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REVIEW

Proecological aspects of citric acid technology

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Abstract

Citric acid (CA) is one of the most important commercial products. The food industry is the largest consumer of the acid, using almost of 70% of the total production, followed by about 12% by the pharmaceutical industry and 18% for other applications. CA is manufactured commercially by the fermentation of carbohydrates, mainly saccharose and molasses, by *Aspergillus niger* using surface, submerged and solid-state fermentation medium. The currently used process causes environmental problems such as production of highly impure post-fermentation waste including dirty $CaSO_4$. The aim of the article was to present alternative production methods for CA, which are more environmental-friendly. Fermentation using the yeast of *Yarrowia lipolytica* is currently undergoing intensive research as an alternative to the classic technology of CA. Extraction by organic solvents is also a promising method of CA production from aqueous solutions. Solvent extraction process is used to eliminate calcium hydroxide and sulphuric acid in the precipitation process. Due to the development of membrane techniques, membranes have been widely used in many branches of industry, including CA technology. CA release and condensation can be obtained by means of electrodialysis, ultrafiltration or/and nanofiltration as well as using liquid membranes. The electrodialysis with a bipolar membrane is another promising method of obtaining CA. Its main strengths are the simplification of technological cycles, waste elimination and creating high-quality products. Selected membrane systems are shown; the BP-A-C system was characterized by the lowest energy consumption (membranes: bipolar, anion exchange and cation exchange). New methods of management of waste biomass from CA production technology towards biogas production are described. Biogas and the biomethane derived from it are widely used: for the production of electricity and heat (cogeneration), as network gas (a substitute for natural gas) and as fuel in vehicles.

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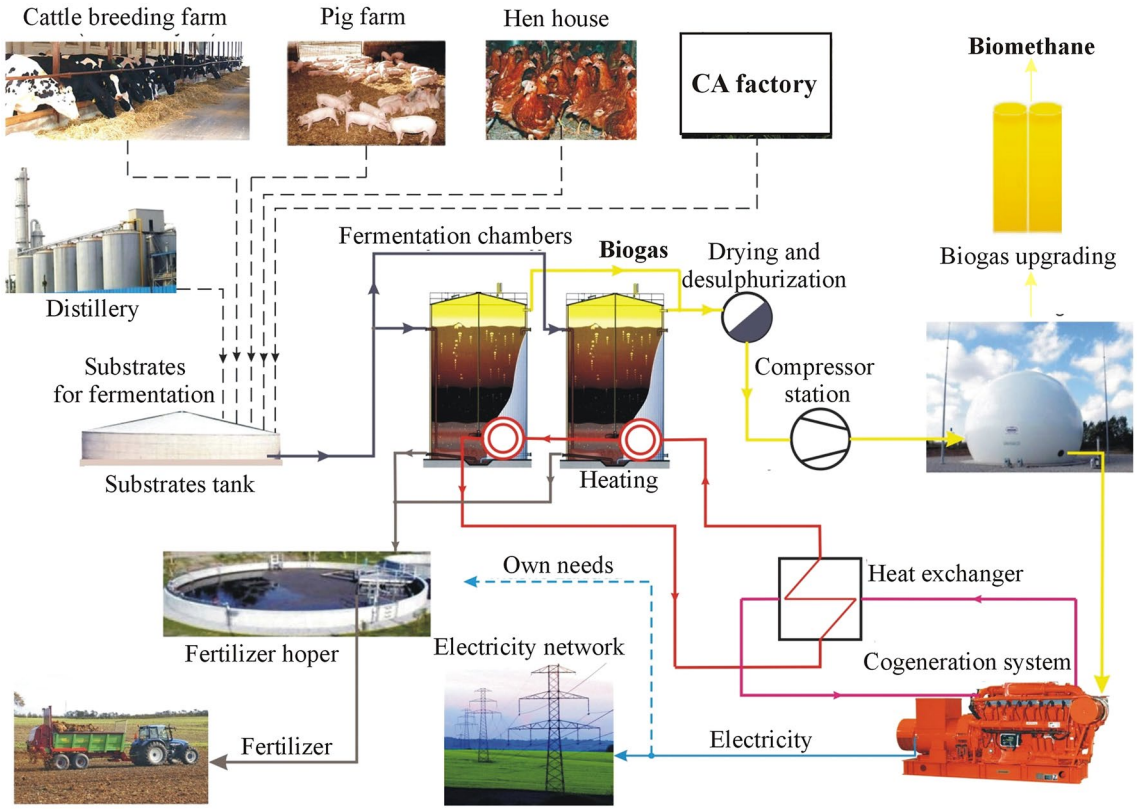
Graphical abstract



Keywords Citric acid · Aspergillus niger · Yarrowia lipolytica · Extraction · Liquid membranes · Electrodialysis · Biogas

Introduction

Intensive civilization development leads to the transformation of the natural environment. Problems related to the negative impact on the environment of production processes have become one of the largest in recent years. Awareness of this state of affairs resulted in the initiation of a series of activities by science, which aims to minimize the amount of pollution, recover or dispose the waste, rationally consume traditional and renewable energy resources and implement "clean technologies". The advanced approach to environmental protection in industry is increasingly switching to integrated systems. These systems are based on the concept of pure production, of which the so-called source reduction is an important element. Its basis is the elimination or reduction of emission streams at the place of their origin and the area of operation for both technical and non-technical elements of the production process. Integrated systems are not only environmentally friendly, but also economically more advantageous. They allow not only to lower or even reduce the generation of waste, thereby reducing the costs associated with their further treatment, but also to increase the economic efficiency of the process by increasing efficiency and reducing the amount of consumed raw materials.

A rapid increase in global birth rate leads to the dynamic development of food industry. When choosing a food product, a consumer thinks not only about the price, but also about favourable organoleptic properties. These are provided by various additives to food, including citric acid (CA). It needs to be stressed that, unlike many other substances used in food industry, CA is non-toxic and easily absorbed by the human organism.

On September 4, 2007, the European Commission initiated antidumping proceeding regulating the import of CA from China, coded CN: 29,181,400 and ex29181500, into the European Union area. The antidumping proceeding was initiated by an appeal placed on July 27, 2007, by the European Chemical Industry Council (CEFIC), representing over 25% of EU CA production. The European Union should defend itself against the flood of Chinese CA not only by issuing the appropriate decrees, but also by supporting the research into rationalization of the conventional technology (Novelli 2008).

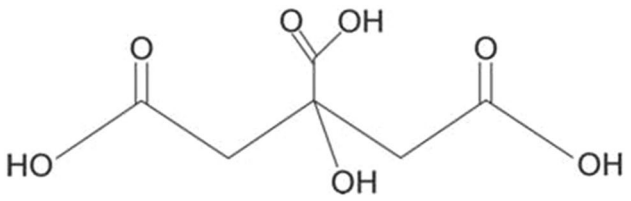


Fig. 1 Chemical formula of CA (own study for (Grewal and Kalra 1995))

Table 1 Physicochemical properties of CA (Leśniak and Kutermankiewicz 1990)

Properties	CA	
	Anhydrous	Monohydrate
Molar mass (g mol^{-1})	192.14	210.16
Crystalline water (%)	0	8.58
Density (g cm^{-3})	1.665	1.542
Melting temperature (°C)	153	70–75
pH 1% solution	2.2	2.2
Solubility at 25°C (g·100 cm^{-3})		
In water	162	209
In diethyl ether	0.75	1.6
In ethanol	38.3	49.8

Thus, it is essential to formulate the most effective method to produce CA (Fig. 1), taking into account an increase in production efficiency and a better product quality as well as lowering of technological and equipment costs, use of resources and energy and waste generation. The major emphasis is on reducing the mass of waste produced throughout all the production stages.

CA can exist in two crystalline forms:

- anhydrous with the formula $C_6H_8O_7$,
- a monohydrate of the formula $C_6H_8O_7 \cdot H_2O$.

Anhydrous CA crystallizes from a hot, concentrated solution, at a temperature above 36.6 °C in the form of a white, crystalline powder. In turn, the monohydrate of CA crystallizes at a temperature below 36.6 °C in the form of colourless, transparent crystals. These crystals are relatively stable in dry air, but gradually lose their crystalline water and disintegrate over time into an amorphous powder. The comparison of the physicochemical properties for the two crystalline forms is presented in Table 1 (Leśniak and Kutermankiewicz 1990).

The aim of the article was to present the conventional CA technology and its modifications—towards cleaner production and waste management. Modifications to conventional CA technology make it possible to obtain CA from a larger variety of substrates, often with less energy requirements and less waste. The "energy" application of waste in CA technology towards biogas and biomethane was also presented.

Short history of CA production

CA was first obtained from citrus fruit by Carl Scheels in 1784. Scheele worked on lemon juice with calcium hydroxide to give calcium citrate. The next step is the reaction of sulphuric(VI) acid on calcium citrate to obtain CA. Particularly high concentration of the acid can be found from lemons and limes; it can constitute to as much as 8% of the dry weight of these fruits. CA started to be obtained on an industrial scale in 1890. CA was expensive at the time, which was due to the price of the raw material and the monopoly of Italy for its production. In 1893, Carl Wehmer discovered that *Penicillium* mould could produce CA from sugar (Peniston et al. 2008).

Until World War I microbiological production of CA did not start to be industrially important, when Italian exports were disrupted. In 1917, James Currie observed that some strains of *Aspergillus niger* produce CA. In the course of the research, Currie came to the conclusion that the highest yield is obtained in an acidic environment (pH 2.5–3.5) and with a high concentration of substrate (sucrose). Around 1929, Pfizer applied surface fermentation techniques to commercially produce CA. In 1948, the cheaper substrate molasses began to be used, which reduced the cost of CA production. Around late 1960s of the XXth, n-alkanes were effectively used as substrate by many bacteria and yeasts for CA production. In 1977, a patent was given to Lever Brothers. It showed for the chemical synthesis of CA starting either from aconitic or isocitrate/alloisocitrate calcium salts under high-pressure conditions; this produced CA in near quantitative conversion under what appeared to be a reverse, non-enzymatic Krebs cycle reaction (Peniston et al. 2008).

Currently, about 80% of CA production is based on submerged fermentation. 2,000,000 tones was in excess in global production in 2018. More than 50% of this volume was produced in China. More than 50% was used as an acidity regulator in beverages, some 20% for detergent applications, 20% in other food applications and 10% for applications other than food, such as cosmetics, pharmaceuticals and chemical (Global Citric Acid Markets Report 2019).

Research is continuing to improve the CA technology. The authors just wanted to present them. Work is underway on new *Aspergillus niger* strains, other CA producing microorganisms, new substrates or the use of membrane techniques. Intensive civilization development leads to transformation of the natural environment.

Applications of CA in industry

Due to its exceptionally pleasant sour flavour and easy assimilation into the human body, CA is widely used in the food industry, which uses 70% of E330 production. It is used as:

- Acid and acidity regulator – it increases the acidity of food products and/or brings in sour flavour,
- Antioxidant – it prolongs life of food products by protecting them against decomposition through oxidation and helps preserve the colour,
- Stabilizer – it helps retain the appropriate physical and/or chemical properties of a food product (Igliński 2006).

The numerous advantages of CA mean that it is also widely used in other industries, as shown in Table 2 (Igliński 2006).

Very good water solubility, typical "lemon" flavour and buffering properties are the major reasons for using E330 as acid and acidity regulator. On the other hand, the complex making and buffering properties imply the application of CA as antioxidant and stabilizer. It complexes the metal ions (Fe, Cu, Zn) (Fig. 2), which catalyse the organic compound decomposition, which leads, among others, to a product colour change (Müller 2004).

CA bonds the metals catalysing the process of fats becoming rancid, and thus, it breaks up the reaction producing peroxides from unsaturated fatty acid oxidation in the process of oils auto-oxidation. In the dairy industry, water solutions of CA are used to remove the milk scale (the sediment of protein, fat and mineral salts) from the apparatus. On the other hand, when added to meat, CA increases the assimilation of macronutrients and micronutrients. As a buffering agent, it ensures stable pH of the environment, due to which virtually no microorganisms develop and enzymatic reactions are slower. CA is a component of many cosmetics, especially elixirs, shampoos, hair fixing agents, etc. It is also widely used in the chemical industry; it is a component of dyeing liquids, detergents (instead of phosphates), electrolytes, photographic paper as well as dyes in photography. It is also used as a polymerization process starter, and most of all, as a component of cleaning products (Igliński 2006).

CA is used in the synthesis of new chemical compounds, such as $BaTi_4O_9$—dielectric of microwave radiation or perovskite catalyst—$LaCoO_3$ (Taguchi et al. 2008) in the production of high-purity compounds, e.g. $CaCO_3$ (Guo et al. 2006). Van Landschoot (van Landschoot et al. 2004) applied CA to increase the area of $LiCoVO_4$ with Fe addition—this material can be used to obtain high-voltage batteries.

The acid is also used in many basic tests, for example when investigating the properties of $(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$, which is used as an oxidant (Huo et al. 2005) or when investigating Ca^{2+} adsorption on goethite (Lackovic et al. 2004a) and kaolinite (Lackovic et al. 2004b). E330 and its esters are used as solvents and plasticizers in the plastics production. For instance, they are components of catalysts preserving ethylene; they are also used in the modification of cellulose fibres (Ghosh and Gangopadhyay 2000). CA is used in the production of the new catalysts (Ni/MgO) used in hydrogenation of carbon dioxide or in methane reforming as well as in the process of hydrogenolysis (Takahashi et al. 2005).

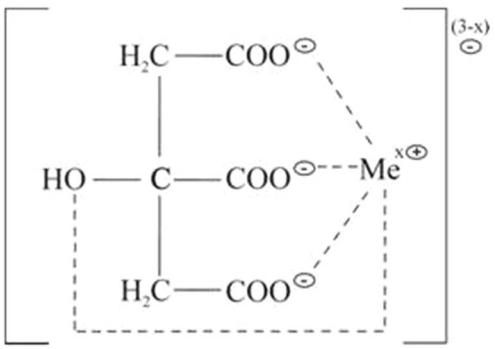


Fig. 2 Scheme of metals (Me) chelating by CA (own study for (Müller 2004))

Table 2 Application of CA in industry (without food industry) (Igliński 2006)

Industry	Application
Chemical	A component of detergents and cleaning agents in the production of plastic masses A component of dyeing liquids in analytical chemistry (buffer, complexing compound)
Cosmetic	Component of many preparations (dyes, cleaners)
Pharmaceutical and medical	Component of effervescent preparations ingredient of medicines and syrups prevents blood clotting
Textile	For fixing and enlivening the colours
Electroplating	In the process of electrolytic electroplating in the metal cleaning process

CA and its salts have a wide application in pharmaceutical industry and medicine as components of transfusion blood medicines, syrups, effervescent preparations, tablets and source of many microelements (potassium citrate, magnesium citrate, bismuth citrate, sliver citrate) used as internal or external medicines. It is used in gastrological investigations, cough investigations (Nurmi et al. 2019), in dentistry to wash root canals, to form collagen biomembranes. Zabiszak et al. (2019) produced new coordination compounds of CA and polyamines with lanthanide ions—potential application in monitoring the treatment of cancer diseases.

CA is also used in the industrial sewage treatment (Lee et al. 2005), as a corrosion inhibitor (Müller 2004) and as a substance facilitating soil reclamation (Chen et al. 2003), including uranium-contaminated soils.

The CA salts also have a wide application in many industries. Among these the sodium salts are of particular interest. In the food industry monosodium citrate, disodium citrate and trisodium citrate are the most important acidity regulators and stabilizers in food products. They buffer the acidity of jellies, help keep CO_2 in sparkling drinks, lending them a salty, cooling flavour. They facilitate the effect of effervescence in the soluble drinks tablets. They prevent foaming, curdling of cream in a coffee and creating agglomerates in nutrients. They are used as stabilizers in the production of cured meat products, edible blood, milk, UHT cream and fruit preserves containing pectine (Vandendriessche 2008). Potassium citrates have similar applications to sodium citrates. They are used in the production of lowered sodium content items. Calcium citrates are used as acidity regulators, carriers and antioxidants. Alkaline metals citrates meet the basic criteria for supplements; that is, they have a high nutritional value, are easily assimilated and have a pleasant flavour and neutral smell.

The conventional method of CA production

At present, virtually the whole production of CA is based on the microbiological method carried out by the selected *Aspergillus niger* strains (Steiger et al. 2019). CA is a by-product of Krebs cycle. In normal conditions, just after being produced, acid becomes involved in further reactions. In pathological conditions acid is accumulated in a cell and then distributed into the solution. The very way of producing CA has not been fully explained. It is supposed that it involves the blocking of reactions in which produced CA should take part or it involves the destruction of regulatory functions of a cell.

Characteristic of *aspergillus niger*

Aspergillus niger is a mesophyll, the optimum temperature for its growth varies between 33 and 37 °C, whilst the optimum temperature for CA biosynthesis is 31–32 °C. The mycelium of *Aspergillus niger* consists of much-branched, colourless, multicellular strings (hyphae) of 3–6 µm diameter. When the surface growth takes place, the mycelium hyphae produces so-called conidiophores up to 2000 µm long, at the end of which beads (heads) of diameter up to 400 µm are created. From the surface of the head cells, called sterigma, grow in a radius. At their ends there are little chains of smaller cells, known as spores (conidia). This shape of the head looks like a brush, which gives the name to the genra—*Aspergillus*. Conidia are of smooth or wrinkly surface, up to 4 µm in diameter and of black colour, which lends the name to the species—*niger*. Mature conidia are very easily separated from the head and on finding the nutrient they initially swell up. Then they start forming a sprout or two, which gradually gain in length and branch out creating new mycelium. After 16–20 h mycelium produces conidiophores, and then conidia, which fully mature after 3–4 twenty-four-hour periods (Leśniak 2002).

Aspergillus niger sources carbon mostly from carbohydrates, especially monosaccharides and disaccharides. The source of nitrogen for *Aspergillus niger* can be both organic substances (amino acids, urea) and inorganic substances (ammonium salts, nitrates), but mineral nitrogen is quicker assimilated. The source of phosphorus can be orthophosphoric acid, its salts and organic substances containing phosphorus. Phosphorus is a part of nucleic acids, phospholipides, phosphoproteins and numerous coenzymes taking part in ADP and ATP synthesis. Other microelements are also essential to the correct development of mycelium. Zinc regulates mycelium growth and its activity, iron enhances its growth, and manganese takes part in many reactions of mycelium metabolism, especially in the synthesis of amino acids, proteins and vitamins (Leśniak 2002).

The intense research into the new strains of *Aspergillus niger* is being carried out up to the present day. The strains used in the commercial production of CA are obtained as a result of mutagenesis and screening selection of natural strains. The physical agents (UV radiation), chemical agents or a combination of both are used as mutagens. Moreover, genetic recombination techniques are used (Mirminachi et al. 2002). Good strains produce almost solely CA in a great amount, with the minimum amount of other organic acids. Rugsassel et al. (1996) obtained a number of the new mutants of *Aspergillus niger*, among which the best mutant marked by symbol CHM I-C3 accumulated 69.4 $mg \cdot cm^{-3}$ of CA from a solution of glucose concentration 120 $mg \cdot cm^{-3}$.

CA was initially produced solely by means of surface fermentation LFS (*Liquid Surface Fermentation*), which is

at present being replaced by submerged fermentation SmF (*Submerged Fermentation*) and solid-state medium fermentation SSF (*solid-state fermentation*).

Surface fermentation

Cultivation is carried out on aluminium or acid-resistant stainless steel trays. Chambers are equipped with a special ventilating apparatus, which keeps slight overpressure in the chamber and also provides oxygen and removes carbon dioxide. When growing, the mycelium covers the surface of a solution with a thin layer and takes nutrients from it; oxygen is taken from the air by means of diffusion. The lower cells of *Aspergillus niger* mould, touching the medium, enjoy an ensured access to nutrients, but have worse oxygen access and carbon dioxide removal. On the other hand, the upper cells, exposed to oxygen, enjoy good breathing conditions, but difficult access to nutrients. These cells breathe more intensively and produce less acid; quite often the complete oxidation of sugar into carbon dioxide and water takes place, which lowers the efficiency of CA production (Roukas and Kotzekidou 2006).

In the surface fermentation, the basic stock for carbohydrates is beet or cane molasses. During the fermentation process, a part of sugar is used for the synthesis of mycelium biomass and its breathing. In the optimum conditions, about 6–8% of sugar is used for mycelium biosynthesis, 11–12% for breathing and 1–2% for the production of other acids. Thus, about 80% of sugar remains for the CA production. It was found that as the thickness of solution layer on the tray grows or the sugar concentration in the fermentation broth increases, more sugar is used for the mycelium biosynthesis and breathing, reaching in unfavourable conditions up to 36–38% of its total amount. The efficiency of CA, in relation to the sugar content in molasses, varies in the surface fermentation between 50 and 70%, and the duration of fermentation can be between 8 and 10 twenty-four-hour periods (Roukas and Kotzekidou 2006).

Submerged fermentation

Submerged fermentation, regardless of technological solutions, is characterized by the development of mycelium not on the surface, but within the whole volume. All the cells of *Aspergillus niger* are provided with the good conditions of development, and consequently, none of the negative phenomena from the surface cultivation occur here. This leads to the faster sugar fermentation into acid and less intensive breathing, which in turn increases the amount of produced CA. In the submerged fermentation, the substrates of high purity are used (most often white sugar). On a commercial scale, fermentation is carried out mainly in fermentation tanks with stirring and aeration or irrotational fermentation tanks. From 10 to 18 h of fermentation, the mycelium hyphae are starting to branch out, and since then, the solution begins to foam, which lasts twenty-four hours. The intensity of foaming is regulated by the manual or automatic batching of chemical antifoaming agents (fatty acids, vegetable oils, silicone oils, etc.). The phase of the intensive mycelium growth takes up to 60–70 h of fermentation, when the nutrient runs out of nitrogen. Fermentation is considered to be finished when sugar concentration in the fermentation broth virtually drops to zero. The process needs to be stopped immediately since prolonged fermentation means that the mycelium would use up CA it previously produced for breathing. In normal conditions, the fermentation duration for 15% sugar solutions is about 120–130 h for sugar media, 140–160 h for molasses media and over 160 h for starch media. The fermentation efficiency is high and varies between 75 and 90%, depending on the stock used and fermentation conditions. As the submerged method is more efficient and safer for workers, it has virtually replaced the surface method (Jeleń 2001).

In research (Ozdal and Kurbanoglu 2019), submerged CA biosynthesis using *Aspergillus niger* was used as the sole carbon and nitrogen sources to reduce the cost of producing CA which was obtained from sugar beet molasses and chicken feather peptone (CFP). To increase the CA production, the parental isolate of *A. niger* MO-25 was increased by mutation using ethidium bromide. CFP concentrations (1–6 $g \cdot dm^{-3}$) significantly affected CA production using molasses. The maximum CA concentration was determined during 168 h and 4 $g \cdot dm^{-3}$ CFP. When CFP was compared to commercial peptones (bacto and casein), the highest CA production was obtained with CFP. By adding KH_2PO_4 (0.15 $g \cdot dm^{-3}$) improved CA production (68.8 $g \cdot dm^{-3}$). The results showed that sugar beet molasses supplemented with mineral salt sources and CFP as organic nitrogen could be utilized for the efficient and economical production of CA.

Solid-state fermentation

The SSF method has been the most commonly used in Japan and is seriously competing with the submerged method (Prado 2004). Waste products (solid but wet) from the food industry can be used as substrates and media, including defective molasses, which due to the wrong composition, including toxic compounds, could not be used in other methods. Fermentation is carried out on trays or directly on the ground (Couto and Sanromán 2006).

Lu et al. (1998) carried out SSF fermentation in a reactor with many chambers, using kumara (*Ipomoea batatas*) as a substrate and the mould of *Aspergillus niger* Yang No. 2, obtained at Waseda University (Tokyo). The authors stresses that the reactor they chose increases acid production due to better mass exchange. In addition, a reactor enables

the precise measuring of CA, carbon dioxide, starch and mycelium biomass concentrations. Lu et al. (1998) found the highest efficiency of acid production on the fourth day; the mycelium biomass growth was the fastest during the first three days of the process, and carbon dioxide production was the biggest between the second and fourth days of fermentation.

Stock for CA production

Fermentation media should contain the components necessary for the growth of mycelium hyphae and their production of CA, and most of all, a source of carbon. A source of carbon for *Aspergillus niger* (Yu et al. 2018) is most often carbohydrates, whilst monosaccharides (glucose, fructose, saccharose) are the quickest to be assimilated. Molasses is a run-off syrup from the rotation of saccharose crystals during the last stage of crystallization, formed in the production of sugar out of sugar beet and cane (Bizukojc and Ledakowicz 2004). The basic component of beet molasses is saccharose, the content of which can vary from 44 to 54%. Among the nitrogen substances present in molasses are mostly betaine, amino nitrogen and proteins. Cane molasses is different from beet molasses in terms of containing less saccharose and more of inert ingredients; it also has a smaller content of nitrogen and raffinose as well as more intense colouring.

Molasses is cheap and readily available, but it causes many technological difficulties as it contains about 20% of non-sugar substances and 8–12% of mineral compounds, including a considerable amount of heavy metals. The presence of heavy metals' cations hampers the CA synthesis, which leads to special preparation of molasses. For this reason, potassium hexacyanoferrate(II) or other complexing compounds are added (Sarangbin and Watanpokasin 1999). Too high amount of nitrogen can cause an excessive growth of mycelium biomass, reducing in this way the amount of CA produced.

White beet or cane sugar is almost pure saccharose, very well fermented by the mould of *Aspergillus niger*. The use of saccharose is mostly supported by its high efficiency and short fermentation duration as well as a very small likelihood of infection due to initially low pH of the fermentation broth. An ecological aspect is of utmost importance too as a pure substrate dramatically reduces the amount of created effluents and waste. The preparation of sugar for fermentation involves diluting it with water to the concentration of $15 \div 20\%$, adding the necessary nutrients (NH_4NO_3, KH_2PO_4, $MgSO_4$) and acidification up to $pH = 2.6 \div 3.0$. Sterilization is usually carried out in the fermentation tank at temperature of 110–120 °C for the time of $0.5 \div 1.0$ h. Next, the solution is cooled down to the temperature of 32–35 °C, and with constant stirring and aeration, the inoculum of *Aspergillus niger* mould, prepared in a propagator, is added (Ilczuk 1987).

Starch in the form of potato or corn starch or even directly as potatoes, wheat, sweet potatoes, sorgo is an alternative for molasses. Starch being a polysaccharide needs to undergo hydrolysis first and the way it is carried out influences the efficiency of CA production.

Since a substrate for CA biosynthesis can be virtually any product containing carbohydrates (Hang and Woodams 2000), extensive research into the new carbon source has been carried out. Progress is being achieved on the use of glucose hydrol (Leśniak et al. 1986), whey (El-Samragy et al. 1996), fruits and their waste (Aravantinoszafiris et al. 1994), agro-wastes (Ali et al. 2016), semolina (Alben and Erkmen 2004), animal products waste (Kurbanoglu 2004), soya (Khare et al. 1995), figs (Roukas 2000), potato starch hydrolyzate (Betiku and Adesina 2013) cellulose (Watanabe et al. 1998), green olive processing wastewaters with white grape pomace (Papadaki and Mantzouridou, 2019).

Purification and crystallization of CA

A post-fermentation solution also contains, apart from mycelium and produced CA, other substances constituting the stock (mineral salts, sugar remnants) or acids produced during fermentation: oxalic, gluconic, apple and others. This solution undergoes treatment in order to separate CA. The first stage (Fig. 3) is mycelium filtering, which is carried out on various types of filters, e.g. frame filters, filter presses or rotary drum-type filters. In the next stage, tricalcium dicitrate is treated with milk of lime. The lowest acid loss, due to citrate solubility, occurs at $pH = 7$, temperature 90 °C and acid concentration over 15%. Rinsing is done with hot water (90 °C) until no sugars, chlorides or colour substances can be found in a reflux. Wet tricalcium dicitrate is directed to the reactor where concentrated sulphuric acid is gradually introduced. After 30 min since CA decomposition started, 10% solution of calcium or potassium hexacyanoferrate(II) is introduced in order to precipitate heavy metals, mainly iron (Leśniak and Kutermankiewicz 1990). The waste product (gypsum) is rinsed till CA concentration drops to 0.1%.

Acid purification is started by decolouring the solution with active carbon. Modern companies do not precipitate heavy metals with potassium hexacyanoferrate(II), but they carry out acid deionization on ion exchange column. It needs to be stressed that the purer carbon source (e.g. saccharose) is used in fermentation, and the purer CA is obtained, which shortens the purification process. The product is purified as a result of rinsing tricalcium dicitrite and if necessary during crystallization itself. Concentration is carried out in two-stage forced-circulation evaporators. In the first stage, the solution is condensated at a temperature of 60 °C and in the second stage at 40 °C. Crystallization is carried out in

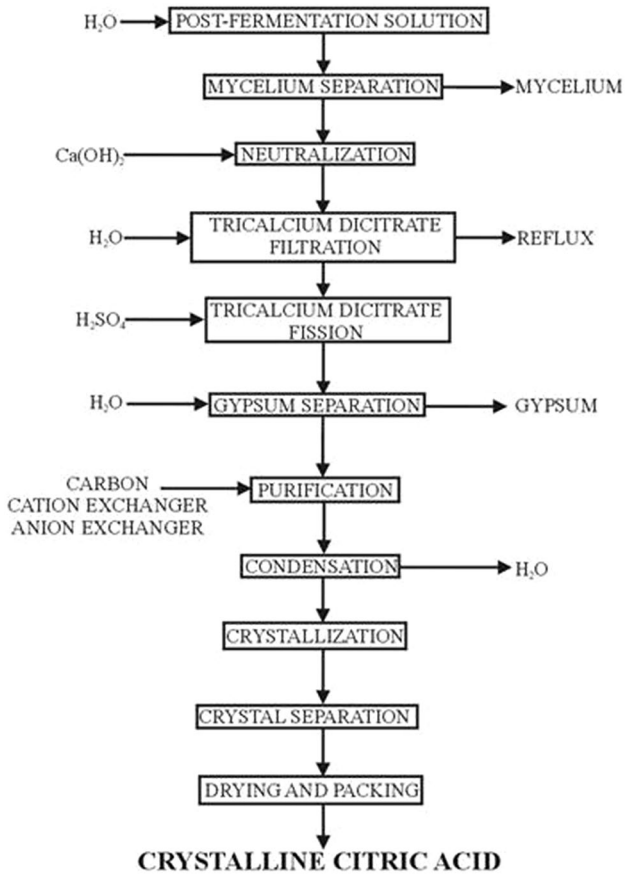


Fig. 3 Scheme of classic method of CA production (own study for (Leśniak and Kutermankiewicz 1990))

vacuum crystallizers with forced circulation of suspension at temperature of 20–25 °C. The solution from an evaporator cools down, which results in further condensation and then acid crystallization in a monohydrate form. CA crystals are continually separated in a centrifuge, then rinsed and dried in a fluidized-solid dryer at the temperature below 36.5 °C (Igliński 2006).

Waste in CA technology

The classic method of CA production involves a great threat to the environment in the form of sewage and waste products. During CA production, heavily polluted sewage is produced, which contains almost the total amount of non-sugar dry mass in molasses as well as remnant sugar. On top of this, there are *Aspergillus niger* mycelium, fermentation by-products (e.g. oxalic acid), active carbon used in decolourization, hexacyanoferrate(II) compounds with heavy metals (Table 3) (Herman 1982). Untreated sewage from the conventional CA technology contributes to the great contamination of waters up to the point of destroying their microbiological balance (biological oxygen demand varies between

Table 3 Sewage composition after CA production (Herman 1982)

Determination	Thin reflux	Reflux condensated under normal pressure
pH	7.8	5.4
Specific gravity ($g \cdot cm^{-3}$)	1.07	1.26
Dry mass content (%)	19.94	55.73
General nitrogen (% of weight)	0.34	1.61
P_2O_5 (% of weight)	4.3×10^{-2}	0.14
Cu (% of weight)	5.6×10^{-3}	1.0×10^{-3}
Mg (% of weight)	2.6×10^{-2}	9.6×10^{-2}
Zn (% of weight)	6.0×10^{-3}	2.4×10^{-2}
Ni (% of weight)	2.6×10^{-4}	1.2×10^{-3}
Pb (% of weight)	2.6×10^{-4}	4.6×10^{-4}
Fe (% of weight)	6.0×10^{-3}	1.6×10^{-2}
K (% of weight)	0.97	3.64
Ca (% of weight)	0.46	1.63

15,000 and 100,000 mg O_2 dm^{-3}. A major waste product in the conventional CA technology is calcium sulphate, which is the greatest drawback of this technology. Gypsum purification is unprofitable, due to which it is dumped at waste sites.

When producing 1 ton of monohydrous CA, about 3.5–4 tons of gypsum are produced (Guilherme et al. 2008). Annually over 3 million tons of this waste product are created worldwide. The research has been carried out worldwide aiming at rationalization of conventional CA technology.

Proecological methods of CA production

Environmentally friendly CA production methods are described below. The management of waste organic matter towards the production of biogas and biomethane was also taken into account.

Waste management

The CA wastewater treatment gives a large amount of waste, which contains more organic matter. It is more complicated to be dewatered by mechanical devices, in comparison with the municipal wastewater sludge. Fenton conditioning was a highly efficient and economical approach to improving the dewater ability of CA wastewater sludge whilst preserving the fertilizing properties (Ding et al. 2018.). Suggested conditions of Fenton treatment were pH 5.0, H_2O_2 dose of 20 $mg \cdot g^{-1}$ dry solids and Fe^{2+} dose of 80 $mg \cdot g^{-1}$ dry solids. The water content of sludge cake was reduced from 85.3 to 73.8% under this condition and capillary suction time was reduced from 19.3 to 10.7 s. In the laboratory-scale and scale-up experiments, there

were no significant differences in capillary suction time and the water content of sludge cake reduction by Fenton treatment.

Recently, research has begun on obtaining biogas from waste biomass using CA technology (Piechota and Igliński 2021). Perhaps soon, agricultural biogas plants will be built at CA factories, which will increase the financial liquidity of the plant. Biogas can be burned to produce electricity and heat (cogeneration), biogas can be used to obtain biomethane, which is a substitute for natural gas, or it can be used as fuel in vehicles (Piechota et al. 2013).

In agricultural biogas plants, a wide spectrum of waste is most often used (Fig. 4). Apart from the waste from the production of CA, agri-food waste can also be used. Part of the energy produced is used for the own needs of the biogas plant, and the rest is sold. As a result of methane fermentation, digestate is produced, which can be successfully used as an agricultural fertilizer (Igliński et al. 2020).

Zhang et al. (2017) proposed an integrated CA–methane fermentation process to solve the problem of wastewater pollution in the CA technology. CA wastewater was firstly treated by anaerobic digestion. After subsequent ultrafiltration and nanofiltration, the anaerobic digestion effluent (ADE) could be recycled as process water for the following fermentation, maintaining excellent CA production efficiency whilst eliminating wastewater discharge and limiting water consumption.

In another study (Xu et al. 2016), wastewater from CA fermentation was used to form methane through anaerobic digestion. Later, the anaerobic digestion effluent was further treated with air stripping and electrodialysis before being recycled as process water for the later CA fermentation. This proposed process was performed for 10 batches and the average CA production in recycling batches was 142.4 ± 2.1 g·dm^{-3}. It was comparable to that with tap water (141.6 g·dm^{-3}). Anaerobic digestion was stable and also efficient in operation.

Fermentation with *Yarrowia lipolytica*

Fermentation with yeasts is being intensively investigated as an alternative for the classic CA technology. When compared to the traditional method, this process seems to be faster, enables the use of a wider choice of stock, is less sensitive to the concentration of mineral components and is more efficient (Zhang et al. 2019). Moreover, the microorganisms' biomass is not a difficult waste product but valuable feed. The biggest number of active in this way species belongs to *Candida*, whilst *Yarrowia lipolytica* creates the greatest interest (Yuzbasheva et al. 2019).

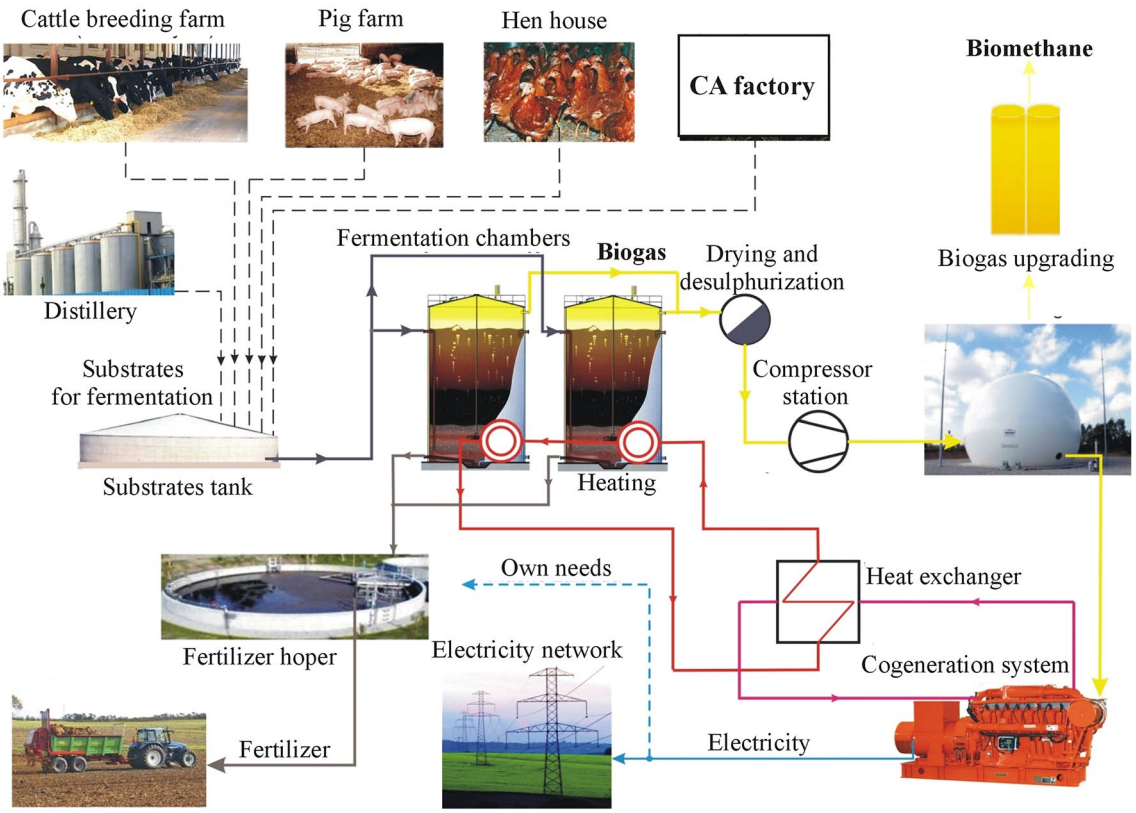


Fig. 4 Biogas and biomethane production using CA technology waste biomass (own elaboration)

Yarrowia lipolytica yeast was isolated for the first time from a gone-off margarine in 1921 (Barnet et al. 2009). Yeast can successfully grow in natural water resources and soil, and are the dominant flora in the food products containing big amounts of fat (Ismail et al. 2001) or proteins (Deak 2001). They are isolated from cheeses and take part in their maturing. *Yarrowia lipolytica* displays a rare among yeasts ability to hydrolyse protein and fat. They propagate by multilateral budding and ascopores.

Acid biosynthesis is usually carried out on simple synthetic media, in which a source of carbon are n-alkanes (Crolla and Kennedy 2004), alcohols (Arzumanov et al. 2000), higher fatty acids and vegetable oils (Venter et al. 2004), finally glucose and glucose hydrol (Robak 2002). The citrate production by *Yarrowia lipolytica* yeast is forced by the lack of nitrogen, sulphur or phosphorus in the medium, and a by-product is isoCA. The research carried out nowadays aims at increasing biosynthesis efficiency, with a negligible amount of created isoCA. The research focuses on the optimization of medium composition, use of new yeast strains, introduction of new carbon substrates, selection and process optimization, use of various cultivation systems (semi-continuous, continuous).

In the research, Cavallo et al. (2017) grade corn syrups and corn steep liquor (CSL) was supstrate in fermentation using *Yarrowia lipolytica*. Besides nutrient sources assay, the effect of C/N ratio and carbon source concentration was evaluated. Authors obtained up to 38 g/L of CA in flasks culture which was formulated with high-fructose syrup and CSL. Additionally, the bioreactor scale-up allowed a 130% increase in drastic fermentation time reduction and productivity. What seems attractive for CA production is the combination of the low-cost nutrient sources of predictable composition derived from the corn processing industry that may be stored at room temperature. The simplicity of the fermentation medium further makes it promising for bigger-than-laboratory-scale production of CA.

Venter et al. (2004) obtained CA with sunflower oil as a carbon source using *Yarrowia lipolytica* UOFS Y-1701. The authors found that sodium acetate addition (10 g·dm^{-3}) positively influences CA synthesis—an increase from 0.5 g·dm^{-3} without acetate to 18.7 g·dm^{-3} with acetate after 240 h of fermentation. The addition of sodium acetate also lowers the amount of produced isoCA; the ratio CA/isoCA increases accordingly from 1.7:1 to 3.7:1.

Crolla and Kennedy (2004) used n-paraffins as a source of carbon (Norpar-15, Imperial Oil Ltd.) and a strain of *Candida lipolytica* NRRL-Y = 1095. The authors found that the optimum speed of mixing is between 800 and 1000 revolutions per minute (rpm) (Table 4).

Papanikolaou et al. (2008) used a strain of *Yarrowia lipolytica* ACA-DC 50,109 to produce CA from so-called olive milk. It is a water fraction of waste obtained during the commercial production of olive oil. It is difficult to utilize due to the presence of phenol compounds. The author found that the strain ACA-DC 50,109 adapted well to a new carbon source, obtaining a high concentration of CA (28.9 g·dm^{-3}).

Table 4 Agitation effect on biomass (%) and CA efficiency [%] after 7 days of fermentation (Crolla and Kennedy 2004)

Parameter	400 rpm	800 rpm	1000 rpm	1200 rpm
Biomass efficiency (%)	30	39	49	44
CA efficiency (%)	22	76	99	88

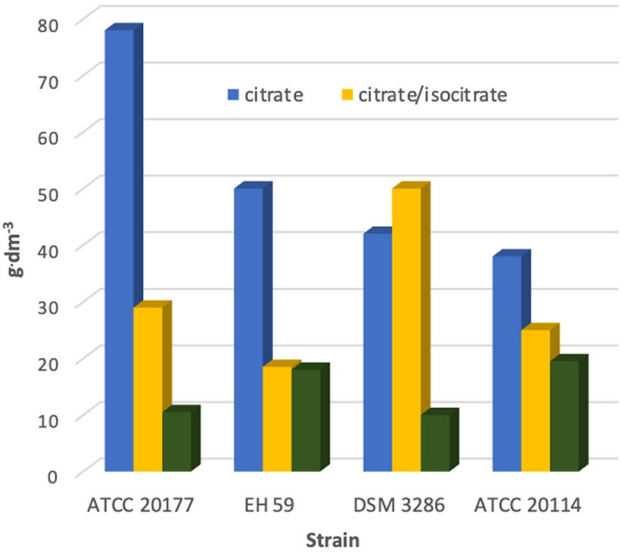


Fig. 5 Citrate concentration (g·dm^{-3}), citrate/isocitrate ratio and biomass concentration (g·dm^{-3}) for selected *Candida* strains (own study for (Anastassiadis et al. 2002))

In recent years, due to increased demand for biofuels, glycerol has become more popular as a carbon source for CA production. Glycerol is a by-product of methyl esters production. Levinson et al. (2007) investigated twenty-seven strains of *Yarrowia lipolytica*, synthesizing CA from glycerol. The research was carried out in nitrate limitation conditions. The highest efficiency was found for NRRL YB-423 strain, producing 21.6 g·dm^{-3} of CA from glycerol of concentration of 40 g·dm^{-3}, reaching the efficiency of 54%. Authors found that acid production efficiency increased along a rise in C/N ratio. The highest efficiency (> 20 g·dm^{-3}) was found for C/N ratio of 686. A further increase in C/N ratio adversely affected the efficiency. A ratio of CA to isoCA for NRRL YB-423 strain was 11.3:1, whilst for other strain s it was between 2 and 6:1.

Candida oleophila is one of the most effective strains that produce CA. Anastassiadis et al. (2002) used four strains of *Candida oleophila* (Fig. 5), among which ATCC 20,177

turned out to be the best (fermentation time 192 h, 30 °C, pH 5).

Simplified method of CA release

Simplified method (without citrate) (Leśniak et al. 1988) of CA release means that the phase of tricalcium dicitrate precipitation is abandoned, but it necessitates the purchase of expensive, pure stock. The stage of acid purification is expanded. Appropriate coagulants (natural and synthetic tannins) as well as potassium hexacyanoferrate(II) are used in order to precipitate protein substances and heavy metals. Diatomaceous earth is additionally used during filtering, due to which protein–tannin sediments can be separated. Post-fermentation solution is decolourized with active carbon and then run through ion exchangers. The simplified method of CA release can replace the conventional method if the price of sugar is low enough.

Method of extraction by solvents

Extraction by organic solvents is a promising method of obtaining carboxylic acids from aqueous solutions. This method is recognized to hold the best prospects in terms of releasing carboxylic and hydrocarboxylic acids from aqueous solutions (Maurer, 2006). Solvent extraction process is used to eliminate calcium hydroxide and sulphuric acid in the precipitation process.

One of these processes, the feed phase (fermented must) is contacted with an organic phase (solvent) in the solvent extraction. These different phases are mutually immiscible and the CA is selectively extracted from the feed to the organic phase. This process can be applied when the fermented musts contain a low number of impurities, since the solvent may extract compounds different than the CA (Araújo et al. 2017).

CA can be easily extracted by many organic solvents, aliphatic amines of high molecular mass are particularly selective. A good solvent needs to be characterized by high selectivity, low ability to create emulsion, good distribution coefficient C_{org}/C_{water}, be non-toxic, cheap and easy to rinse with water (Mauer 2006).

A few authors have discussed the CA extraction mechanism, and there is no consensus between them. Malmary et al. (2001) suggested that the formation of the complexes between the tertiary amine (triisooctylamine) and the CA occurs with the non-ionized acid form (amine acting as a solvation extractant). Bauer et al. (1989) claim that the complexation reaction happens with the citrate ions and trialkylamine in MIBK (methyl isobutyl ketone) by an ionic association mechanism.

Ion exchange method

Ion exchangers are employed when pure stock is used for CA production. In the simplest scenario, a closely packed bed is an adsorbent, which is rinsed in turn with post-fermentation liquid or a desorbing agent. CA is most often reclaimed from an adsorbent by desorption with diluted sulphuric acid. Kulprathipanja (1989) suggested adsorbents based on styrene cross-linked with divinylbenzene. The author gained a better selectivity by using anion exchange resins, impregnated with tertiary amines or pyridine.

Edlauer et al. (1990) suggested using a system of mobile beds installed in a counter-current system. In this system, the apparatus consists of two solid beds connected by appropriate pipes so that a supplying liquid goes through adsorbent's one bed whilst a desorbing substance flows through the other bed. In such a system, adsorption and desorption operations occur continuously, which facilitates simultaneous production of raffinate and extract stream and continuous use of supplying stream. Recently, research has been carried out into a considerably more efficient method of adsorption/absorption, which makes it possible to release acid in one stage.

Membrane methods of CA production

Due to the development of membrane techniques, membranes have been widely used in many branches of industry, including CA technology. CA release and condensation can be obtained by means of electrodialysis, ultrafiltration or/and nanofiltration as well as using liquid membranes (Handojo et al. 2019).

Membranes can be made of organic or inorganic, synthetic or natural materials. The choice of material and the method of making the membrane depends on its intended use, as well as the conditions in which the membrane is to work (Igliński 2006).

Harasym (2003) in his doctor's thesis presents the improved non-citrate method using ultrafiltering (Fig. 6). Due to the properties of ultrafiltering technique, at this stage a post-fermentation solution is partially purified from cations and anions. Due to the chelating properties of proteins, they are stopped on a filtering membrane. In addition, a retentant obtained from ultrafiltration process, containing proteins and trace amount of sugars, can become a source of precious proteins, e.g. enzymes, or when combined with mycelium, it can be a valuable feed addition.

Choi et al. (2008) used nanofiltration technique to reclaim organic acids, CA including, from sewage

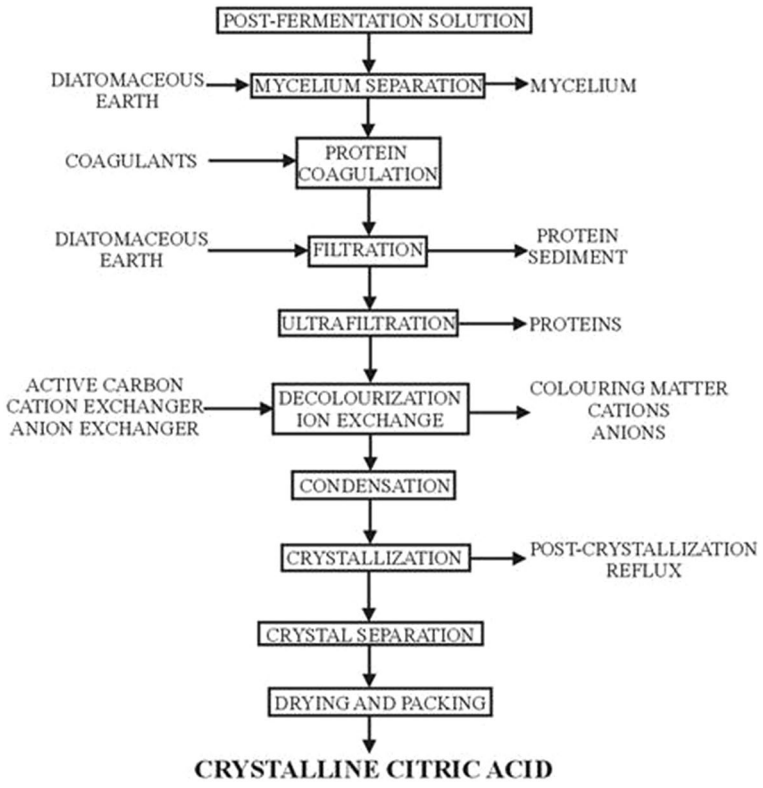


Fig. 6 Scheme of improved non-citrate method of CA production (own study for (Harasym 2003))

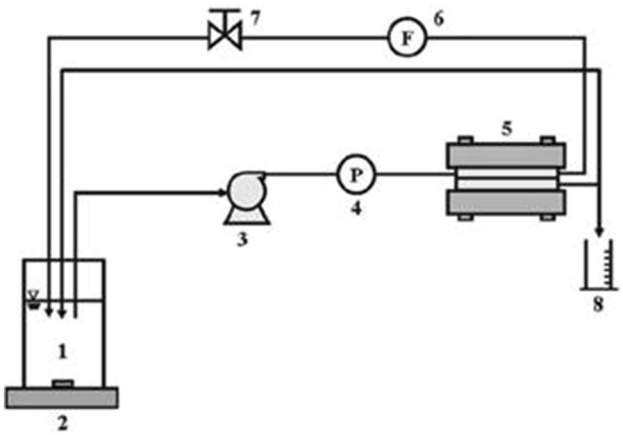


Fig. 7 Schematic diagram of the nanofiltration reactor: **1** feed tank, **2** stirrer, **3** pump, **4** pressure gauge, **5** membrane module, **6** flow rate meter, **7** cross-flow control valve, **8** mass cylinder (own study for (Choi et al. 2008))

(Fig. 7). The authors used commercial membranes ES10 and NF270. Choi et al. (2008) found that for ES10 CA was virtually totally reclaimed, regardless of pH whilst for membrane NF270 recovery increased along rising pH. In comparison with other organic acids, CA recovery was the greatest, reaching almost 100% for pH > 7. Similarly to pH, the pressure and concentration of supplying solution did not exert a big influence on CA recovery, which in all cases reached almost 100%.

The research has been carried out for more than twenty years into using liquid membranes in CA release. A liquid membrane is a layer of liquid separating two other liquid or gaseous phases (Konzen et al. 2014). There are three basic types of liquid membranes: bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM). A liquid membrane separates two solutions, namely a supplying solution (*f*), also known as a donor phase, from a receiving solution(*s*), in other words, an acceptor layer. In most cases supplying and receiving solutions are aqueous solutions whilst a membrane consists of organic hydrophobic liquid. A decrease in liquid membrane volume in relation to external solutions can be obtained in case of supported liquid membranes SLM.

Juang et al. (1997) investigated the transport of CA from aqueous solutions through SLM. The mechanics of transport through SLM containing tri-n-octylamine (TOA) and its salt (TOA salt) is presented in Fig. 8. CA diffuses through the interphase $x = 0$, where it forms complexes H_3R-TOA and H_3R-TOA salt. Those complexes diffuse then through a liquid membrane to the interphase $x = L$, where acid was released from complexes into the acceptor phase (deionized water or sodium carbonate solution). This stage regenerates carriers, which then diffuse into the interphase $x = 0$, the cycle of "carrying" CA is closed. Juang et al. (1997) concluded that the greatest CA transport occurs when the acceptor phase is not deionized water, but sodium carbonate of concentration of 100 mol·m^{-3}. The optimum TOA

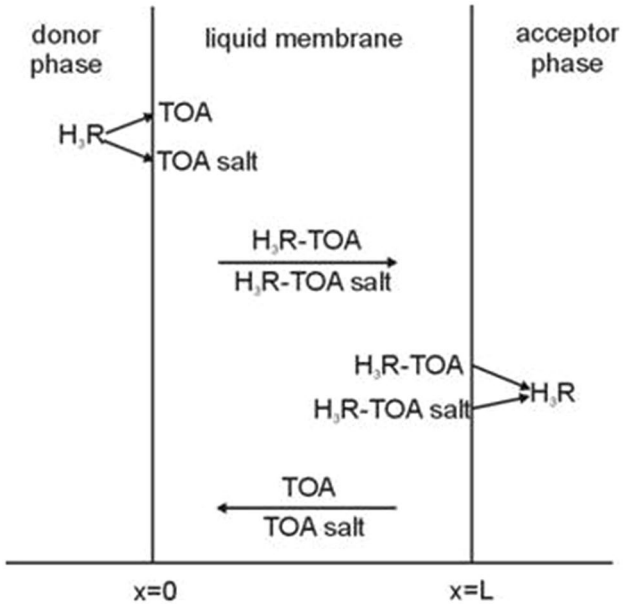


Fig. 8 Transport of CA across SLM membrane containing TOA and TOA salt as carriers (own study for (Juang et al. 1997))

concentration was 200 mol·m^{-3}. The acid transport depends on the salt that is used and increases in the following order: chlorate < sulphate < nitrate < citrate.

Yordanov and Boyadzhiev (2004) obtained CA using emulsion liquid membranes. The authors used Alamine 336 as a carrier and as the acceptor phase sodium alkaline in stoichiometric concentration to acid. The membrane (membrane phase) consisted of Alamine 336, chloroform and an inactive diluent—a surface-active agent, which was alkanes of boiling point 180–210 °C. Yordanov and Boyadzhiev (2004) used C9232 emulsifier in order to obtain emulsion and ensure its durability. The composition of ELM corresponds to double emulsion water/oil/water, which is a result of the emulsification of organic phase in excess (that is membrane) by aqueous solution (here trisodium citrate), being a receiving solution for the membrane system (Fig. 9). In

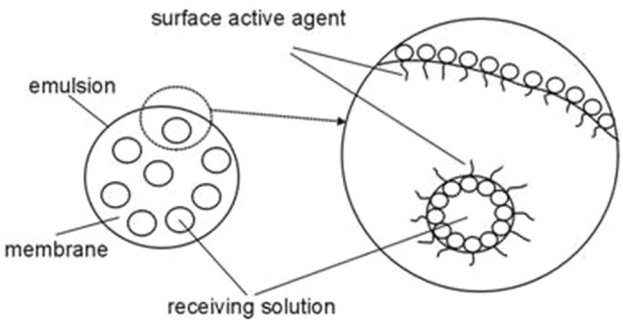


Fig. 9 ELM composition (own study for (Yordanov and Boyadzhiev 2004))

the next stage, the obtained emulsion dispergates further in excess of a supplying solution. CA of concentration [HR] is carried from the donor phase through the border layer to the donor–membrane interphase. In the interphase, acid reacts with a carrier (Alamine 336) dissolved in membrane. The obtained complex is carried through a membrane and disintegrates in the membrane–acceptor interphase. A carrier returns to the donor–membrane interphase, where it links up with another CA molecule. Acid is accumulated in the form of trisodium citrate. Yordanov and Boyadzhiev (2004) found that an increase in Alamine 336 concentration from 5 to 40%, at constant chloroform concentration (8%) results in a 100 times greater transport of acid of constant concentration c_{H3R} = 0.048 moldm^{-3}. On the other hand, when Alamine 336 concentration is 40% and chloroform concentration increases from 2 to 8%, a 2.5 times rise in acid transport occurs. Using the optimum process parameters, that is, $c_{Alamine\ 336}$ = 40%, $c_{chloroform}$ = 8%, $c_{surface\ active\ agent}$ = 4%, mixing rate v = 180 rpm, the efficiency of acid production is 97%.

In the electrodialysis process (ED), ion exchange (Fig. 10) and bipolar membranes are used (Igliński et al. 2020). An ion-selective membrane is a barrier made of cross-linked polymer, through which selective transport in an electric field is possible. The counter-ions neutralize the charge of the polymer network and the co-ion, ensuring the electroneutrality of the membrane as a whole. Due to the charge of the network, membranes are divided into:

- Cation exchange – containing ionic groups with a negative charge (-SO_3^-, -COO^-, -PO_2H^-, -AsO_3^-) (Balster et al. 2005),
- Anion exchange – containing positively charged ionic groups
- (-NR_3^+, -NR_2H^+, -NRH_2^+, -NH_3^+, -PR_3^+, -SR_2^+) (Sata 2000).

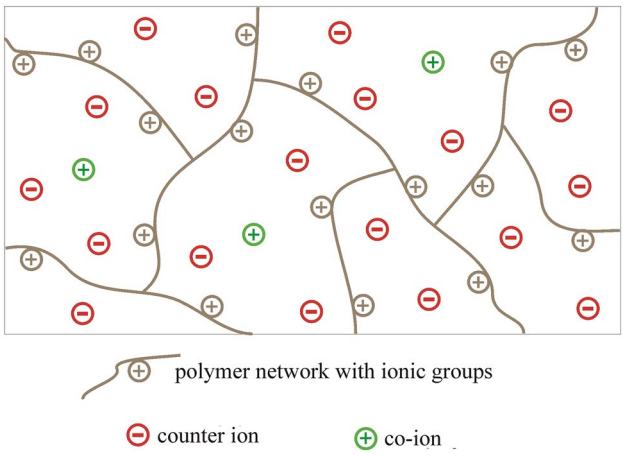


Fig. 10 Structure of ion exchange membrane (own study)

As its name implies, in an electric field, an ion-selective membrane enables the selective transport of a specific ion (counter-ion) between membrane solutions, whilst the co-ion transport remains negligible. The self-ions, located in the membrane solution, prevent the co-ion "intrusion" by electrostatic repulsion (Igliński et al. 2020).

Bipolar membranes (BP) are a special type of ion-selective membranes, they consist of a cation exchange and anion exchange layer. In electrodializers, bipolar membranes are oriented in such a way that the cation exchange layer is facing the cathode (Fig. 11).

The external electric field causes the cations to flow from the cation exchange layer to the cathode solution. Due to the excluding effect of the anion exchange layer, this loss is not compensated by the migration of cations from the anode solution—there is a decrease in the cation concentration in the interlayer space compared to the membrane–outer solution interface. The changes in the anion concentration in the anion exchange layer are analogous. At the junction of the cation and anion exchange layers (Figs. 12 and 13), a thin ion-free layer is formed, in which ions (H_3O^+ and OH^-) are generated as a result of increased dissociation (splitting) of water. When using electrodialysis with bipolar membrane, CA and an alkaline (usually it is a sodium alkaline NaOH) can be obtained from their salts.

In the production of acids, different membrane layouts are used: bipolar (BP), anion exchange (A) and cation exchange (C) (Igliński 2006). In the construction of the bipolar membrane, we distinguish two oppositely charged layers: anion exchange and cation exchange. In the process of producing acids and bases, the bipolar membrane is a basic element of the electrodializer; however, it additionally works with at least one type of monopolar membrane.

In the layout C-BP-C: cation exchange membrane–bipolar membrane–cation exchange membrane (Fig. 14a), salt (Na_3A) is directed into chamber 3, in which sodium cations

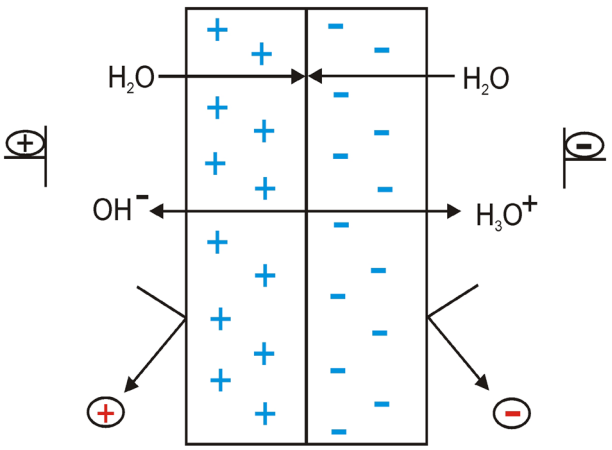


Fig. 11 Principle of operation of a bipolar membrane (own study)

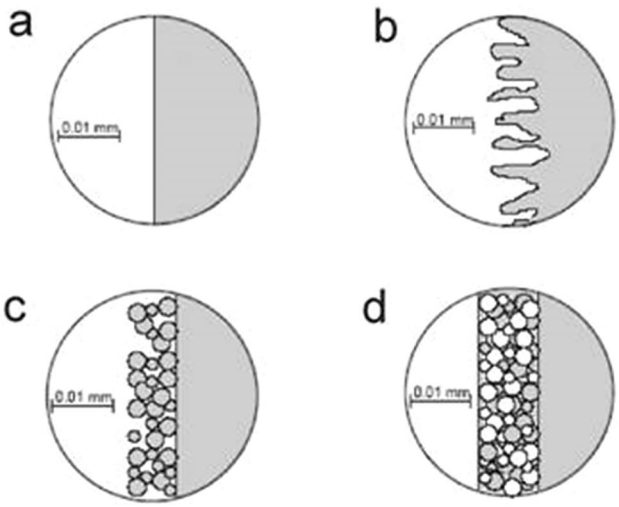


Fig. 12 Interface structure of bipolar membrane: **a** smooth, **b** corrugated, **c** heterogeneous, **d** heterogeneous with binder (own study for (Kemperman 2000))

are replaced by hydronium cations (Bailly 2002). In chambers 2 and 4, alkaline is created (neutral salt, most often Na_2SO_4, is introduced into chambers 1, 2 and 4). CA (H_3A) is formed in chamber 3. It needs to be noted that chamber 3 is also a salt chamber, due to which CA will be polluted with sodium ions (Pinacci and Radaelli 2002).

Igliński et al. (2006) obtained CA working in the layout BP-A-C (Fig. 14b). Trisodium citrate is introduced into chamber 3. In a constant electric field, citrate ions migrate to chamber 2, where they link with hydronium ions, producing CA. A layout BP-A-BP (Fig. 14c) allows salt fission (Xu and Yang, 2002). The initial input solution is directed to chamber 3, in which a metal cation (most often Na^+) is replaced by

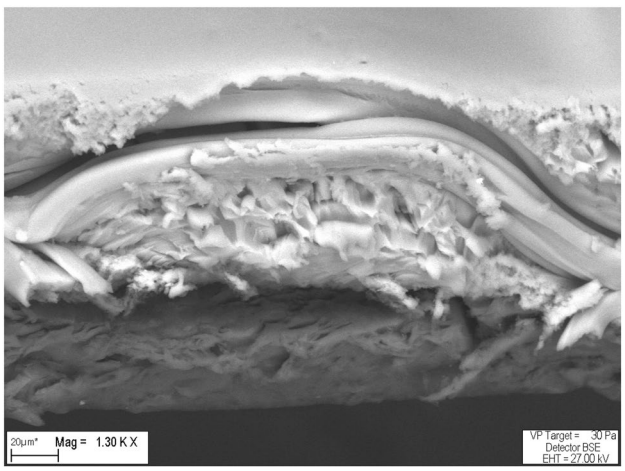


Fig. 13 Bipolar membrane (SEM—scanning electron microscope, photograph: B. Igliński)

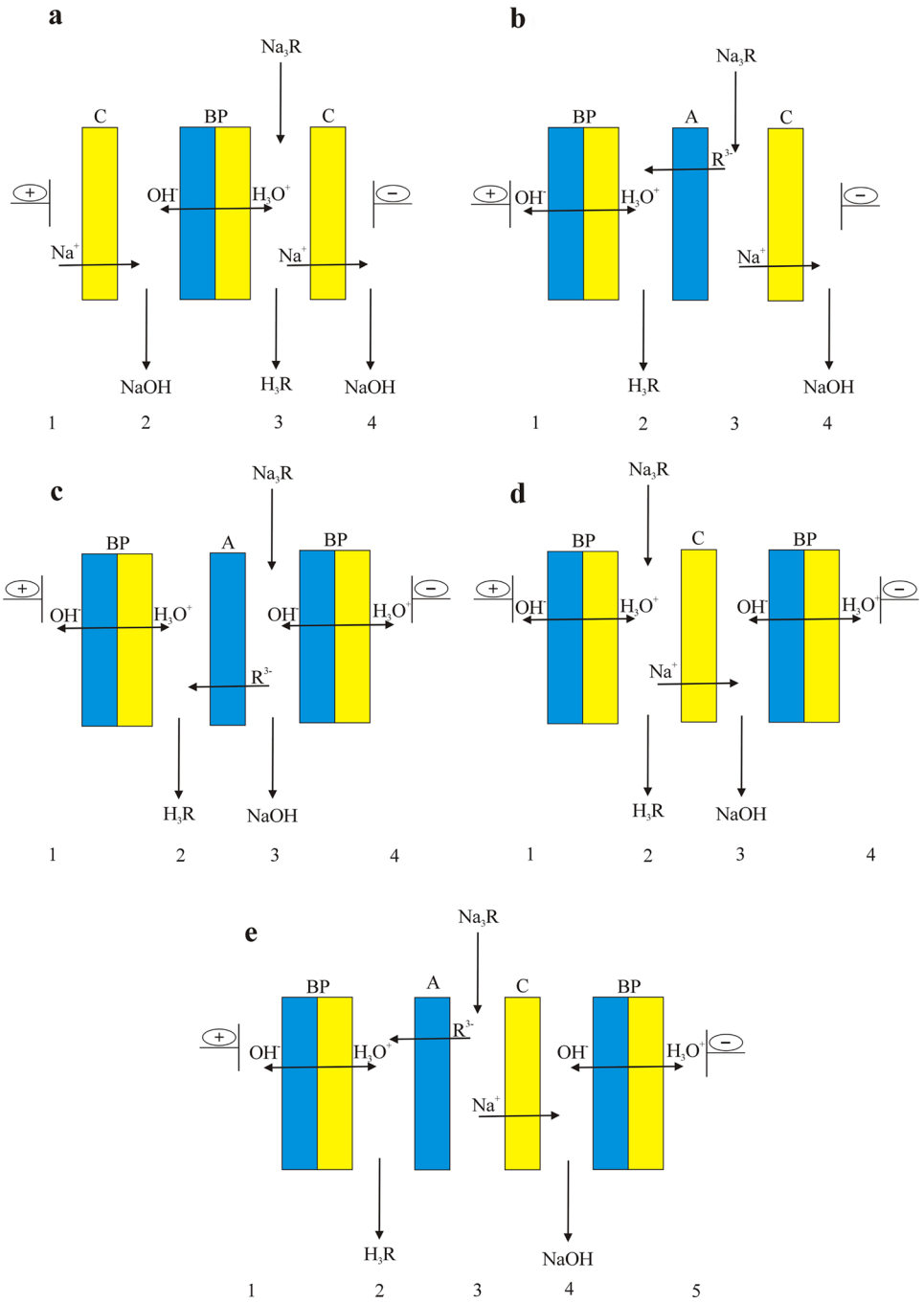


Fig. 14 Membrane systems applied in electrodialysis with bipolar membrane: **a** C-BP-C, **b** BP-A-C, **c** BP-A-BP, **d** BP-C-BP, **e** BP-A-C-BP) (own study for (Bailly 2002; Pinacci and Radaelli 2002; Xu and Yang 2002; Igliński 2006))

a hydronium cation (from water fission in BP membrane). In chamber 3, an alkaline is created whilst in chamber 2 an adequate acid.

Xu and Yang (2002) used the layout BP-C-BP. In this case, a citrate is directed to chamber 2, in which Na^+ is replaced by a hydronium cation from water fission in a bipolar membrane. Chamber 2 is simultaneously a salt and acid chamber whilst an alkaline is created in chamber 3. In a layout BP-A-C-BP (Fig. 12e), salt is directed to chamber 3. An acid radical anion migrates to chamber 2, producing acid, whilst a cation (Na^+) migrates to chamber 4, producing an alkaline. Authors found that an increase in acid concentration in time is linear. (They used membranes produced in the Institute of Chemical Engineering, Shandong.) In case of a layout BP-C-BP, Xu and Yang (2002) obtained the highest increase for salt concentration $C_{s,0} = 0.5–1.0$ mol·dm^{-3} and sodium sulphate concentration $C_{Na2SO4} = 0.5–1.0$ mol·dm^{-3}. On the other hand, the lowest increase was obtained for $C_{s,0} = 0.1$ moldm^{-3} and $C_{Na2SO4} = 0.5$ mol·dm^{-3}. Xu investigated how current

efficiency changes in time, depending on the used membrane layout. Authors concluded that for a layout BP-C-BP efficiency virtually does not change.

Pinacci and Radaelli (2002) and also Novalic et al. (2002) worked using Tokuyama membranes. Pinacci and Radaelli (2002) obtained satisfactory current efficiencies for cation exchange and bipolar membranes as well as for cation exchange, anion exchange and bipolar membranes. (They did not specify the layout.) Pinacci and Radaelli (2002) found that a level of salt conversion should not exceed 80% since later electric energy consumption rises sharply. Novalic et al. (2002) found that an increase in current density is followed by an increase in energy consumption, which is also confirmed by the presented results. Researches suggests combining conventional electrodialysis (initial condensation of salt solution) with electrodialysis using bipolar membrane (salt fission).

Buczkowski et al. (2007) showed that the energy consumption E ($kWh \cdot kg^{-1}$) is the lowest in the layout BP-A-C (Fig. 15). It was also calculated how many kilowatt hours is needed to obtain 1 kg of CA monohydrate by cleavage of trisodium citrate (pattern 1). The electricity consumption $\overline{E}_{el}$ of the pumps and the power supply was comparable per time unit for all electrodialysis; therefore, it differed in energy demand:

$$\overline{E}_{roz} = \frac{\overline{E}_{el}}{m_k} = \frac{\overline{U}It}{3,6 \cdot 10^6 \Delta n \overline{CE}_{k,n} M_k} \quad (1)$$

where $\overline{E}_{el}$ – electricity [J], m_k – the mass of acid formed during electrodialysis [kg], Δn – increase in the number of moles of acid, M_k – molar mass of the product [$kg \cdot mol^{-1}$], $\overline{U}$ – medium voltage [V].

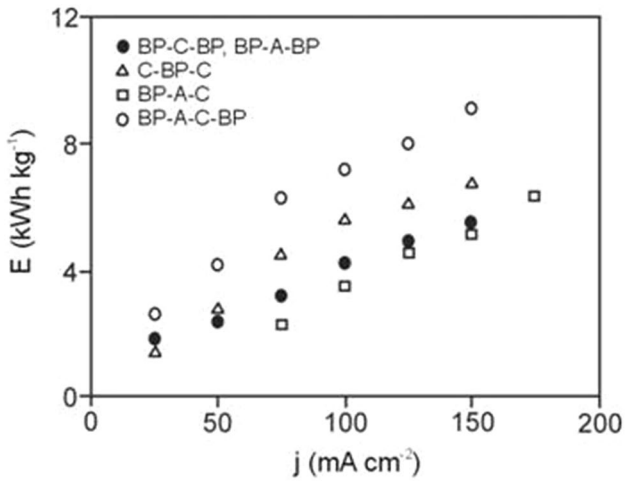


Fig. 15 Energy consumption vs. current density in ED with bipolar membranes (own study for (Buczkowski et al. 2007))

Conclusions

The conventional method of CA production involves a massive burden on the natural environment in the form of sewage and waste. During CA production, highly contaminated sewage is created, which contains almost the total amount of dry non-sugar mass in molasses as well as remnant sugar. This is followed by *Aspergillus niger* mycelium, fermentation by-products (e.g. oxalic acid), active carbon from decolouring, hexacyanoferrate (II) compounds with heavy metals.

An alternative to the conventional technology is a simplified (non-citrate) way of CA production. In this method, a stage of acid purification is extended. Appropriate coagulants (natural and synthetic tannins) and potassium hexacyanoferrate(II) are applied in order to precipitate protein substances and heavy metals.

During filtration, diatomaceous earth is additionally used, due to which protein–tannin sediments are separated. Post-fermentation solution is decolourized by active carbon and then run through ionites. A simplified method of CA release can replace the conventional method if the sugar price is low enough.

Extraction by organic solvents is a promising method of CA production from aqueous solutions. CA can be easily extracted by many organic solvents, and aliphatic amines of big molecular weight are particularly selective.

Fermentation using the yeast of *Yarrowia lipolytica* is currently undergoing intensive research as an alternative to the conventional technology of CA. When compared to the traditional method, this process seems faster, allows the use of a wider choice of stock and is less sensitive to the concentration of mineral components and more efficient. In addition, the biomass of microorganisms is not a noxious waste product but valuable feed.

The electrodialysis with a bipolar membrane is another promising method of obtaining CA. Its main strengths are the simplification of technological cycles, waste elimination and creating high-quality products.

The authors of this article think that each of the presented modifications of CA technology should be further investigated and improved so as to be able to compete against the flooding of cheap, low-quality CA from China. The combinations of innovative methods are particularly desirable, for example obtaining citrate with *Yarrowia lipolytica* and acid production with electrodialysis with a bipolar membrane. Thanks to intensive research on the optimization of CA production, it will soon be possible to obtain it in cleaner production, with high efficiency from many waste substrates. A very good solution is to use waste from the production of CA for biogas production. Biogas is used for energy production, for powering vehicles or injected into the gas network.

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Data availability Enquiries about data availability should be directed to the authors.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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