Vinegar Production Technology – An Overview

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1. INTRODUCTION

Vinegar is an acid liquid produced from the fermentation of ethanol in a process that yields its key ingredient, acetic acid (ethanoic acid). The acetic acid concentration typically ranges from 4% to 8% by volume for table vinegar and up to 18% for pickling. Natural vinegars contain small amounts of tartaric acid, citric acid, and other acids.

Vinegar has been used since ancient times and is an important element in European, Asian, and other cuisines. The word "vinegar" derives from the Old French vin agre, meaning "sour wine". Vinegar has been made and used for thousands of years. Traces of it have been found in Egyptian urns dating from around 3000 BC. In 1864, Louis Pasteur showed that vinegar results from a natural fermentation process.

Vinegar is primarily used to flavor and preserve foods and as an ingredient in salad dressings and marinades. Vinegar is also used as a cleaning agent. Natural vinegar is a superior food additive over synthetic vinegar as it carries essential amino acids from its fruit source and is reported to act as a medicine for aches and gastric troubles. However, it is generally ignored by both the consumer (due to the higher price) and the producer (due to the long fermentation time of 5–6 weeks). Moreover, vinegar can be more than an addition to any dish; it can be a source of income, a promising business.

In this paper work aims to elaborate the different types of vinegars and major vinegar processing methods used for commercial production. As an example a flow chart for the production of cane vinegar is included and possible improvements for cane vinegar production are discussed.

2. TYPES

There are many different types of vinegars. The classification is usually based on the raw material used for its production. Malt vinegar, Wine vinegar, Apple cider vinegar, Balsamic vinegar, Fruit vinegar and many other types of vinegar exist in today's global market. The most common types of vinegars and their origin are discussed below.

✓ **Wine Vinegar**

Wine vinegar is made from red or white wine and is the most commonly used vinegar in Mediterranean countries and Central Europe. As with wine, there is a considerable range in quality. Better quality wine vinegars are matured in wood for up to two years and exhibit a complex, mellow flavor. Wine vinegar tends to have a lower acidity than that of white or cider vinegars. There are more expensive wine vinegars that are made from individual varieties of wine, such as Champagne, Sherry, or pinot grigio.

✓ **Beer Vinegar**

Vinegar made from beer is produced in the United Kingdom, Germany, Austria, and the Netherlands. Although its flavor depends on the particular type of beer from which it is made, it is often described as having a malty taste. That produced in Bavaria, is a light golden color with a very sharp and not-overly-complex flavor.

In Beer vinegar and Wine vinegar production only one type of fermentation takes place; for the conversion of ethanol in to acetic acid. But other types of vinegars, discussed later, are grouped under a production process where there are two types of fermentations; one for ethanol formation and another conversion of the ethanol in to acetic acid.

➢ **Fruit Vinegars**

Fruit vinegars are made from fruit wines, usually without any additional flavoring. Common flavors of fruit vinegar include apple, black currant, raspberry, quince, and tomato. Typically, the flavors of the original fruits remain in the final product. Most fruit vinegars are produced in Europe, where there is a growing market for high-priced vinegars made solely from specific fruits (as opposed to non-fruit vinegars which are infused with fruits or fruit flavors). Several varieties, however, also are produced in Asia. Persimmon vinegar, called *gam sikcho* is popular in South Korea. Jujube vinegar and wolfberry vinegar are produced in China. *Jamun Sirka* is vinegar produced from the *Jamun* (or rose apple) fruit in India. It is considered to be medicinally valuable for stomach, spleen and diabetic ailments.

➢ **Balsamic Vinegar**

Balsamic vinegar is an aromatic, aged type of vinegar traditionally crafted in the Modena and Reggio Emilia provinces of Italy from the concentrated juice, or must, of white grapes (typically of the Trebbiano variety). It is very dark brown in color and its flavor is rich, sweet, and complex, with the finest grades being the product of years of aging in a successive number of casks made of various types of wood (including oak, mulberry, chestnut, cherry, juniper, ash, and acacia). Originally a product available only to the Italian upper classes, a cheaper form of balsamic vinegar became widely known and available around the world in the late twentieth century. True balsamic vinegar (which has Protected Designation of Origin) is aged for 12 to 25 years. Balsamic vinegars that have been aged for up to 100 years are available, though they are usually very expensive. The commercial balsamic sold in supermarkets is typically made with concentrated grape juice mixed with strong vinegar, which is laced with caramel and sugar. Regardless of how it is produced, balsamic vinegar must be made from a grape product. Balsamic vinegar has a high acidity level but the tart flavor is usually hidden by the sweetness of the other ingredients, making it very mellow.

➢ **Malt Vinegar**

Malt vinegar is made by malting barley, causing the starch in the grain to turn to maltose. Then ale is brewed from the maltose and allowed to turn into vinegar, which is then aged. It is typically light brown in color.

Rice Vinegar

Rice vinegar is most popular in the cuisines of East and Southeast Asia. It is available in "white" (light yellow), red, and black varieties. The Japanese prefer light rice vinegar for the preparation of sushi rice and salad dressings. Red rice vinegar traditionally is colored with red yeast rice. Black rice vinegar (made with black glutinous rice) is most popular in China, and it is also widely used in other East Asian countries. White rice vinegar has a mild acidity and a somewhat "flat", uncomplex flavor. Some varieties of rice vinegar are sweetened or otherwise seasoned with spices or other added flavorings.

➢ **Others**

Coconut vinegar, Palm vinegar, Raisin Vinegar, Honey Vinegar, Sugar Cane Vinegar and many other different types of vinegar are produced in different parts of the world. The Coconut vinegar, a cloudy white liquid, with a sharp acidic taste is famous in Southeast Asian cuisine, particularly in the Philippines. Palm vinegar is another type most often used in the Philippines, where it is produced. Vinegar made from raisins called *khal 'anab* in Arabic is used in cuisines of

the Middle East. Though Vinegar made from honey is rare, commercially available honey vinegars are produced in Italy, France, Romania and Spain.

3. VINEGAR PRODUCTION

3.1. Raw Materials

The major raw materials for the production of vinegar are alcohol containing liquid, Acetobacter, a genus of aerobic bacteria, oxygen, and some times herbs and fruits as a flavoring agent.

Alcohol Containing Liquid

Vinegar can be made from a variety of diluted alcohol products, the most common being wine and beer. Alternatively an alcohol product can be prepared through fermenting carbohydrate in rice, sugar cane, or malt anaerobically by yeast. The resulting alcohol product is pasteurized, filtered and then diluted to adjust the alcohol content and then used for vinegar production.

Bacterial Cultures

Acetobacter acetii cultures are used for vinegar production. These perfectly work at a temperature of 28 °C (82 °F) with full air injection. The lowest temperature that the bacteria can tolerate is 20 °C (68 °F) and the maximum temperature is 33 °C (91 °F). Below and above these temperatures, there is no conversion from alcohol into acetic acid. The starting alcohol should be lower than 7.5 % (v/v) and there should be no free Sulfites.

In the natural processes, Acetobacters are allowed to grow over time. However, mother of vinegar is added as a source of Acetobacter for commercial production. Mother of vinegar is the gooey film that appears on the surface of the alcohol product as it is converted to vinegar. Mother of vinegar is skimmed off the top and added to subsequent batches of alcohol to speed the formation of vinegar. It consist natural carbohydrate called cellulose and this film holds the highest concentration of Acetobacters. Sometimes in the vinegar factory acetozym nutrients are added in to the alcohol liquid as a bacterial culture. Acetozym nutrients are manmade powdered form of mother of vinegar.

Flavoring Agent

Herbs and fruits are often used to flavor vinegar. Commonly used herbs include tarragon, garlic, and basil. Popular fruits include raspberries, cherries, and lemons.

Processing Methods

Vinegar is the product obtained as a result of impartial oxidation of alcohol in a fermenting sugar containing fruit or cane juice, molasses, fermented mash of malted grain, honey, syrups, etc. It is made from the fermentation of ethanol by acetic acid bacteria. The ethanol may be derived from many different sources including wine, cider, beer or fermented fruit juice. For wine vinegar and beer vinegar the production process only includes fermentation for the conversion of the alcohol present in the raw materials in to acetic acid. However, in other types of vinegar such as fruit vinegars or cane vinegars two major processing steps are carried out; one for the production of ethanol alcohol from raw materials and the other for the conversion of the ethanol produced in to acetic acid. Vinegar contains, mainly, acetic acid by weight and small quantities of alcohol, glycerol, easters, sugars, and salts. To find pure acetic acid the vinegar is subjected to purification by distillation.

The transformation of wine or fruit juice to vinegar is a chemical process in which ethyl alcohol undergoes partial oxidation that results in the formation of acetaldehyde. Then, the acetaldehyde is converted into acetic acid. Thus, it can be said that the production of vinegar involves two types of biochemical reactions: alcoholic fermentation and oxidation of alcohol in to acid.

Alcoholic fermentation of carbohydrate is the first critical step in the production of vinegar and takes place under anaerobic condition. In this step sugar is fermented to alcohol by the action of yeast species as follows.

$$C_6H_{12}O_6\ (\text{Glucose}) \xrightarrow{\text{Yeast}} 2C_2H_5OH\ (\text{Ethyl Alcohol}) + 2CO_2 + \text{Energy}$$

Oxidation of alcohol to acid is the second major step in the production of vinegar and is aerobic process. In this step alcohol is oxidized to acetic acid by the action of acetic bacteria; the species of Acetobacter.

$$2C_2H_5OH\ (\text{Ethyl Alcohol}) + O_2 \xrightarrow[\text{Bacteria}]{\text{Acetic Acid}} CH_3COOH(\text{Acetic Acid}) + H_2O + \text{Energy}$$

Commercial vinegar is produced either by fast or slow fermentation processes. In the slow, or natural, process, vats of cider are allowed to sit open at room temperature. During a period of several months, the fruit juices ferment into alcohol and then oxidize into acetic acid. Slow methods generally are used with traditional vinegars; fermentation proceeds slowly over the course of weeks or months. The longer fermentation period allows for the accumulation of a nontoxic slime composed of acetic acid bacteria and soluble cellulose, known as the mother of vinegar.

Fast methods add mother of vinegar (i.e., bacterial culture) to the source liquid before adding air using a Venturi pump system or a turbine to promote oxygenation to obtain the fastest fermentation. In fast production processes, vinegar may be produced in a period ranging from 20 hours to three days. In the modern commercial production of vinegar, the generator method and the submerged fermentation method are employed. These methods are based on the goal of infusing as much oxygen as possible into the alcohol product

The three common methods used for vinegar production are the generator or trickling method, the submerged fermentation or the Acetator method and the Orleans traditional method. Traditionally natural spontaneous fermentation is also used. The Generator method is the quicker one and is generally used in commercial vinegar production.

3.1.1. The Orleans Method

The Orleans process is one of the oldest and well known methods for the production of vinegar. It is a slow, continuous process, which originated in France. High grade vinegar is used as a starter culture, to which wine is added at weekly intervals. The vinegar is fermented in large (200 liter) capacity barrels. Approximately 65 to 70 liters of high grade vinegar is added to the barrel along with 15 liters of wine. After one week, a further 10 to 15 liters of wine are added and this is repeated at weekly intervals. After about four weeks, vinegar can be withdrawn from the barrel (10 to 15 liters per week) as more wine is added to replace the vinegar. One of the problems encountered with this method is that of how to add more liquid to the barrel without disturbing the floating bacterial mat. This can be overcome by using a glass tube which reaches to the bottom of the barrel. Additional liquid is poured in through the tube and therefore does not disturb the bacteria. Wood shavings are sometimes added to the fermenting barrel to help support the bacterial mat.

Manufacturing Steps

1) Wooden barrels are laid on their sides. Bungholes are drilled into the top side and plugged with stoppers. Holes are also drilled into the ends of the barrels.
2) The alcohol is poured into the barrel via long-necked funnels inserted into the bungholes. Mother of vinegar is added at this point. The barrel is filled to a level just below the holes on the ends. Netting or screens are placed over the holes to prevent insects from getting into the barrels.
3) The filled barrels are allowed to sit for several months. The room temperature is kept at approximately 85°F (29°C). Samples are taken periodically by inserting a spigot into the side holes and drawing liquid off. When the alcohol has converted to vinegar, it is drawn off through the spigot. About 15% of the liquid is left in the barrel to blend with the next batch.

3.1.2. The Generator Method

Because the Orleans process is slow, other methods have been adapted to try and speed up the process. This method uses a generator (figure 1), which is an upright tank filled with beech wood shavings and fitted with devices which allow the alcoholic solution to trickle down through the shavings in which the acetic acid bacteria are living.

Generators of various sizes (15 feet in diameter and 20 feet in

length) are used. The generator consists of a cylindrical tank with a perforated false bottom supporting beech-wood shavings or similar material that will help increase the flow of air from this bottom that has an exit at the top. A mix is prepared which consist of an adjusted solution of alcohol acidified with acetic acid and special nutrients for the growth of acetic acid bacteria. The latter, spies of the genus Acetobacter, are inoculated into the beech-wood shavings. The mix is applied in a trough at the top of the chamber and allowed to trickle down over the shavings. The mix is collected at the bottom of the generator and is re-circulated over the shavings resulting in more oxidation of alcohol until vinegar of the desired strength is obtained. Oxidation of alcohol by bacteria may result in the development of temperatures high enough top kill them. In order to keep the temperature down to 25 to 30^{0}C, cooling coils need to be provided. The generator method is quicker in comparison to other methods and the vinegar may be produced within a period of 10 days. This method is usually used to manufacture distilled vinegar. After collection of the vinegar distillation process takes place to concentrate the product.

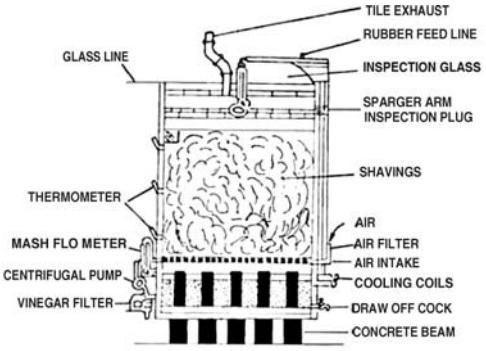


Fig1: ***Generator for Vinegar Production (Source: www.studentsguide.in)***

Manufacturing Steps

1) Tall oak vats are filled with vinegar-moistened beech wood shavings, charcoal, or grape pulp. The alcohol product is poured into the top of the vat and slowly drips down through the fillings.
2) Oxygen is allowed into the vats in two ways. One is through bungholes that have been punched into the sides of the vats. The second is through the perforated bottoms of the vats. An air compressor blows air through the holes.
3) When the alcohol product reaches the bottom of the vat, usually within in a span of several days to several weeks, it has converted to vinegar. It is poured off from the bottom of the vat into storage tanks. The vinegar produced in this method has very high acetic acid content, often as high as 14%, and must be diluted with water to bring its acetic acid content to a range of *5-6%.*
4) To produce distilled vinegar, the diluted liquid is poured into a boiler and brought to its boiling point. A vapor rises from the liquid and is collected in a condenser. It then cools and becomes liquid again. This liquid is then bottled as distilled vinegar.

3.1.3. The Submerged Fermentation Method

In the submerged fermentation method a tank filled with alcohol is pumped with oxygen and maintained at warm temperature. Primarily used to produce wine vinegars, this process was developed in the 1950s, using tanks called acetators. The wine is kept at a temperature between 26 and 38 degree centigrade while nutrients and air are pumped in to the mixture. The submerged fermentation method is commonly used in the production of wine vinegars.

Submerged vinegar systems are most commonly used by corporations who produce high quantities of vinegar with a high content of acetic acid. Submerged vinegar processing systems work with the continuous aeration of the liquid. The vinegar bacteria are floating in the liquid and do not produce a vinegar mother. Using this system, there is no slime in the machine and the ready vinegar is exceptionally clean and typical. Two systems are used:

Turbine Systems

work with a turbine at the bottom of the tank and bring the air into the liquid. Those turbine machines can be controlled automatically with an electronic system: The vinegar is pumped out of the machine when it is ready and is then refilled with wine. These systems are suitable for producers who plan to make more than 50,000 liters of vinegar per year.

Venturi Air Systems

are smaller and cheaper than turbine systems. The processing is done with a pumping system in a closed stainless steel tank. The air is brought into the liquid with a Venturi air nozzle, which brings air into the pumped liquid. The air bubbles have the same size like the turbine bubbles. The processing time of venturi systems is around 30 % longer than turbine systems, but this is better for quality, because of the lower aeration there is not so much flavor loss. As tastings showed, vinegars from these machines are always better and fruitier.

The changing is done after manual controlling of acetic acid content with a pump or with the pump inside the machine. The refilling is done with an external pump. These machines are very competitive and are available from 20 liters filling up to 600 liters filling. At the moment the venturi air system is the most common processing system for small and medium vinegar makers around the world.

Manufacturing Steps

1) Production plants are filled with large stainless steel tanks called acetators. The acetators are fitted with centrifugal pumps in the bottom that pump air bubbles into the tank in much the same way that an aquarium pump does.
2) As the pump stirs the alcohol, acetozym nutrients are piped into the tank. The nutrients spur the growth of Acetobacter on the oxygen bubbles. A heater in the tank keeps the temperature between 80 and 100°F (26-38°C).
3) Within a matter of hours, the alcohol product has been converted into vinegar. The vinegar is piped from the acetators to a plate-and-frame filtering machine. The stainless steel plates press the alcohol through paper filters to remove any sediment, usually about 3% of the total product. The sediment is flushed into a drain while the filtered vinegar moves to the dilution station.

3.2. Quality Control

Two factors require special attention when making vinegar: oxygen supply and temperature. Oxygen should be spread throughout the mixture. The temperature of fermenting cider should be kept at around 28 °C.

In the Orleans Method, bungholes must be checked routinely to ensure that insects have not penetrated the netting. In the generator method, great care is taken to keep the temperature inside the tanks in the 80-100°F range (26-38°C). Workers routinely check the thermostats on the tanks. Because a loss of electricity could kill the Acetobacters within seconds, many vinegar plants have backup systems to produce electrical power in the event of a power shutdown. Sometimes in the generator method undesirable microorganisms might spoil the vinegar. For example the vinegar eelworm (Turbatrix aceti) causes deterioration of flavor and appearance. Therefore, care should be taken to check contamination by undesirable bacteria or moulds or establishment of eelworm. The generator may be periodically disinfected to avoid contamination.

When the vinegar is fully fermented, it should be stored in separate containers or wooden barrels. The best place is cool (under 10°C) and dark. Before using the vinegar, it should be cleaned by filtering.

4. Cane Vinegar Production

Cane vinegar, made from sugar cane juice, is most popular in the Philippines, in particular, the Ilocos Region of the northern Philippines, although it is also produced in France and the United States. It ranges from dark yellow to golden brown in color and has a mellow flavor, similar in some respects, to rice vinegar, though with a somewhat "fresher" taste.

Sugarcane is well known and grown widely in Ethiopia and its juice is a good choice for natural vinegar because of its high sugar

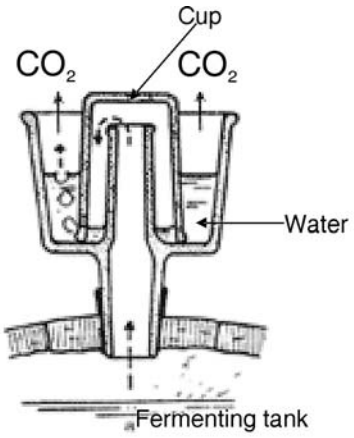
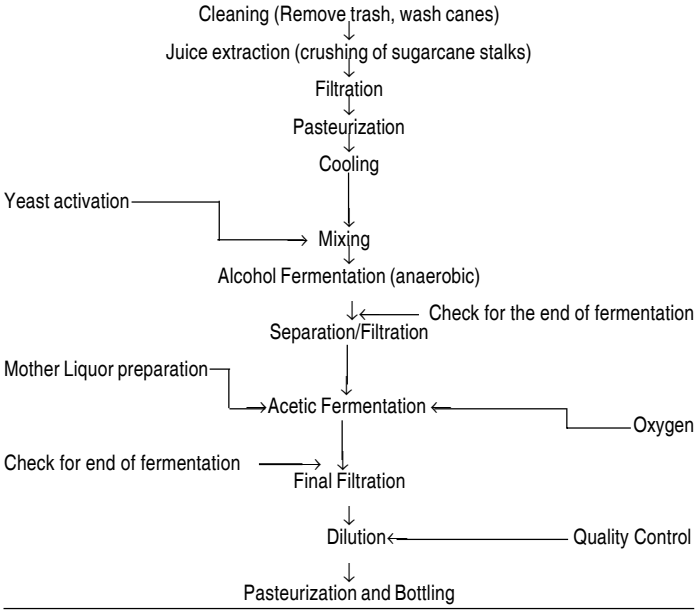


Fig 2: ***Air Lock***

content and availability. Generally, vinegar production allows utilization of over-riped fruits, sugarcane rejects, ethyl alcohol rejects and cane by-products such as molasses and bagasse. In sugar producing areas where leftover canes rejected by mills are available, it is recommended to utilize the leftovers and produce a product such as vinegar. It is possible to produces naturally fermented sugarcane vinegar from sugarcane juice. Young canes may also be used for vinegar making. If the juice extracted is below 15-16 degrees brix, small amounts of sugar or optionally molasses may be added.

A general flow diagram for the production of sugarcane vinegar is shown below.

Processing Steps



Cleaning step is vital to obtain a good quality cane juice. During juice extraction focus should be given on efficiency during pressing. Contamination should be avoided. To avoid microbial contamination the juice should be filtered and pasteurized as soon as possible. Then the juice should be cooled down and maintained at a suitable temperature for yeast growth (28 – 32 °C). *Saccharomyces cerevisiae* strains are used for producing alcohol. One and half gram of yeast is added per liter of juice. The yeasts should be activated in a separate batch so that they finish the lag phase. The activated yeasts are then mixed with the pasteurized cane juice, allowed to multiply for 2 – 3 hours, and then kept under anaerobic condition. To create the anaerobic environment different simple airlock designs could be applied (Figure 2).

Figure 2 shows how CO_2 gas from the fermenting tank passes through the water filled gap to escapes in to the environment. Since CO_2 is a light gas and due to the fact that there is greater pressure in side the tanker, it will not be difficult for the gas to boost out from the tanker by penetrating the water filled gap. But external air will not be capable of entering the tanker through this gap due to the presence of water. After some time all the O_2 in the tanker will be utilized by the microbes and the environment within the tanker will be completely anaerobic.

To check whether the alcohol fermentation is over or not a hydrometer is used. If no hydrometer is available, by observing the movement of gases in the liquid one can decide to proceed to the next step when fewer gases are produced. Filtration process is needed to remove yeasts. The alcohol should be diluted to around 8% by volume before adding the mother liquor. Since oxygen is very important, its supply should be monitored through out the fermentation. Samples should be taken after wards to check the acetic acid content at different time intervals. When the desired level of acid is reached a final filtration is carried out; standardizing, quality check and pasteurization bottling steps are the final steps in the manufacturing process. Labeling is necessary.

Further Possible Improvements

Studies show that cell immobilization provides a means to improve the fermentation process by increasing biomass, option of reusability, protection of cells from toxic effects of low pH, temperature, and inhibitors. Cell immobilization also helps in early clarification of the product. Further, the choice of immobilization material in the form of inexpensive easily available inert biological materials can help reduce the cost of the process.

A study was undertaken to develop an efficient process using immobilized cells of *Acetobacter aceti* for vinegar production from cane juice. In the study different inert materials (i.e. bagasse, corn cobs and wood shavings) were compared for immobilization of the *A. aceti* cells. First sugarcane juice was converted to ethanol by free *Saccharomyces cerevisiae* producing 8% (v/v) ethanol. This ethanol was used for vinegar production using adsorbed and entrapped cells of *Acetobacter aceti*.

The result of the study shows that all three adsorbed carrier materials were statistically similar for acetic acid production and produced acidity from 5.9 to 6.7% after 28 days of submerged fermentation. By recycling bagasse adsorbed cells, the time of acetic acid fermentation was reduced to 13 days. Semi-continuous fermentation of bagasse adsorbed cells using a packed bed column further reduced the fermentation time to 80 hours.

CONCLUSION

Vinegar is the product obtained as a result of impartial oxidation of alcohol in a fermenting sugar containing fruit or cane juice, molasses, fermented mash of malted grain, honey, syrups, etc. Vinegar is primarily used to flavor and preserve foods and as an ingredient in salad dressings.

The three common methods used for vinegar production are the generator or trickling method, the submerged fermentation or the Acetator method and the Orleans traditional method. The generator method is quicker in comparison with the others. Submerged vinegar systems are most commonly used by corporations who produce high quantities of vinegar with a high content of acetic acid.

Generally, vinegar production allows utilization of over-riped fruits, sugarcane rejects, ethyl alcohol rejects and cane by-products such as molasses and bagasse. Since sugarcane is well known and grown widely in Ethiopia, it is feasible to use cane juice as a raw material for vinegar production. Especially in sugar producing areas, where leftover canes rejected by mills are available, it is recommended to utilize the leftovers for the production of vinegar.

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