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POSSIBILITY AND NECESSITY OF TARTARIC ACID PRODUCTION IN THE REPUBLIC OF MOLDOVA

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Abstract. The wine industry has been and remains a source of natural- tartaric acid. The tartaric acid can be obtained from such wastes as grape marcs, yeast, vinasse and wine stone. But the use of these wastes was limited in the Republic of Moldova by the production of tartaric acid lime (calcium tartrate) and wine stone, which were shipped to Ukraine and Armenia where the finished product is obtained. Currently, tartaric acid is used in considerable quantities in the winemaking and food industry, being a quite expensive imported product. The Department of Oenology and Chemistry has developed a complete technological scheme for the use of wine wastes to obtain the finished product – tartaric acid. The realization of the proposed tartaric acid production in the Republic of Moldova is important for the country's economy and it does not require large investments. Wineries can also help to organize tartaric acid production by providing calcium tartrate, wine stone, pressed or dried yeast, and other ingredients.

Keywords: *tartaric acid, calcium tartrate, winemaking, circular bioeconomy, vinasse, wine stone.*

Rezumat. Industria vinului a fost și rămâne o sursă de acid tartric natural. Acidul tartric poate fi obținut din deșeuri precum tescovina de struguri, drojdia de vin, vinasa și semințele de struguri. Dar utilizarea acestor deșeuri a fost limitată în Republica Moldova la producția de tartrat de calciu și piatră de vin, care erau expediate în Ucraina și Armenia, unde se obținea produsul finit. In prezent acidul tartric este folosit in cantități considerabile in vinificație și industria alimentara, fiind un produs de import scump. Departamentul de Oenologie și Chimie a elaborat o schemă tehnologică completă de utilizare a deșeurilor de vin pentru obținerea produsului finit – acid tartric. Realizarea producției propuse de acid tartric în Republica Moldova este importantă pentru economia țării și nu necesită investiții mari. Cramele pot recurge, de asemenea, la organizarea producției de acid tartric, oferind tartrat de calciu, piatră de vin, drojdie presată sau uscată și alte ingrediente.

Cuvinte cheie: *acid tartric, tartrat de calciu, bioeconomie circulară, vinasă, piatră de vin.*

Introduction

The wine industry has been and remains a source of tartaric acid in wine wastes. The use of wine wastes in Moldova was limited to the production of tartaric acid lime (calcium tartrate), wine stone and dried yeast. So, tartaric acid remains to be a quite expensive imported product. Considering that only 30 - 40% of wine wastes currently are reused globally, the recycling strategy must be reassessed. When properly managed, secondary wine products may be used to generate value-added goods. The physicochemical characteristics of wine wastes indicate that they contain a wide variety of extractable substances used by food, pharmaceutical, and other industries. The usage of wine industry generated by-products would result in fewer wastes and develop rich bioactive component extracts with various uses [1]. The environmental impact should be taken into account, when processing wastes into tartaric acid.

The goal of this research was to develop a complete technological scheme for the use of wine waste to obtain the finished product - tartaric acid. The article includes an in-depth study of current developments in the field, both internationally and nationally.

The implementation of the proposed production of tartaric acid in the Republic of Moldova has an essential significance for the country's economy. It does not require large investments. Wineries can also participate in organizing the production of tartaric acid by supplying calcium tartrate, wine stone, pressed or dried yeast.

1. Tartaric acid

Tartaric acid is an organic acid, mainly found in grapes but also in a wide variety of fruits. L(+)-tartaric acid is the most common type of acid found in nature, while D(-)-tartaric acid sources are limited [2]. The main sources of tartaric acid on the market are: recovery from winery waste, chemical synthesis (from maleic anhydride) or of microbiological origin [3].

L(+)-tartaric acid is traditionally formed as a solid crystals in the wine fermentation process, and this mode of manufacturing is heavily influenced by grape maturity and environmental factors. Chemical synthesis of L(+)-tartaric acid using maleic acid is possible, but this results in a significantly less soluble racemic DL-form that is not acceptable for inclusion in foods. The D(-)-tartaric acid presence makes it hazardous to human health. High production cost also limits the commercial utilization of the chemical process. For the manufacture of both tartaric acid forms, microbial methods are currently considered to be more simple and cost-effective [2].

Utilizing tartaric acid is more expensive than citric and malic acids, and in comparison to most other organic acids, it has the least antimicrobial properties. Furthermore, when it is dissolved in hard water, an unwanted insoluble precipitate of calcium tartrate might occur [4].

As a winemaking additive, principle of action is based on part of the tartaric acid added to the wine will lead to the precipitation of potassium bitartrate and thus a drop in the pH of the wine. Possible side effects are increased tartaric instability in wine, and at high doses, can impart a bitter flavor and give wine astringency. Verification of the effectiveness of the treatment is done by measuring total acidity and pH of wine. Cost of this additives varies from 5 to 6 €/kg i.e., between 0.5 and 0.6 $€\cdot hL^{-1}$ of treated wine (dose 100 $g\cdot hL^{-1}$) [5].

L(+)-tartaric acid is consumed in different industries, including food, pharmaceutical, chemical, and polyester production. In the pharmaceutical industry, D(-)-tartaric acid is also important [2]. Tartaric acid is preferred in cranberry or grape-based foods, such as wines, jellies, and confectioneries [4].

Main winemaking application, according to the International Code of Oenological Practices is acidification of musts and wines i.e., increasing the titrating acidity and real acidity (decreasing the pH). Tartaric acid addition develops balanced wines from the point of view of taste sensations, promotes good biological development and smooth maturation of the wine and fixes a lack of natural acidity [5].

In recent years, green extraction technologies for obtaining high-value bioactive chemicals from raw natural materials and wastes have gotten a lot of interest. A natural deep eutectic solvent was explored - L(þ)-tartaric acid, as a possible solvent for extracting phenolic compounds [21, 22].

Polytartaric acid, a novel polymer having several pendant negatively charged carboxylate groups, was investigated as a potential coating material for magnetic nanoparticles. Polytartaric acid is produced by simply heating tartaric acid as a sustainable natural product under controlled conditions without the need for a solvent or a catalyst [8]. The utilization of wine by-products as a substrate for the production of polymer building blocks and as polymer reinforcing fillers is investigated [9].

Esters/ethers produced from tartaric acid, were obtained, thoroughly described, and evaluated as PVC plasticizers. They found to be completely compatible with PVC, have an acceptable plasticizing effect, have a minimal migration potential, and have no effect on the polymers' thermal stability. Traditional phthalate plasticizers may be replaced by these biobased compounds [10].

The magnesium oxychloride cement (MOC) production aids in the CO emissions reduction and recycling of potash industrial waste. Biobased chitosan (CS) and tartaric acid (TA) were used as organic chelating components to enhance the MOC's compressive strength and water resistance, as they give more active sites for Mg ions in the cement [11].

1.1 Composition of winemaking by-products

Winery wastes can differ in composition, depending on harvesting period and conditions. Table 1 shows the content of tartaric compounds in the main wine wastes.

Table 1

Content of tartaric compounds (recalculated in tartaric acid) in the main wine wastes

Wine wastes	Tartaric compounds
Winemaking marcs:	
- white wine, g/kg	0.5-2.0
- red wine, g/kg	0.7-2.5
- fortified wine, g/kg	12-30
Pressed yeast, g/kg	10-60
Dried yeast, g/kg	Min 25
Wine stone, g/kg	Min 520
Vinasse, g/dm^3	2.9

Grape stalks (leaves and shoots), grape seeds, wine lees, and grape marc (pomace) are solid residues produced by the winemaking industry, and their chemical composition varies depending on the source.

Grape marc (pomace) is a solid product produced during the primary grape juice production process, that comprises both water-soluble and water-insoluble components. It contains a significant amount of protein, pectin and cellulose, and has a moisture level of 40-81 %. Monosaccharides, polysaccharides, and oligosaccharides are water-soluble compounds, but polysaccharides incorporated in cell walls are water-insoluble [12].

In the Table 2 the main characteristics of the tartaric raw materials are presented.

Table 2

Characteristic of tartaric raw materials [13]

Raw material	Humidity, %, max	Tartaric acid content, %, min	Insoluble impurities content, %, max	Medium
		Liquid yeast sediment:		
dry	97	2.5	1.0	acidic
fortified	97	3.5	1.0	acidic
		Dry yeast sediments:		
I grade	5.0	25.0	50	acidic
II grade	5.0	20.0	55	acidic
		Calcium tartrate:		
I grade	3.0	45.0	8	neutral
II grade	3.0	40.0	15	pH 6.5-7.0
		Wine stone:		
I grade	2.0	65.0	3.0	acidic
II grade	3.0	55.0	10.0	acidic
		Lime sediment:		
I grade	3.0	40.0	10.0	neutral
II grade	3.0	30.0	10.0	neutral

Wine lees form at the end of the fermentation in the winemaking process. They contain inorganic components, organic acids, and phenolic compounds. Solid part of wine lees is represented by cellulose, hemicellulose, lignin, seeds, grains, organic and inorganic salts.

Vinasse, which is made up of leftover fermentation broth, is the liquid fraction of wine lees. It is the primary source of polyphenol chemicals and includes around 58 % water by weight, with a pH of 3.5 [12]. Vinasse should be used immediately after the distillation of wine and its clarification.

The yeast, obtained by pressing the rotating drum filter, can be immediately transported to the tartaric acid production plant or can be pre-dried. After extraction, pressed yeast can be washed with water and then used as a food additive for animals or as compost.

2. Previous experience in the field

According to a 2006-year survey of European wineries on waste disposal:

Grape stalks were mainly land-spread in Italy, Spain, and France, and mostly disposed of (in landfills) in Greece. The pomace was distilled in Italy, France, and Spain. In Spain still, 50% was land-spread, and in Greece, 67% of pomace ended up in landfills. Wine lees were mostly used for distillation in all mentioned countries. In Spain, filter cakes were used for tartaric acid production, in France for land-spreading, and composted in Italy. In Greece, they were discarded.

In the US, Canada, and Australia, winemaking wastes are preferred to be composted. South Africa also composts the majority of wineries' wastes, but some refineries produce cream of tartar, calcium tartrate, and grape wine spirit. Most of the winemaking countries are also producing grapeseed oil [14].

2.1 Situation in the Republic of Moldova

In 2021, the questionnaire was held, in which participated wineries, that cumulatively generate approximately 25-30% of the total by-products in the sector. In the set of questions on the main challenges of transition and implementation of the circular business model within the enterprise, the following ranking was obtained:

- Lack of technological and technical solutions for the recovery of wine by-products - 64%
- Lack of adequate and clear information on circular economy opportunities - 43%
- Lack of employment and financial risks obtained equal scores - 14% each
- Other transition and implementation issues were not identified, 0%

57% of wine companies do not capitalize on wine by-products, and 43% do so. Among that 43% of enterprises, more than 66% process small quantities (less than 50%) of the total amount of by-products generated [15].

China imports from Moldova grape seeds, oil and tartaric acid, because the EU has banned the import of tartaric acid synthesized from petroleum products. Now China starts producing natural tartaric acid. The EU market is only 60% satisfied with this product. The current shortage of tartaric acid at 40% creates good opportunities for our country. Also, a Spanish investor "Agrovin" placed his production in Gagauzia and buys wine yeast from Moldova. Ethanol and tartaric acid are extracted from them, so almost everything is recycled [16].

Nevertheless, out of the total volume, only a small part of the by-products of winemaking is processed. At some enterprises, wine-making waste is stored outside the settlements. They heat up, the surface is covered with billions of spores that spread to farmland. This leads to the fact that it is necessary to increase the load of phytoncides and pesticides [16].

2.2 Amount of wasted resources (winemaking waste)

In developed wine-making countries, wine-making waste is processed to obtain from them other necessary products. For a long time, this topic was not of interest to manufacturers in Moldova, apart from isolated cases. But the European Union allocated money for the implementation of a cross-border project, in which Moldova and Ukraine are involved, in order to create clusters for the processing of secondary wine products.

According to the ONVV, for 2010-2017 in our country, an average of 250 thousand tons of grapes were processed. Of these, 18 million decaliters of wine and 3.5 million decaliters of wine materials for distillate worth $200 million were produced.

Also, from this amount of wine and cognac production, secondary products were obtained: 80 thousand tons of pomace, 40 thousand tons of stillage, 25 thousand tons of seeds, 20 thousand tons of yeast and 10 thousand tons of ridges [16].

For 1000 decaliters of wine materials, the following amount of yeast sediments is formed: liquid yeast at the first removal of wine - 50 decaliters; precipitation during the subsequent removal of wine - 15 dal; squeezed out (pressed) yeast sediments - 200 kg [17].

3. Demand for tartaric acid on the market

In 2013, Europe was the largest regional market, accounting for 39.4 % of market volume. This market is predicted to develop due to high tartaric acid demand in winemaking countries [17, 18]. Because of its antioxidant effects, tartaric acid is increasingly being used in functional foods and energy drinks [18].

Antibiotics and cardiotonics both include tartaric acid as an excipient. Its rising use as a component of gypsum in the construction industry, in soil fertilizers and metal cleaning is likely to contribute to the market growth [19]. In the coming future, the market is projected to benefit from tartaric acid's adoption in niche applications [20].

The COVID-19 pandemic has impacted nearly every industry in every location, with the majority of manufacturing enterprises either shutting down or functioning with minimal production and staff. Despite this, there's still a demand for food. Food and beverage sales were observed to be high, prompting producers to adapt their sales tactics and transfer to online platforms [21].

Increased pricing has resulted from decreased availability in Europe and North America, which is projected to provide problems to market players [19]. The negative impact of the COVID - 19 pandemic is expected to inhibit the natural tartaric acid market's growth [20].

The worldwide tartaric acid market is predicted to develop at a sustainable rate during 2020 - 2030. The global tartaric acid industry is being fueled by rising wine and processed food consumption. The tartaric acid market is expected to rise 1.5 times in volume by the end of 2030, owing to the growing wine sector [21].

4. Methods for tartaric acid production

Wine lees have been mainly used as a raw material for the extraction of tartaric acid and ethanol since they cannot be used as animal feed due to high polyphenol content [22]. The reported yield for tartaric acid production is 100 – 150 kg per ton of wine lees. Among winery wastes, recovery of tartaric acid has been well established for wine lees and grape marc [23].

4.1 Basic methods

L(+) tartaric acid can be extracted from tartar, wine lees, and grape pomace, according to industry information. Tartaric acid usually represented by monopotassium tartrate (80–90 % in tartar) and calcium tartrate in these products.

These secondary raw materials are firstly neutralized by CaOH or $CaCO_2$, followed by concentration and centrifugation, resulting in calcium tartrate. In a decomposing tank, it is then treated with sulfuric acid to generate tartaric acid, which is refined through concentration and crystallization (Figure 1) [10, 12]

Determined optimum values for tartaric acid extraction from solid wastes are: pH (2.0), temperature (45°C), contact time (30 min), and solid to solvent (ethanol) ratio (1:6 w/v) for red and white tartar wastes respectively [24].

After filtration and purification (especially demetallization), the tartaric acid is concentrated by vacuum evaporation; then tartaric acid is transformed in solid form by crystallization, washing and drying. The resulting gypsum, as well, can be used as a building material [3, 4].

In cognac production, as a result of the extraction of tartaric acid from vinasse by precipitation with milk of lime, tartar (salts of tartaric acid) is formed. The remainder of the stillage after removing tartaric acid from it (and when bringing the active acidity to an optimal level) can be used as fertilizer for some types of soils without contaminating them [27].

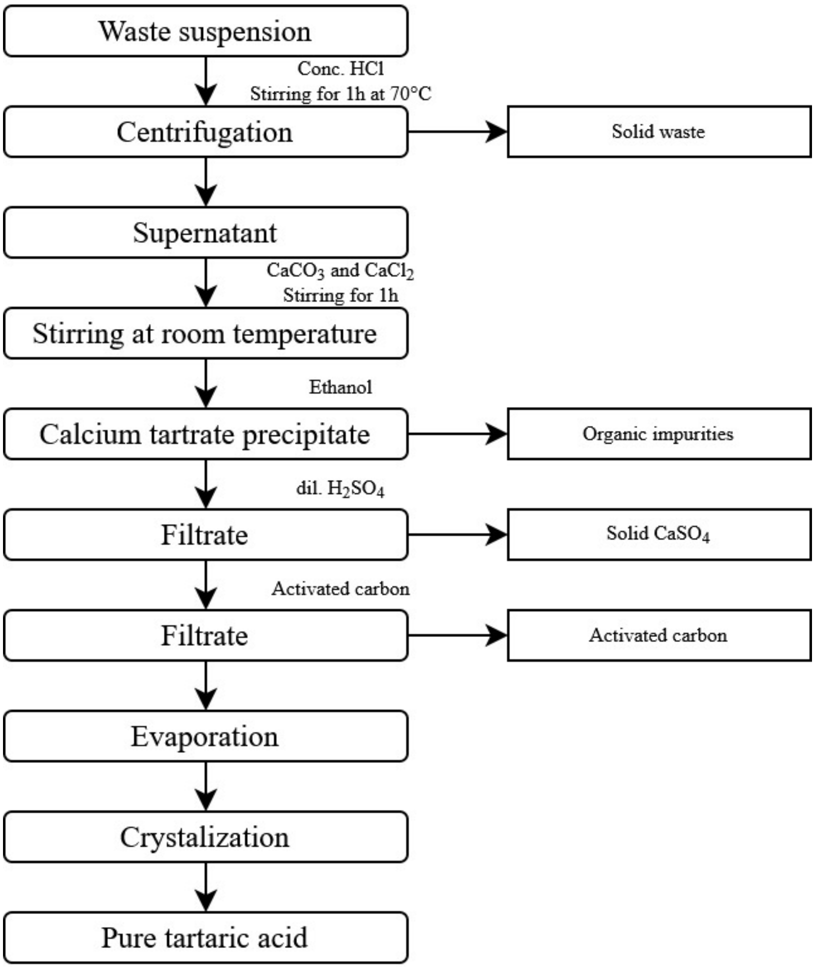


Figure 1. Recovery of tartaric acid from red and white tartar wastes [28].

For such materials, as dregs and marc, calcium tartrate is extracted in an ensuing manner: they are first mixed with water and then ethanol is removed in fractioning columns. Calcium tartrate is formed when wine marc is neutralized with calcium salts and remains suspended in the form of crystals then the wine marc is centrifuged through a series of cyclone separators. Due to the abrasive effect of the tartrate crystals on the pumps and cyclones, frequent stops for maintenance and repair are also required, resulting in significant downtime expenses [14].

Patent EP1288288 provides a solution to this problem.

Vibration makes tartrate crystals precipitate easier since it significantly reduces the friction between the tartrate crystals and the liquid medium. Calcium tartrate gathers at the outflow conduit in this procedure. Crystals have high purity and the possible tartrate recovery rate is nearly 100%. The plant is thought to be easy to build, cost-effective, quiet, and has an unlimited lifespan [29]. An alternative method of tartaric acid recovery exists. Firstly, the wine waste materials are treated with KOH solution (80°C and pH 8) and possible contaminants are eliminated with activated carbon. Then, potassium tartrate precipitation is done by the addition of saturated tartaric acid solution. Sulfuric acid (pH 2) is added to the obtained precipitate to redissolve it at 70°C. Removal of interfering K+ and SO_2− ions is performed by ion exchange resins. After removing the impurities, the solution is concentrated by evaporation, following crystallization at 4°C [34, 35].

Those conventional recovery methods let to obtain a high yield. Nevertheless, the process has its disadvantages: complexity, cost, laboriousness, and environmental impact caused by higher quantities of produced calcium sulfate deposit [23]. Solvent extraction yield is up to 90%. Adsorption method is easy to operate, but has low capacity and adsorbents have short lifetime. Adsorption methods let to achieve the 75 – 99% yield [32].

4.2 Environment friendly methods

4.2.1 Electro-membrane method for tartaric acid recovery

To enhance process efficiency and reduce production costs, it is essential to reform the technological aspects of organic acids recovery. Electro-membrane processes let to separate organic acids from mixed solution, avoiding usage of any solvent, so the main purifying elements are ion-exchange membranes. This method also provides elevated product purity and yield.

The main known electro-membrane process for the recovery of the tartaric acid is electrodialysis. The operation parameters for electrodialysis for tartaric acid recovery are: temperature (25 – 40°C) and feed solution (10 kg m^{-3} tartaric acid and 60 kg m^{-3} glucose). As a result, final acid concentration achieved is 170–300 $kg{\cdot}m^{-3}$ with energy consumption of 5.103–12.103 $kJ{\cdot}kg^{-1}$ [32].

There are also studies on electrochemical reduction of oxalic and glyoxylic acids for development of a feasible green and sustainable synthesis of tartaric acid in aqueous and/or acetonitrile solvent utilizing silver and lead electrodes [33].

In a GB756854 patent, a process of extracting potassium hydrogen tartrate from wine lees was proposed. According to technology, tartrate ions are removed from the wine lees solution by passing it through anion-exchange material in the hydroxyl form and its elution with KOH or NaOH or H_2SO_4. Then, adsorbent effluents are electrolyzed in separate cells. The tartaric acid separation takes place in the anode compartment from the anion exchange material effluent. Similarly, in another cell, KOH is separated in the cathode compartment from the cation exchange material effluent. The reaction of tartaric acid and KOH results in obtaining the tartar cream. The advantages of this solution are recovering tartar cream from byproducts and limited usage of chemicals in the process [14].

For rich in potassium hydrogen tartrate (KHT) vinasses, anionic- (AEM) and cationic-exchange membranes (CEM), as well as bipolar ones (BPM), can be used to concentrate KHT in the pre-distilled solution. Firstly, standard membrane electrodialysis (CEM-AEM-CEM configuration), followed by bipolar membrane one (using (anode)-CEM-BPM-AEM-CEM-(cathode) configuration). The high efficiency and purity of the product were shown applying a combination of membranes during electrodialysis [34].

The high selectivity of membranes allows producing tartaric acid with relatively high purity, without discards of solid wastes, compared to the traditional process. At the same time, if strong acid resin filling is used, this method provides a high production rate and relatively low energy consumption [35].

The conductive spacer can be very efficacious in assisting the transport of the hydrogen ions in the product compartment. It is supposed, that this technology can be integrated effortlessly into the production of tartaric acid by bipolar membrane electrodialysis. The application of the conductive spacer can also cause some unanticipated issues, such as the decreasing production rate and current efficiency, caused by “hydrogen ion short circuit” [36].

4.2.2 Ultrasound-assisted extraction

Tartaric acid can be extracted from wine lees also by ultrasound-assisted extraction (in combination with H_2SO_4). The optimal conditions for the process were determined. Raw materials' solid to liquid ratio should be of 1:3, using the H_2SO_4 solution of concentration 0.06 mol·L^{-1}. Ultrasound treatment duration should be 6 minutes, with magnetron power of 500W. The total extraction time reaches 15 - 20 min, holding the 75 – 80°C temperature. Retaining mentioned conditions, the final tartaric acid yield may reach 74 g·kg^{-1} [37].

4.2.3 Ion-exchange resins

This method for treating a liquid discharge from the wine-alcohol industry includes contacting the discharge with an anionic exchange resin and obtaining a cationic solution containing potassium cations and chloride anions, which is concentrated to produce a potassium-enriched solution suitable for fertilization. It further includes renewing the anionic exchange resin with a sodium chloride solution to create an anionic tartrate solution from which a tartaric acid-enriched solution or a calcium tartrate precipitate can be formed. Any liquid waste originating from the wine-alcohol sector, both from the winemaking industry and from the vinification by-product exploiting industry, characterized by tartrate anions and potassium cations, can be used in this technique. It is preferred that liquid discharge to be the vinasse [38].

Kontogiannopoulos et al. (2016) invented a cost-effective approach for recovering tartaric acid from wine lees employing a cationic exchanger to make the process more environment-friendly. The determined optimal method for the extraction is maintaining the pH of 3.0, the addition of 10 ml·g^{-1} of water in the dry material, and the addition of a cation exchanger of 3.5 g·g^{-1} to dry lees. Cation exchange resin usage under ambient temperature allows avoiding the calcium sulfate waste generation, attributable to the standard process. Following the described method may result in a tartaric acid yield of 74.9% and 98.8% efficiency of potassium elimination [39].

4.2.4 Crystallization

Salgado et al. propose a different tartaric acid recovery scheme. To achieve a rich in tartaric acid solution, the liquid raw material gets concentrated (up to 1/3 of the starting volume) in rotavapor (50◦C). Thereafter, tartaric acid precipitation with ethanol (1:1 v/v) takes place, and crystallization is performed at −20◦C for 24 h. After warming up to 4◦C, crystals are isolated by centrifugation and washed [31].

4.2.5 Nanofiltration

Some studies propose that nanofiltration with a membrane pore size of around 1 kDa can provide excellent separation filtration. In this case, the filtrate will contain a quite high concentration of tartaric acid, which could be later refined by evaporation and crystallization. The remaining concentrate will be a substance, rich in polyphenols, which can be further used as a source of antioxidants [40].

4.3 Local developments

There were several Moldovan patents issued in last 20 years, showing that the tartaric acid extraction from winemaking wastes already was in the field of scientific interest, but, unfortunately, did not find their application on a large scale.

The first mentioned invention is for a method of tartaric acid production from winemaking waste-provided calcium tartrate. The technological process includes mixing calcium tartrate with water at 85 - 90°C and dissolving it in 5.0 - 8.5% H_3PO_4 solution. Next, neutralizing the excess acid with $CaCO_3$ and filtering the resulting precipitate. The remaining solution should be treated with calcium hexacyanoferrate(II), with further removal of the precipitate, and eliminating impurities using activated charcoal. The final product is obtained by crystallization [41].

The second invention is in the field of organic compound purification, specifically tartaric acid purification. The invention is summarized as tartaric acid dissolution in water, treatment with 5% activated charcoal, filtration, and xylene addition. Azeotropic distillation is used for separation, followed by crystal washing (with ether or acetone) and drying at 60-80°C. The implementation of the tartaric acid crystallization process from an azeotropic mixture allows for faster crystallization and separation of the finished product, as well as higher yields (95 - 96%) [42].

The next invention is in the field of wine industry waste processing and utilization for tartaric acid production. The procedure involves dissolving tartrates with pure water and proof-filtering the solution. This is followed by the ion-exchange extraction of tartaric acid, using Amberlite LA-2 as an anionite. Finished by crystallization of the tartaric acid, utilizing butyl acetate as a polar solvent. The invention effects by boosting the efficiency of the tartaric acid production process, increases the purity of the resulting tartaric acid, with reduced usage of chemical solvents [43].

Duca (2011) proposed a technological process of obtaining tartaric acid in the pilot plant. Calcium tartrate with a concentration of 52% tartaric acid was analyzed as the starting material. Thus, the potential of the installation is as follows: processing 850 kg of calcium tartrate, obtaining 450 kg of tartaric acid. The basic steps for obtaining tartaric acid are the following: dissolution of the raw material in the reactor; filtration of the mixture under pressure; purification of the filtered solution with activated carbon and mineral sorbent; reactive extraction of tartaric acid in the plate extractor; re-extraction of tartaric acid in the plate extractor; crystallization in an azeotropic medium in crystallizer-evaporator; filtering crystals and washing them; drying the crystals in the vacuum drying plant and capturing the solvent in the refrigerant [13].

4.4 Proposed recovery scheme

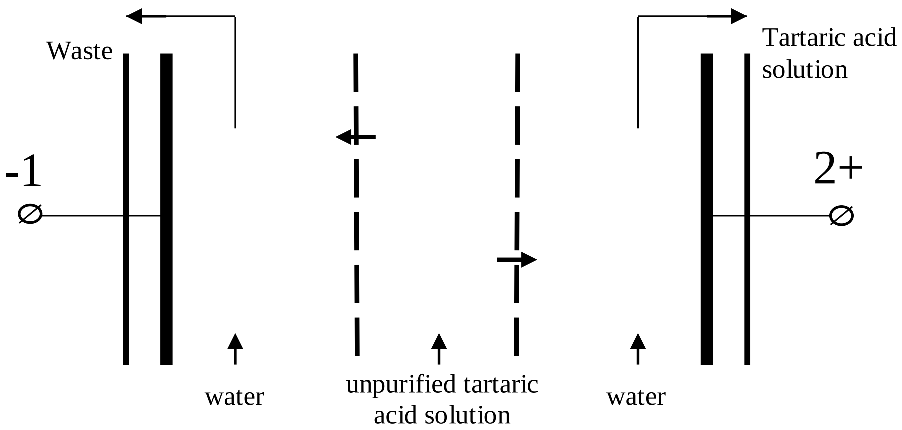
A conventional method for tartaric lime obtaining is proposed. Drinking water at room temperature is mixed with the solid-type tartaric raw material. Of course, the efficiency of extracting tartrates will be more efficient at 60-70℃, but in this case, energy consumption is rising. The diffusion juice of raw material is mixed with $CaCO_3$ introduced to the mixing chamber. In the case of a liquid by-product (vinasse), the washing step is unnecessary, and $CaCO_3$ is added right away.

As a result of treatment:

$$H_2C_4H_4O_6 + CaCO_3 \rightarrow CaC_4H_4O_6 \downarrow + H_2O + CO_2$$
$$KHC_4H_4O_6 + CaCO_3 \rightarrow CaC_4H_4O_6 \downarrow + KOH + CO_2$$
$$K_2C_4H_4O_6 + CaCl_2 \rightarrow CaC_4H_4O_6 \downarrow + 2KCl$$

For the accumulation of calcium tartrate, treatment can be carried out several times in the same vessel. Then, the tartaric lime is washed with water, dried and transferred to the tartaric acid production plant. The washed pomace can be used for further seed separation or as an addition to animal feed, compost, etc.

For the purification of tartaric acid, the staff of the Department of Oenology and Chemistry suggests using electrodialysis to separate cations, especially Ca^{2+}, and to concentrate the tartaric acid solution until the final evaporation (Figure 2).



Note: 1, 2 – anode (+) and cathode (-) electrodes
M - selectively permeable membrane with (-) and (+) charge

Figure 2. Diagram of purification and concentration of tartaric acid solution by electrodialysis.

Electrodialysis can be used to separate and concentrate tartaric acid from diffusion juice. Under the action of electric current, cations will be separated from the semi-permeable membrane with positive charge, while the anions of tartaric acid from the semi-permeable membrane with negative charge. The use of electrodialysis, except the purification of tartaric acid, will reduce energy costs when concentrating the tartaric acid solution by evaporation [13].

The implementation of proposals for the production of tartaric acid can be carried out at one of the wineries, which is currently not engaged in grape processing activities. This implementation brings not only economic support, but also has social and environmental value.

Conclusions

- The main wine wastes from which tartaric acid can be produced are pomace, yeast, wine stone and vinasse.
- The production of tartaric acid from wine waste is possible and necessary without large investments, and will lead to the solution of economic, social and ecological issues.
- To solve ecological issues when using wine wastes in technological processes, it is necessary to exclude the use of aggressive and expensive reagents.
- For every one million dal of wine produced, 50 - 80 tons of tartaric acid can be obtained from the processing of wine wastes.
- The implementation of electrodialysis is recommended for the purification and concentration of tartaric acid solutions.

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References

1. Musteață G., Balanuță A., Filimon R., Băetu M. Capitalization of secondary wine products-an opportunity for the wine sector of republic of Moldova and Romania. In: *Journal of Social Sciences*, 2021, 4(2), pp. 117–127.
2. Xuan J., Feng Y. Enantiomeric Tartaric Acid Production Using cis-Epoxysuccinate Hydrolase: History and Perspectives. In: *Molecules*, 2019, 24(5), p. 903.
3. Younes M., Aquilina G., Castle L., Engel K., Fowler P., Frutos Fernandez M., FÜRST P., Gürtler R., Gundert-Remy U., Husøy T. Re-evaluation of L(+)-tartaric acid (E 334), sodium tartrates (E 335), potassium tartrates (E 336), potassium sodium tartrate (E 337) and calcium tartrate (E 354) as food additives. In: *EFSA Journal*, 2020, 18(3), p. e06030.
4. Gurtler J., Mai T. Preservatives. Traditional Preservatives – Organic Acids. In: Batt, C. – Patel, P., ed *Encyclopedia of Food Microbiology: Second Edition*. Academic Press, 2014, pp. 119–130.
5. IFV - intrants bio [online]. 2021. [accessed: 27.12.2021]. Available: http://www.vignevin.com/pratiques-oeno/index.php?etape=1&operation=7&onglet=Origine
6. Koutsoukos S., Tsiaka Th., Tzani A., Zoumpoulakis P., Detsi A. Choline chloride and tartaric acid, a Natural Deep Eutectic Solvent for the efficient extraction of phenolic and carotenoid compounds. In: *Journal of Cleaner Production*, 2019, 241, pp. 118-384.
7. Makris D., Passalidi V., Kallithraka S., Mourtzinos I. Optimization of polyphenol extraction from red grape pomace using aqueous glycerol/tartaric acid mixtures and response surface methodology. In: *Preparative Biochemistry & Biotechnology*, 2016, 46(2), pp. 176–182.
8. Nan A., Filip Xe., Dan M., Marincaş O. Clean production of new functional coatings of magnetic nanoparticles from sustainable resources. In: *Journal of Cleaner Production*, 2019, 210, pp. 687–696.
9. Nanni A., Parisi M., Colonna M. Wine By-Products as Raw Materials for the Production of Biopolymers and of Natural Reinforcing Fillers: A Critical Review. In: *Polymers* 2021, 13(3), p. 381.
10. Howell B., Sun W. Biobased Plasticizers from Tartaric Acid, an Abundantly Available, Renewable Material. In: *Industrial & Engineering Chemistry Research*, 2018, 57(45), pp. 15234–15242.
11. Han Y., Ye Qi., Xu Y., Li J., Shi Sh. Bioinspired Organic-Inorganic Hybrid Magnesium Oxychloride Cement via Chitosan and Tartaric Acid. In: *ACS Sustainable Chemistry and Engineering*, 2020, 8(51), pp. 18841–18852.
12. Bharathiraja B., Iyyappan J., Jayamuthunagai J., Kumar R., Sirohi R., Gnansounou E., Pandey A. Critical review on bioconversion of winery wastes into value-added products In: *Industrial Crops and Products*, 2020, 158, p. 112954.
13. Duca G. *Produse vinicole secundare* [Secondary wine products]. Chișinău: Știința, 2011.
14. Galanakis C. *Handbook of grape processing by-products*. Elsevier, 2017.
15. Bugaian L., Arpentin G., Diaconu C. Perception of the circular economy by the wine sector of the Republic of Moldova. In: *Competitiveness and sustainable development in the context of European integration*, Chişinău, 2021. pp. 95–101.
16. Taran A. The hidden reserves of the wine industry [online]. 2018. [accessed: 08.01.2022]. Available: https://wine-and-spirits.md/tajnye-rezervy-vinnoj-industrii/
17. Sviridov D. Development of technology for the use of secondary resources of the viticulture and wine industry in order to increase the biological value of food products: Ph.D. Thesis. Moscow, 2017 [in Russian].
18. Grand View Research. Tartaric Acid Market Size Worth $425.0 Million by 2020 [online]. 2015. [accessed: 20.12.2021]. Available: https://www.grandviewresearch.com/press-release/global-tartaric-acid-market
19. Grand View Research. Global Tartaric Acid Market Size, Share & Trends Report, 2020 [online]. 2015. [accessed: 20.12.2021]. Available: https://www.grandviewresearch.com/industry-analysis/tartaric-acid-market
20. Mordor Intelligence. Tartaric Acid Market | 2021 - 26 | Industry Share, Size, Growth [online]. 2021. [accessed: 20.12.2021]. Available: https://www.mordorintelligence.com/industry-reports/tartaric-acid-market
21. Persistence Market Research. Global Tartaric Acid Market: Industry Analysis & Forecast [online]. 2020. [accessed: 20.12.2021]. Available: https://www.persistencemarketresearch.com/market-research/tartaric-acid-market.asp
22. Kokkinomagoulos E., Kandylis P. Sustainable Exploitation of By-Products of Vitivinicultural Origin in Winemaking. In: *Proceedings*, 2020, 67(1), p. 5.
23. Ahmad B., Yadav V., Yadav A., Rahman M., Yuan W., Li Zh., Wang Xi. Integrated biorefinery approach to valorize winery waste: A review from waste to energy perspectives. In: *Science of The Total Environment*, 2020, 719, p. 137315.
24. Aryal M., Liakopoulou-Kyriakides M. Optimization studies for tartaric acid, phenolics, sugars, and antioxidant activity from industrial red and white tartar wastes. In: *Engineering Research Express*, 2020, 2(2), p. 025042.

25. Popa Gh., Parasca P. Improvement of Technology for Obtaining Tartaric Lime from Yeast Sediments. In: *Sadovodstvo, vinograd i vinodeliye Moldavii*, 1985, 9, pp. 39–41 [in Russian].
26. Razuvayev N., Nechayeva P., Belyayev V. Technology of Complex Processing of Grape Pomace and Yeast Sediments in the Stream. In: *Voprosy vinogradarstva i vinodeliya*, 1971, pp. 434–437 [in Russian].
27. Găină B. Winemaking: Waste into income? [online]. 2005. [accessed: 06.01.2022]. Available: http://www.vinmoldova.md/reviews/vinodelie-othody-v-dohody/ [in Russian].
28. Moschona A., Ziagova M., Aryal M., Iliadou A., Liakopoulou-Kyriakides M., Kyriakidis D. Recovery of Tartaric Acid and Added-Value Phenolics from Wine Wastes Towards an Integrated Treatment and Commercial Valorisation. In: *5th International Conference on Environment Science and Engineering*, 2015, pp. 116–120.
29. BALICE DISTILLATI S.R.L., IT. Process and plant for calcium tartrate extraction from wine-making by-products. Patent no. EP1288288B1. Inventor: Gennaro BALICE. Int. cl.: C12F3/00; C12H1/06. Publ.: EPO, 2005-12-14.
30. Yalcin D., Ozcalik O., Altiok E., Bayraktar O. Characterization and recovery of tartaric acid from wastes of wine and grape juice industries. In: *J Therm Anal Calorim*, 2008, 94(3), pp. 767–771.
31. Salgado J., Rodríguez N., Cortés S., Domínguez J. Improving downstream processes to recover tartaric acid, tartrate and nutrients from vinasses and formulation of inexpensive fermentative broths for xylitol production. In: *Journal of the science of food and agriculture*, 2010, 90(13), pp. 2168–2177.
32. Handojo L., Wardani A., Regina D., Bella C., Kresnowati M., Wenten I. Electro-membrane processes for organic acid recovery. In: *RSC Advances*, 2019, 9(14), pp.7854-7869.
33. Garcia A., Sánchez-Martínez C., Bakker I., Goetheer E. Sustainable Electrochemical Production of Tartaric Acid. In: *ACS Sustainable Chemistry and Engineering*, 2020, 8(28), pp. 10454–10460.
34. Vecino X., Reig M., Gibert O., Valderrama C., Cortina J. Integration of Monopolar and Bipolar Electrodialysis Processes for Tartaric Acid Recovery from Residues of the Winery Industry. In: *ACS Sustainable Chemistry & Engineering*, 2020, 8(35), pp. 13387–13399.
35. Zhang K., Wang M., Wang D., Gao C. The energy-saving production of tartaric acid using ion exchange resin-filling bipolar membrane electrodialysis. In: *Journal of Membrane Science*, 2009, 341(1-2), pp. 246–251.
36. Zhang K., Wang M., Gao C. Ion conductive spacers for the energy-saving production of the tartaric acid in bipolar membrane electrodialysis. In: *Journal of Membrane Science*, 2012, 387–388(1), pp. 48–53.
37. QU H. Optimization of Ultrasound-Assisted Extraction of Tartaric Acid from Wine Lees. In: *Food Science*, 2014.
38. Pedros Llevata Francisco ES. *Method for treating wine-alcohol industry liquid discharges*. Patent no. EP1832649A1. Inventor: Pedros Llevata Francisco. Int. cl.: C07C51/02; C07C59/255; C12F3/00; C12F3/06. Publ.: EPO, 2007-09-12.
39. Kontogiannopoulos K., Patsios S., Karabelas A. Tartaric acid recovery from winery lees using cation exchange resin: Optimization by Response Surface Methodology. In: *Separation and Purification Technology*, 2016, 165. pp. 32–41.
40. Kontogiannopoulos K., Patsios S., Mitrouli S., Karabelas A. Tartaric acid and polyphenols recovery from winery waste lees using membrane separation processes. In: Journal of Chemical Technology & Biotechnology, 2017, 92(12), pp. 2934–2943.
41. PUBLIC INSTITUTION "SCIENTIFIC-PRACTICAL INSTITUTE OF HORTICULTURE AND FOOD TECHNOLOGIES", MD. Procedeu de obţinere a acidului tartric din tartratul de calciu obţinut din deşeuri vinicole [Process for obtaining tartaric acid from calcium tartrate obtained from wine waste]. Patent no. 4504. Inventor: Tudor Bounegru. Int. cl.: C07C 59/255; C07C 51/02. Publ.: BOPI, 2018-03-31.
42. STATE UNIVERSITY OF MOLDOVA, MD. Procedeu de purificare a acidului tartric [Tartaric acid purification process]. Patent no. 2428. Inventor: Aliona Mereuţă, Corneliu Oniscu, Tamara Ceban, Gheorghe Duca. Int. cl.: C07C 51/42. Publ.: BOPI, 2004-11-30.
43. STATE UNIVERSITY OF MOLDOVA, MD. Procedeu de obţinere directă a acidului tartric din produsele vinicole secundare [Process for the direct production of tartaric acid from by-products]. Patent no. 2407. Inventor: Aliona Mereuţă, Corneliu Oniscu, Victor Covaliov, Gheorghe Duca, Liviu Vacarciuc. Int. cl.: C07C 51/42; C07C 51/43. Publ.: BOPI, 2004-03-31.