



A REVIEW ON CITRIC ACID PRODUCTION AND ITS APPLICATIONS

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ARTICLE INFO

Article History:

Received 17th June, 2017
Received in revised form 3rd
July, 2017 Accepted 18th August, 2017
Published online 28th September, 2017

Key words:

Citric Acid, Fermentation, Extraction, Citrus
Fruits, Lemon

ABSTRACT

Citric acid has high economic potential owing to its numerous applications. This work provides a review about the production of citric acid and its various applications specially in pharmaceuticals, foods and industrial. Citric acid is weak organic acid that occurs naturally in various fruits and vegetable, especially in the citrus fruits. Different manufacturing processes of citric acid were discussed in this review. This review presents the effect of various parameters on production of citric acid. The global market consumption of citric acid were discussed later stage and also market pattern. The detail application of citric acid is discussed in this review.

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INTRODUCTION

Citric acid (C₆H₈O₇) is a weak organic tricarboxylic acid found in citrus fruits. Citrus fruits (lemons, oranges, tomatoes, beets etc.) are those fruits which contains sufficient amount of citric acid and they are classified as acid fruits. It is a natural constituent and metabolite of plants and animals, is versatile and widely used organic acid in the field of food and pharmaceuticals industries. Citric acid is a good preservative and acidic in taste. Citric acid can be easily manufacture and easily soluble. It is used in flavouring agent and increases stability of the fruit [1-3]. Citric acid as non-agricultural allowed non-synthetic under 'acids', with annotation that must be produced by microbial fermentation of carbohydrate sources. Olden days citric acid is produced by three methods fermentation, chemical synthesis and extraction from citrus fruits [4]. Recently wide range of production of citric acid has been reported in response to different levels of nutrient supplementation produce. Almost 50% citric acid produce worldwide. Global production of citric acid in 2004 was about 1.4 million tonnes and annual growth is 3.5- 4% in demand of citric acid [5-6]. Citrus fruit production was estimated as 120 million tons per year globally. India ranks 6th position for the production of citrus fruits in the world. Worldwide the citrus fruit wastes are also generated in millions of tons after extraction of juice [7].

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The development of citrus processing unit in India has increased problems of effective disposal of wastes. In India more than 1.7 million metric tons of citrus fruits are produced annually (FAO 1984), which after extraction of juice consists of peels, pulp and seeds. These wastes dumped indiscriminately after extracting the edible portion and this uncontrolled activity leads to environmental pollution and health problems to human beings. Thus we need to carry out studies on suitability of orange and sweet lime wastes as the substrates for the production of citric acid [8-9].

Historical Background

The history of citric acid was started in 1784 with W. Scheele. He was first isolated from the lemon juice as calcium citrate, which treated with sulphuric acid gave citric acid in the liquid phase. Wehmer in 1893 was the first he observed the presence of citric acid by product of calcium oxalate produce by a culture of penicillium glaucum fermenting sugar. The world production of this citric acid by fermentation is rapidly increasing. Although in south America, Mexico and Greece there still some exits factors where citric acid isolated from unripe citrus fruits, today over 99% of the world's output of citric acid. The crystalline structure of anhydrous citric acid, obtain by cooling hot concentrated solution of the monohydrate from, was first discovered by Yuill and Bennet in 1934 by X-ray diffraction. In 1960 Nordman and co-workers further two molecules of acid are linked through hydrogen bond between two -COOH group of each monomer. Bichara and co-workers published the outcome of structural and vibrational theoretical study for citric acid dimer into

2011. Citric acid plays a central role in the biochemical cycle found by Kerbs in 1937. The production of citric acid lemon juice peaked in year 1915-1916 at 17,500 tonnes. In 19th century the acid was directly extracted from concentrated lemon juice mainly in sicily. In Europe, Palermo in 1930 hosted the largest citric acid plant.

MATERIAL AND METHODS

There are three principal methods which are available for the production of citric acid i.e., extraction from Citrus Fruits, Chemical Synthesis and fermentation. Recently submerged technique is widely used for the production of citric acid. It is estimated that about 80% of world production is obtained by submerged fermentation. It also presents several advantages such as higher productivity and yields lower labour costs, lower contamination risks and labour consumption.

Extraction from Citrus Fruits

In this process, the citrus fruits especially lemons are washed the peeled and crushed in between squeezer to obtain juice. The filter juice containing 3-4% citric acid is limed to get calcium citrate. The calcium citrate with sulphuric acid to form a solution from which citric acid is crystallised.

Chemical Synthesis

In this process, twofold excess of hydrogencyanide added rapidly to a slurry of 15g of symmetrically dichloroacetone in 10 ml. Ethanol at 0 °C about 100 mg of sodium cyanide added and the mixture is stirred at 0-10 °C for 2 hours and then 60 °C for 2 hours. After cooling 250 ml of cold concentrated hydrochloric acid is continuously added with stirring. The solution is kept at 0 °C overnight and finally boil under reflux for 24 hours. The hydrochloric acid evaporated and water is added. The formed mixture is extracted with ether. For the above quantity of chemicals approximately 117gm of product is reported.

Fermentation

Fermentation process is generally regarded as a biological method for citric acid production. Citric acid production using *Aspergillus niger* in submerged fermentation using as substrate. Literature regression equations used to model the fermentation for determining the optimum fermentation conditions. For fermentation process the medium is taken as 250 ml in flask with 50 ml medium and 1 ml of spore inoculum, incubated in a rotary shaker at 150 rev./min. The Maximum citric acid is reported in the literature. Many researchers working on the fermentation process and finding out optimized parameters. By using optimized parameters such as pH, temperature, sugar concentration, ammonium nitrate concentration and potassium ferrocyanide concentration got the maximum citric acid.

Factors Affecting Citric Acid Production

The condition for citric acid fermentation established during 30's and 40's when the effects of various components of the fermentation media. The accumulation of the citric acid is strongly influenced by the composition medium. Especially fermentation processes, with the expectation of early studies by Currie. There were no other systematic studies on the composition medium until the 40's. These authors developed the medium was basis for further research on production of citric acid. It was shown that the factor affecting citric acid

fermentation are the type and the concentration of carbon source, nitrogen and phosphate limitation, pH, aeration, oligo elements concentration and others.

The main factors affecting of citric acid production are given below

Carbon Source

The carbon source for citric acid fermentation has been subject many studies especially regarding use of polysaccharides. In sugar are quickly assimilated by the microorganism allow high final yield of citric acid. The mostly used carbon sources in industry fermentation are glucose syrups from starch hydrolysis sugar beet molasses and low-quality sugarcane by products are contaminated by high level cations.

Nitrogen and Phosphate Limitations

Complex media such as molasses are rich in nitrogen and rarely need to be supplemented with nitrogen source. The highly pure media used in laboratory scale research are usually supplemented with ammonium salts, partially ammonium nitrate and sulphate. Other sources of nitrogen are urea and yeast extract have been employed successfully. Phosphate not need to be limiting for citric acid production.

Trace Elements

Trace metal ions have been significant impact on citric acid accumulation by *A. Niger*. Divalent metal ions such as zinc, manganese, iron, copper have been found to affect citric acid production.

Lower Alcohols

Lower alcohols added in pure material inhibit citric acid production but added into crude carbohydrates these alcohols enhance production. Methanol, ethanol, n-propanol, Iso-propanol.

pH of Culture Medium

The pH of medium is important in two stages of the process. All fermentation starts from spores and their germination require pH>5.

Aeration

The industrial producers of citric acid have long known variations in the rate of aeration can detrimental effect of performance. If the aeration rate is too high, the partial pressure is dissolved CO₂ in the broth may be too low.

Applications of Citric Acid

Citric acid mainly used in food industry, pharmaceuticals, chemical industry, cosmetics, printings, food preservative, electro pickling, copper plating, beverage & others. Some specific applications are given below

1. Citric acid monohydrate is widely used as organic acid & pH control agent, flavouring and preservative in food production like as candy, cookies, biscuits, jams, jellies, snacks, instant foods and sauces.
2. It is used as acidity regulator and antioxidant in beverage such as alcoholic beverage, carbonated soft drink, syrups, juice drinks, tea & coffee, ice-cream, sports & energy drink.
3. It can be used in thrombin inhibitor and fungicide in pharmaceutical.

4. It can be used as antioxidant & pH regulator in agriculture/ animal food/ poultry food such as chicken feed, boiler feed.
5. It is widely used in cleaning agent, surfactant in various industries such as cleaning agent & anticrease agent.
6. Remove metal oxide from surface of ferrous & non-ferrous for operational cleaning of iron & copper oxides.
7. In electroplating, copper plating, metal cleaning, leather tanning, printings inks, bottle washing compounds, floor cement, textiles, photographic reagent, plaster.
8. It can be use in tartness and complements fruits & barriers flavours in beverage.
9. It is used as an acidulent in creams, gels & liquid of all kinds.
10. It is used as acidifying agent in many cheese products & as an antioxidant in dairy products.
11. It can be used as an alternative to nitric acid in passivation of stainless steel.
12. It is used as an odorless alternative to white vinegar for home dyeing with acid dyes
13. It is used as one of the active ingredients in the production of antiviral tissues
14. It is an alpha hydroxy acid and used as an active ingredient in chemical peels.
15. It can be used in food colouring to balance the pH level of a normally basic dye.
16. It can be added to ice cream as an emulsifying agent to keep fats from separating, to caramel to prevent sucrose crystallization, or in recipes in place of fresh lemon Juice.

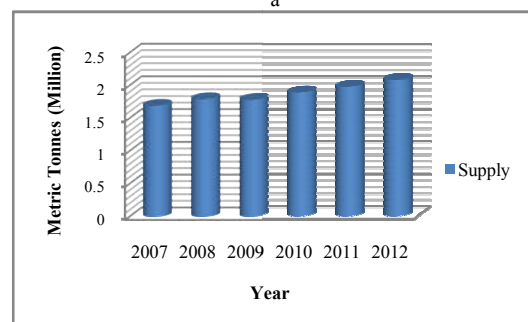
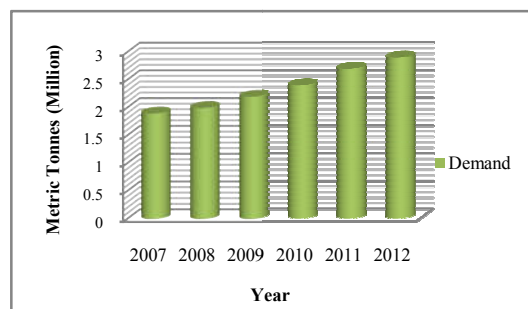


Fig. 1 (a) & (b) Global Citric Acid Demand and Supply

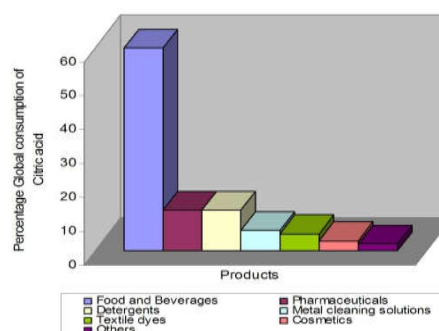


Fig. 2 Global Consumption Pattern of Citric Acid

Global Production and Consumption Pattern of Citric acid

The worldwide demand of citric acid is about 6,00000 tons per year and it is bound to increase day by day. With an estimated annual production of 1,000,000 tons citric acid is one of the fermentation products with the highest production level worldwide. The first successful commercial development of the citric acid in fermentation process was achieved in the United states. The World’s greatest production continentally belongs to Europe and produced in other sixteen countries.

The food industry and beverage consumes about 60% of total citric acid produced, while the pharmaceutical and detergents industries consume 30%. and remaining consumes for metal cleaning solution, textile dyes, cosmetics and other purposes. From this point of view, it is necessary to use inexpensive and readily available raw materials for industrial production process. The high demand in citric acid is the wide use in food, pharmaceutical and beverage Industry. In the 1980s USA has been leading country in producing citric acid. The Global Citric Acid Demand and Supply, Global Consumption Pattern as shown in fig 1 & 2. Fig 1 (a) shows that the demand of citric acid is increases day by day. The supply value of citric acid in the market is less as compared to the demand of citric acid. The future scope is high for the manufacturing of citric acid. Many researchers are working on the manufacturing of citric acid and finding out the most suitable, high efficiency process and parameters for the citric acid.

Global Market Pattern

The world global market percentage share pattern is shown in fig 3. It shows that US and Europe countries have large production and market share percentage for citric acid. The 20% contribution is for china. Now day by day the production rate of citric acid is increasing and also consumption increases.

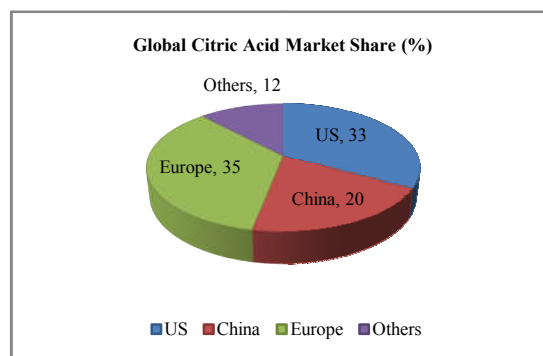


Fig. 3 Global Market Pattern of Citric Acid

CONCLUSION

Citric acid production has been studied during last decade and great alternatives to this process have been found to follow its great demand. Reviewing broad research achievements and market trends, this study provides a critical overview on citric acid. Citric acid is the most produced organic acid. The raw material cost (molasses, *A. niger* water and sulphuric acid) is low and their availability is easily in market. So production of citric acid is economically feasible by different methods. The production of citric acid now more than 1.4 million tonnes per year and day by day that rate is increasing. The important reason for increases the large numbers of applications that can be found citric acid mainly in food and pharmaceutical industry.

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How to cite this article:

Nitin G. Kanse *et al* (2017) 'A Review on Citric Acid Production And its Applications', *International Journal of Current Advanced Research*, 06(09), pp. 5880-5883. DOI: <http://dx.doi.org/10.24327/ijcar.2017.5883.0825>
