

# VINEGAR

The topic vinegar will be discussed under 5 subunits such as

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## 1. INTRODUCTION

Vinegar is a liquid consisting mainly acetic acid ( $\text{CH}_3\text{COOH}$ ) and water. The acetic acid is produced by the fermentation of ethanol by Acetic acid bacteria. Vinegar must have been known to man for thousands of years since he apparently learnt to produce alcoholic beverages some 10,000 years ago. Basically vinegar may be regarded as wine spoiled by the Acetic acid bacteria, but for which other uses have been found. Historically, as the most easily available mild acid, it had a great variety of industrial, medical and domestic uses, some of which (such as its use as a general household cleanser) are still promoted today.

Although acetic acid is the major component of vinegar, the material cannot be produced simply by dissolving acetic acid in water. When alcoholic fermentation occurs and later during acidifications many other compounds are produced, depending mostly on the nature of the material fermented and some of these find their way into vinegar. Furthermore, reactions also occur between these fermentation products. Ethyl acetate, for example, is formed from the reaction between acetic acid and ethanol. It is these other compounds which give the various vinegars their bouquets or organoleptic properties. The other compounds include non-volatile organic acids such as malic, citric, succinic and lactic acids; unfermented and unfermentable sugars; oxidized alcohol and acetaldehyde, acetoin, phosphate, chloride, and other ions.

Commercial vinegar is produced either by fast or slow fermentation processes. In general, slow methods are used with traditional vinegars, and fermentation proceeds slowly over the course of months or a year. The longer fermentation period allows for the accumulation of a nontoxic slime composed of acetic acid bacteria. Fast methods add mother of vinegar (bacterial culture) to the source liquid before adding air to oxygenate and promote the fastest fermentation. In fast production processes, vinegar may be produced in 20 hours to three days.

## 2. TYPES OF VINEGAR

Vinegar is normally a product of two fermentations: alcoholic fermentation with a yeast and the production of acetic acid from the alcohol by acetic acid bacteria. There is no distillation between the two fermentations, except in the production of spirit vinegar, which is described below. The vinegar may or may not be flavored. The substrate for the alcoholic fermentation for vinegar productions varies from one locality to the other. Thus, while wine vinegar made from grapes is common in continental Europe and other vine growing countries, malt vinegar is common in the United Kingdom; the United States on account of its great variety of climatic regions uses both malt and wine vinegars. Rice vinegar is common in the far Eastern countries of Japan and China and pineapple vinegar is used in Malaysia. In some tropical

countries vinegar has been manufactured from palm wine derived from oil or raffia palm. The composition and specifications of various types of vinegars are defined by regulations set up by the governments of different countries. In the United States, for example, vinegar should not contain less than 4.0% (w/v) acetic acid and not more than 0.5% ethanol (v/v).

The various major vinegars are defined briefly

- (a) *Cider vinegar, apple vinegar*: Vinegar produced from fermented apple juice (US) and non-grape fruits.
- (b) *Wine vinegar, grape vinegar*: Fermented grape juice malt.
- (c) *Malt vinegar*: Produced from a fermented infusion of barley malt with or without adjuncts.
- (d) *Sugar, glucose, dried fruits*: In the US vinegar from sugar syrup or molasses should be labeled sugar vinegar, while that from glucose (which should be dextroserotatory) and dried fruits should be labeled with 'glucose' or the particular dried fruit involved.
- (e) *Spirit vinegar*: Vinegar made from distilled alcohol. In the US synonyms for spirit vinegar are 'white distilled vinegar' and 'grain vinegar'. The alcohol used in the distillation is denatured for tax reasons with ethyl acetate. One gallon of ethyl acetate is usually added to 100 gal of 95% alcohol. The ethyl acetate is not deleterious and in any case is present in vinegar by the alcohol acetic acid reaction. It should be noted that in the United States the term 'distilled' refers to the ethanol used; in the United Kingdom, however, 'distilled' vinegar refers to a distillate of malt vinegar.
- (f) Some specialty vinegars: Specialty vinegars make up a category of vinegar products that are formulated or flavored to provide a special or unusual taste when added to foods.

Specialty vinegars are favorites in the gourmet market:

- (a) Herbal vinegars: Wine or white distilled vinegars are sometimes flavored with the addition of herbs, spices or other seasonings. Popular flavorings are garlic, basil, and tarragon, but cinnamon, clove, and nutmeg flavored vinegars can be tasty and aromatic addition to dressings.
- (b) Fruit vinegars: Fruit or fruit juice can also be infused with wine or white vinegar. Raspberry flavored vinegars, for example, create a sweetened vinegar with a sweetsour taste.
- (c) Balsamic vinegar: Traditional balsamic vinegar of Modena, Italy is made from white and sugary Trebbiano grapes grown on the hills around Modena. The grapes are harvested as late as possible to take advantage of the warmth of the weather. The traditional vinegar is made from the cooked grape 'must' (juice) matured by a long and slow process of natural fermentation, followed by progressive concentration by aging in a series of casks made from different types of wood and without the addition of any other spices or flavorings. The color is dark brown and the fragrance is distinct. Production of traditional balsamic vinegar is governed by the stringent standards imposed by the quasi-governmental Consortium of Producers of the Traditional Balsamic Vinegar of Modena.
- (d) Raspberry red wine vinegar: Natural raspberry flavor is added to red wine vinegar, which is the aged and filtered product obtained from the acetous fermentation of select red wine. Raspberry red wine vinegar has a characteristic dark red color and a piquant, yet delicate raspberry flavor.

- (e) Other specialty vinegars: Coconut and cane vinegars are common in India, the Phillipines and Indonesia with date vinegar being popular in the Middle East.

### **3. ORGANISMS INVOLVED**

Pasteur confirmed that acetic acid is produced only in the presence of the bacteria, but he did not identify them. The genus name *Acetobacter* was put forward by Beijerinck in 1900. Suffice it to state that although *Acetobacter* spp are responsible for vinegar production, pure cultures are hardly used, except in submerged fermentation because of the difficulty of isolating and maintaining the organisms. The only member of the genus which is not useful, if not positively harmful in vinegar production is *Acetobacter xylinum* which tends to produce slime. Recently a new species, *Acetobacter europaeus*, was described.

Strains of acetic acid bacteria to be used in industrial production should

- (a) Tolerate high concentrations of acetic acid;
- (b) Require small amounts of nutrient;
- (c) Not overoxidize the acetic acid formed; and
- (d) Be high yielding in terms of the acetic acid produced.

The bacteria converting alcohol to acetic acid under natural conditions are film forming organisms on the surface of wine and beer. The film was known as 'mother of vinegar' before its bacteriological nature became known. The bacteria were first described as *Mycoderma* (viscous film) in 1822. Later other workers classified them in *Mycoderma vini* (forming film on wine) an *Mycoderma acetic* (forming film on beer).

### **4. MANUFACTURE OF VINEGAR**

The three methods used for the production of vinegar are the Orleans Method (also known as the slow method), the Trickling (or quick) Method and Submerged Fermentation. The last two are the most widely used in modern times.

#### **1. The Orleans (or Slow) Method**

The oldest method of vinegar production is the 'let alone' method in which wine left in open vats became converted to vinegar by acetic acid bacteria entering it from the atmosphere. Later the wine was put in casks and left in the open field in the 'fielding process'. A small amount of vinegar was introduced into a cask of wine to help initiate fermentation. The introduced vinegar not only lowered the pH to the disadvantage of many other organisms but also introduced an inoculum of acetic acid bacteria.

The casks were wooden and of approximately 200 liter capacity. It was never filled beyond about two-thirds of its capacity so that there was always a large amount of air available above the wine. A thick film of acetic acid bacteria formed on the wine and converted it in to vinegar in about five weeks. About 10-20% of the vinegar was drawn off at weekly intervals and replaced with new wine. The withdrawal and replenishment were done from the bottom of the cask so that the film would not be disturbed. Often a series of casks was present and the transfer was done from one cask to another. The process had a number of disadvantages:

- (a) It was slow in comparison with later methods, taking up to five weeks sometimes as against days, hence it is also known as the slow method.
- (b) It was inefficient, yielding 75-85% of the theoretical amount.
- (c) The 'mother of vinegar' usually gradually filled the cask and effectively killed the process.

## **2. The Trickling Generators (Quick) Method**

Credit for devising the fore-runner of the modern trickling generator is usually given to the Dutch Boerhaave who in 1732 devised the first trickling generator in which he used branches of vines, and grape stems as packing. Improvements were made by a number of other people from time to time. Later ventilation holes were drilled at the bottom of the generator and provided a mechanical means for the repeated distribution of the alcohol acetic acid mixture over the packing. The heat generated by the exothermic reaction in the generator caused a draft which provided oxygen for the aerobic conversion of alcohol to acetic acid. This latter model of the quick method (sometimes called the German method) enabled the production of vinegar in days instead of in weeks.

The modern vinegar generator consists of a tank constructed usually of wood preferably of cypress and occasionally of stainless steel. A false bottom supports the coils of birchwood shavings and separates them from the collection chamber which occupies about one fifth of the total capacity of the generator. A pump circulates the alcohol-acetic acid mixture from the reservoir through a heat exchanger to the top of the generator where a spray mechanism distributes it over the packing in much the same way as a trickling filter functions in waste-water treatment. Air is forced through the false bottom up through the set-up. The cooling water in the heat exchanger is used to regulate the temperature in the generator so that it is between 29°C and 35°C; this is determined with thermometers placed at different levels of the generator.

The top of the generator is covered but provision exists for exhaust air to be let out. Meters measure three parameters: (a) the circulation of the mash, (b) the flow of cooling water through the heat exchange, and (c) the amount of air delivered through the system. If the air flow rate is too high alcohol and vinegar are lost in effluent air.

The trickling or circulating Frings generator is reasonably efficient, achieving, when operating maximally, an efficiency of 91-92% and it is capable of producing 500–1000 gallons of 100-grain (i.e. 10%) vinegar every 24 hours. The finished acidity of the vinegar is about 12%; when it is higher, production drops off. In order not to exceed this level of acidity, when drawing off vinegar, the amount of alcohol in the replacement should be such that the total amount of alcohol is less than 5%.

## **3. Submerged Generators**

With knowledge in submerged fermentation gained from the antibiotics and yeast industry it is not surprising that vinegar production was soon produced by this method. Several submerged growth vinegar generators have been described or are in operation. The common feature in all submerged vinegar production is that the aeration must be very vigorous as shortage of oxygen because of the highly acid conditions of submerged production, would result in the death of the bacteria within 30 seconds. Furthermore, because a lot of heat is released (over 30,000 calories are released per gallon of ethanol) an efficient cooling system

must be provided. All submerged vinegar is turbid because of the high bacterial content and have to be filtered.

Some commonly used submerged generators will be discussed below.

### **a. Frings acetator**

First publicized in 1949, most of the world's vinegar is now produced with this fermentor. It consists of a stainless steel tank fitted with internal cooling coils and a high speed agitator fitted through the bottom. Air is sucked in through an air-meter located at the top. It is then finely dispersed by the agitator and distributed throughout the liquid. Temperature is maintained at 30°C, although some strains can grow at a higher temperature. Foaming is interrupted with an automatic foam breaker. Essentially it is shaped like the typical aerated stirred tank fermentor.

#### *Advantages*

- (a) The efficiency of the acetator is much higher than that of the trickling generator; the production rate of the acetator may be 10-fold higher than a trickling unit. Values of 94% and 85% of the theoretical have been recorded for both the acetator and the trickling filter.
- (b) The quality is more uniform and the inexplicable variability in quality noted for the trickling generator is absent.
- (c) A much smaller space is occupied (about one-sixth) in comparison with the trickling generator.
- (d) It is easy and cheap to change from one type of vinegar to another.
- (e) Continuous production and automation can take place more easily with Frings acetator than with trickling.

#### *Disadvantages*

- (a) A risk exists of complete stoppage following death of bacteria from power failure even for a short time. Automatic stand-by generators have helped to solve this problem.
- (b) It has a high rate of power consumption. Some authors have however argued that in fact in terms of power consumed per gallon of acetic produced the acetator is less power consuming.

### **b. The cavitator**

The cavitator was originally designed to treat sewage: it was then modified for vinegar production. In many ways it resembled the acetator. However, the agitator was fixed to the top and finely dispersed air bubbles are introduced into the liquid. It operated on a continuous basis and was quite successful in producing cider and other vinegars as long as the grain strength was low.

### **c. The tower fermentor**

The tubular (tower) fermentor developed in the UK has been used on a commercial scale for the production of beer, vinegar, and citric acid. It has a working volume of 3,000 liters and aeration is achieved by a stainless steel perforated plate covering the cross section of the tower and holding up the liquid. The unit can produce up to 1 million gallons (450,000 liters)

of 5% acetic acid per annum. The *Acetobacter* sp requires a month to adapt to the new system. The system can be batch, semi or fully-continuous without noticeable differences in the quality of the product.

## PROCESSING OF VINEGAR

- (a) **Clarification and bottling:** Irrespective of the method of manufacture, vinegar for retailing is clarified by careful filtration using a filter aid such as diatomaceous earth. Vinegar from trickling generators are however less turbid than those from submerged fermentations because a high proportion of the bacterial population responsible for the acetification is held back on the shavings. After clarification it is pasteurized at 60-65°C for 30 minutes.
- (b) **Concentration of vinegar:** Vinegar can be concentrated by freezing; thereafter the resulting slurry is centrifuged to separate the ice and produce the concentrate. With this method 200° grain (i.e., 20% w/v) acetic acid can be produced. Concentration is necessitated by two considerations. One is the consequent reduction in transportation costs. The other is the need to prevent loss of activity of the vinegar when cucumbers were pickled in it after first being soaked in brine.

## 5. USES OF VINEGAR

(i) **Ancient uses:** The ancient uses of vinegar which can be seen from various records include a wide variety of uses including use as a food condiment, treatment of wounds, and a wide variety of illnesses such as plague, ringworms, burns, lameness, varicose veins. It was also used as a general cleansing agent. Finally, it was used as a cosmetic aid.

(ii) **Modern uses:** Vinegar is used today mainly in the food industry as;

- (a) A food condiment, sprinkled on certain foods such as fish at the table;
- (b) For pickling and preserving meats and vegetables; vinegar is particularly useful in this respect as it can reduce the pH of food below that which even spore formers may not survive;
- (c) It is an important component of sauces specially renowned French sauces many of which contain vinegar;
- (d) Nearly 70% of the vinegar produced today is supplied to various arms of the food industry where it finds use in the manufacture of sauces, salad dressings, mayonnaise, tomato productions, cheese dressings, mustard, and soft drinks. Most of the vinegar used in industry is the distilled or concentrated.

**Conclusion:** Throughout history, vinegar has proved to be the most versatile of products. The dictionary defines versatile as capable of turning with ease from one thing to another, and from more than 10,000 years ago to today, consumers continue to use vinegar in a variety of ways. Vinegar is now mainly used as a cooking ingredient. Historically, as the most easily available mild acid, it had a great variety of industrial, medical and domestic uses, some of which (such as its use as a general household cleanser) are still promoted today.