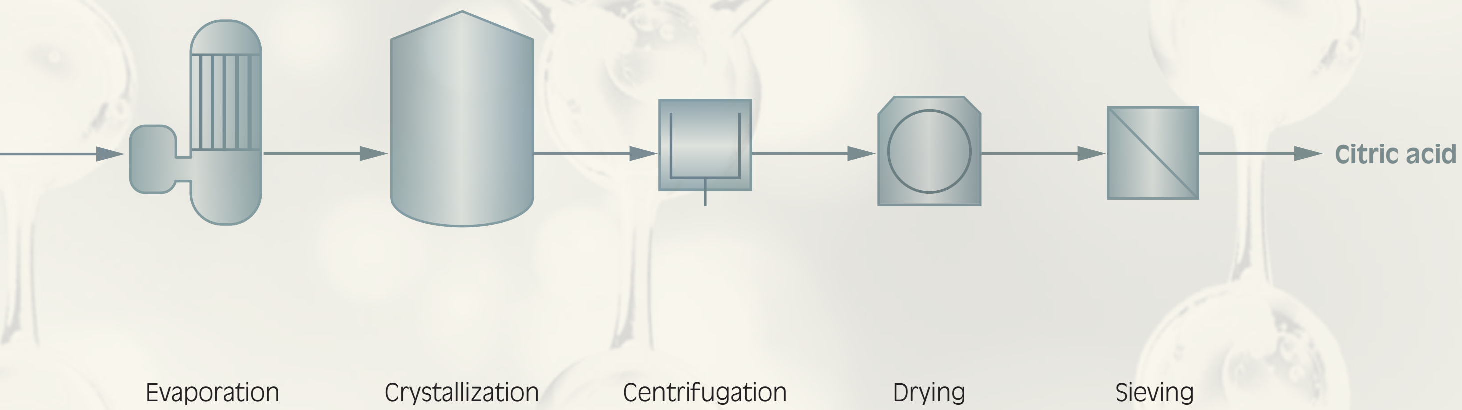

Special equipment has been developed to produce and test spores in a safe and efficient way. The patented Vogelbusch Sporebox comprises a closed system for the propagation, harvesting and bottling of the dried spores, improving both storage stability and the ease of dosing in application.

A pilot fermentation system is used to test substrates and microorganisms for their suitability in production, enabling test series for process optimization to be carried out in a timely manner, for instance regarding the addition of nutrients, trace elements, and inhibitors.

FERMENTATION

Citric acid synthesis is carried out by means of submerse fermentation. Using sets of bubble column (air-lift) fermenters with static sparger systems to disperse the air, the Vogelbusch citric acid fermentation sets itself apart with its simple design and its particularly low energy consumption.

To start the process, the sterilized substrate in the fermenter is inoculated with spores that have been propagated and pilot tested in the on-site laboratory. The fermentation procedure is precisely matched to the raw material used to regulate the metabolic activity of the microorganism so as to ensure the best possible substrate yields and consistently high production rates.

DESIGN OPTION

Batch | Fed batch fermentation

Batch fermentations are employed for all types of pure substrates and high-quality molasses. The production fermenters are inoculated directly with the spores. Alternatively, small pre-fermenters may be used for germination of the spores to avoid the lag phase in the production fermenters and to shorten the cycle time there accordingly.

Fed-batch fermentation is more suitable for low-quality molasses to overcome the inhibiting effects of substances contained in the raw material.

ISOLATING CITRIC ACID

The aim of isolating the citric acid is to obtain a largely pre-purified citric acid raw solution from the fermented mash, thereby not only facilitating its downstream processing, but also ensuring the quality of the finished product. The mycelium is separated from the raw solution in a series of filtration and decantation steps, which are combined depending on the case.

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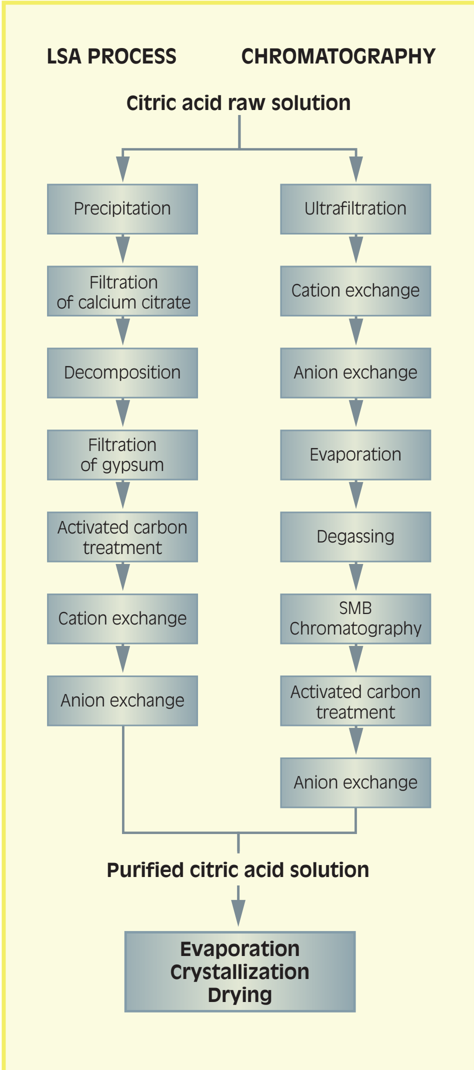
PURIFICATION

The isolated citric acid solution can be purified in two different ways: chromatography is used for pure substrates, while the lime-sulfuric acid (LSA) process is suitable for all types of feedstocks.

DESIGN OPTION
LSA process
The LSA process requires significant amounts of lime hydrate and sulfuric acid and a by-product, gypsum, is formed in corresponding quantities. The wastewater from the calcium citrate filtration process must be treated. It is possible to utilize the gypsum in some way, depending on the options available locally, such as for cement production in the construction industry.

The advantages of the LSA process are its high purification efficiency and the high concentration of the citric acid solution obtained after decomposition. This has a positive effect on the sizing of evaporation and crystallization units and in combination with lower energy demand reduces costs. Thanks to the purity of the citric acid solution, the mother liquor from crystallization can be completely recycled within the process.

DESIGN OPTION
Chromatography process
In comparison, the chromatography process uses fewer chemicals and there are no solid by-products. Only hydrochloric acid and sodium hydroxide are required for the regeneration of the ion exchangers, along with small amounts of sulfuric acid for the simulated moving bed (SMB) chromatography. Process and demineralized water are required for chromatography and ultrafiltration; the raffinate is wastewater that must be treated. Given that there is a higher accumulation of impurities in the mother liquor, the production of trisodium citrate serves as a sink.



EVAPORATION, CRYSTALLIZATION AND DRYING

The final processing of the purified citric acid solution involves concentrating it in a multistage falling film evaporator that combines the advantages of delicate product handling with high energy efficiency. The specific energy requirement can be reduced even further by means of thermal vapor compression or, alternatively, by means of mechanical vapor compression.

Continuously operated forced-circulation vacuum crystallizers are used to crystallize the citric acid. Appropriate measuring and control strategies, along with a crystallizer design matched to suit them, enable Vogelbusch plants to produce both citric acid monohydrate and anhydrous using the same equipment. Sophisticated strategies for recirculating the mother liquor, separated from the crystal mash in a continuous centrifuge, make it possible to effectively control the quality of the final product.

Fluidized bed drying takes full account of the high demands for the quality of the final product by ensuring that the product is handled gently. Subsequent screening of the dried final product allows customer-specific fractioning according to particle size.

Product yield

Depending on raw material quality and the degree of impurities in the fermented mash, a final yield in the range of 90 to 92% can be achieved in the downstream process.

AUTOMATION

Vogelbusch citric acid plants incorporate a combination of batch and continuous process stages that have to be coordinated. Reliable and stable plant operations are ensured by means of control systems and automation solutions, adding another layer to the high level of reproducibility of the process, which is essential for the quality of the final product.

PRODUCT QUALITIES

Citric acid is made in both crystalline and liquid forms. Our product purification and crystallization processes are compatible with a wide range of product configurations including:

- Citric acid monohydrate (CAM)
- Citric acid anhydrate (CAA)
- Syrup
- Trisodium citrate (TSC)

They comply with international quality standards for food, industrial and pharmaceutical grades, including BP, USP and FCC.

AVERAGE CONSUMPTION FIGURES

The table below shows the average consumption and by-product figures for a process plant when producing 1,000 kg of CAM, based on pure substrate. The figures are typical examples, and consumption may vary depending on plant configuration. Process water consumption is contingent on wastewater and condensate recycling solutions.

PARAMETER	UNIT	LSA PROCESS	CHROMATOGRAPHY
Chemicals			
Slaked lime (70% CaO)	kg	700	0
Hydrochloric acid (30%)	kg	170 - 190	230
Sulfuric acid (94%)	kg	940	60
Caustic soda (50%)	kg	140 - 160	240
Utilities			
Deionized water	m^3	11 - 14	9
Cooling water 24°C	MJ	10,350 - 11,300	10,350 - 11,300
Cooling water 32°C	MJ	13,600 - 14,600	15,000 – 16,000
Cooling water 5°C	MJ	1,050 - 1,250	1,050 - 1,250 (excluding TSC)
Steam 9 bar	kg	8,500 - 9,000	9,800
Electrical energy	kWh	1,950 - 2,100	dependent on technical solution
By-products			
Mycelium (20% DS)	kg	550	550
Trisodium citrate (as dihydrate)	kg	0	140
Gypsum (as dihydrate)	kg	1,500	0

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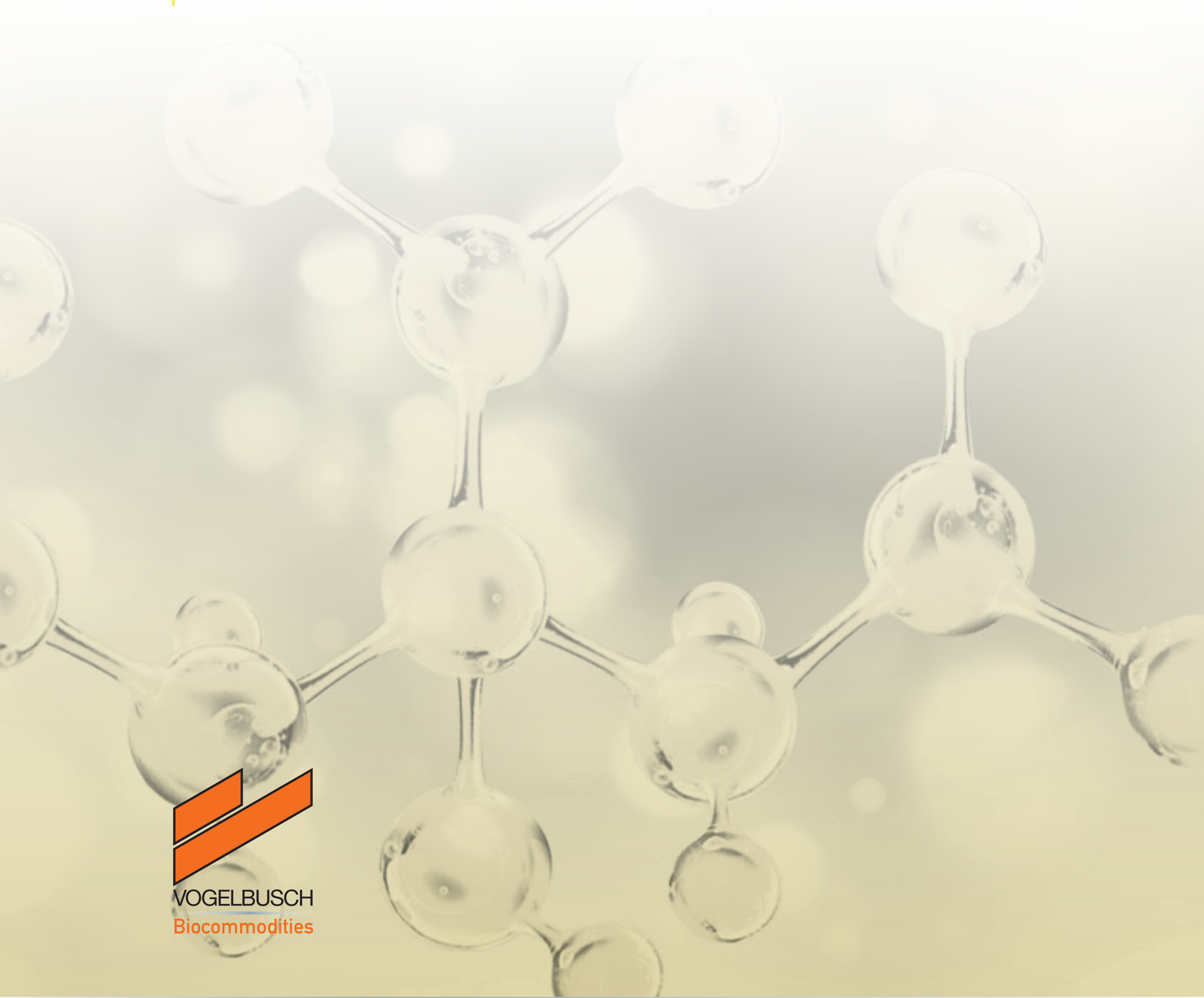
Citric acid occurs naturally in citrus fruits. Discovered in the 18th century, it used to be made by precipitating its calcium salt from juice. Industrial production using a microbial process began in 1919 and has been the subject of continuous improvement and enhancement ever since.



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VOGELBUSCH Biocommodities GmbH | Blechturmgasse 11 | 1051 Vienna | Austria
T +43 (0) 1 54661 | vienna@vogelbusch.com | www.vogelbusch-biocommodities.com

VOGELBUSCH USA Inc. | houston@vogelbusch.com
VOGELBUSCH Hong Kong Ltd. | hongkong@vogelbusch.com

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