

EXECUTIVE SUMMARY

1. Citric acid is a biodegradable, environmentally acceptable, and versatile chemical. It is universally accepted as a safe food ingredient additive. It is available internationally as well as in India as anhydrous and monohydrate. Initially, in India it was available as monohydrate. However, with the indigenous R & D efforts supported by the technology supplier, the anhydrous grade of citric acid has also been developed in India now.
2. Citric acid used in the food industry, especially in processing, is generally dissolved beforehand. For such applications the use of the expensive crystalline citric acid can be avoided. Recently, 50% solution of citric acid, both technical grade as well as for food processing, has been introduced in the international market. In India this grade is not marketed at present.
3. Citric acid is used in food processing, pharmaceuticals and industrial usage like plasticizers in plastics industry, detergents, metal cleaning, textile printing and dyeing, photography, sulfur dioxide absorption and others. The end-use pattern of citric acid in India, and internationally is as follows:

	International	India
Food, beverages and confectionery	70%	40%
Pharmaceuticals	12%	55%
Industrial applications	18%	5%

4. Industrial applications of Citric acid in India are limited to only 5%, which has a substantial scope for growth. Developmental efforts are needed for promoting industrial applications in India.
5. Mycelium and gypsum are the by-products obtained. Mycelium is dried, to be used as animal feed or as fertiliser. The wet gypsum is required to be dumped outside the factory premises. After several years of seasoning of the gypsum, it can be utilised by specialising firms for building purposes.
6. Citric acid can be manufactured by three different kind of processes:
 - (a) Extraction from citrus fruits
 - (b) Synthesis
 - (c) Fermentation.

In case of extraction, yields are low and costs of production high. It is uneconomical and rarely used. At present about 7% of world production is by extraction.

Technically, it is quite feasible to produce citric acid by purely chemical reactions with no elements of bioconversion. However, the present level of production costs practically rules out this method of producing citric acid. All the synthetic methods proposed have eventually turned out to be expensive, hazardous and low yielding.

Fermentation continues to be the predominant way of producing citric acid and accounts for over 90% of the world production. Fermentation is obviously a complex process because several reactions are sandwiched into one single bio-reaction, for which operating conditions have to be tailored precisely and controlled severely. Variations in results often occur even under apparently similar operating conditions. All plants prefer to rely upon their own experience rather than the so-called 'proven' facts.

7. Presently, there are three different types of fermentation processes in use. These are:

- (a) surface fermentation
- (b) submerged fermentation
- (c) solid state fermentation.

Surface and submerged fermentation processes are used quite extensively, while solid state process is still being developed, particularly in Japan.

Despite fermentation being a relatively old technology, interestingly, advances in Science and Technology have kept it in the forefront - the modern molecular biology, or the biotechnology as it is known, has facilitated precise failuring of microbes for specific bioconversion tasks.

The solid state fermentation is being developed because of the localised availability of wastes arising from fruit processing. In Japan, it is being developed for utilising starch containing residual pulps from starch manufacture, e.g. sweet potato fibrous residues, rice or wheat bran and others.

The surface and submerged processes continue to co-exist though the submerged process has steadily increased its share. The surface process still accounts for a substantial part of fermentation capacity worldwide. From yield (obtainable) point of view, surface and submerged processes are rated equally. The yield depends upon several factors, such as the origin of the

molasses, the chemical treatment, the height of the substrate in the trays, activity of the micro-organism and the conditioning of the air.

8. From a practical point of view, pure sugars such as glucose and sucrose are generally too expensive to use industrially. The raw materials can be classified into two groups:
- (i) Raw materials with low ash content like corn sugar, cane or beet sugar, and refined starch hydrolysates yielding very pure dextrose qualities.
 - (ii) Raw materials with high ash content and high amounts of other non-sugar substances, such as cane and beet molasses, high test molasses etc.

Sugarcane juice is in fact, a better raw material for citric acid production by fermentation, compared to beet or cane molasses, particularly for large plants with capacities of over 10,000 tonnes of citric acid per annum.

Molasses is one of the most widely used sources of sugar, for production of citric acid. Being a by-product of sugar refining, it is relatively cheap. There are several kinds of molasses obtained as by-products of different types of sugar production, such as beet, cane etc. They vary widely in quality and composition, depending upon the stage of sugar production at which molasses have been taken out. Composition also varies from season to season and factory to factory. In Europe and North America, beet molasses is used widely for citric acid production.

9. In India, 1st, 2nd molasses and refiners molasses are not available. Molasses available from sugar factories in India are very impure, though they generally contain 40 to 45% fermentable sugar. Several salts and other impurities are contained in the sugarcane juice, which eventually produces molasses. Normally, these molasses cannot be used directly for fermentation. Khandesari molasses are available but yet not tested in India.
10. Eversince Curie's discovery of *A. Niger* in the second decade of the current century, *A. Niger* has been used most extensively for manufacturing citric acid. However, it is now recognized that many species of yeasts also accumulate citric acid in their growth, albeit alongwith relatively large amounts of iso-citric acid. Fermentation by *A. Niger* under surface or submerged conditions continues to be the predominant process even today.
11. The fermented liquid contains, besides citric acid, several unwanted materials, including oxalic acid, residual sugars and mycelium extraction from the fermented liquid is, therefore, a complex process, carried out in several

stages. There are three different processes that can be followed for recovering citric acid from the fermented liquor. These are:

- (i) precipitation (classical process)
- (ii) ion exchange
- (iii) solvent extraction.

Precipitation is the most commonly used method. As it is more economical to remove calcium citrate by lime precipitation than it is by ion-exchange treatment, the ion exchange method may be used for treating lime juice rather than filtered acid juice.

Solvent extraction is a possible alternative to the classical method but because the available solvents tend to extract some of the impurities too, it is easier to apply to products from glucose or alkane based substrates. The advantage of this process is that it avoids the use of lime and sulfuric acid and the concomitant problem of gypsum disposal.

12. The waste fluid left after calcium citrate precipitation can be concentrated and used as animal feedstuff or cultivation of yeasts can be carried out on this concentrated effluent for producing a material suitable for animal feed. An aerobic digestion can also be carried out of this effluent to generate bio-gas (methane) as by-product. In India, one manufacturer has already installed a bio-gas generator.

13. At present, there are two major manufacturers of citric acid in India - Citurgia Biochemicals Ltd. and Citric India Ltd. Citurgia has an installed capacity of 4,950 TPA and Citric India 1,500 TPA.

The total installed capacity at present is around 6,500 TPA and production 4,500 TPA. Over and above the proposals already approved, about 20 parties have shown interest in this project but no concrete progress towards implementation appears to have been made by any party including the approved projects.

It would be worth mentioning here that Andhra Citrates Ltd., Hyderabad installed a plant to manufacture 400 TPA of citric acid starting from sugar based technology developed by RRL, Jammu. However, they could not produce acceptable quality and closed down their unit.

14. The domestic demand of citric acid is expected to grow at a rate of 10% per annum to around 8,000 TPA by 1994-95. A large export potential remains untapped due to present production, meeting only the domestic demand. World demand at present is in excess of 300,000 tonnes and India is in a unique position to meet a significant part of the same, because of the molasses being the cheapest in India. Under the circumstances, the indigenous production

would have to exceed domestic demand before exports can pick up to a noticeable extent. However, in this context, it may be noted that plants of 3,000 to 5,000 TPA capacity are hardly likely to be competitive internationally. In order to compete in world markets, India would have to plan plants of above 10,000 TPA capacity with most sophisticated microprocessor based control of fermentation process. The present price of citric acid in the indigenous market is around Rs.30-32 per Kg and Rs.14 per Kg in the international market.

15. Present world capacity is about 4,00,000 tonnes out of which USA has 1,70,000 tonnes and West Europe 1,00,000 tonnes. Some 30 countries produce citric acid.

Pfizer and Miles Laboratories are the majors, together accounting for 40% of world capacity. Both have plants in several countries - directly or through subsidiaries. Japan has no large production. Small quantities are being produced in Japan by Solid State Fermentation. East Europe's production is small. USSR produces about 20,000 to 25,000 tonnes yearly.

Other sugarcane producing countries are Brazil, Cuba, Pakistan, China, Mexico etc. but India is the largest producer.

16. It would be worthwhile to mention that bulk of the production worldwide is out of beet molasses. The most predominantly used process is the surface fermentation employed by West Germany and the East European countries. Citric acid technology absorption becomes all the more desirable and necessary in view of the fact that India is in a position to manufacture a large part of the plant and machinery required. Thus, technology imports by themselves are unlikely to result in any large scale foreign outgo on account of capital goods, though import of design and drawings of more sophisticated plant and machinery would be required in order to improve the overall performance and yields.

17. The present technical research efforts are principally targeted towards the following areas:

- (i) Search for new and different organisms that would perhaps be able to operate in still cheaper substrates or at least do away with some part of elaborate media preparation or shorten the fermentation cycle.
- (ii) Search for a continuous fermentation process.
- (iii) Search for production techniques, that would reduce operating costs, including energy consumption.

The Indian Industry still depends upon overseas sources, for high yielding strains or new process techniques and, to some extent, sophisticated equipment and instruments.

It has now become necessary for the industry to adopt new techniques, such as, clarification of molasses, reduction of B.O.D. of waste with development of biogas, reduction of energy consumption per unit of produce, etc.

18. Internationally, the process control systems are well advanced and automated. Computerised control systems are very common. But there is no basic change since the fifties in the process technology; raw material, micro-organism remain unaltered. Process cycle time has also not reduced. While West Germany and East European countries use surface fermentation process, elsewhere submerged process is employed. Present research efforts are directed at finding out new micro-organisms, a continuous process (against the present batch process) and search for cost reduction. A. Niger continues to be the most common micro-organism all over the world. Several attempts have been made for continuous fermentation but no real breakthrough has as yet been achieved.
19. The best technologies in the world for citric acid are still not available to India. Offers received are not proven for Indian type of sugarcane molasses.

Only a few countries, majority of them developing countries, produce sugarcane. Most of the countries having sugarcane do not have large capacity plants of citric acid based on sugarcane molasses. In the past, a number of trials have been made to achieve better yields, using Indian cane sugar molasses but without much success. Considering that indigenous research efforts have not been able to produce any concrete results, technology imports are obviously unavoidable.
20. Industrial applications for citric acid are yet to develop. Efforts are required to be made in the direction of developing industrial applications.
21. A large export potential exists, because Indian molasses are perhaps the cheapest. Efforts should therefore be made to develop technology suitable for Indian molasses, for which own R&D is necessary, because most of the international production is out of beet molasses. Cane molasses supposedly contain more impurities; need different treatment and handling.
22. As equipment fabrication capability for this industry is well developed within the country, technology absorption and development is very much desirable.
23. At least one more project of capacity 4,000 to 5,000 TPA is desirable to meet domestic demand.
24. Solid state fermentation is to be closely examined. It is more suitable for India and a large potential for this process exists in the country.