Citric Acid Production

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Citric Acid: Applications

- Citric acid (CA) is an organic acid that is generally found in a variety of fruits such as limes, lemons, oranges, pineapples, and grapefruits.
- It is a natural ingredient that aids in detoxification, maintaining energy levels, and supporting healthy digestion and kidney function.
- It has a slightly tart and refreshing flavor and is employed for balancing the sweetness in soft drinks, juices, and other beverages.
- Citric acid used in food and beverage (F&B) industry due to its antioxidant properties to preserve the food or as an acidifier enhances the flavors and aromas of fruit juices, icecream, and marmalades.
- In the pharmaceutical industry, it is used as an antioxidant to preserve vitamins, effervescent, pH corrector, blood preservative, iron citrate tablets as a source of iron for the body, ointments and cosmetic preparations, and so forth.

... Applications

- In the chemical industry, for softening and treatment of textiles, it is used as a foaming agent.
- In metallurgy, certain metals are utilized in the form of citrate.
- Because of less eutrophic effect, CA is used in the detergent industry as a phosphate substitute.
- Further, CA is frequently incorporated in facial packs and masks as it naturally brightens and lightens the skin tone, minimizes break-outs and oiliness, and regenerates the dead skin cells.
- Currently, the global CA market is projected to reach USD 3.2 billion by 2023 and is expected to witness a Compound Annual Growth Rate (CAGR) of 5.1% during the forecast period (Market report world.com, 2020).
- The global production of CA is estimated to be around 736,000 tones/year, and the entire production is carried out by fermentation.

Applications	Industry	Uses
Food	Animal feed	Complementary feed
	Candies	Acts as acidulant. Prevention of sucrose crystallization provides dark colour in candies, sucrose inversion. Provides tartness
	Dairy products	Emulsifier (ice creams and processed cheese), antioxidant and acidifying agent (cheese products)
	Fats and oils	Stabilizing action. Synergist for other antioxidants as a sequestrant
	Frozen fruits	Inactivates trace metals to protect ascorbic acid. Lowers pH to inactivate oxidative enzymes. Neutralizes the residual lye
	Jellies and jams	Adjusts pH (to the range where pectin acts as a gelling agent). Acts as an acidulant. Provides tartness, tang and flavour. Increases the effectiveness of antimicrobial preservatives
Beverages	Fruit and vegetable juices	Stabilizer in commercially prepared juices
	Soft drinks and syrups	Simulates fruit flavour and tartness. As an acidulant in carbonated and sucrose-based beverages
	Wines and ciders	Browning prevention in some white wines. Turbidity prevention. Oxidation inhibition. pH adjustment
Pharmaceutics	Pharmaceuticals	Provides rapid dissolution of active ingredients. Acidulant in mild astringent formulations, anticoagulant. Effervescent in powders and tablets in combination with bicarbonates, solubilization action for cathartics, antioxidant in vitamin preparations
	Cosmetics and toiletries	Metallic-ion chelator and buffering agent. Adjusts pH. Antioxidant
Other	Other	Buffering agent, sequesters metal ions, neutralizes bases
		Metal oxide removal from ferrous and non-ferrous metal surfaces, operational cleaning of iron and copper oxides
		In electroplating, copper plating, metal cleaning, leather tanning, printing inks, bottle washing compounds, floor cement, textiles, photographic reagents, concrete, plaster, adhesives, paper, polymers, tobacco, waste treatment, chemical conditioner on teeth surface, ion complexation in ceramic manufacture, etc.

Properties

- CA is a colorless white crystalline powder that is practically odorless and exists in:
  - anhydrous form ($C_6H_8O_7$, molecular weight 192.12)
  - monohydrate form ($C_6H_8O_7.H_2O$, molecular weight 210.14)
- Anhydrous CA is highly soluble in water, freely soluble in ethanol, and sparingly soluble in ether
- Whereas monohydrate CA is soluble in water and sparingly soluble in ether.
- It is solid at room temperatures, melts at 153◦C, and boiling temperature is 310◦C.
- It decomposes with loss of carbon dioxide (CO_2) above about 175◦C.

Microorganisms Known to Produce CA

- Bacteria, such as *Arthrobacter paraffinens*, *Bacillus licheniformis*, and *Corynebacterium* sp., are known to produce large amounts of CA.
- Yeasts that can produce CA are *Candida*, *Hansenula*, *Pichia*, *Debaromyces*, *Torula*, *Torulopsis*, *Kloekera*, *Saccharomyces*, *Zygosaccharomyces*, and *Yarrowia*.
- One drawback of yeast fermentation is that they produce substantial quantities of Iso-citric acid, an undesired by-product.
- Fungi that are reported to produce CA are *Aspergillus*. niger, *A. awamori, A. clavatus, A. nidulans, A. fonsecaeus, A. luchensis, A. phoenicus, A. wentii, A. saitoi, A. flavus, Absidia* sp., *Acremonium* sp., *Botrytis* sp., *Eupenicillium* sp., *Mucor piriformis, Penicillium citrinum, P. janthinellu, P. luteum, P. restrictum, Talaromyces* sp., *Trichoderma viride*, and *Ustulina vulgaris*

Microbes	CA producing species
Bacteria	*Bacillus licheniformis, Arthrobacter paraffinens, Corynebacterium* sp., *Bacillus subtilis, Brevibacterium flavum, Corynebacterium* sp., and *Penicillium janthinellum*
Fungi	*Aspergillus niger, A. aculeatus, A. awamori, A. carbonarius, A. wentii, A. foetidus, Penicillium janthinelum*
Yeast	*Saccahromicopsis lipolytica, Candida tropicalis, C. Oleophila, C. Guilliermondii, C. Parapsilosis, C. Citroformans, Hansenula anamola, Yarrowia lipolytica, Torulopsis, Hansenula, Debaromyces, Torula, Pichia, Kloekera,* and *Zygosaccharomyces*

Productions

- Raw materials used for CA production can be divided into two groups:
  - With a low ash content from which the cations could be removed by standard procedures (e.g., cane or beet sugar, dextrose syrups, and crystallized dextrose)
  - raw materials with a high ash content and high amounts of other non-sugar substances (e.g., cane and beet molasses, crude unfiltered starch hydrolysates).
- Industrial CA fermentation can be carried out with different substrates in three different ways such as surface, sub-merged, and solid-state fermentation with some advantages and dis-advantages (Table2).

Table 2.

Fermentation	Advantage	Disadvantage	Material
SSF	Lower energy and cost requirements, higher yield, low-cost natural media, better oxygen circulation, less susceptible to trace elements inhibition, low risk of bacterial contamination, less amount of post-recovery waste	Difficulties in scale-up, difficult control of process parameters higher recovery product costs	Pineapple waste Apple pomace Banana peels Coffee husk Corn cob Grape pomace Corn husk Kiwi fruit

Fermentation	Advantage	Disadvantage	Material
SF	Less effort in operation, installation, and energy cost	Large amount of heat generation, time-consuming and needs large area/space, sensitive to contamination by *Penicillia*, other *Asperigilli*, yeasts, and lactic acid bacteria	Brewery waste
			Turnip whey (supplemente with molasses)
			Sweet potato starch hydrolysate
SMF			Beet molasses
	Sophisticated control mechanisms, lower labour cost, higher productivity and yield	High media cost, sensitive to trace metal inhibition, high waste water generation	Cane molasses
			Date syrup
			Corn cobs
			Coconut oil
			Soybean oil
			Orange peel

Surface fermentation

- Surface fermentation is a stationary batch fermentation process known as the beginning of CA fermentation process completed within 8 to 12 days.
- It is carried out in fermentation chambers, with a number of trays arranged in shelves made in stainless steel.
- The fungal mycelium develops
- on the surface of the medium on those trays. After sterilizing the fermentation medium contained in trays, it is inoculated with spore suspension and incubated at 28–30◦C for 24h.
- Spores germination started with drops in pH of medium from 6.0–6.5 to 1.5–2.0
- In this process, a huge amount of heat is generated during fermentation, which is controlled with proper aeration.
- The CO_2 generated during the fermentation process would inhibit the production of CA in concentrations higher than 10%.
- Surface fermentation has some disadvantages such a slow yield and labor-intensive with higher maintenance cost compared to submerged fermentation.
- It is also sensitive to changes in the composition of the media.
- The advantage are lower energy consumption and foam free.

Submerged fermentation

- In this process, the broth medium inside the nutrient substratum is in liquid form and the organism can grow through out the broth medium.
- The fermentation is carried out in bioreactors and completed within 5–12 days.
- The organism, after 1 to 2 days of inoculation, grows as pellets of approximately 0.5 cm diameter and suspended freely in the medium.
- Thus, the organism with a huge contact surface area can take up the nutrients and O_2.
- The air flow is introduced into the vessel at high speed, and the agitation equipment mixes and breaks the air bubbles to increase oxygen levels.
- The carbon source present are decomposed anaerobic or partially anaerobically by microorganisms present in the medium.
- The advantages of submerged fermentation include better control of the fermentation process and the maximum use of a wide range of substrates.
- It provides higher yields; lower capital, maintenance, labor costs, and contamination risks make it more suitable for CA production.
- In contrast, the disadvantage of submerged fermentation is the formation of foam, which can be avoided using antifoam agents such as animal or vegetable fats and chambers with a volume of upto one-third of the total fermenter volume.

Solid-state fermentation

- The condition parameters for solid-state fermentation are substrate used is solid and moistened to about 70% moisture, pH between 4.5 and 6.0, and a temperature between 28–30◦C.
- The process is completed within 4–5 days.
- The major advantages of solid-state fermentation are low energy requirements, higher yield, low risk of contamination, less efforts in down stream processing, less effluent generation, simple operation, operable under less water, and less operating costs as compared to submerged fermentation.
- Besides, in solid-state fermentation, cheap and widely available agro-industrial substrates can be easy utilized without any pre-treatment as the system is less sensitive to the presence of trace elements compared to submerged fermentation.
- On the other hand, this method has some disadvantages such as difficulties to scale up, low amenability of the process to standardization, difficult control of process parameters, and problems with heat build-up.
- It cannot utilize available nutrients completely owing to poor heat and oxygen transfer in the substrate.

Recovery of Citric Acid

- Recovery of CA is generally performed through three major procedures such as:
  - precipitation,
  - Extraction and
  - purification
- Oxalic acid is formed during the CA fermentation, which can be removed by increasing the pH upto 3.0 with calcium hydroxide at 72–75◦C.
- Subsequently, calcium oxalate is formed, which can be further precipitated and eliminated by centrifugation or filtration process.
- The CA that remained in the form of calcium salt (calcium citrate) can be recovered through precipitation by adding calcium oxide at 90°C and pH nearly equal to 7.0 .
- Tri-calcium citrate tetra hydrate is formed, which is then treated with 70% sulfuric acid to form CA and insoluble calcium sulfate (gypsum).
- After filtering off the gypsum, a solution of 25%–30% of CA is obtained.
- To remove residual impurities, the filtrate is treated with activated carbon or can be purified in ion-exchange columns.
- Now concentrated by evaporation in a vacuum at 40◦C, and crystals of CA monohydrate can be formed in a vacuum crystallizer at a temperature of 20–25◦C or anhydrous.
- CA can be formed at crystallization temperatures above 36.5◦C

... Recovery of Citric Acid

- Purification and crystallization of CA from fermentation broth can be alternatively performed by solvent extraction method in which insoluble or sparingly soluble solvent such as n-octyl alcohol, tridodecylamine, and isoalkane, alanine 336 in heptane or xylene, mixture of butylacetate and N,N-disubstituted alkylamide, aliphatic alcohols, ketones, ethers or esters,organophosphorus compounds, such as tri-n-butylphosphate, alkylsulphoxides, and water-insoluble amines or a mixture of two or more of such amines are used.
- The advantage of the solvent extraction method is to prevent the use of lime and sulfuric acid , and thus the production of gypsum can be avoided.
- In this process, CA is recovered from the aqueous solution by washing off the extract with water, subsequently crystallized and concentrated.
- The concentrated CA solution dissolved in acetone is passed with compressed CO_2.
- The anti-solvent effects of CO_2 remove the residual impurities and food-grade CA is obtained by simple decolorization and crystallization.

THANKS