Artisan Distilling

A Guide for Small Distilleries



Kris Arvid Berglund, Ph.D.

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Kris Arvid Berglund, Ph.D.
University Distinguished Professor
Department of Chemical Engineering & Materials Science
Department of Agricultural Engineering
Michigan State University
East Lansing, MI 48824 USA
berglund@msu.edu

and

Professor and Division Head
Division of Biochemical and Chemical Process Engineering
Department of Chemical Engineering and Geosciences
Luleå University of Technology
SE-971 87 Luleå, Sweden
kris.berglund@ltu.se

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Dedication

To my wife Dianne, my son Erik, and my daughter Lisa, without your support this book would not have been possible.

Forward

Production of distilled spirits is certainly one of the oldest practiced biotechnological processes. In recent years there has been rapid increase in interest in the production of spirits at smaller, artisan scale in the U.S. and other countries. This type of distillation is widely known and practiced in the French and German speaking countries of Europe, but there is a general lack of literature written in English. This work, which draws heavily from the widely popular book written in German by H. Tanner and H. R. Brunner, is aimed at filling this void. These authors are thanked and acknowledged for their work. Dr. Klaus Weispfennig translated the Tanner and Brunner book into English which allowed its use as a reference. His efforts were invaluable since the author is not fluent in German and this book would not be possible without his assistance.

This book is aimed at the production of white spirits (fruit brandy/ eau de vie, vodka, gin, rum, etc.). While there is a large group of products that are stored in oak for color and flavor components, I do not attempt to cover the nuances of oak treatment for these products in any depth. It should be noted that all oak stored products start as white spirits, so the production of white spirits is common to the distilled beverage business.

I have chosen to produce this book in electronic format. This choice keeps the cost down and allows it to be kept current. I expect to be continually updating it and welcome any comments or suggestions for new or expanded topics.

I would like to thank all the people who have helped me learn about small scale distillation, and in particular, Jörg Rupf of St. George Spirits in Alameda, CA USA who help me start and continues to be a great friend and colleague; my good friends and colleagues at the various artisan distilleries in Michigan and Sweden; and Alexander, Christian, and the entire Plank family of Christian Carl Ing. GmbH, Göppingen, Germany, who continue to be valued collaborators and friends.

As we say in Sweden, ***skål!***

Kris Arvid Berglund
Luleå, Sweden and East Lansing, MI USA
March 2004



The author (KAB) in the foreground with former MSU graduate student, Matt Berg, in the background at the MSU distillery in East Lansing, MI USA. This 150 liter working volume still is a typical still used by the artisan distillers in Michigan.

RAW MATERIALS

General Requirements

Any sugar containing material can be the basis for the production of spirits. Starch containing materials such as grains and potatoes are fermentable and are acceptable for whiskey, vodka, and gin production; however, in the U.S. they cannot be used for brandy production[1]. The following raw materials will be considered in the present work:

For brandy

Seed fruit (apples, pears)
Stone fruit (cherries, plums, apricots)
Berry fruit (raspberries, currants, blackberries, juniper berries etc.)
Pulp (grape and other fruit pulp)
Seed fruit and grape wine
Yeast sediment products
Roots and tubers.

For vodka, gin, whiskey:
Grains (corn, wheat, barley, and rye)
Roots (potatoes], not whiskey

For rum:
Molasses

The raw materials necessary for the production of excellent spirits need to meet certain quality demands, but the more common physical criteria for table fruits such as color, shape, size and surface shine are less important. It is the chemical composition of the fruit or grain which is decisive for both a qualitative and quantitative satisfactory outcome including:

1. high sugar content
2. strong developed, typical aroma (in fruits)
3. clean, healthy, sound material (no mold or rot).

In general, optimal sugar and aroma content can only be achieved through good ripening of the fruit or grain. Upon addition of sugar (forbidden by regulations in a wide number of countries in Europe and North America for brandy production) the lack of sugar content in unripe fruit can be corrected: however, because of the lack in aroma the resulting brandy would likely be of poor quality. Moreover, the increased level of tannin materials in unripe fruits can lead to fermentation hold-up

[1] In the U.S., the controlling legisalation for production of distilled spirits. is the Code of Federal Regulations and lists the standards of identitiy for distilled spirits.

or faulty fermentations. Overly ripe fruit tends to rot and mold, which results in poor brandies. Furthermore, the fruits or grains used ought to be free of any secondary odors and flavors (e.g. oils, sprays, pesticides, etc.) In summary, the condition of the raw material is of fundamental importance for the production of good spirits. Superior distillates can not be obtained using low-grade material even with the most careful processing. Distillation should never be considered a remedy for utilization of damaged or unsound fruit or grains.

Table. 1: Sugar content and alcohol output of various raw materials (from *Tanner and Brunner*)

	Sugar content (%)		Yield (liters of pure alcohol per 100 kg raw material)	
Raw material	Range	Mean	Range	Mean
Apples	6-15	10	3-6	5
Apricots	4-14	7	3-7	4
Pears	6-14	9	3-6	5
Blackberries	4-7	5.5		3
Gentian roots	5-13		3-5	
Windfalls (Seed fruit)	2-5			2.5
Yeast deposits			2-5	
Blueberries	4.5-6	5.5		3
Raspberries	4-6	5.5		3
Elderberries	4-6	5		3
Currants	4-9	red 4.5 black 6.5		3.5
Pomace	2-4		2-3	
Cherries, sweet	6-18	11	4-9	6
Peaches	7-12	8		4.7
Plums	6-15	8	4-8	
Quinces	4-8		2.5-4	
Marc	2-4			3
Juniper berries (dried)		20	10-11	
Topinambour	13-18*		6-8	
Grapes	9-19	14	4-10	8
'Zwetschgen' (Plums)	8-15	10	4-8	6

- **predominantly inulin**

Components of the Raw Materials

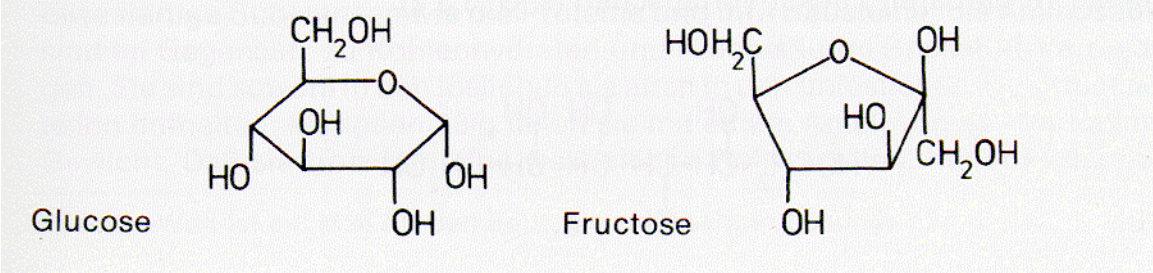
The principal components of fruits and grains can be classified into three groups:

1. water
2. solids/ insolubles
3. soluble constituents.

The water content of fresh fruit is normally between 80 and 85%while in grains it is usually less than 20%. The solid, insoluble constituents such as stems, shells, cores, stones and protopectin are less important for distillation; they remain as residue in the still. Hexanol can be obtained from the stem and leafs in the mash which can lead to undesirable leafy flavor. In practice it is necessary to remove, for example, the leaves and stems of cherries before marinating. The "cement substance" protopectin will be decomposed during ripening or storage through enzymes (softening of fruits); also, the poisonous methyl alcohol (methanol) can be produced through further decomposition of pectin. Care is to be taken with stone fruit inasmuch not more than 5% of the stone are being broken in order to avoid an obtrusive bitter almond taste in the distillate.

Water soluble substances are present in 10-20% in fruit and can be catergorized as carbohydrates, acids, proteins and nitrogen containing compounds, phenolics, vitamins, aromatics, and minerals.

Carbohydrates. Carbohydrates constitute the main part of the water-soluble fruit substances. The primary sweet tasting sugars are glucose (grape sugar), fructose (fruit sugar) and sucrose (cane and beet sugar).



Glucose and fructose are monosaccharides (simple sugars) and are fermented by yeasts. However, sucrose (a disaccharide, i.e. a double sugar) has to be decomposed first into glucose and fructose by means of enzymes and/or acids in order to be fermentable. This process is called inversion and proceeds during fermentation such that the residual sugar content of fermented musts and mashes is usually only glucose and fructose. The sum of glucose, fructose, and sucrose, i.e. the total sugar content, sets the potential alcohol yield. The yield can be calculated based on the fermentation equation:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

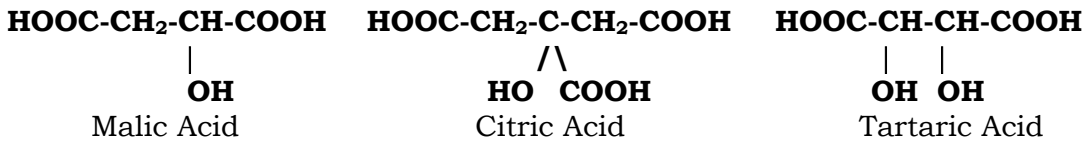
Sugar (Glucose, Fructose)	Alcohol (Ethyl Alcohol)	Carbon Dioxide (Fermentation Gas)

Theoretically, 100 kg sugar (glucose, fructose) will yield approximately 51 kg or 64.5 l alcohol. In practice, however, this number is actually not achieved, because the above equation is a simplified description of the actual processes. Less than theoretical yield is caused by sugar consumption by the yeast, incomplete fermentation, the formation of fermentation side products (e.g. fusel alcohols), and alcohol loss in the distillation process. For these reasons a yield of only 56 liters of pure alcohol per 100 kg glucose or fructose is generally realized in practice.

Another carbohydrate present in fruits is the unfermentable sugar alcohol sorbitol. It is present in all seed and stone fruits whereas it is practically absent in grapes, berry fruits and citrus fruits. Sorbitol content can be incorrectly interpreted as fermentable sugar in fermented pomace fruit mashes and stone fruit mashes.

Grains also possess fermentable sugars, but generally they are not in the form of simple sugars like those found in fruits. The predominant form of sugars in grains is starch. Starch is a polymer composed of repeating units of glucose; therefore, it is necessary to break the starch down to the basic glucose unit for the yeast to convert the sugar into alcohol. This process is called hydrolysis and can be accomplished by use of enzymes or acids.

Acids. The taste of fruit is also determined by the content of non-volatile acids in addition to the sugars. During ripening, the sugar content increases at the expense of the acid content. However, fruit with an acid content too low (high sugar/acid ratio) not only affects the taste in an unsatisfactory way; but the resulting mashes are more susceptible to contamination by undesired micro organisms which may lead to faulty fermentations. Mashes lower in acid, such as those made with Bartlett pears, should be fermented using pH adjustment by acid addition. The primary acids present in fruits are malic acid, citric acid, tartaric acid, and isocitric acid:



Malic Acid | Citric Acid | Tartaric Acid

Malic acid is widely distributed in fruits, but is particularly present in seed fruit and in stone fruit. Citric acid is dominate in the majority of berries and in citrus fruits whereas tartaric acid is present in a

significant concentrations only in grapes. Isocitric acid is found in blackberries, but in other fruits is only present in trace amounts.

During primary fermentation and subsequent aging fruit acids are decomposed through bacterial activity. In most cherry mashes the decomposition of malic acid to lactic acid occurs without adversely changing the mash. In the production of wine the conversion of the "hard" malic acid into the "softer" lactic acid is in sometimes desired and a secondary malo-lactic fermentation in undertaken intentionally. The bacterial decomposition of citric acid leads to formation of lactic acid, acetic acid, formic acid, and acetaldehyde which can be detrimental to the mash and can appear in the resulting distillate. Decomposition processes are associated with an increase of the pH which increases the susceptibility of the mash to bacteria.

Proteins and Nitrogen Containing Substances. In contrast to carbohydrates and organic acids, proteins and their components, amino acids, contain nitrogen. These compounds are important nutrients for the fermentation as the yeast needs a nitrogen source for growth and maintenance. If the nitrogen available to the yeast is not sufficient, fermentation hold-ups can occur and fermentation aids or nutrients must be used. In the wine industry this is sometimes referred as a "stuck" fermentation. The yeast fermentation is believed to convert certain amino acids to the formation of aromas and flavors.

An important nitrogen containing group is enzymes, which are proteins that catalyze or accelerate chemical processes in living organisms (metabolism) without being used up at the same time. They are effective in small amounts and usually very specific for a reaction. Thus, complicated metabolic processes take place through the use of several enzymes. As an example the enzyme system for alcoholic fermentation consists of 12 different enzymes formed in the yeast cells. Every one of those enzymes participates in a specific reaction in the formation of alcohol from glucose and fructose.

Many enzyme-controlled reactions lead to undesired changes including browning and oxidation reactions, increased methanol and cyanide contents. Enzymes are heat sensitive like all proteins, a characteristic that can be exploited for the reduction of their activity.

Phenolics. This large group of compounds is often described by the generic name "tanning agents". It contains plant colors as well as combinations which condense to larger molecules and can cause the well-known harsh and astringent taste. For elevated contents of phenolic substances the danger of fermentation hold-ups exists because flocculations/ precipitates are formed through deposition onto protein substances

VitaminsAscorbic acid (vitamin C) is a major vitamin present in fruits, but does not, however, have great importance in fermentation. Contact with oxygen in the air oxidizes vitamin C and converts it to dehydroascorbic acid.

The aroma of fruit is composed of a multitude of various substances. For example, in grapes the existence of more than 200 aromatic substances could be demonstrated even though their total share is mostly under 0.1 %. Aroma components are predominantly alcohols, volatile acids, esters, aldehydes, acetals, and ketones which form during both ripening, fermentation, and distillation. Many factors influence the aroma in the fresh fruit like geographical location, climate, and storage conditions.

Some aroma agents, e.g. isoamyl alcohol from the amino acid leucine, form in the course of the fermentation, whereas others present in the fresh fruit are partly converted into different ones. This leads to the fact that the aroma of a fermented mash (fermentation bouquet) mat differ greatly from the corresponding fruit bouquet. The distillation of the mashes as well as the subsequent storage of the distillates leads to further changes of the bouquet.

Minerals. All fruits and grains contain minerals like potassium, calcium, magnesium, iron, phosphorus etc., which also serve as nutrients for the yeast. Fermentation hold-ups caused by excess mineral contents are not common.

Raw Materials

Seed Fruit.

Generally, surplus apples and pears are used for processing. But specialties from pure types of fruit are also produced. A well-known apple variety is “Golden Delicious” and the pear variety is “Bartlett”, also known as “Williams” in Germany. Pear brandy has one of the most characteristic flavor and aroma of the original fruit of any of the fruit brandies.

The sugar content of seed fruit generally fluctuates very strongly (cf. Table 1), but has a mean of about 9-10 % both for apples and pears. Pears contain less acid than apples which causes them to be more susceptible for infections; therefore, acid adjustment is generally required. Must pears often contain a high level of tanning agent. In general, healthy seed fruit is stored for a while before use (decomposition of the tanning agent, softening of the fruit, aroma development), whereas damaged raw materials have to be processed fairly soon because of risk of infection. Several processing possibilities exist:

1. Mashing after preceding mincing (healthy fruit)

2. Fruit pressing and fast fermentation (foul, unripe fruit; hail damaged fruit; surplus use)
3. Usage of overaged fruit wines (consider total SO_2-content, as high sulfur content can leave to very poor distillates).

Stone Fruits

Cherries which are richer in sugar and in aroma than table cherries are desired for the production of cherry brandy (Kirsch). Early harvested fruit generally does not have full sugar and flavor development; therefore, it is recommended to use fully ripe and even overly ripe fruit. Tart cherries often possess a higher (the taste being masked by the acid) sugar content than sweet cherries, but they can low in aroma. Experience with the Montmorency tart variety in Michigan has shown that an excellent distillate can be produced from this variety.

Cherries usually contain 20-40 g sorbitol/kg, a non-fermentable, sweet tasting sugar alcohol. In case of faulty fermentations the non-fermentable sugar alcohol mannitol can also be formed from fructose such that refractometer measurements can wrongly indicate fermentable sugar. The stone content is approximately 10% of the total weight. The cherries should be picked without stems and leaves should be removed. Cracked fruit needs to be processed immediately.

Plums are more round in contrast to the longish 'Zwetschgen'; their flesh is moreover softer and is less easily to separate from the stone. Sugar and acid content are rather somewhat lower compared to 'Zwetschgen' and the aroma is - except of some special sorts - less developed. Plums are more susceptible for decay than 'Zwetschgen' since their skin is thinner and thus easily crack and become rotten faster because of their lower acid content. It is not uncommon to obtain impure distillates but with proper processing (e.g. addition of acid to the mashes) it is possible to obtain satisfactory results.

Apricots are also an excellent raw material for distillate production. The processing and treatment should generally follow the guidelines set out the other stone fruit mentioned above.

Berries

Berries are not as widely used for distillation as compared to stone fruit or seed fruit. Cultivated berries possess a relatively low sugar content of 4-8% (exceptions: Grape and rose hip) as compared to wild growing ones. This low sugar content results in relatively low yield of distillate and subsequently makes the raw material cost quite high. Berries are more widely used for the production of liqueurs.

Raspberries, blackberries, and currants are the most widely used raw materials for distillate production. Cranberries and elderberries are rich in tanning material and partially low on nitrogen; therefore, supplementation using fermentation aids should be used to avoid fermentation hold-ups. Juniper berries are commonly used in dried condition, their sugar content is around an average of 20%. Due to the high content of tanning agents and resins it is difficult to ferment juniper mashes.

Pulp

Marc is the residual from the pressing of the fruit. Its sugar content depends to a great extent on the moment of the pressing as well as the associated conditions in addition to the quality of the base material. White grapes are pressed while sweet and the resulting sugar content of the marc is thus higher than for red grapes which are pressed during decreasing fermentation in order to gain the color. In some cases the sugar content can be so low that the use of the marc is no longer profitable for distillation raw material. Heating of the mash can increase the sugar content for the marc of red grapes. The press conditions have a significant influence on the sugar content: higher pressure, renewed loosening and pressing, hot pressing etc. are factors which contribute to the juice yield; however, improved juice yield results in lower sugar content in the marc.

Marc is highly perishable and should be processed quickly after production. Increased contact with air can be avoided through a good pulping. It is recommended to avoid the usage of marc already containing compounds that result in poor quality (e.g. marc with butyric acid tinge or an aldehyde content which is too high), because the recovery of their distillates is associated with tremendous expenditure or not anymore possible at all. While present day practices and regulations often prohibit it, previously residuals of sprays could be found in the marc, especially sulfur and organic sulfur constituents. During the course of the fermentation this sulfur is converted to hydrogen sulfide such that the odor of rotten eggs is formed. Marc mostly yields distillates with increased aldehyde and methanol content. An important element to consider in both marc and pomace use it that the sugar content is always low relative to other feedstocks and there will always be a much higher concentration of flavor and aroma components in the final distillation process.

The pulp of apples and pears (i.e. pomace) generally contains less sugar than the marc of grapes and their processing is often not very profitable. Pomace distillates are also known for their relatively high methanol content. Methanol forms during the fermentation through the influence of a fruit specific enzyme (pectin methyl esterase) from pectin present

mostly in large quantities in pears. High methanol contents can pose a problem in the US as the allowable limits are lower and the regulations are more closely enforced than in some other countries.

Wines

Often faulty wines or low-grade wines are used for distillation. Special care must be employed during distillation and the addition of specific technical measures (elimination of the sulfur compounds, lowering of an excessive acetic acid content, etc.). Bitter wines and wines with mercaptan, butyric acid, or oil taste are unusable.
The most well-known brandies made from wines are of French origin. The applelations "Cognac" or "Armagnac" are used exclusively for the products stemming from the wines of the particular growing areas. Moreover there are regulations regarding the distillation process and storage in oak barrels. The designation "Wine brandy (i.e. brandy)" indicates a distillate from wine.

Yeast Sediment Products

Lees and yeast sediment products can be used for distillates. It is recommended for them to be collected in barrels, to fill the barrels to the neck, and to distill those raw materials as soon as possible. Prolonged waiting periods should be avoided at all costs in order to avoid the formation of yeast decay products.

Starch based materials

Grains (corn, barley, wheat, rye) and potatoes are widely used for the production of vodkas and whiskeys. Because all of these materials contain high concentrations of starch, there is never a problem relative to the amount of sugar available for fermentation. Rather, the problem is actually the opposite as compared to fruit fermentations. Yeast can only perform up to concentrations of alcohol of around 15% because of the toxicity of alcohol on yeast; therefore, if the sugar source is too high, the sugar will be wasted because the yeast will not ferment it. This feature allows the separate optimization of the amount of grain or potatoes in a given process.

As mentioned previously, starch is a polymer of repeating glucose units; therefore, it is necessary to break down the starch into it component glucose units prior to fermentation. This pretreatment will be discussed further in the following chapter.

MASHING AND FERMENTATION

Mash and Fermentation Containers

Mash and Fermentation Container Materials of Construction

The traditional oak barrel used as a mash and fermentation container is no longer used for distillate production even though it retains its role for the preparation of wines and for the storage of certain distillates. Wooden barrels are very labor intensive with respect to starting operations, cleaning and maintenance; also their storage in empty conditions poses problems which include the establishment of undesired micro-organisms and undesired influences on the taste.

A several materials are available as alternatives for the wooden barrel, including metal and plastic containers, concrete and stone materials, and glass. In comparison to the wooden barrel these materials possess advantages with respect to cleaning, maintenance, and sealing. It should be noted, though, that not all materials are suitable for the direct contact with mashes and in such cases it is necessary to apply an interior lining of the container walls. Mashing and fermentation containers made of high-grade stainless steel (high-chrome steel) are recommended without restrictions, but lower grades of stainless steel may lead to problems if using gaseous SO_2. Different restrictions apply for mild steel and aluminum. Since these materials are corroded by fruit acids, an interior lining, made of plastic or glass enamel is required.

Fiber-reinforced polyester resins and low-pressure polyethylene tanks are widely used due to their low weight and high corrosion resistance. Plastic containers can also be installed outdoors; however, ultraviolet light from the sun can cause significant degradation leaving to brittleness and cracking. Models suitable for stacking are also available. No interior lining is necessary for the fermentation and storage of fruit mashes in plastic containers because such tanks are usually neutral with respect to taste of the products. If in doubt this assertion should be checked. In general, plastic tanks can be purchased with prior approval for food use by the FDA in the US and the supplier should be consulted.

Glass and concrete also have importance as fermentation vessels. The direct contact of concrete by the mash should be avoided because fruit acids spall or corrode concrete. In such cases epoxy-resins can be used as linings for concrete containers.

Cleaning and Maintenance

Barrels and vats made of wood have to be sealed against leakage. Sealing is achieved by thorough soaking with water to sweel the wood and this is particularly necessary if they have been empty for some time. The water should be renewed every 1-2 days. However, it is not possible to achieve airtight wooden barrels and loss of alcohol has to be taken into account when wood is used.

The interior should be cleaned immediately after emptying to avoid the formation of dried mash crust. The barrel should be flushed thoroughly with cold water and then brushed with a hot cleaning agent (e.g. 2% sodium solution). Afterwards the barrel needs to be flushed again with cold water until it drains clear and without any foreign taste. Care needs to be taken also of the exterior cleanliness. In particular, the formation of mold can be avoided through a periodical treatment of the exterior wall with an impregnating salt or oil, but chlorine should be avoided.

The barrels need to be dried after cleaning and empty containers should never be closed. If they are not used for some time, a barrel conservation is required to protect against undesired microorganisms. A proven classical method is the burning of a non-dripping sulfur bar according to the size of the barrel or the filling with water containing sulfuric acid (500 ml 5% SO_2/hl water). A 1-2 % solution of formalin serves the same purpose. The effect of the sulfuric acid decreases with time such that the procedure has to be renewed every 1-2 months. Before reuse the wooden barrels should be carefully examined for their condition.

The cleaning of containers not made of wood does not pose any difficulties. The sequence: cold water - cleaning agent - cold water also applies. In this case alkaline, acidic or chlorine-containing agents can be used and it is recommended to make sure the reagents are food grade. It is not recommended to use these cleaning techniques for mild steel or aluminum without great care. In any case a thorough flushing with water has to follow. The use of soft brushes is recommended for plastic material and high-grade steel in order to maintain a smooth surface.

Sealing of the Fermentation Containers

Lids for containers of any size should prevent inflow of air because external air (containing oxygen) contact with the mash promotes the formation of undesired microorganisms, e.g. film-forming or acetic bacteria, while the yeast used for the fermentation of the sugar does not require any oxygen. A fermentation in an open container will inevitably result in an infection of the mash as well as alcohol losses. As it can be seen from the governing equation for the fermentation (in a following section) the most important side product of alcohol fermentation is gaseous carbon dioxide (CO_2) which is produced in large quantities and

has to be released from the fermentation container*. This venting of carbon dioxide is achieved through the use of an air lock as shown in Fig. 1. The air lock is constructed in such a way that the barrier liquid (usually water) does not allow air inflow whereas the escape of the carbon dioxide is possible because of the slight elevated pressure present inside the vessel. The observance of gas bubbles moving through the air lock can be used to follow the course of the fermentation. While pure water is often used, a 1:1 solution of water and glycerin or, after completed fermentation, a 2% sulfuric acid can be used as barrier liquids if evaporation is a problem.

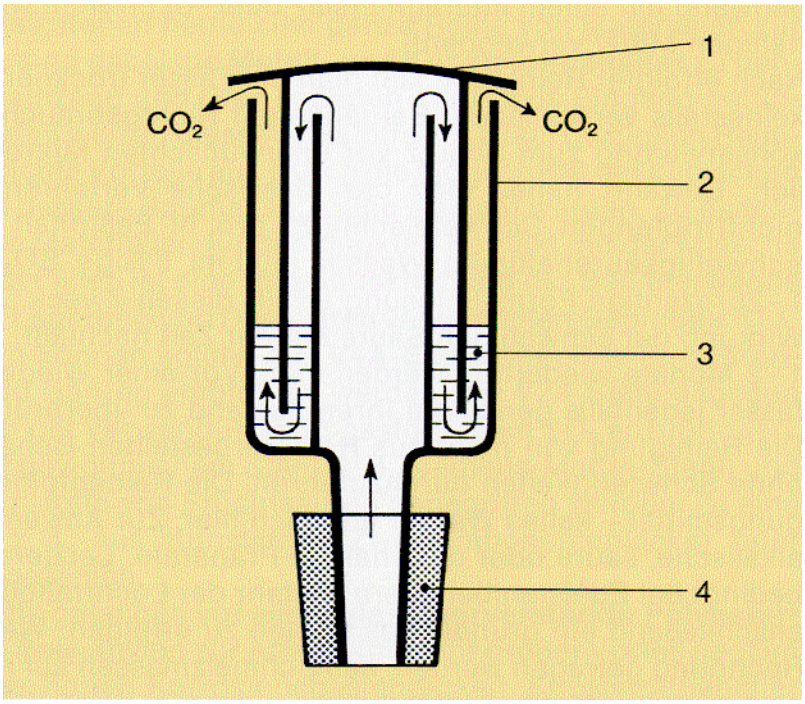


Figure 1: Air lock

Designation
1 Bell
2 Bottom Part
3 Barrier Liquid
4 Rubber Plug
(from *Tanner and Brunner*)

MASHING AND MASH TREATMENT

Mashing and Mash Treatment of Fruits

The individual steps at the beginning of the fermentation process play as an important role as the requirements regarding the raw materials which should be met to obtain flawless distillates. They all serve the purpose to provide optimal conditions for the yeast to proceed with the fermentation process. The steps include: washing and crushing of the fruit and the addition of acids, pectin-reducing enzymes and fermentation aides (fermentation salts, combined nutrient preparations for yeast). Of course, not all those measures have the same importance regarding the different kinds of fruit or grain. It is not possible to specify a general "correct" procedure for the mashing because too many factors like the

* Example: A fermentation of 300 kg fruit mash (must weight of 60°) yields 8000-9000 liter, i.e. 8-9 m^3 carbon dioxide. Care should to be taken for appropriate ventilation in the fermentation room (danger of suffocation).

condition of the raw material and the expected storage time of the fermented mash.

Cleaning and Crushing of the Raw Materials

If possible, the raw material should be washed. Fruit picked up from the ground contains leaves, soil, stones, grass and micro-organisms which can largely be removed through washing if the fruit is undamaged. Through injuries of the skin- either through mechanical contacts or through decay- large amounts of bacteria might end up in the mash, i.e. the juice, despite washing. In such cases, e.g. with very soft or slightly rotten fruit, the advantage of washing is not realized and acids are added to the mash to avoid faulty fermentations. Rotten fruit should not be used. In small enterprises which do not have special washing equipment, the fruit is introduced into water-filled containers into which fresh water is injected at the bottom. The heavy stones collect at the bottom and the dirty water overflows at the top. Stone and berry fruit can also be flushed with water in sieves or baskets.

A general principle is that the fermentation proceeds better and is more complete depending on the maceration of the raw material, i.e. the higher the degree of crushing of the fruit. An additional advantage is that through the crushing the mash becomes less viscous and can be more easily pumped. Also the through mixing of additives like pure yeast, yeast nutrient salts and acids is more easily accomplished Fast liquefaction can be achieved through the use of pectinase enzymes.

The mechanical crushing of the raw material can be done through squeezing, grinding or mixing. There are several kinds of commercially available motor-driven or hand mills. Two important basic types are:

- **Rolling mills** are used primarily to crush stone and berry fruit. They can be used for seed fruit with additional cutting tools. They consist of parallel, counterrotating rollers made of stone, metal or hard rubber. The distance between the rollers can be adjusted according to the fruit to be processed (see Fig. 2a).

- **Rätz mills** serve the crushing of seed fruit. The fruit are being pressed against a grinding casing by means of a rotor with several blades. This casing has milling blades and slits at the bottom which are arranged axially. The crushed fruit is pressed through the slits to the outside (see Fig. 2b).

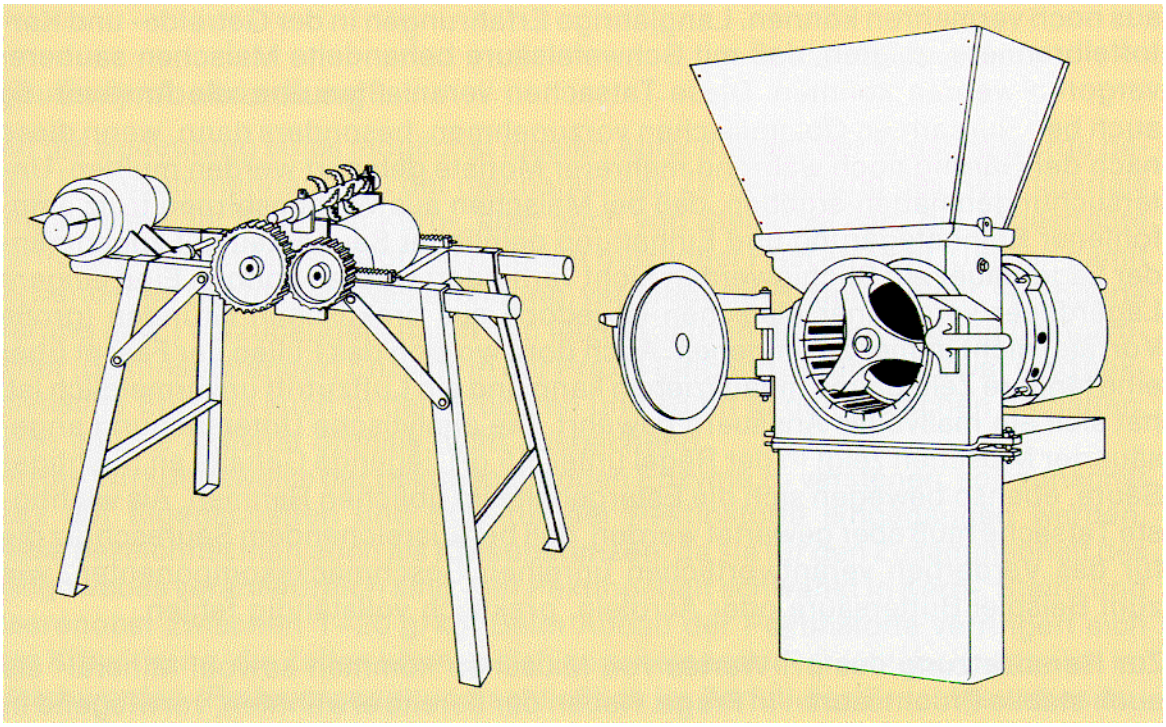


Figure 2: Rolling Mill (Funnel removed), 2a to the left and Rätz Mill, 2b to the right. (Adapted from *Tanner and Brunner*)

Acidification

With their combined sugar content, amino acids, and mineral agents, fruit juices and mashes provide the ideal nourishing ground for many microorganisms. In addition, an average pH-value of 3-4 does not inhibit most bacteria. Undesired microorganisms like *acetobacter*, *lactobacilli*, and butyric acid bacteria are not very viable at pH-values below 3, whereas yeasts can still reproduce at pH-values around 2.8-3. Long-standing experience in distilling cereals and potatoes has shown that mashes which have been sulfonated (pH reduction) can be fermented better. These observations have led to the acidification of fruit mashes low in acid especially if they had to be stored for several months after fermentation. Investigations revealed that with increasing storage time mashes from Bartlett pears were degraded even though only purest yeasts were used and extreme cleanliness prevailed. For practical reason it is, however, not always avoidable to store fermented mashes for longer periods of time (large stocks). In cases when the filling of barrels takes a longer time such that air contact affects the mash a reasonable acidification has proven to be helpful. The analysis of acidified mashes generally shows volatile acid contents under 1.5 g/l, the contents of esters is also in normal ranges. The most important fact is that with a sufficient acid protection the impure flavor components like butyric acid or acrolein which are responsible for the decay are at very low concentrations.

The reduction of the pH-value of mashes is usually achieved through mineral and stable fruit acids. Besides the already mentioned sulfuric acid which is mostly used in Germany acid combinations such as phosphoric acid/butyric acid or malic acid/lactic acid have proven valuable. An additional advantage of the phosphoric acid/butyric acid mixture commonly used in Switzerland is the fact that phosphoric acid also provides a nourishing ground for yeasts and thus promotes a speedy fermentation. The acid combinations mentioned above are less problematic to use than concentrated sulfuric acid which is extremely corrosive and poses some hazard in its use.

The required dosage for acidification depends on the type and condition of the raw material as well as the expected storage period of the fermented mash. The range for sulfuric acid (96%) lies around 100-200 g (55-110ml) per 100 kg mash. The concentrated acid has to be carefully diluted with a 10-20 fold amount of water (add acid to water and use protective glasses!) and added in portions to the mash after cooling; the addition can be done during the mashing. Good mixing is essential to obtain almost uniform pH-conditions within the mash.

The phosphoric acid/butyric acid mixture is mostly used in a dosage of 100-250 g phosphoric acid/butyric acid per 100 kg mash. The amount required for 100 kg is diluted with 2 l of water. The dilution and addition to the mash is done in the same way as for the sulfuric acid.

Enzyme Treatment

It was already mentioned in combination with the mechanical crushing of the raw material that a good maceration of the fruit mash is very important. The desired liquefaction of mashes from seed fruit and stone fruit is often not achieved within a desired period of time. To counteract these disadvantages (reduced ability for pumping, delayed fermentation etc.) the use of pectolytic (i.e. decomposing pectin) enzymes has been introduced, primarily in Europe. Such pectolytic enzymes are also contained in fruit and thus in the mashes but their activity is often insufficient.

In order to understand the function of pectolytic enzymes the properties and structure of pectin materials is explained. These materials are structural agents because they are responsible for the cohesion of cell material. The content of pectin fluctuates in seed, stone and berry fruit between 1 and 20 g/kg. During the decomposition of the pectin their cohesive effect is reduced, the cells can move relative to each other which leads to the maceration (ripening) and eventually to the decay of the fruit

flesh. The designation pectins is used for a variety of agents. According to *Gierschner* it is used for the following classification:

Pectin acid is a polygalacturonic acid consisting of galacturonic acid molecules (see Fig. 3a).
Pectates are salts (mostly salts of calcium) of the galacturonic acid.

Pectins are partially or full methylated (esterified with methanol) polygalacturonic acids. A highly esterified pectin is esterified to above 50%, a low esterified to below 50% with methanol.

Protopectin is an insoluble higher-molecular pectin. Besides the partial methylation the polygalacturonic acid chain shows side chains whose exact structure is to a great extent still unknown.

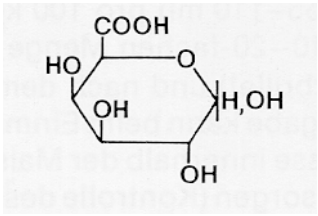


Figure 3a: Galacturonic Acid (Simplified Formula)

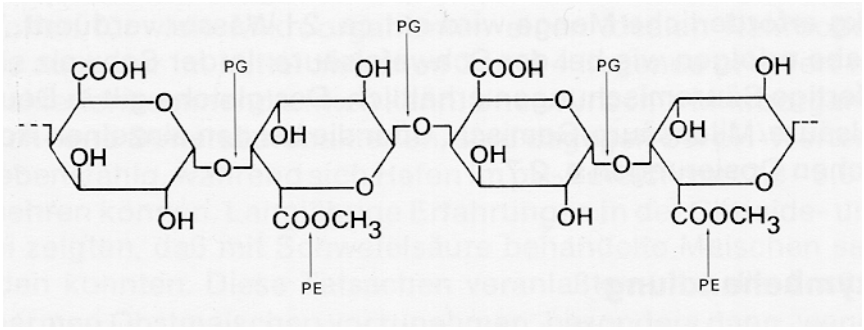


Figure 3b: Pectin (Simplified Formula). The points where the enzymes pectinmethylesterase (PE) and poly galacturonase attack are indicated by the arrows.

In simplified terms there are two types of pectolytic enzymes:
- Poly galacturonase splits the connections between the elements of the galacturonic acid of the pectins: out of large molecules smaller ones are created (in case of complete decomposition even galacturonic acid, see Fig. 3b). This leads to the reduction of the cohesive effects already mentioned.
- The pectinmethylesterase splits off methanol (methyl alcohol) from the methylated poly galacturonic acids. Methanol is toxic and also ends up in the distillate during distilling.

What happens then with the pectin in the course of the fermentation?

1. With increased alcohol content pectin agents are precipitated. The large molecules (protopectin) are hardly soluble in water as such and precipitate after some time.
2. Pectin is de-esterified by pectin methylesterase which is contained in the fruit (the formation of methanol is a natural process!). This phenomenon is demonstrated in Fig. 4 where the production of methanol during cherry mash fermentation is shown.

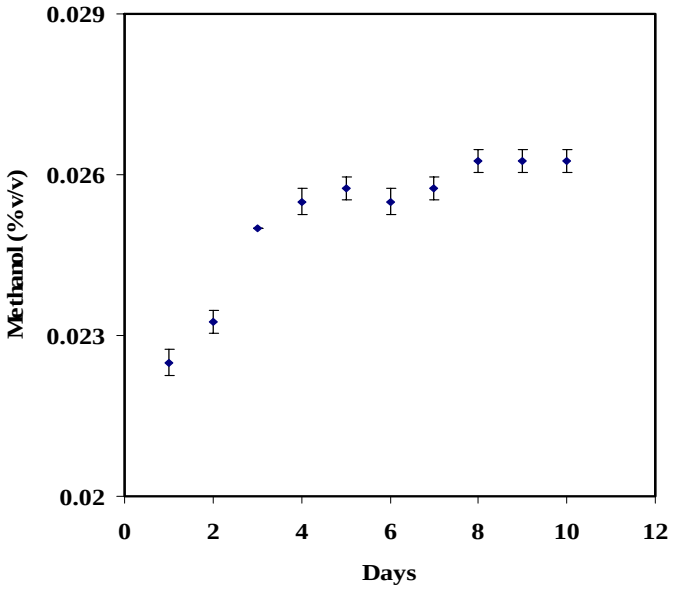


Figure 4. Methanol generation during cherry mash fermentation (A. Maghasi, M. S. Thesis, Michigan State University, 2001.)

Because the precipitation and decomposition of the pectin proceeds very slowly initially, the fruit mashes remain unchanged in their consistency during the starting period of the fermentation; they are very viscous and impede the rapid course of the fermentation. These drawbacks can be counteracted through the use of commercially available pectolytic enzymes which are obtained from molds or from bacteria. Whereas the use of enzymes has become indispensable for the fruit and vegetable technology and nowadays also for the production of wines, it is not quite as clear how they are suitable for the treatment of mashes in distilleries.

The ease of pumping mashes in the first fermentation phase is improved because the insoluble pectin is decomposed. Investigations by *Kolb* regarding the flow properties of apple and pear mashes revealed that the best flow behavior after the addition of enzymes is achieved after two days for the pear mash and after five days for the apple mash compared with five and ten days without the use of pectolytic enzymes, respectively.

The advantages of a fast liquefaction of the mash are apparent; the formation of covering turbid layers consisting of larger fruit parts is

reduced, viscous mashes - as a consequence of high pectin contents, the use of unripe or partially dried fruit - are macerated in a short period of time and can be pumped. The introduction of further additives for the mash is facilitated, the process speed of the fermentation is higher, the formation of nests is reduced and stones are easily removed from the flesh.

The methanol concentration of mashes treated with enzymes is increased as compared to the ones which are not treated because the formation of methanol takes place through pectinmethylesterase which is already contained in the fruit. In this sense the use of commercial enzymes 'free of methylesterase' does not have any meaning. A set of experimental studies demonstrating the formation of methanol by commercially available enzymes is shown in Tables 3 and 4. In this study significant increases in methanol were obtained by the use of liquefaction enzymes. A partial inactivation of the pectinmethylesterase through heating of the mash offers itself as a solution.

Investigations have shown that the use of pectolytic enzymes yields at most a minimal increase in alcohol content in terms of tenths of a percent. Similar results were obtained by *Kolb* who achieved an increased alcohol content by 0.5 % by volume through a Pectinex-treatment of plums. Moreover, the amount of sugar remaining is hardly influenced by enzymes. Differences are only noted in the apparent degree of fermentation. This degree is slightly higher for mashes treated with enzymes because the galacturonic acid produced through the decomposition of the pectin increases the TDS content. No disadvantages were noted regarding the sensory properties through the use of enzymes.

The practical use of enzymes does not pose any particular problems. It is advantageous to prepare a 2-10% solution of the amount of enzymes as recommended by the manufacturer in tap water or juice. This is added to the mash in small portion, for example during the beginning of the mashing. The durability of enzymes is limited; therefore it should only be prepared when used. Commercially available products are also subject to activity loss in the course of time; enzymes in powder form, esp. vacuum-packed, are more durable than liquid ones. The specifications of the manufacturer regarding storage and durability should be noted.

Table 2 A series of liquefaction enzymes studied by J. Andraous, M. S. Thesis, Michigan State Univeristy, 2002.

Liquefation Enzymes Utilized					
Name	Identification	State	Source	Activity (with respect to Spirizm FM)	pH Limit
Spirizm FM	(FM)	Liquid	Concntrated pectolytic enzyme.	N/A	N/A
VP 0956/2	0956/2	Liquid	Polygalacturonase from *Aspergillus niger*.	3 time higher	up to pH 5
VP 0996/2	0996/2	Liquid	Polygalacturonase from *Aspergillus niger*.	2 times higher	up to pH 6
VP 0996/9	0996/9	Powder	Polygalacturonase from *Rhizopus oryzae.*	8 times higher	up to pH 5.5
Available from Erbsloh Geisenheim. Getranke-Technologie Gmbh & Co. KG					

Table 3. Methanol concentrations is final fruit distillates for mashes treated by liquefaction enzymes (J. Andraous, M. S. Thesis, Michigan State University, 2002)

Fruit Used		Ethanol Volume		Methanol Concentration	
		ml of 40% EtOH	Std. Dev.	mg/100 ml of 40% EtOH	Std. Dev.
Gala Apples	Control	68.8	1.2	87.5	8.9
	FM	75.1	1.0	530.6	5.3
	0956/2	69.2	1.1	525.2	4.8
	0996/2	86.6	0.2	508.7	3.3
	0996/9	79.2	0.9	423.7	2.5
Red Delicious Apples	Control	46.3	1.1	91.0	0.7
	FM	78.9	3.2	417.9	1.2
	0956/2	56.0	1.6	424.0	3.9
	0996/2	41.5	1.8	460.1	0.3
	0996/9	56.8	1.7	320.4	1.6
Granny Smith Apples	Control	73.4	1.3	136.5	7.8
	FM	89.2	4.3	519.0	12.7
	0956/2	63.9	0.9	634.5	41.7
	0996/2	92.7	5.2	506.0	16.4
	0996/9	86.4	2.2	464.5	31.8
Bartlett Pears	Control	58.9	2.2	452.1	0.4
	FM	67.0	2.3	607.4	17.1
	0956/2	70.6	1.7	615.3	2.4
	0996/2	60.5	0.9	656.4	4.5
	0996/9	N/A		N/A	
Note: Legal U.S. methanol limit is 280 mg/100 ml of 40% ethanol					

The dosage of enzymes depends on various factors:

- **Consistency** of the raw material: hard fruit with a large content of protopectin naturally require a higher dosage;
- **Temperature**: the optimal effect of pectolytic enzymes is around 45-50°C. Above 55°C they could be inactivated, whereas at temperatures below 10°C the decomposition of pectin is very slow or does not take place at all;

- **pH-value:** besides other factors such as increased SO_2- and tanning agent content extreme pH-values impede enzymes. The optimal effect of Ultrazym 100 is, for example, at a pH of 4.5-5. Below a pH of 3 or above a pH of 6 its activity is reduced significantly.

These influences can be compensated through the adjustment of the enzyme dosage according to the respective conditions while the relevant product information of the manufacturers should be considered. It is also important to know the activity of individual products, see for example Table 3.

Acidification and the use of enzymes provide the distiller with two powerful procedures to treat the mashes about whose capabilities and limits he should though be well aware. It can be stated that the use of enzymes with regard to the liquefaction of the mash, its motion and transport as well as the development of the fermentation is advantageous. A protection of fermented mashes against acetobacters, esp. at outdoor temperatures which are too high and at extended storage periods, can only be achieved through acidification; the use of enzymes does not provide a stabilizing effect. Because the acidification slows down the effect of enzymes as the result of a decreased pH-value an addition of acid after completed enzyme-supported fermentation would be ideal. Unfortunately, the later addition of substances is accompanied with difficulties, especially with the use of large fermentation containers. For this reason a combined enzyme and acid treatment is recommended while attention should be paid that the enzyme solution is added after acids have been introduced and well mixed. The pH-value of the mash should not be below 3.

Fermentation Aides

A prerequisite for an optimal fermentation process is a sufficient nutrient supply for the yeast for their reproduction and fermentation. . The key nutrients include nitrogen-containing compounds such as amino acids, phosphorus compounds, and vitamins. Sufficient concentrations are not present in all raw materials such that the nutrients must be supplemented through the addition of fermentation salts in order to prevent fermentation hold-ups and delays (esp. using pomaceous fruit and berry fruit). In practice ammonium salts like ammonium sulfate or diammonium hydrogen phosphate are emplyed where the latter not only provides nitrogen but also phosphorus. A dosage of 20 g per hl mash is usually sufficient. The fermentation salt dissolved in a small quantity of water or juice can be added during the beginning of the mashing while care should be taken for a good mixing.

Additional Mash Additives

Besides the acidification with concentrated mineral acids and fruit acids they are - even though not widespread in practice - additional possibilities at hand to reduce the pH-value and to increase the durability of the mashes.

Sulfuration as commonly used during the production of wines (addition of sulfur dioxide or sulfuric acid[*]) has lost its early importance for distillation probably because the acidification provides a less problematic method. Sulfuration is still widespread for the production of distillates from pomace fruit. Disadvantageous is the danger of a too high sulfuration; SO_2 content which are too high can lead to fermentation hold-ups and faulty distillates. Moreover, the protective effect of the sulfuric acid is gradually reduced due to oxidation and reaction with the constituents of the mash, thus limiting the storage capability. A combination of acidification and sulfuration is not recommended. Due to the limiting capability for exact dosage the oldest form of sulfuration, the burning of bars of sulfur, is nowadays used at most for the conservation of barrels. There is also the problem of formation of sulfur containing compounds during distillation. Humans have the ability to sense very low concentrations of sulfur containing compounds as aromas so the use of sulfur in mashes should be carefully considered.

The entry of air after completion of the fermentation can not be entirely avoided if wooden barrels are used. To limit the contact with oxygen and thus the formation of acetobacter in case of long storage periods *Bruchmann* and *Kolb* showed that the addition of glucose-oxidase is suitable. This enzyme which is added to the mash after the main fermentation in a dosage of 2 g/hl promotes the oxygen-consuming oxidation of glucose which is accompanied by an additional protection achieved through the produced hydrogen peroxide which possesses disinfecting properties. Mashes treated in this way did not show any increased levels of volatile acids after 6 months of storage; the alcohol yields were about 1-1.5 % higher than those of untreated mashes with the same storage period. As an alternative to the already mentioned malic acid/lactic acid-mixture the addition of 150 g fumaric acid/lactic acid per hl, respectively, is possible. However, the prompt distillation of the mash is always the preferred approach.

Mash Heating for the Production of Low-Methanol Brandies

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[*] Trading forms of sulfur dioxide (SO_2) are a) **potassium disulfide** ($K_2S_2O_5$) in powder form (10 g are equivalent to 5 g SO_2), to store dry and air tight; b) **sulfuric acid** (5-6 percent watery SO_2-solution), full barrels should be well closed and protected against sun light; c) **pure sulfur dioxide** liquefied under pressure (in pressure containers with dosage adjustment).

The formation of methanol from pectin through pectinmethylesterase contained in the fruit is a natural, but undesired process. This is the reason why in some countries restrictions exist regarding the maximal permissible methanol content in spirits. The problem of producing brandies low in methanol can not be solved through simple distillation- even though it has a lower boiling point compared to ethanol (64.7 °C and 78.3 °C) methanol appears in the forerun (heads) as well as the middle (hearts) and afterrun (tails)(tails). A separation is possible through the use of special distillation columns with a large number of trays, the result is a brandy that approaches a neutral spirit and is low in aroma.

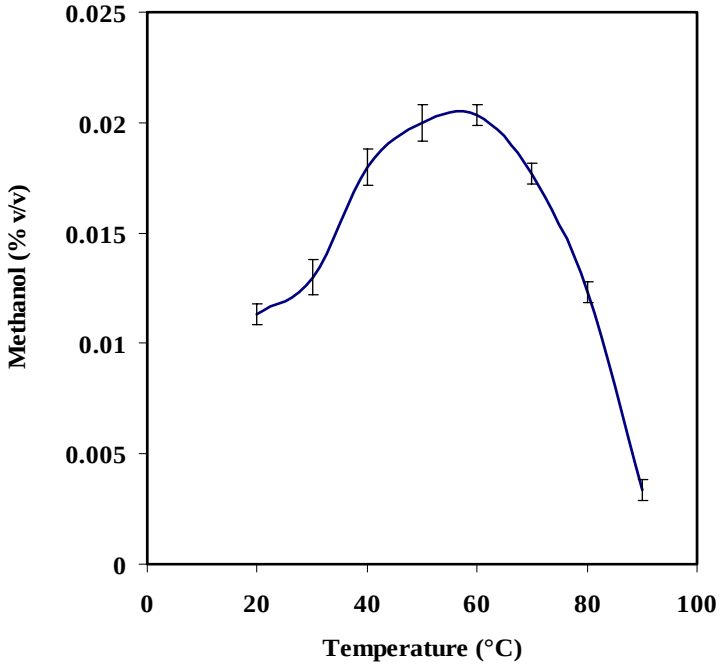


Figure 5. Reduction of methanol production during cherry mash fermentation by thermal deactivation of enzymes (A. Magahsi, M. S., Michigan State University, 2001.)

The more obvious way is to prevent the formation of methanol or to limit it significantly by heating of the mash (inactivation of pectin methylesterase) to a temperature of 80-85 °C for about 30 minutes. Figure 5 shows the effect of temperature on the deactivation of the pectin methylesterase in cherry mashes. Because the main part of the methanol is formed within less than 1 hour after the initial mashing the heating has to proceed very rapidly. The difference regarding the taste of distillates obtained from heated mashes and those produced in a normal way is insignificant. The need for such a procedure is left to the distiller's judgement.

Special Processing Information

Seed Fruit

Seed fruit has to be washed before processing and crushed. The crushing can be omitted only for very soft fruit such as aged, doughy Bartlett pears because the fruit is squashed after the breaking through their own weight. An acidification of the mash is recommended for table fruit and problematic raw material (approx. 50 g sulfuric acid or 100 g phosphorus acid/lactic acid/hl, respectively). According to the condition of the raw material and the expected storage period of the fermented mash the acid content has to be increased (e.g. doubled). Bartlett pears which are low in acid require double or triple the recommended amount in order to obtain a sufficient protection against infection. A combined acid/enzyme treatment is possible, for example with 15-25 g Pectinex forte and 200 g phosphorus acid and lactic acid per hl, respectively (Attention: Addition of enzyme solution only after a thorough mixing of mash and acid!). The use of nutrient salts for yeasts, e.g. 10-30 g ammonium sulfate or ammonium phosphate has will aid in the progress of the fermentation. Sulfuric acids should not be used to treat the mash for reasons outlined earlier.

An alternative processing method is the production of juices from seed fruit with subsequent fermentation. This procedure should be used if the fruit is subject to an increased danger for infection, as with unripe, slightly rotten or hail-damaged fruit. The disadvantage compared with mash fermentation is a loss in bouquet which is balanced against the reduced infection danger. The washed and crushed raw material is pressed and the juice obtained is immediately distilled with 100 ml 5% sulfuric acid or 10 g potassium disulfide (equivalent to 50 mg SO_2/l) per hl juice. The fermentation can be initiated 8 to 12 hours later after addition of 20 g ammonium sulfate or ammonium phosphate per hl using pure yeast.

Rapid fermentations with fresh compressed yeast is only recommended if the juice to be fermented has a temperature of 20 °C and can be distilled directly after the fermentation in highly-effective column distilleries. In order to prevent the formation of acrolein the acidification of the juice with equivalent 50 mg SO_2/hl should be done.

Stone Fruit

Stone fruit should be processed without stems and leaves to prevent faulty distillates. Very soft and fully ripened fruit crush themselves through their weight and therefore do not require additional crushing;

compact fruit flesh can in the easiest cases be crushed using a wooden pestle. Mixers and roll crushing mills are mostly used in commercial enterprises where a too large amount of crushed stones can be avoided by adjusting the distance between the rolls. In principle not more than 5% of all stones should be crushed because they contain amygdalin which can be decomposed through enzymes in the stone to glucose, benzaldehyde and the toxic hydrogen cyanide. Therefore, benzaldehyde and hydrogen cyanide are present in distillates from stone fruit as volatile substances where an excess of benzaldehyde - also designated as bitter almond oil - causes a flavor ('stone flavor') overpowering the fruit aroma. There is no need to mention that content of hydrogen cyanide in brandies which are too high are undesired.

When using cherries the fermentation should in general be done under acid protection, especially if the filling of the barrels extends over a longer period of time or if the raw material shows different quality. Moreover the distillation of acid-treated mashes can be postponed. In these cases an acidification with 200 g sulfuric acid or 150 g phosphorus acid and lactic acid per hl, respectively, has proven to be advantageous. A combined treatment with 10 g Pectinex forte and 100 g phosphorus acid and lactic acid per hl, respectively, has likewise proven advantageous. It should be mentioned that an acid treatment is not necessarily required if the cherries are healthy, fermented with fermentation salts and pure yeast and distilled within 3-4 weeks.

In warm years and in times of large harvests cherry brandies with higher contents in esters (higher fermentation temperature, storage of mashes outdoors etc.) are produced. Too high an ester content causes a penetrant touch to the distillates: a certain ester content is, however, typical and even desired for cherry and other stone fruit brandies. From these considerations it is recommended that a portion of the cherry crop is also acidified in companies which normally do not produce extremely unharmonic distillates. Blends of distillates rich in esters or volatile acids with less aggressive ones should be considered in order to obtain a better quality and to adjust current flavor trends. Other stone fruit such as ‘Zwetschgen’ (plums), peaches and apricots are mixed preferably with pectolytic enzymes and fermented with pure yeast. Good experience was made with enzyme-treated ‘Zwetschgen’ (plums) (dosage 3 g Ultrazym 100/hl mash).

A fermentation under acid protection is recommended if slightly rotten and/or low-acid fruit are used (plums!). Mashes with an expected storage period of more than 3-4 weeks should be acidified with 150 g lactic acid and phosphorus acid/hl, respectively, after completed fermentation. If

the mash has been treated with enzymes a later mixing does not pose any problems.

Berry Fruit

The production of brandies made from berry fruit is only occasionally done by mash fermentation, for once because the effort is not profitable due to low sugar contents and on the other hand because the fermentation is complicated by various factors (fermentation-impeding substances, unfavorable nutrition conditions, dry state). In order to ferment a berry mash within a useful time period increased levels of nutritive salts for the yeast (e.g. 40 g di-ammonium phosphate/hl) and pure yeast as well as elevated fermentation temperatures (20-25 °C) are required. Besides this dry sorts of berries have to be ground and mixed with water (juniper berries, for example, with 200-250 l water per 100 kg according to *Pieper*) for a sufficient mash liquefaction. To prevent influences on the aroma the berries should be processed without stems and stalks.

For some berry types a far more common way is the production to spirits. These designate brandies which are obtained from fresh or frozen fruit by coating with alcohol with subsequent distillation. Best known are raspberry spirits which belong to the aroma richest fruit brandies in general. Forest raspberries which are mixed immediately after crushing with 0.5 l of fine spirit per kg fruit are used in the first place. This preparation should be done in fully filled glass or high-grade steel container which can be tightly closed and the time period for TDSion should not exceed 2 days.

Pulp

Fruit and berry pulp ought to be immediately spread by rubbing after pressing and mixed with approx. 20% water. Contact with air should be avoided because pulp is generally susceptible to contamination and oxidations. For this reason the fermentation should be done in closed containers (put on a fermentation top!). It is recommended to initiate the fermentation with pure yeast, for pomaceous pulp also with 20-40 g ammonium sulfate/100 kg. Red wine pulp made from mash-fermented grapes can be stored in open casks as long as the filling is done within a useful time and the surface is afterwards covered with a sufficiently thick layer of sand (above plastic foil!). The addition of yeast can be omitted here.

After completed fermentation the distillation should not be postponed for too long. Pulp from strongly rotten raw material is not suited for further processing. It is advised against the often practiced procedure of filling

the pulp into plastic sacks because the resulting distillates show increased levels of aldehydes.

Mashing and Mash Treatment of Grains

The production of distillates from grains or other starch based materials follows similar strategies to use of fruit with the primary difference the conversion of the starch to sugar which can be fermented by the yeast. The following discussion will present some general principles which will be adjusted depending upon whether the goal is the production of neutral spirits for the vodka, gin, etc. or as the initial steps to production of whiskey.

Milling

Grains that can be considered include corn (maize), wheat, barley, and rye. The grain should be passed over a magnet to remove iron and then cleaned to remove dust and foreign material. Various mill types are possible, but a hammermill is common. Corn contains a significant amount of oil in the germ and there my be some interest in using degermed corn, but at the small scale this is less important.

Mashing

The ground grain is then mixed with water and then cooked at temperatures between 100 and 140°C to liquefy the starch and sterilize the mash. It is then cooled to around 60 to 70°C and either malt or enzymes (α– and β-amylases) are added to hydrolyze the starch into glucose. The resulting mash is then ready for yeast addition.

Mashing and Mash Treatment of Molasses

Molasses is received as a liquid so no milling is required as for the solid starting materials. The molasses is generally heated to precipitate calcium salts and to sterilize it prior to use. Since molasses contains so much unfermentable solid materials that can inhibit the yeast, it is usually dilute to around 10-12% sugar. The pH should be checked and adjusted to around 5.5. Molasses is generally deficient in nitrogen so some nitrogen supplementation is generally required to ensure the yeast have sufficient nutrients. Typical nutrients are diammonium hydrogen phosphate or urea and should be added to achieve a level of around 200mg/100ml of nitrogen for a molasses that has been diluted to a sugar concentration of 10-12%.

Fermentation

Yeasts

Without proper conservation mashes and fruit juices will start fermenting sooner or later due to the presence of wild yeasts. Yeasts belong botanically to the class of fungi and are capable of transforming sugars like glucose and fructose into ethyl alcohol and carbon dioxide under the exclusion of oxygen. A variety of more or less desired substances such as glycerin, succinic acid or higher alcohols (fusel oil) are produced as side products. The various types of yeasts are categorized according to their properties like appearance, fermentation capability, kind of reproduction etc. into genus and groups through which the indication is given that not all kinds of yeasts are suited for the fermentation of distillation raw materials. Like other micro organisms also 'wild' yeasts adhere to the raw material. Because they can propagate quickly spontaneous fermentations can result, a fact which is associated with risks for various reasons. This applies for example to the often encountered 'Apiculatus' yeast which can be recognized under the microscope by their typical form (see Fig. 6). Their low alcohol-forming capability is disadvantageous and an increased level of fermentation side products such as acetic acid and fusel oils can be expected. In addition, wild yeasts are not very temperature stable which can lead to fermentation hold-ups at cold weather. It is recommended to initiate the fermentation of mashes using pure bred yeast.

Most kinds of yeasts (Fig. 7) can reproduce in a sexual (generative) as well as non-sexual (vegetative) way. Under the nutrient conditions prevailing in fmashes the reproduction takes place through budding**,** i.e. vegetative. This happens through the formation of a daughter cell at the cell wall. After completed development the daughter cell can

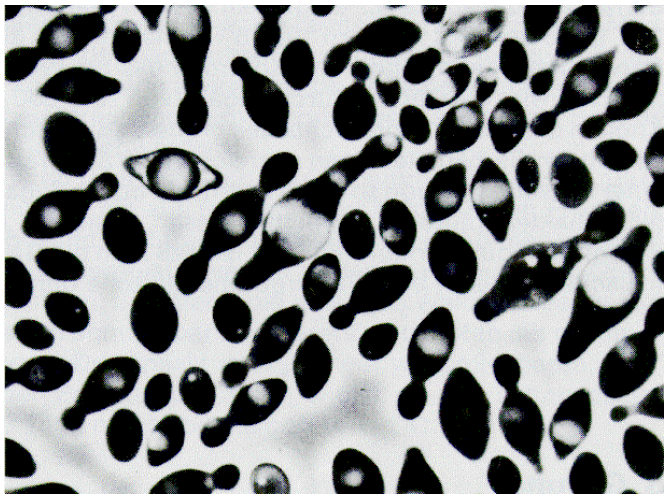


Fig. 6:'Apiculatus'-Yeast (Magnification 1200x)

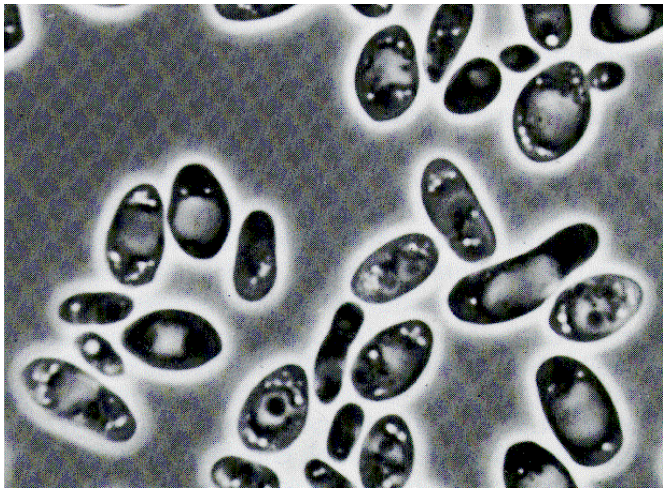


Fig 7 Yeast-Pure Culture (Magnification 1200x)

be separated and is capable to form further daughter cells. The time period for this process extends to 3-6 hours depending on the type of yeast and ambient conditions (temperature, pH-value, supply of minerals etc.), i.e. after this time the amount of yeast cells have doubled. The fermentation process starts when the amount of living yeast cells has increased to 100.000-1.000.000 per cm^3. Regarding the generative reproduction by means of formation of spores, cross-breeding different types of yeast can be cultivated which combine various desired properties such as alcohol, SO_2 and coldness resistance or weak tendency towards foam creation.

The fermentation is an exothermal process, i.e. heat is generated; for this reason increase in mash temperature is to be expected. The optimal fermentation temperature is approx. 18-20 °C, for mashes which are difficult to ferment somewhat higher. In special cases (low mash temperatures, no heating possibility) the use of so-called cold fermentation yeasts is possible which allow a complete fermentation at even 8-10 °C. Higher temperatures generally accelerate the fermentation process, but also favor the growth of undesired micro organisms. With a stormy fermentation there exists moreover the danger of alcohol and aroma loss. Fermentation temperatures above 27 °C should therefore be avoided. Above 43-45 °C yeasts are neither reproductive nor fermentable. The fermentation is impeded by a high SO_2 level (more than 50 mg free SO_2/l).

Fermentation Initiation

After mashing the fermentation should be initiated without delay using pure bred yeast. The addition of yeast can principally be done in

combination with addition of other treatment agents as long as a homogeneous mixing in the mash is guaranteed. Especially during acidification concentrations which are locally too high can lead to low pH-values which are detrimental even for yeasts. Where processing with sulfuric acid is still done the addition of yeast has to take place at the earliest 6-8 hours after the sulfuration. It is crucial to add the yeast before the onset of a spontaneous fermentation; addition of pure yeast during a fermentation which has been initiated by wild yeasts is useless. It would principally be possible to kill wild yeasts and other micro organisms through heating and to carry out the inoculation afterwards. However, because of technical difficulties and the potential for degradation of the aroma this procedure is not commonly used in practice. As a reminder, the first condition for a successful fermentation is still the raw material. A suitable mash treatment can also contribute; however, it is misleading to assume that the addition of pure bred yeast is a general recipe against bad raw material or mistakes during the mashing.

Cultivated yeasts

Cultivated yeasts are commercially available in different forms (liquid, dry). Dry yeasts possess significant advantages regarding technical applications if compared to liquid yeasts. While liquid yeasts have to be increased using a pitching culture before they can be used to ferment large quantities of mashes or juices due to costs, the dry yeasts can be added directly or after a brief soaking. The reproduction under process conditions does - in addition - bear the risk of bringing in undesired micro organisms so that the main advantage of using cultivated yeasts would be void. An additional advantage of the dry yeasts is their better durability during storage.

Dry Yeast

The production of commercially available granulated dry yeasts is done by specialty companies. The cultivated yeast is washed and carefully dried without additives (rest water content is approx. 8%). This process itself causes the granulation. The product is immediately packed under a protective gas, e.g., nitrogen. Fermentation activity (amount of living cells) and microbial purity (absence of foreign organisms) are guaranteed through continuous quality control. The dry yeast does not experience any significant loss of activity for a year in the closed original package stored in a refrigerator. Opened packages should be closed immediately after use; however, their durability is limited. Since several different package sizes are available a longer storage period of opened packages is usually avoidable.

The addition of dry yeast to mashes can be done directly during a thorough pumping. In case of mashes which may not be easily pumped

it is recommended to mix the required amount of yeast slowly with the five- to tenfold amount of water. The water temperature should be approx. 40 °C (to be checked with a thermometer!). After completed swelling (let the preparation sit for 10-15 minutes) the suspension is mixed again and added evenly to the mash. It is important that the fermentation container is filled at most to 9/10 and closed with a fermentation top after addition of the yeast suspension. Dosage of the dry yeast depends on the product (notice the specifications of the manufacturer). As a guideline the following amounts can be taken: with liquids as juices 10 g/hl and with mashes 20 g/hl. Thick mashes or fruit types rich in tanning agent (danger of fermentation hold-ups) require a higher dosage, e.g. 40 g/hl.

Fermentation Course

Before the sugar fermentation can start a certain yeast concentration has to be achieved. The duration of the required reproduction phase depends on a variety of factors, especially on the mash or must temperature as well as on the nutrients condition. If sugar rich raw materials are used a significant temperature increase can be noted. After the main portion of the sugar is fermented the gas production and the temperature gradually decrease; finally the CO_2-production stops entirely. In well fermented mashes normally only 2-3 g sugar/l remain. It is recommended to monitor the fermentation progress by means of a refractometer. For the commonly used pitching temperatures of 15-20 °C - even in the case of easily fermented raw materials - a fermentation period of 10-20 days can be expected. Fruit with a significant content of fermentation-inhibiting agents (e.g. berry types rich in tanning agent) requires significantly longer for the fermentation to complete at the same temperature. It is recommended to increase the pitching temperatures, the amount of yeast and fermentation salt in order to prevent delays in the fermentation or even fermentation hold-ups. The most important causes for fermentation hold-ups are summarized briefly:

- **Temperatures too low**: Heating of the room. Musts can be heated using an immersion heater. Mashes can be heated through careful injection of steam (danger of aroma loss!).

- **Lack of nitrogen substances**: Addition of fermentation salts like ammonium sulfate.

- **Acid contents too high**: can have several causes, e.g. stemming from the raw material (acid rich fruit or formation of volatile acid) or through incorrect procedures (too strong of an acidification or sulfuration). Remedy through partial neutralization with calcium carbonate. Afterwards again addition of pure yeast.

- **Increased content of tanning material**: Yeasts precipitate. Prevention through fining with gelatin (30-50 g/hl) or blending with raw material low in tanning agents.

Increased levels of metals (iron, copper), conservation agents (sorbic acid, benzoic acid) and pesticides are additional causes for fermentation hold-ups. They are, however, less frequently encountered.

Faulty fermentations can occur if undesired yeast and bacteria are present due to mash infections and lack of acid protection. In the widest sense they are all the result of undesired changes in musts and mashes due to micro organisms*. Among those changes can be decompositions of sugars, fruit acids and amino acids as well as fermentation products. Since these processes often progress under CO_2-formation they are often mistaken for alcohol fermentations. Besides acetic acid, products of faulty fermentations can be lactic acid, butyric acid, and acrolein. Besides the fact that faulty fermentations can cause significant yield losses these substances often influence the mashes and the distillates stemming from them in terms of flavors and aromas in a negative way. The recovery of those faulty distillates is not always possible or at least associated with enormous effort. It is far more efficient to prevent faulty distillates caused by micro bacteria, a fact easily achievable through high quality raw material, proper mash treatment, and an appropriate fermentation procedure.

Measures after Completion of the Fermentation

Testing of Fermentation Completeness

After completion of the gas development it is advised to check the completeness of the fermentation. This is best done through an hydrometric determination of the TDS. Because the TDS content is not only influenced by sugar, but also by other unfermentable substances completely fermented juices indicate a certain 'must weight'. In addition the produced alcohol influences the TDS content and thus the indicator of the hydrometer.

In cases of doubt it is recommended to mix the mash filtrate intended for TDS determination with bakery yeast (Dosage: approx. 5 g yeast per 200 ml filtrate; mix yeast without lumps) and leave it at 20-25 °C in a glass flask closed with a fermentation lid. The yeast ought to be whirled up 1-2 times a day through tilting of the flask. After 2-3 days it is filtered again and the TDS determination is repeated. A measured value below

* Fermentation processes in a closer sense designate sugar decompositions which proceed without air (oxygen).

the one before yeast addition indicates that the fermentation is not completed; through adequate measures it can be restarted again.

Storage of Fermented Mashes

Fermented mashes can be stored before distillation for about 3-4 weeks without significant problems. Storage containers should be kept full up to the neck and closed airtight. Juices should be separated from the yeast after fermentation and distilled without delay. A longer delay is often accompanied with a bacterial decomposition of the mash. Thus, an increased formation of propanol (up to 2 g/100 ml a.A.) can be noted; the content in acetic acid increases also significantly. This is at the cost of alcohol. It is therefore recommended to distill the mashes with the highest acetic acid content first. Mashes low in acid most often yield neutral distillates with an ethyl acetate content which is too low. In these cases a somewhat longer storage of the mash (of course under aroma and analytical control) has a positive effect.

If mashes have to be stored for a longer period of time cool places should be chosen and the mashes should be acidified if this has not yet been done before the fermentation. Wooden barrels should be used for longer storage of fermented mashes because of the loss of alcohol.

DISTILLATION

General Remarks

Distillation separates the alcohol and the aroma agents produced in the mash from the remaining components of which water is the predominant compound. Depending on the type of distillation equipment, heating apparatus, and operating procedure of the still a relatively neutral alcohol or a distillate enriched with undesired less volatile components (fusel oil) is obtained. Volatile components like aldehydes, ketones, and esters can be present in the mash in high concentrations. It is left to the skills of the distiller to separate undesired components without loss of aroma. The enrichment of the alcohol is achieved because its boiling point of 78.3 °C is substantially lower than that of water which boils at 100 °C. The heating of the mash therefore causes an enrichment of the more volatile alcohol in the gas phase.

Distillation Apparatus

Although the various distillation devices may appear different the principle construction with still, top, distillate transfer tube (which is referred as a "spirit tube" in the German speaking countries), and condenser are the same. The differences mainly concern the kind of heating of the still and the rectification devices. In the following sections the types of apparatus used for fruit distillation will be introduced.

Simple distillation with direct heating

This classical distillation apparatus integrates the copper still - i.e. the part containing the mash to be distilled - into the device such that it is surrounded directly by the flame or the heating gases (see Fig. 8). This type of direct heated device is often referred as an alambic style still. Variations of such still are used for the production of Cognac and Scotch whiskey. Copper is often used as the material of construction for the still for a number of reasons: first of all copper is a very good heat conductor, secondly this metal shows optimal resistance to acids and thirdly copper affects the quality of distillates positively. It is mainly the last aspect which causes copper to stand out in comparison to other acid resistance materials. One reason for the fact that copper stills produce cleaner and aromatic distillates compared to such made of high-grade steel or glass is that copper forms non-volatile products with volatile sulfur combinations arising during the fermentation which then remain in the slops. A well-known example of such a quality-reducing sulfur combination is hydrogen sulfide.

A disadvantage for distillation equipment with direct heating is that thick (i.e. viscous) mashes tend to burn due to the very high surface temperature. Distillates made from such mashes often have a burnt-bitter taste (Furfural formation) which is hardly removable. Despite this disadvantage this kind of equipment is still in use today probably because of its very good energy usage. Modern distillation devices of this kind are also equipped with a sieve tray, a mixer and a large mash outlet. The direct heating allows a fast control of the distillation process. It is advised to be cautious with older distillation stills because they may burn out (i.e. burn through) such that explosions may happen. Thus, direct heated distillation devices should only be used for distillation conversions of raw distillates (i.e. production of fine distillates).

The more wide use of alambic style stills is in the Cognac and Scotch whiskey industries wherein either wines or beers are distilled avoiding the difficulty of burning of mashes. An additional feature of such stills is that they are essentially reaction distillation devices because the high temperature copper surface actually catalyses a series of chemical reactions that contribute to the flavors and aromas of specific brandies and whiskeys.

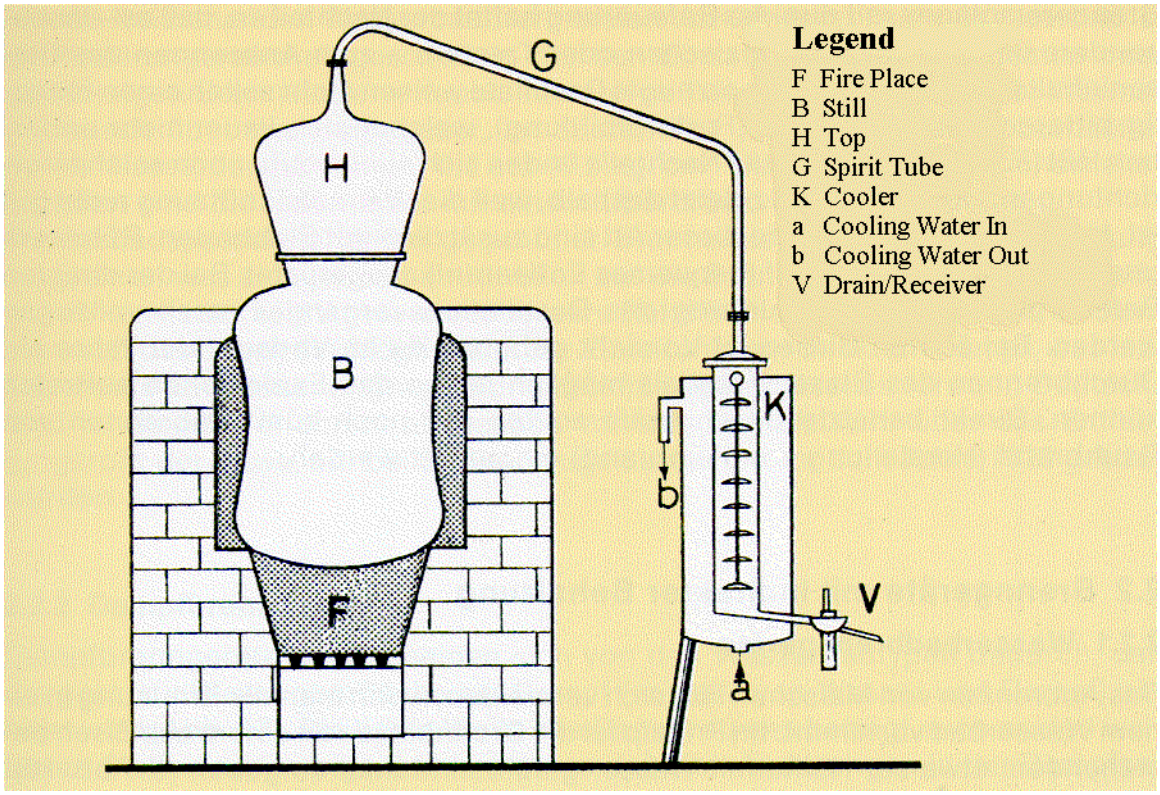


Figure 8: Simple distillation with direct heating (reproduced from *Tanner and Brunner*).

Distillation Devices with indirect Heating

Distillation Devices in a Water Bath

Burning of a mash can be avoided if the heating is done in water baths. In principle the still is surrounded by an iron casing which is filled half-way with water (see Fig. 9). In earlier times those devices were built into brick, nowadays the use of free- standing water bath distillation

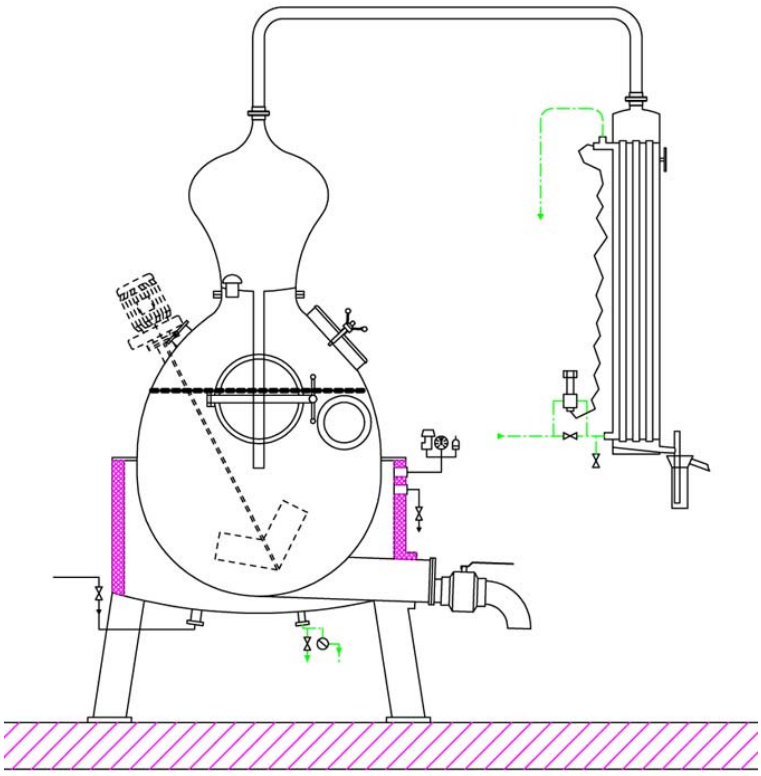


Figure 9: Water bath distillery with alambic style top (figure courtesy of Christian Carl, Ing. GmbH).

devices is widespread. A fireplace is inserted into the water bath allowing the use of liquid, solid or gaseous fuels. The heat transfer through the hot water takes place in the lower part of the still, in the upper part (above the water surface) through steam of about 0.5 atm (0.5 kg/cm^2 pressure above atmosphere). Safety regulations require that the heating apparatus be equipped with safety valves.

Compared with distilleries using direct heating the water bath devices operate slightly slower which, however, is favorable for quality of the brandy (no burning, better rectification).

Steam Distillation Devices

Steam distillation devices are distinguished from the water bath type devices through the fact that the entire surface is heated using steam (instead of water and steam). The nominal width of the space available for steam amounts even at wider locations to only a few centimeters such that changes in the steam supply affect the distillation process fairly fast. Such systems are easily controlled. Sometimes one encounters steam distillation devices with heating coils integrated into the still. Those types, however, involve the danger of burning during distillation of the mash; moreover, they are difficult to clean. However, there are no reservations about their usage for the distillation of fine distillates.

Continuous distillation devices are used in situations wherein much higher volume is desired. Some examples of continuous devices are shown in Figure 11.

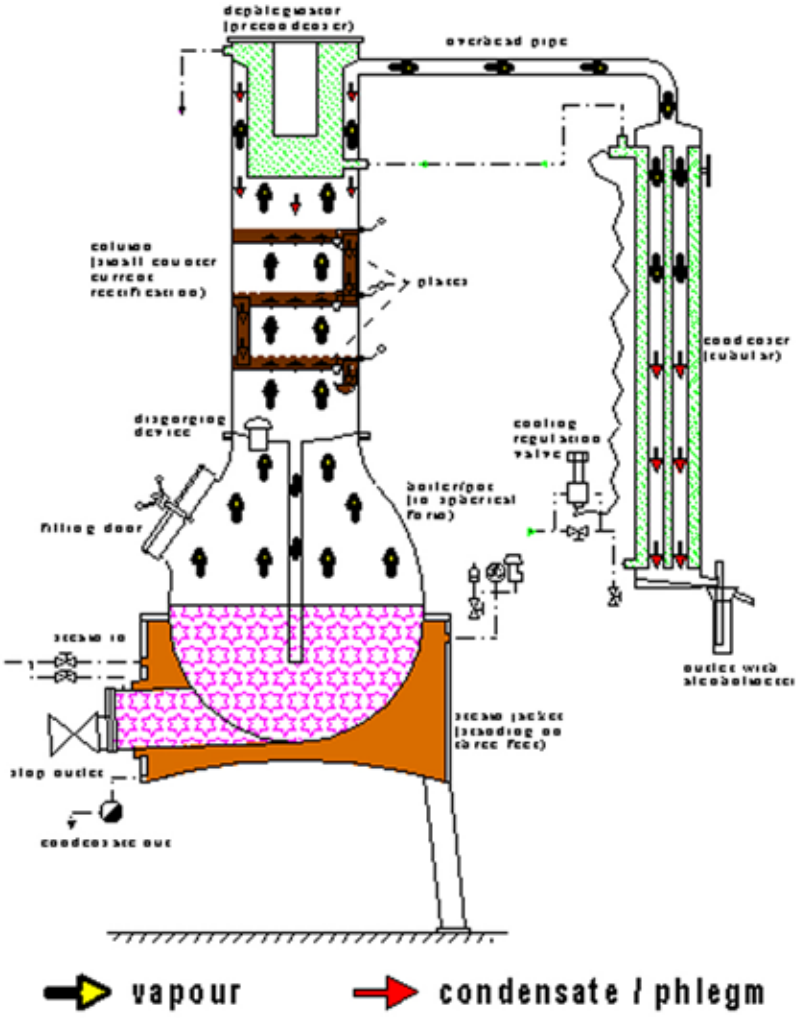


Figure 10: Steam Distillery with Intensification Unit (figure courtesy of Christian Carl, Ing. GmbH).

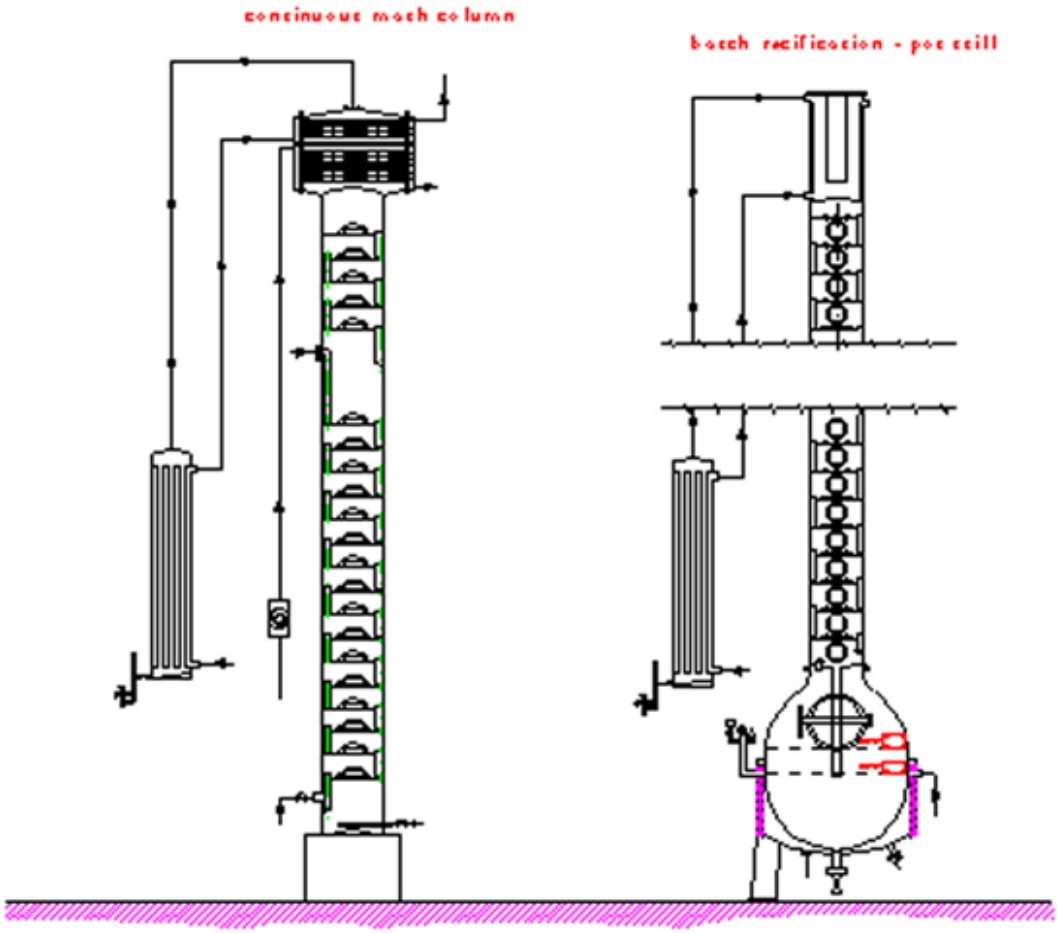


Figure 11: Continuous mash distilling column (beer stripper), plus copper pot still with rectification column for producing double distilled neutral spirits (figure courtesy of Christian Carl, Ing. GmbH).

Intensification/ Rectification Equipment

Only low-proof brandies can be obtained with the classical stills consisting of still, top, distillate transfer tube and cooler (coarse spirit) such that they have to be distilled a second time (fine spirit).

The reason for this restricted enrichment is that these devices do not have intensification capabilities. Because of costs and to reduce the process duration, the use of special intensification devices for distillation for a single distillation step has been developed. The higher enrichment of the gaseous component is achieved in comparison to the cocurrent distillation through a partial withdrawal of the distillate and a reentering of a portion into the still. This return of part of the distillate in liquid form in countercurrent flow to the vapor is referred a reflux. The concept of increasing the concentration by this countercurrent flow is known as rectification. Reflux and rectification are well known and widely practiced concepts in the petrochemical industries. For high process

efficiency, it has to be assured that almost complete heat and mass transfer between the reflux and the rising gas is given. Such intensifiers/rectifiers consist of a cylindrical container which is surrounded by a second somewhat larger container. Cold water is fed through the spacing between them in order to cool the inner container. Sieve trays or interim trays are installed in this inner container in order to divert the entering steam and have it partially condense at the cooled walls. Other partial condensers (intensifier) consist of a system of horizontal or vertical pipes which are surrounded with a container. The steam of the alcohol/water-mixture flows through the pipes while the outside is in contact with the cold water. Besides the concentrating effect the additional 2-4 trays inserted into those intensifying devices take over the task of a partial rectification (cleaning of the alcohol/water steam). Concentration and rectification are indivisibly connected.

The distiller has the task to decide according to the raw materials to which extent the intensification device should be used to obtain an optimal distillate. In practice this is done through bypassing of one or more trays as well as the regulation of the cooling water temperature, i.e. the reflux in the partial condenser or precooler.

Spirits and herbal extracts are generally distilled without trays, precooler and partial condenser. This kind of distillation already uses rectified and higher-proof brandy in addition to the flavorant such that the separation of fusel oil can be omitted for the most part. Raw materials like wine yeast, pulp and fruit wine in which undesired substances disadvantageously affect the taste require the full use of all concentration devices, i.e. trays. If stone fruit (esp. cherries) or Bartlett pears are used only two bell trays are usually used whereas the partial condenser is run with reduced effectivity (instead of using cold water cooling water of 35°C is used).

For production of neutral spirits such as vodka, columns containing numerous trays are necessary. An example is shown in Figure 11. While it is possible to produce vodka using a still with a small number of trays, it requires repeated redistillation that is both expensive and inefficient with low yield.

Distillate Transfer Tube

The connection between the top or intensifier unit and the cooler is designated as distillate transfer tube. These tubes are manufactured from high-grade steel because copper and tin are corroded by acetic acid steams stemming from mashes resulting in the formation of tin or copper acetate. This green-blue compound ends up in the distillate and

is a defect. Besides acetic acid, sulfuric acid from distilled wines and musts can have a corrosive effect on tin-plated copper tubes.

During the installation of the spirit tube (high-grade steel) onto the intensifier (copper) care needs to be taken that the copper and the steel is separated by nonconductive material because otherwise electrochemical contact corrosion occurs.

Cooler and Spirit Outlet (Drains)
The requirements of the materials for the distillate transfer tube are likewise valid for the cooler and the outlets.

The choice for a suitable cooler depends mostly on the still used. Thus, the simplest devices use a coil cooler which is led through a water container. Tube coolers made of high-grade stainless steel are recommended. They consist of bundles of tubes surrounded by water and merge into plenums at the top and bottom. Cleaning is relatively easy.

The cooling water flow should be directed from the bottom to the top with all types, i.e. counter-current. Thus, better heat transfer and therefore better cooling performance is achieved. The end of the cooler is to be equipped with 'drain' made of high-grade steel which should allow to control the amount, temperature, grade strength and clarity of the distillates to be removed. To reduce alcohol losses the outlet should be covered with a glass top. It is strongly recommended to control the distillate temperature and to increase eventually the cooling rate because significant evaporation losses have to be expected at higher temperatures. For the same reason it is advised to cover the receiving container (e.g. bottle in a basket) with a suitable material. It is also recommended to avoid large amount of distillate evaporation to avoid fire and explosion hazards.

Distillation Technique

Depending on whether the stills are equipped with or without intensification devices the production of distillate is done in a single-stage, double-stage, or possibly a multiple stage distillation.

Distillation without Intensification Device

Production of Coarse Distillate
The still vessel is filled with mash, wine, or beer up to 65-75 % and closed. For distillation of sediment yeasts the still is only to be filled half

way (Foaming!). Viscous mashes which tend to burn with direct heating (e.g. Bartlett pear) are diluted with 20 % water. Pomaces which yield a low alcohol content are mixed preferentially with 20 % coarse spirit.

The heating of the still is done in such a way that the range of the last 10 degrees below the boiling point are passed through slowly such that strong foaming is prevented. It is also recommended to add so-called anti-foaming agents in dosages of 2-4 g per hl volume. After the first portions of the distillate are obtained the heating power can be increased.

At the beginning of the distillation the coarse distillate contains alcohol of 40-60 % vol. After approx. 2 hours the alcohol content in the drain reduces to 2-3 % vol.[*] . At this point in time the distillation is interrupted; further distillation of the small portion of the alcohol remaining in the slops is not profitable anymore due to the heating costs. Moreover, a unnecessary dilution of the distillate would result. A too vigorous distillation of the coarse distillate is a mistake. Besides the damage to the aroma many unnecessary steam volatile components such as higher alcohols and fatty acids are entrained through excess amounts of distilled water.

Production of Fine Spirit

With the distillation of coarse spirit to fine spirit an intensification of the alcohol content as well as a purification (rectification) is achieved.

Depending on the size of the still 2-4 coarse spirit distillates are further distilled. To achieve a successful separation of undesired constituents the distillation of fine spirit has to be carried out much more careful than the one for coarse spirit. For example, in the beginning of the distillation the distillate should be received in dropwise quantities. The first portions are received separately and collected as forerun (heads). Generally this amounts to 1-1.5 l per hl coarse spirit. A somewhat different determination of the switching moment can be done if the distillate is collected in amounts of 200 ml and continuously tested through tasting (taste control). If the mashes used for brandies were damaged it may be necessary to collect up to 2.5 l from the forerun (heads). In the forerun (heads) the enrichment of the highly volatile components acetaldehyde and ethyl acetate is done both of which possess a sharp and pungent smell if present in excess. Eventually some turbidity may be observed in the forerun (heads). Its disappearance, however, must not be taken as the criteria for switching to the middle run (hearts).

During the onset of the middle run (hearts) the distillation should also not be forced because the separation of undesired fusel oils is only guaranteed in an acceptable way if the equilibrium between alcohol and

[*] In all cases described it is necessary to have a hydrometer available to confirm the choices to be made.

water is achieved. Over time the alcohol content of the middle run (hearts) decreases. Just before a turbidity can be noted the spirit is collected in a different container. The alcohol grade strength serves as a guideline for the switching to the afterrun. For cherries the limiting values are around 55 % vol. and for Bartlett pears, plums and pomaceous fruit around 45 % vol. In addition to both criteria (clarity, alcohol strength) the results from smell and taste have to be taken into consideration. Portions of fusel oil, higher fatty acids and their esters which are distilled into the distillate at an initial alcohol content which is too low give a faded, dull character to the brandy ('blasé character'). If those changes are noted switching to the afterrun (tails) has to be done. Bad experiences were obtained when the switching to the afterrun (tails) was done for average alcohol contents of the fine spirit as low as 45 % vol.

The distillation of the afterrun (tails) can be forced; approximately a quarter of the coarse distillate is in the afterrun. The average alcohol content fluctuates between 15 and 25 % vol.; for stone and seed fruit it is rather between 20 to 25 %. The distribution of the fractions from the fine spirit distillation of 100 l coarse distillate from plums is given in the following overview:

1-2 l	Forerun (heads) (75 % vol.)
30 l	Middle run (hearts) (60-65 % vol.)
20-25 l	Afterrun (tails)(20-25 % vol.)
40-45 l	Still residuum (0.1-0.3 % vol.)

For fruit brandies distilled in simple stills - in comparison to distillations with intensification devices - higher alcohols end up primarily in the middle run (hearts). Even though those substances can partially be considered as aroma-giving components excess can disturb the harmony of the distillate significantly (palatal scratching, metal-kind flavor). It seems therefore advisable to switch to the afterrun (tails) rather earlier than later. The often practiced method to add all forerun (heads)s and afterruns to the next distillation step is not recommended. The impairment resulting from the addition is in opposition to the original purpose of cleaning the fine distillate. Foreruns (heads) and afterruns are preferably collected and distilled again into forerun (heads) and afterrun (tails) after appropriate treatment (carbon treatment, separation of esters). The middle run (hearts) thus obtained can be added to the distillates in small amounts.

Distillation with Intensification Devices

In earlier years the opinion was widespread that only common brandies from inferior fruit could be distilled in a one-step distillation whereas due to reasons of quality the time- and energy-consuming coarse/fine spirit

distillation was preferred if specialties were to be obtained. This opinion still prevails for Cognac and Scotch whiskey, but as noted earlier, these products have strong tradition and the actual desire for the high temperature reaction products for flavor and aroma. More recently, stills equipped with intensification devices have been significantly improved not only with respect to the functionality but also the materials used such that distillates obtained in a one-step distillation distinguish themselves rather positively from those obtained in common stills. After the reduction with water the middle run (hearts) yields drinkable fruit brandy. The distillate is obtained with approx. 80 % vol. It is recommended to initiate a slow distillation and to throttle the cooling in the partial condenser temporarily such that undesired volatile components can be concentrated in the forerun (heads) and eventually be separated.

With a one-step distillation the alcohol content both of the middle run (hearts) and the afterrun (tails) is higher as compared to a fine spirit distillation (65-70 and 25-30 % vol.). Time and fuel savings are cost reducing factors and the distillation itself is easier. Through the use of automatic cooling water adjustments (the cooling water inflow is controlled by the cooling water outflow of the partial condenser) the operator is relieved to the extent that one person alone can supervise several stills. This efficient process is the reason why more and more companies switch to the one-step distillation. The distillation is interrupted if the distillate has an alcohol content of approx. 5-10 % vol. The alcohol content remaining in the mash can be neglected for practical purposes; it is not profitable anymore.

Production of Flavored Products

Raspberry Vodka or Spirit

Mash 100 kg raspberries (to thaw if frozen) and pour 35-40 liters fine spirit/ neutral spirit over them. Leave preparation after being well mixed in entirely filled, well closed containers. The best results regarding the aroma are obtained if the preparations are distilled after 24 hours

(preceding water addition of 50 l per hl mash). Already distilled mashes can be prepared once more: 100 kg are covered with 20 l fine spirit. Leave standing for 24 hour and add the afterrun (tails) from the first distillation before distilling again. The resulting distillate has lost aroma and should therefore only be used in small amounts.

Raspberries prepared with fine spirit can be distilled without intensifiers and the separation of the forerun (heads) is generally not required. Switching to the afterrun (tails) occurs at 45 % vol.. The amount of afterrun (tails) is significantly smaller than the one of distillation of

mashes. Raspberry spirit is commercially available with a minimum alcohol content of 40 % vol.*

Gin (Juniper Berry Brandy)

For a process without fermentation 20 kg juniper berries are first slightly squeezed and then prepared with 100 l 30% drinkable alcohol. After a resting period of approx. 12 hours (repeated stirring of the preparation is recommended) the distillation is initiated.

In enterprises where juniper mashes are still fermented the production of the brandy is done in a two-step distillation. The fermented mash is distilled without intensification devices and without separation of forerun (heads) and afterrun. The resulting coarse spirit is mixed with 5-10 % water and 1 kg magnesia (magnesium oxide) per hl and filtered through kieselgur. Oil eventually excreted should be skimmed off before the treatment with magnesia. In the fine distillation step the switching to the afterrun (tails) is done at 65 % vol. Disturbing flavor agents and oils are best eliminated in this way.

Other Botanicals

This class of spirits includes flavored vodkas and gins. The base material is a well rectified spirit with neutral aroma. After filling the still, water is added in order to obtain a still content with approx. 30 % vol. The commercially available herbs are set on a sieve tray or sieve basket which are hung into the still. The distillation is best done using a fine distillation apparatus. Using a different procedure the herbs are added directly to the neutral spirit or hung into the still packed in linen sacks. A mixture of 1-5 kg of herbs is required for 100 l spirit. The optimal dosage is best obtained through a taste check of already distilled brandy.

The distillate (alcohol content 70 % vol.) is reduced to approx. 37 % vol. using softened water. The turbidity thus resulting can be removed through filtration. The almost clear filtrate can now be adjusted to 42 % vol. using high-proof drinkable alcohol.

The list of botanicals that have been employed for making gins and vodkas is quite lengthy. Some typical gin botanicals include: juniper berries, coriander seeds, angelica root, orange peel, lemon peel, cinnamon bark, cardamom, aniseed, nutmeg, fennel, etc. These same spices are used in production of akva vit, ouzo, and pastis. A typical recipe for gin is 45.4 kg juniper berries, 22.7 kg coriander seeds, 4.5 kg

* This depends on the choice of marketing country.

cinnamon bark, 4.5 kg angelica root, 0.45 lemon peel, and 0.45 kg cardamom added to 115 hl of 50% (v/v) neutral spirit.

Cleaning and Maintenance of Distillation Devices

New stills or stills not used for a period of time regardless of the design should be flushed by boiling several times before operating. For this purpose the still is filled up to the rim with water. After closing the water is distilled without cooler. The steam exiting the cooler is passed into a drain or led into the ambient air using a tube. After daily operation the stills should be cleaned in general. Very dirty stills as they are encountered after distillation of yeast brandies need to be brushed out thoroughly using suitable cleaning detergents (e.g. 1 kg sodium carbonate or per filling of the still). The 'spirit tube' is best cleaned with a bottle brush. This brush is connected to a rope and led through the tube several times. Tube coolers are to be cleaned in the same manner whereas the coil coolers which are difficult to clean should be closed at the bottom and filled with a hot sodium carbonate solution and left for 1 hour. A thorough rinsing with cold water is required in any case (The rinse water ought to be checked for remains of basic material using indicator paper!). It is inevitable to steam-clean a distillation device until it remains aroma neutral after the distillation of aroma rich distillant (juniper, herbs etc.). It is recommended to distill common fruit brandy before expensive raw materials (cherries, Bartlett pears) are distilled. During the annual dismantling of the apparatus (main cleaning) the main cooler and the partial condenser are to be checked for onsets of limestone and eventually to be treated using 10% formic acid (water immediately after the decomposition of the cake!). Inexplicable alcohol losses can sometimes be attributed to leakages in the cooler. It is therefore recommended to subject connections as well as welding seams - if necessary with a pressure test -to a thorough check. In cases of doubt the water leaving the cooler should be examined for alcohol content.

For the cleaning of the outer parts (still, intensification unit) a 10% citric acid solution has proven successful. This solution is best applied to the parts still warm and flushed thoroughly with cold water after a short period of contact.

Weakly alkaline or synthetic means are often sufficient to clean the exterior of high-grade steel parts. Water spots can be removed with a little vinegar. It is important not to clean high-grade steel with abrasive materials (steel brushes, steel wool).

Usage of the Slops

The usage of the slops or distillers grains as fodder is common. The fruit slops have a significantly lower protein content than for slops from potatoes or rye such that its value for fodder is rather modest. In addition, fruit mashes contain relatively a high content of fruit acids which makes them usable for fodder only in limited amounts; otherwise indigestion has to be expected. For the same reasons slops from acetic mashes or acidified mashes are not suitable for fodder at all. Draining of sewage water has to be approved; moreover the sewage water has to be within certain fixed concentration limits. Residuals from grains, on the other hand, are high in protein and widely used for high quality animal feed.

In small enterprises agricultural usage is possible for fruit slops: the slops are used as fertilizer either directly or mixed with manure. According to experience one hectare of land can absorb 100 m^3 of slops without impairment. It is important to neutralize the slops after the distillation directly in the still using slaked lime or sodium hydroxide (mixing can be done through direct steam injection). General requirements for the neutralization of 100 l slops are:

600 g slaked lime (calcium hydroxide) or
1.6 l 30% sodium hydroxide

The control of the pH-value (guideline pH 8; allowed range pH 6.5-9.0) has to be done using indicator paper.

Examples of Distillation Apparatus



Figure 12. An electrically heated still with rectification column directly mounted above the pot. (Figure courtesy of Christian Carl, Ing. GmbH)



Figure 13. A steam fired still with the rectification column set to the side. This configuration allows a complete bypassing of the column to approximate an alambic or Rayleigh distillation. This same bypass configuration would be appropriate for the production of gins and flavored vodkas. The red arrow indicates the valve allowing the bypass. (Figure courtesy of Christian Carl, Ing. GmbH)

General Theory of Distillation

(Author's note: This section is largely aimed at engineers with an interest in the underlying theory of distillation.)

Overview

Rayleigh Distillation

The most basic type of distillation is a simple binary distillation also known as a Rayleigh distillation and for the most part this is described in the distilling industry as alambic distillation. Two compounds with different boiling points can be distilled under simple distillation conditions. A simple distillation involves no trays, i.e., no rectification, the pot for boiling the mixture is connected to the condenser. When the liquid in the pot is boiled, the vapor is removed at each time interval and condensed in the condenser. The vapor becomes richer in the more volatile component than the liquid remaining in the pot, thus reducing the concentration of the more volatile component present in the pot. The vapor condensed in the condenser increases in the concentration of the more volatile component. As time increases the two components are separated into two separate vessels, the more volatile in the distillate and the less volatile in the pot. Figure 14 shows a schematic diagram of the Rayleigh distillation apparatus.

The mass balance around the entire system for the entire operating time is:

$$F = W_{final} + D_{total}$$

$$Fx_F = x_{W,final} W_{final} + D_{total} x_{D,avg}$$

where F represents the feed, D represents the distillate W represents the bottoms, and x_f represents the mole fraction of the feed.

The variables F, x_F and the desired value of either $x_{W,final}$ or $x_{D,avg}$ are specified requiring an additional equation to solve for the three unknown variables D_{total}, W_{final}, and the unspecified variable above. The Rayleigh equation is derived from a differential mass balance. The assumption is made that the holdup in the accumulator and column are negligible[2]. The differential amount of material -dW of concentration x_D is removed from the system, resulting in the differential mass balance:

$$-x_D dW = -d(Wx_W) = -Wdx_W - x_W dW$$

Rearranging and integrating gives:

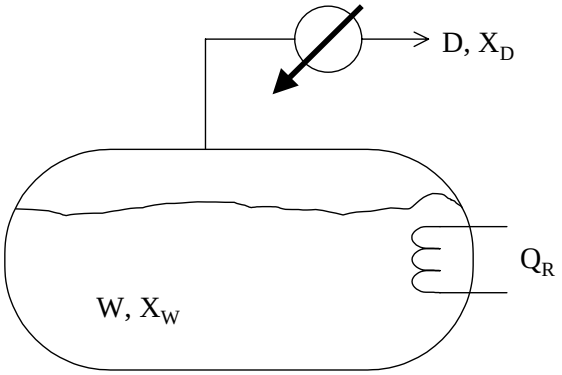
$$\int_{W=F}^{W_{final}} \frac{dW}{W} = \int_{x_F}^{x_{W,final}} \frac{dx_W}{x_D - x_W} \quad \text{or} \quad \ln\left[\frac{W_{final}}{F}\right] = -\int_{x_{W,final}}^{x_F} \frac{dx_W}{x_D - x_W}$$

The vapor product is in equilibrium in simple batch distillations. Because a total condenser is used, the substitution of $y = x_D$ can be made. Then:

$$\ln\left[\frac{W_{final}}{F}\right] = -\int_{x_{W,final}}^{x_F} \frac{dx}{y - x} = -\int_{x_{W,final}}^{x_F} \frac{dx}{f(x) - x}$$

where x and y are in equilibrium which can be expressed as y = f(x,p)

By integrating the above equations it is now possible to find a solution for the unknown variables D_{total}, W_{final}, and $x_{W,final}$ or $x_{D,avg}$. Time is implicitly present in these equations because W, x_W, and x_D are time dependent.



W	Bottoms
D	Distillate
X_D	Mole Fraction of Distillate
X_W	Mole Fraction of Bottoms
Q_R	Reboiler Heat Load

Figure 14 Simple batch distillation schematic (Rayleigh/ alambic).

Multistage Batch Distillation

For multistage systems x_D and x_W are no longer in equilibrium, and the Rayleigh equation can not be integrated until a relationship between x_D and x_W are found. Stage by stage calculations must be made to obtain

the relationship between x_D and x_W. By assuming that the holdup is negligible at each tray, the condenser, and the accumulator, mass and energy balances around any stage *j* and the top of the column can be performed as shown in Figure 15. At any time *t* these balances become:

$$V_{j+1} = L_{j+1} + D$$
$$V_{j+1} y_{j+1} = L_j x_j + D x_D$$
$$Q_C + V_{j+1} H_{j+1} = L_j h_j + D h_D$$

The molal flow rates are expressed in these equations by V, L, and D. The energy balance is not needed if constant molal overflow is assumed, because the vapor and liquid flow rates will be constant. The equation for constant molal overflow then becomes:

$$y_{j+1} = \frac{L}{V} x_j + \left(1 - \frac{L}{V}\right) x_D$$

This represents a straight line on a y-x diagram. The slope will be L/V and the intercept with the y = x line will be x_D. Either x_D or L/V will need to vary during the batch distillation, and the operating line will be constantly changing. The 150 L Christian Carl still is based on a varying reflux ratio, attempting to keep the concentration of x_D at a maximum.

For variable reflux ratio operation of a batch distillation, the equation for constant molal flow rate holds, with the slope varying, and the intersection with the y = x line at a constant x_D. Figure 16 shows the McCabe-Thiele diagram for multistage batch distillation with variable reflux. The McCabe-Thiele diagram relates x_W and x_D allowing integration of the Rayleigh equation.

The feed concentration x_F is found by identifying the initial value of L/V is found by trial and error, and specifying the number of stages and the distillate composition x_D. The final value $x_{W,final}$ occurs when L/V is in total reflux, or $L/V = (L/V)_{max}$. Once $x_{W,final}$ is found, W_{final} is determined from integration by the equation:

$$W_{final} = F \exp\left(- \int_{x_{W,final}}^{x_F} \frac{dx}{y - x} \right)$$

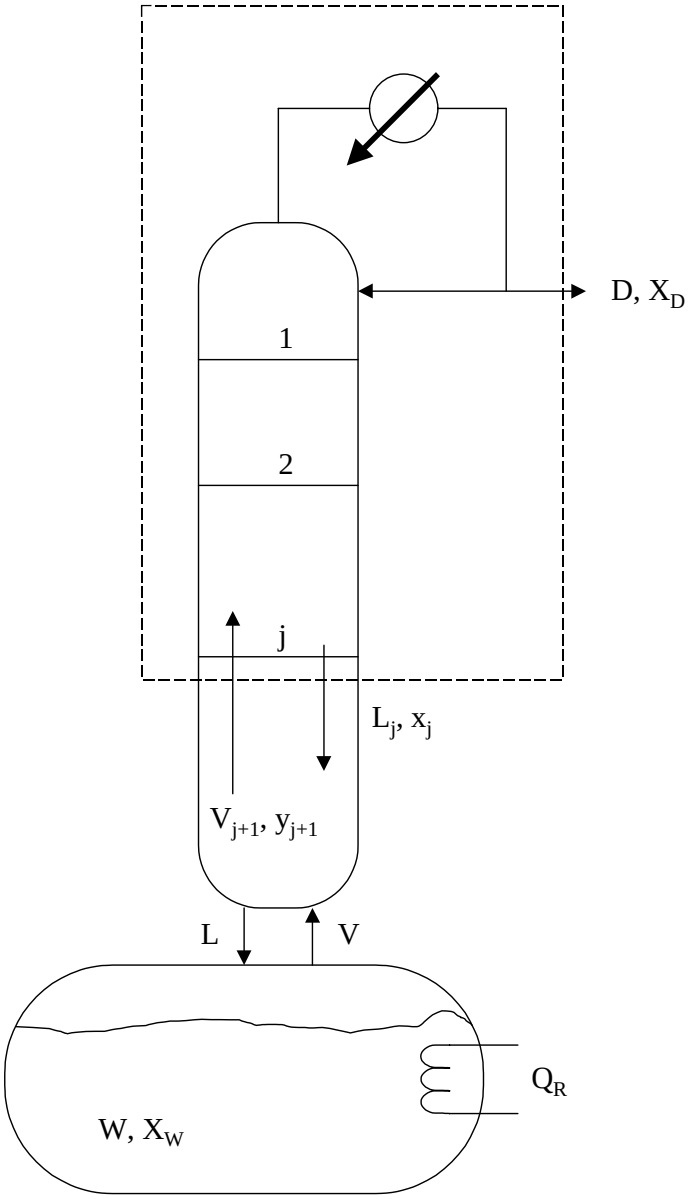


Figure 15 Schematic of a multistage batch distillation apparatus.

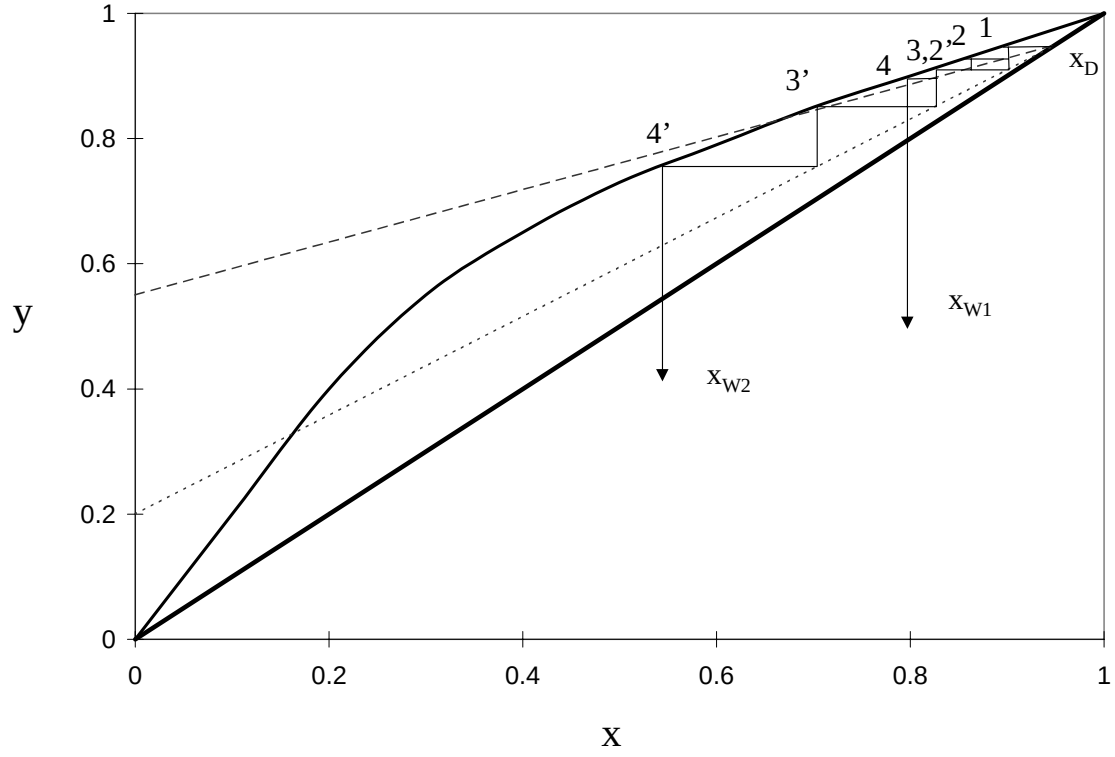


Figure 16 McCabe-Thiele diagram for multistage batch distillation with variable reflux.

Multicomponent Batch Distillation

The additional degrees of freedom associated with the addition of more compounds to the mash make the modeling of multicomponent batch distillations difficult. By increasing the number of components from two to three the number of degrees of freedom increases to account for the composition of the feed. Each additional compound included in the feed will in turn increase the complexity of the interactions of the components. Each interaction between each component must be taken into account for modeling these types of distillations. The variety in compound interactions (e.g. polar and non-polar, size, hydrogen bonding, etc.) require many different types of models to explain the behavior of the components present in the multicomponent distillations. These models rely upon large sets of coupled, nonlinear ordinary differential equations and are available in commercial software packages such as CHEMCAD™, HYSIM™, and ASPEN™.

In multicomponent distillation, neither the distillate composition nor the bottoms composition is completely specified because there are not enough variables to allow complete specification. The calculation procedure is greatly affected by the inability to completely specify the distillate and bottoms composition. It is possible to identify components in four classifications. Those components for which the fractional recoveries in the bottoms or distillate are known as key components, the most volatile of which is known as the light key (LK) and the least volatile of which is known as the heavy key (HK). The other compounds are known as the non-key components. Those non-key components that are more volatile than the LK component are known as light non-key (LNK) and the compounds less volatile than the LK compound are the heavy non-key compounds (HNK).

The overall balance equation is:

$$F = B + D$$

The component balance equations become:

$$Fz_i = Bx_{i,bot} + Dx_{i,dist}$$

and the mole fractions must sum to 1.

$$\sum_i^C x_{i,dist} = 1.0$$

$$\sum_i^C x_{i,bot} = 1.0$$

For a three component mixture the component balance equation is written three times, and must then sum to meet the overall balance equation.

The problem of solving for the external mass balances arises. The unknowns are B, D, $x_{2,dist}$, $x_{3,dist}$, $x_{2,bot}$, and $x_{3,bot}$. This leaves six unknowns with five independent equations. The additional equations of energy balances or equilibrium expressions always add additional variables. Internal stage-by-stage calculations for tertiary systems rely on the compositions of the components at one end of the column, and these as mentioned earlier are unknown. By assuming one of them is known, the problem becomes a trial-and-error exercise.

Many formulae for these trial-and-error calculations have been developed for mixtures of three or more components. Additional variability to the

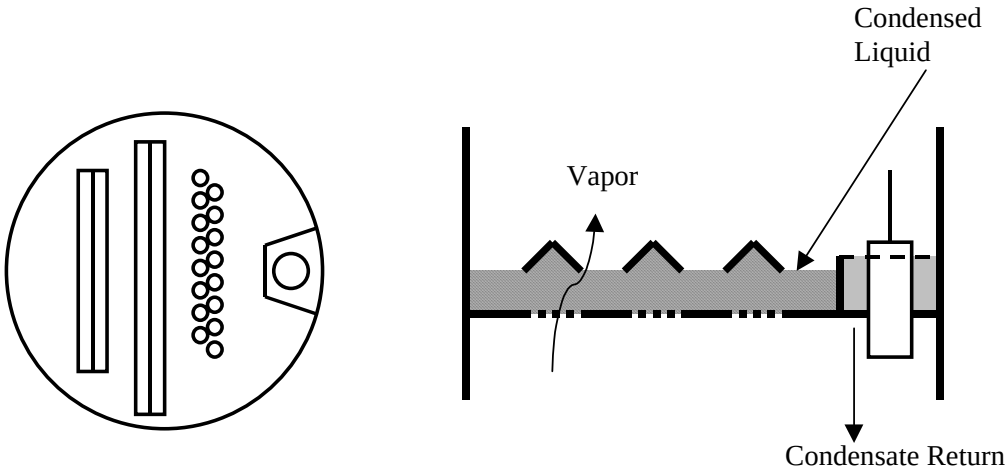
molal flow rate of each component and chemical interactions further complicate the problem resulting in the need for a software suites like CHEMCAD™, HYSIM™, and ASPEN™ to perform these calculations using a variety of these distillation models.

Trays and Usage

Distillation trays rely on the principle of reflux for increasing the separation of the compounds present. Reflux is the partial condensation of vapor and the return of the liquid down the column. At every interface between the liquid layer and the condensed layer, contact is occurring causing greater separation of the compounds present.

As the name implies, sieve trays have numerous small holes in the plate of the tray which, for the Christian Carl still used in this experiment, are capped by a plate as illustrated in Figure 17. These holes are small enough that the pressure of the vapor from the tray below causes only the upward flow of vapor and liquid does not flow downward. The liquid phase flows across the top of the tray until it reaches the downcomer (the opening for the liquid to flow downward) and the vapor from the tray below is forced to pass through the holes and the liquid, and then onto the next tray. This configuration leads to excellent contacting between the two phases and makes the composition approach vapor-liquid equilibrium.

The Holstein still uses bubble cap trays. Bubble cap trays use the same idea of passing the vapor from the tray below through the condensed layer on the tray above. As seen in Figure 18 a bubble cap tray has a cap over a tube from the lower tray. The vapor must pass through the condensed liquid in order to get through to the next tray. Both types of trays can be modeled by the commercial software programs.



Top View Side View

Figure 17 Sieve tray. The sieve tray has a number of holes along the tray through which the vapor from the tray below must pass. This action forces the vapor to pass through the condensed liquid on the tray, increasing the separation of the components present.

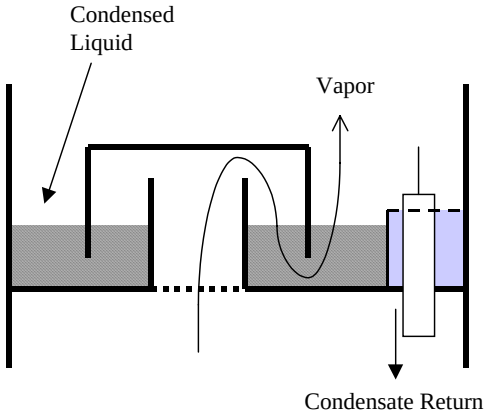


Figure 18 Bubble cap tray. This tray design traps the condensed liquid on the surface of the tray without allowing it to flow through to the tray below. The design also forces the vapor from the tray below to pass through the condensed liquid layer, increasing the separation of the components present.

Flavor Components

Overview

Organic acids, esters, and fusel alcohols form the main body of the congener compounds (all compounds other than ethanol and water) in the distilled spirits. Some other compounds are also present in the distillate, but the above organic compounds account for the majority of congeners present. The formation of most of the congeners in the distillation occurs in the fermentation of the mash in the presence of yeast. The fermentation process is controlled to prevent an excess of undesired compounds, and increase the yield of ethanol. Control of the

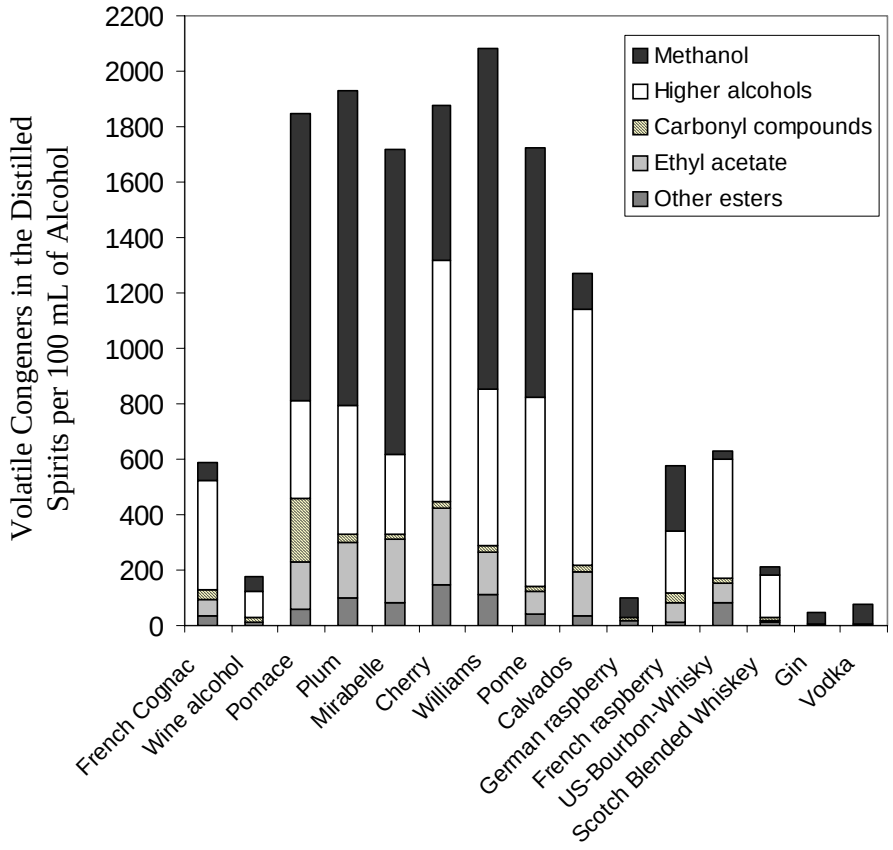


Figure 19 Volatiles in distilled spirits. The concentration of volatile congeners in the distilled spirits (mg/100 mL of alcohol). Fruit spirits have higher concentrations of volatiles than other distilled beverages.

fermentation includes temperature control, fermentation duration, and mixing. High temperature fermentations have reduced ethanol yield and increased congener concentrations. If the temperature of the fermentation is too low, the yeast activity decreases, requiring a longer duration of fermentation. Common fermentation conditions include a temperature range of 13°- 18°C and a two week fermentation time.

Stirring the fermentation can decrease the time required for complete fermentation, and decrease the mash viscosity.

Any wild strains of yeast, molds, or other microbes may cause increased concentrations of undesired compounds. Over-inoculation of the mash with the desired strain of yeast is the best method for preventing other microbes from producing undesired compounds. Over-inoculation requires adding an amount of yeast greater than the minimum amount required to ferment the mash. The desired yeast will out-compete the wild microbes for the nutrients needed for growth and reproduction. This method reduces the production of undesired flavors at a cost of more yeast.

Ethanol

The distillation of fruit spirits relies on the conversion of fruit sugars to ethanol by yeast. The Embden-Meyerhoff-Parnas Pathway (EMP) is the well know process for the conversion of sugars to ethanol by yeast. This pathway proceeds by degrading the sugar to acetaldehyde where it is then reduced to ethanol. The yield of ethanol is dependant upon the initial concentration of the total sugar present in the fruit which is measured as total dissolved sugar present in the liquid mash. The total dissolved solids (brix), however, also includes unfermentable compounds such as sorbitol, and must only be used as a guide to determine the approximate concentration of the sugars present in the mash. The EMP process yields two moles of ethanol for every one mole of glucose present in the fruit. Other sugars present in the fruit include fructose, maltose and sucrose.

Methanol

Methanol is a very important compound in the production of fruit brandies. The United States Food and Drug Administration (FDA) and Alcohol and Tobacco Tax, and Trade Bureau (TTB) regulate the methanol concentration in distilled spirits at 0.35% v/v (2.765 g/L). Methanol is a positive flavor component of brandies; therefore, its complete elimination from brandies is not the aim of the regulations. Methanol is similar to ethanol in taste and smell; however, it is toxic and potentially dangerous if present in high concentrations. These regulations are primarily a consequence of the use of methanol by unlicensed distillers to adulterate beverages by addition of methanol to increase the alcohol concentration.

The regulation of methanol is based on associated health hazards. Methanol is a poison that interrupts nerve impulses. Methanol causes headache, nausea, and can attack the optic nerve blurring vision or even causing blindness. Chronic exposure to methanol can cause kidney and liver dysfunction. Methanol is metabolized in the body to formaldehyde, which is also toxic to humans. Interestingly, the antidote for acute methanol poisoning is administration of ethanol; therefore, the low

regulated levels of methanol in high proof fruit brandies pose little or no health hazard.

Methanol is a side product of the fermentation process along the EMP process. However, a larger concentration of the methanol comes from an enzymatic interaction of pectinesterase with the pectin of the fruit as discussed previously. This is part of the natural decomposition process of the fruit, which is designed by nature to prevent animals from removing the seed from the nutrients of the fruit because of the poisonous methanol that is present. The whole fruit is used in the fermentation of fruit spirits which increases the amount of pectin and pectinesterase in the mash and consequently increases the concentration of methanol in fruit spirits when compared with other distilled spirits. This problem is generally not encountered in grape or grain mashes.

Fusel Alcohols

Fusel alcohols are defined as those alcohols larger than ethanol (e.g. C>2) and compose the largest group of aroma compounds in alcoholic beverages. The most common fusel alcohols in distilled spirits include 1-propanol (*n*-propanol), 2-methyl-2-propanol (isobutyl alcohol), and 3-methyl-1-butanol (isoamyl alcohol). Isoamyl alcohol is the main fusel alcohol synthesized during fermentation by yeast accounting for 40 to 70% of the total fusel alcohol concentration in distilled spirits depending upon the type of mash. Formation of these fusel alcohols is thought to be independent of the raw materials used in the mash in that the formation of these longer chain alcohols can occur in whiskeys as easily as in tequila, gin, or fruit spirits. N-propanol, and branched C_4 and C_6 alcohols are formed from valine, leucine, and isoleucine in the presence of yeast. α-keto acids are thought to act as key intermediates in the formation of higher alcohols. The α-keto acids are first decarboxylated to aldehydes and then reduced to the corresponding alcohol. Fusel alcohols are thought to form in fermentation under both anaerobic conditions from amino acids and aerobic conditions from sugars.

Carbonyl Compounds

Aldehydes

Aldehydes are the intermediates in the production of alcohols by yeast. The aldehyde concentration in the distilled spirits is due to the inefficiency of the yeast in reducing the aldehydes to their corresponding alcohol. The yeasts are making the aldehydes as well as reducing them to alcohols; however, the reduction of the aldehyde to alcohol is not as efficient as the production of the aldehydes.

The most common aldehyde present in the distilled fruit spirits is acetaldehyde. Acetaldehyde is an intermediary in the EMP pathway and

is present in all distilled spirits. Acetaldehyde has a low boiling point and is soluble in both water and ethanol, and is at its highest concentration in the early (heads) portion of the distillation.

Benzaldehyde, sometimes referred to as bitter almond oil, is another important aldehyde present in stone fruits. Benzaldehyde comes from the amygdalin present in the pit of stone fruit. The hydrolysis of one mole of amygdalin yields two moles of glucose one mole of cyanide and one mole of benzaldehyde. Benzaldehyde is considered a positive aroma characteristic in stone fruit brandies. It is present in the late hearts and tails of the distillate due to the relatively high boiling point.

Ketones

Ketones are produced in the yeast cells as an oxidation product of alcohols and excreted as an unwanted side product. The most common keytone present in the distilled spirits is acetone, which has a negative aroma associated with it in fruit spirits. Acetone may be produced from oxidation of 2-propanol as well as other microbes present in the fermentation media. *Clostridium acetobutylicum* for example, is used in the industrial fermentation of acetone, butanol, and ethanol.

Esters

Esters are formed during the distillation and storage of the spirits and generally add positive flavor aromatic qualities to the distilled fruit spirits. The highest concentration esters present are ethyl formate and ethyl acetate. Ester formation is due to the esterification of alcohols with organic acids. The formation of ethyl acetate and ethyl formate involve the reaction of acetic acid with ethanol and methanol respectfully. These two esters are present in the highest concentration in the distilled spirits because they are derived from the two highest concentration alcohols.

Congeners in Distillate Fractions

An interesting phenomenon is the manner in which the congener compounds distribute themselves as a function of distillate fractions during a batch distillation. Figure 20 shows data obtained for different distillate fractions collected during a batch distillation with reflux. As expected the very volatile compounds such as acetaldehyde and ethyl acetate are concentrated in the early head fractions and are easily separated. The fusel oil compounds, 1-propanol and isoamyl alcohol, have low concentrations at early fractions, go through a maximum, and trail off in the tail fractions. Methanol exhibits a much more complex behavior in that it behaves early on as expected and reduces in concentration since it has a lower boiling point than ethanol. The very unusual behavior commences in the hearts cuts where unexpectedly the concentration goes through a minimum and actually starts to increase in concentration even though all the other alcohol concentrations (including ethanol) are decrease. This behavior is due to the multicomponent

interactions of the system and underscores the inability to apply simple binary reasoning or predictions to a complex system.

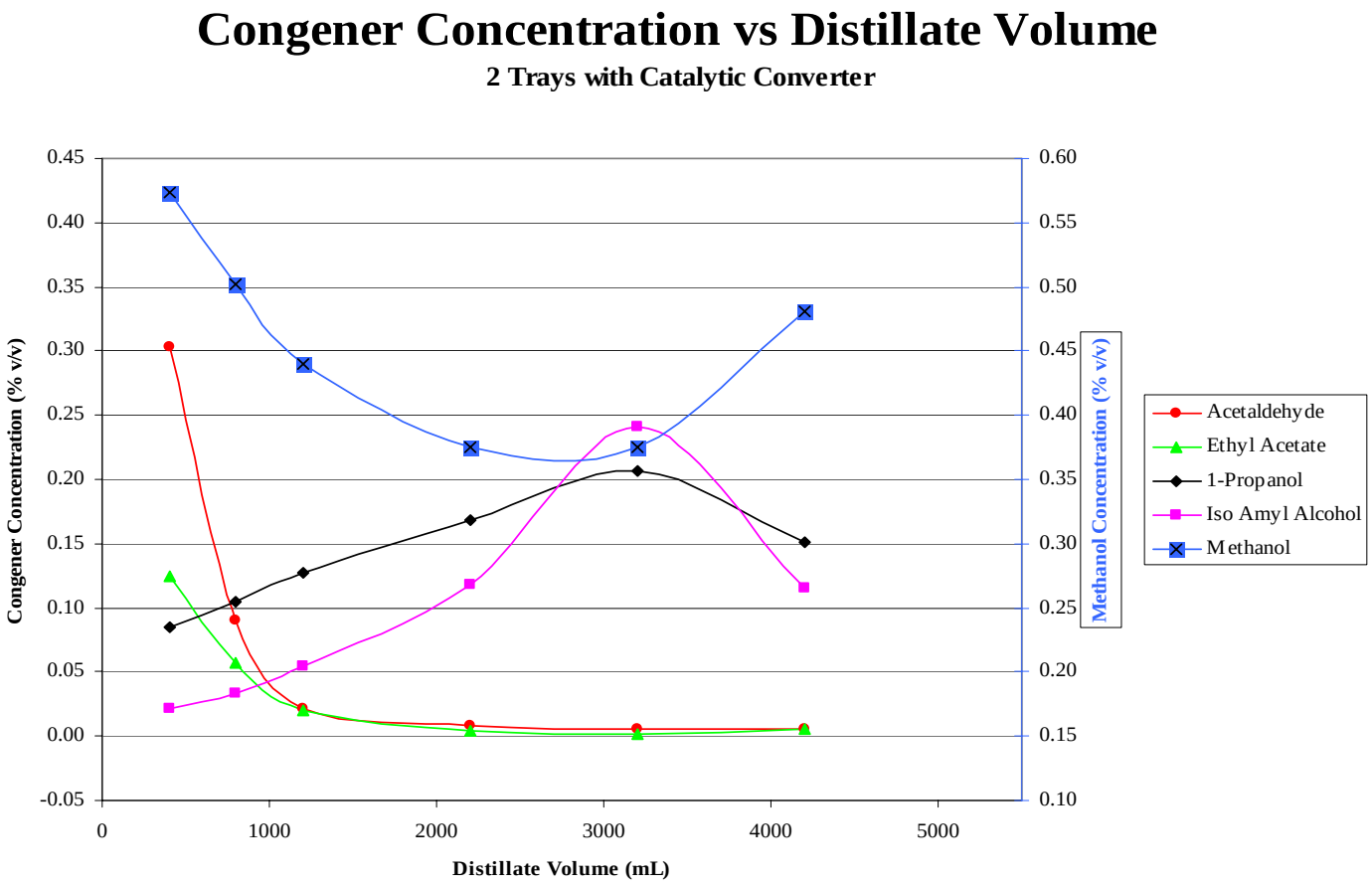


Figure 20. Congener concentration as a function of cumulative distillate volume for a cherry distillate (M. Claus, M. S. Thesis, Michigan State University, 2000).

AGING OF SPIRITS

General Remarks

Freshly produced distillates seem to appear in general less tastable and discordant. An immediate reduction (dilution) to drinking strength is therefore not recommended; an old rule rather says that high-proof spirits ought to be kept in the loft for some time, namely in bottles which are closed with slits in the corks. In this way two conditions crucial for aging are achieved: on the one hand the contact with air promotes the oxidative change of substances, i.e. their reaction with oxygen is promoted, on the other hand it is the influence of heat which accelerates those conversions[*] . The "aging" of spirits is thus considered quite positive; it is usually associated with the decomposition and conversion of undesired substances in such which are more pleasant and refined in aroma and flavor.

The aging process of fruit brandies like kirsch, plum spirit and Williams proceeds differently than, for example, of Cognac, Calvados (apple brandy in barrel storage), or Scotch whiskey. The main difference is that the barrel storage of spirits promotes the transfer of constituents like tanning agents, hemicellulose, lignin and minerals from the oak into new, more pleasantly smelling components or such which act accelerating as catalysts during the reaction. Often new acids are formed, the pH-value decreases in the course of time and the formation of ester or acetal is accelerated. Not all the brandies show the same reaction under the influence of heat and oxygen; the aging of Bartlett pear brandy is associated with an early decline of the bouquet (it becomes rancid, i.e. the natural oils become resinous) such that a forced ripening process should be disregarded.

In summary it can be stated that for Calvados-like apple spirits, marc and brandies a short storage in oak barrels proved to be best. Instead of oak barrels the storage can also be done in high-grade steel tanks, enamel or glass containers (but not in plastic containers). Kirsch and plum distillates are only kept in partially filled and non-hermetically closed glass carboys or tanks in a warm environment for aging. Fast temperature oscillations are not favorable for the aging process. Occasional injection of air and a brief immersing of a clean copper sheet can accelerate the aging process. Brandies which are obtained in a one-step distillation in modern stills and not through a forced distillation procedure are generally not required to be subjected to an extended

[*] A rule of thumb states a doubling of the reaction rate for a temperature increase of 10 °C.

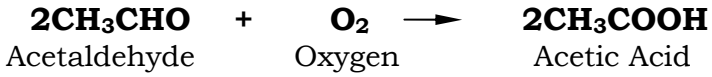
storage period. One to two month storage is considered sufficient for those distillates; however, the length of this storage period is certainly a point of contention among producers.

Important Aging Processes

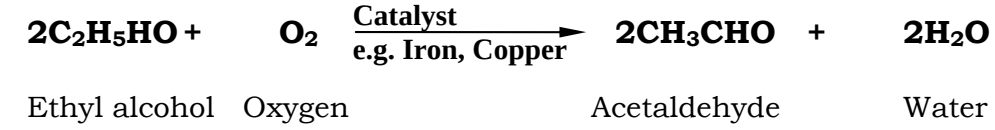
Oxidation

The best known example of an oxidation process in daily life is the formation of rust. Iron reacts with the oxygen present in the air to form ferric oxide which is a compound with different properties than the ones from the starting materials. Distillates also contain substances which can react with oxygen. These processes are called oxydative aging. Inaddition to the main components (ethyl alcohol, water), several alcohols are contained including methanol (stemming from the pectin) and a variety of higher alcohols such as propyl, butyl, isobutyl and amyl alcohol. In addition there are aldehydes with acetaldehyde being the dominant member. Acetic, propionic, and butyric acids constitue the lower molecular weight acids; caproic and capric acid form the higher molecular weight fatty acids. The examples of the primary oxidative reactions for aldehydes and alcohols are:

- Oxidation of acetaldehyde
  Acetaldehyde is easy oxidizable; the reaction with oxygen produces acetic acid:



– Oxidation of ethyl alcohol
  Mainly through barrel storage the following reaction can occur with the participation of catalysts:



Acetaldehyde can then oxidized in a later phase to acetic acid as shown by the first reaction.

Esterification

Esters are reaction products which are formed from the reaction of an alcohol and an acid wherein water is formed as a side product. Large amounts of acetic esters arise in brandies due to the high concentration of ethyl alcohol that drives the equilibrium reaction to the right:

C_2H_5OH	+	CH_3COOH	→	$CH_3COOC_2H_5$	+	H_2O
Ethyl alcohol		Acetic Acid		Acetic Ester		Water

Esterification is possible for all alcohols and esters. The completeness of their reactions depends on the initial concentration of the reaction constituents as well as the temperature and the pH-value. Because the esters produced possess an aromatic and fruity smell the distillates lose their herbal, scratchy notes through storage. Processes of esterification are reversible; for example, acetic ester can be decomposed into ethyl alcohol and acetic acid in alkaline solutions ("soaping") or acidic solutions. This phenomenon has been exploited for the treatment of distillates with excessive ester content.

Acetalization

Acetals are formed through the reaction of alcohols and aldehydes. For example, in the presence of a small amount of acid acetaldehyde and ethyl alcohol react to form acetaldehyde-diethylacetal which is a fruity substance smelling like flowers.

CH_3CHO	+	$2C_2H_5OH$	→	$CH_3CH(OC_2H_5)_2$	+	H_2O
Acetaldehyde		Ethyl Alcohol		Acetaldehyde-Diethylacetal		Water

This reaction sequence is a parallel reaction to oxidation processes. This reaction pathway provides a means to convert the pungent acetaldehyde into a pleasant bouquet component. Acrolein present in spirits loses its pungent smell during the course of some months through a polymerization process.

COMPLETION OF THE DISTILLATES

Reducing to Drinkable Grade Strength

Most distillates (middle run (hearts)) have an alcohol content of more than 40-45 % vol. and have to be reduced in concentration after storage, i.e. blended with water* . The water to be used has to satisfy two main requirements:

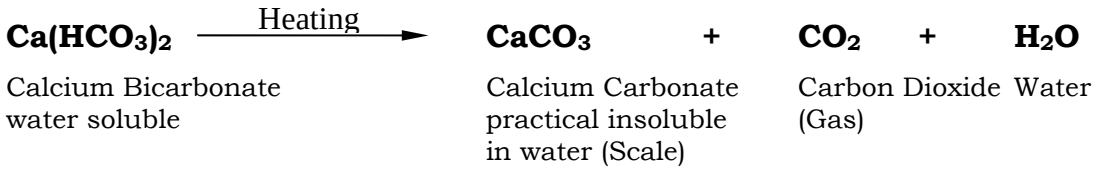
- Aroma and flavor neutrality (the character of the distillate must not be influenced in any way)

- lowest possible content of hardness forming components such as calcium and magnesium (these can lead to undesired precipitation)

The use of freshly distilled water is best; but for reasons of costs (energy consumption) water softening methods are employed. In principle, rain water is excellently suited for this application assuming it is free of any contaminants (air pollution!), but the challenge of its collection makes it less than a practical alternative. Use of spring or natural waters should be approached with care and based on their mineral content. The treatment with ion exchangers for softening has proven successful in practice. The amount of water needed for the reduction to a certain alcohol grade strength can easily be determined using tables.

Constituents of Tap Water

If spring water or tap water is heated, insoluble substances precipitate at temperatures above 60 °C which adhere to the surfaces of the heating containers and pipes ('scale'). The main constituent is lime (calcium carbonate, $CaCO_3$). In addition small amounts of magnesium carbonate ($MgCO_3$), gypsum (calcium sulfate, $CaSO_4$), bitter salts (magnesium sulfate, $MgSO_4$) as well as traces of additional salts can be found. These substances arise from the rock layers the water had to pass before reaching an aquifer. These are naturally constituents in water. During the formation of scale the following reaction proceeds:



* In US the minimal alcohol content of most spirits has to be 40 % vol.

Methods of Water Softening

Only very soft water should be used for dilution to drinking strength. Several methods exist in practice to remove mineral constituents from tap water. A full de-ionization as possible through distillation or combined application of cation and anion exchangers is not required for the purposes of fruit distillation. For the usage as blend water the removal of the hardness-forming substances calcium and magnesium (partial desalination) is sufficient. In case the cooling water needs softening (with medium cooling capacity of the distillation device the cooling water outflow can easily achieve temperatures of 60-65 °C) sodium polyphosphate (approx. 1-2 g/m^3) can be added using a dispensing pump. This method does not remove the hardness-forming substances, but transforms them into a water soluble form for temperatures of even 65 °C such that lime deposit in the cooler does not occur. It is very safe and it often used in drinking water systems in of municipal water supplies.

Determination of Blend Water Amount

If alcohol and water are mixed in arbitrary amounts the volume of the mixture is smaller than the sum of the individual volumes. This phenomenon is called contraction* and for this reason the determination of the required blend water amount makes use of tables (Gauging Manual in the US). Calculations would give an inaccurate result would.

For spirit strengths not listed in the table the required amount of blend water can be obtained through interpolation. It is generally recommended to proceed with the blending using a somewhat smaller amount in blend water and to carry out a fine correction after a renewed determination of the alcohol content. It is important to mix the liquids thoroughly and to consider the measured temperature. Occasionally a partial reduction with intermediate storage is carried out.

Cool Storage

Even with the use of completely softened blend water turbidity can occur in reduced distillates. The reason is the lower solubility of certain ingredients, e. g. terpenes, at a lower alcohol concentration. The solubility diminishes with decreasing temperature and the reduced distillates are subjected to a cool storage for some time. In this way the turbidity-forming constituents can mostly be precipitated and separated through subsequent filtration. A cloudiness in the bottle should not occur, assuming of course, that this bottle is not stored at even lower temperatures.

* The contraction is largest if approximately equal volume portions of alcohol and water are mixed.

Storage temperatures between 0 and -10 °C have proven suitable in practice for the precipitation of turbidity. A storage time of approx. 14 days has to be considered for a storage temperature of 0 °C whereas at -10 °C only half the time is required. Even lower temperatures are not recommended because the distillates become more viscous which complicates the filtration if it does not become entirely impossible. Using cooling temperatures above the freezing point does not guarantee a complete precipitation in all cases. It is important that the filtration following the cool storage is done at the same temperature because a renewed heating would otherwise cause the precipitated particles to dissolve again. For the cooling of small amounts of brandy the containers (e.g. glass carboy) are best stored in a freezer.

Filtration

Funnel filters and cylinder filters as well as layered filter with hand pumps have proven suitable for the filtration of small amounts of spirits.

Funnel filters use pleated filters with different porosities. Their performance is better the more filter area can be used.

Distillates with a high content in natural oils such as juniper brandies, Bartlett pear brandies or herbal brandies are preferably adjusted to approx. 5 % vol. below drink strength before the cool storage. After the filtration at the cool storage temperature the alcohol content is increased using the same well-rectified distillate used as the base.

Bottling

The bottling of the completed brandies does usually not pose any difficulties. As with all beverages only impeccably clean, well rinsed bottles are to be used (dishwater has to be removed!). No danger of microbial infections is present due to the high alcohol content but mechanical impurities such as dust or glass splinters are easy recognized in the clear, colorless distillates. This means that even brand-new bottles delivered direct from the manufacturer should be checked for impurities and eventually be flushed and blown out. The bottling process and the closing of the bottles can naturally be done in a manual way for small producers. In the easiest case a simple outflow apparatus for bottom broaching consisting of a hose and squeeze clamp suffices. For top broaching a siphon with a manual pump is suited.

For small-sized and medium-sized companies a variety of semi-automatic bottling machines are commercially available with which, despite their

simplicity, respectable capacities of several hundred bottles per hour can be achieved. Similar equipment exists for the capping of the bottles, for example with twist caps.

Preservation of Marinated Fruit

Brandies which contain the entire fruit according to their flavor are considered popular specialties (e.g. Bartlett pears, apples). Often they are grown into the bottle directly on the tree. However, at alcohol concentration around 40 % vol. the preservation of those fruit is not guaranteed; the appearance of brown spots can be expected.

A somewhat higher alcohol concentration normally extends the durability (approx. 45 % vol.). In addition the following measures have proven useful:

- Bottles with grown fruit should be filled with sulfuric acid (1%) and left standing for one hour
- Fruit should be flushed extensively with softened water; drain well
- Add 1 g ascorbic acid (vitamin C)/l to the brandy and mix until dissolved
- Fill brandy into bottles (fruit has to be entirely immersed)
- Evacuate bottles before closing briefly (e.g. water jet pump). If air bubbles escape from the fruit ventilate the bottle at once again. Repeat procedure 2-3 times
- Cap bottle in the usual way.

In practice it may happen that the bottle-grown fruit has to be stored for some time before the brandy to be filled in is available. In this case the fruit should be immersed entirely in a solution which contains 10 g citric acid, 1g ascorbic acid and 100 mg SO_2 (= 2 ml SO_2-solution [5 %]) per liter as a preservation-extending measure. In this way the fruit can be stored for at least 6 months without significant quality loss.

FLAWS

General Remarks

There are an uncountable number of spirits which are rejected because of visible inadequacies or shortcomings in aroma and flavor. Among those reasons are not only the actual mistakes but shortcomings like a weak aroma or too little of the typical character. The blame is usually attributed to the raw material or the deliverer even though the causes can be in the processing as well. The importance of the quality of the raw material as a first prerequisite for clean and typical distillates is critical, but practice has shown that faulty spirits can often be traced to errors during mashing, to inadequate fermentation development or unfavorable distillation conditions. Many of these mistakes have already been mentioned in preceding chapters in combination with the corresponding processing steps, but it seems reasonable to summarize them, to address their causes and treatments, and to provide preventive measures to avoid them. Not all mistakes can successfully be eliminated. The use of corresponding treatment agents may show only a partial improvement and in certain cases correction is not possible. The phrase "prevention is the best cure" seems appropriate here.

Visible Mistakes

Cloudiness through Metals

Cloudiness through Hardness-Forming Substances

White flakes or white sediments are to be expected in almost all brandies which have been reduced using hard or incompletely softened well water. These turbidities consist of calcium salts or magnesium salts. It is most often a calcium sulfate (gypsum) precipitation which can be recognized under the microscope by the needle-shaped crystals (Fig. 21). The natural hardness-forming agents of the water are practically insoluble in alcoholic solutions. Unfortunately their precipitation takes place very gradually such that a filtration, even after a brief cool storage, does not offer a guarantee against recurring cloudiness.

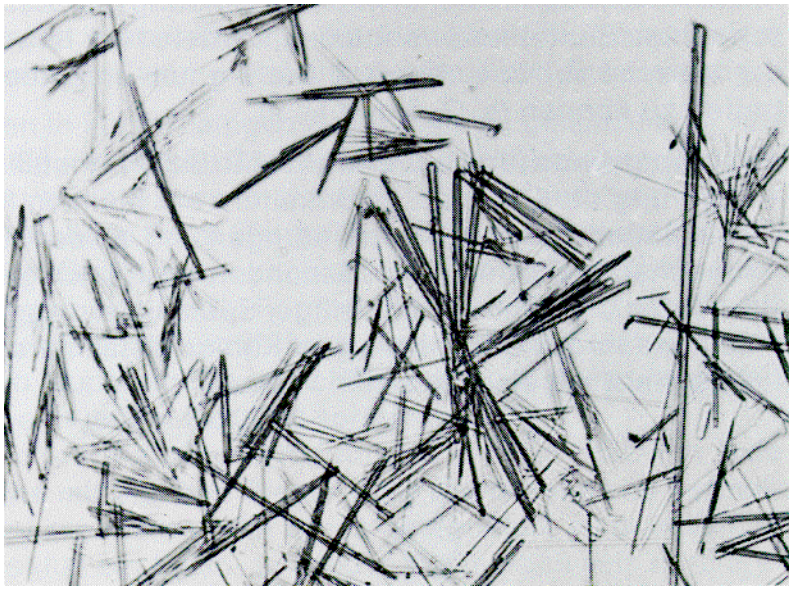


Figure 21. Calcium sulfate crystals (magnification approx. 400x) ***from Tanner and Brunner***

Trouble can be avoided if distilled water or softened water obtained through the treatment with cation exchangers is used for the reduction of the spirits.

The removal of turbidity caused by hardness-forming agents can of course be done through repeated distillation with subsequent reduction using softened water. The treatment with a acid form cation exchange (e.g. Dowex 50 W) after preceding filtration of the cloudy components already precipitated would be easier, though. This method practiced in Switzerland does not affect the aroma and can be carried out analogous to the water softening. The exchange volume to be used is approx. 1% of the volume of the brandy to be treated. In cases of doubt special institutes should be consulted.

Cloudiness through Heavy Metals

These mistakes appear in different forms which could be slight discoloration, but also heavy cloudiness. In contrast to the always white precipitation caused by hardness-forming agents, the cloudiness from heavy metals occurs in different colors. Originally clear, colorless distillates can change color and become turbid with color changes if corresponding storage conditions are given (contact with light or oxygen). All these observations can be attributed to the presence of the heavy metals copper and iron which form combinations with various partner constituents which are difficult to dissolve. Higher amounts of heavy metals also affect taste. In the first place, care should be taken that no heavy metals end up in the distillate. A higher concentration of the partner constituents (above all acetic acid and sulfuric acid) should be avoided as well.

The main reasons for the undesired presence of heavy metals are:

- Storage of the distillates in containers with exposed copper or iron parts.
- Distillation in stills with poorly tinplated copper coolers or damaged iron coolers. Acetic mashes or mashes with higher contents in sulfuric acid cause aggressive vapors which can dissolve metal during the condensation in the cooler.
- Blending with iron-containing water.

Iron cloudiness is often formed only through intense contact with air through which the spongy, amorphous precipitates gradually take on a brown color. The black combinations of iron/tanning material give the distillate an unsightly color whether they are present in dissolved or undissolved form. Besides the iron, the presence of tanning material which ends up in the distillate through the storage in oak barrels (brandy, marc) is required. Similar effects occur during storage of clear brandies which are closed with a cork. Through the pressing of the cork plug, tanning material contained in the plug is released and leads to the same appearance in the presence of iron.

In distillates containing copper the influence of light and the presence of sulfuric acid produce reddish copper-sulfite precipitations. Their formation is reversible, i.e. they disappear in the dark but can reappear again into the insoluble form after a short exposure to light. In distillates from sour, acetic mashes a blue or blue-green cloudiness can be observed, partly in form of small pellets which can be attributed to copper/fatty acid combinations. In a first phase the formation of copper acetate sets in after which the decomposition to higher fatty acids occurs which are present in all distillates.

Any contact between the brandy and open iron or copper parts is to be avoided to prevent heavy metal precipitations. Damaged devices should be repaired or replaced by more appropriate ones. In cases of doubt the distillate should be examined with respect to the presence of iron and/or copper.

Two methods are available for the treatment of heavy metal cloudiness:
- Additional distillation of the brandy using an appropriate facility, if necessary after preceding neutralization of the major portion of acids. The salt precipitations remain in the distillation residuum.
- Treatment with cation exchanger.

Cloudiness caused by Natural Oils, Fusel Oils and Terpenes

In contrast to the turbidity caused by metals, cloudiness is caused through precipitations of natural constituents of the distillates. They appear at the time of the reduction of the high-proof brandies and can be formed even after prolonged cool storage.

Natural oils are mixtures of combinations with various chemical compositions which participate in the aroma formation of the unfermented fruit. There they can be found together with terpenes, fats and waxes. Pure natural oils are easily soluble in high-proof alcohols, but rather insoluble in diluted distillates. In the case of relatively high amounts of terpenes (this is very pronounced in citrus fruit products), fats and waxes the precipitations during reduction of the alcohol content may be unavoidable. These components can be found especially in juniper, Bartlett pear, kirsch, yeast and herbal brandies.

Fusel oils are side products of the alcoholic fermentation. The higher alcohols consisting of amino acids belong to this group; but also higher fatty acids and their esters are inlcuded. The boiling temperatures of higher alcohols are above those of ethyl alcohol (78.3 °C); however, with common stills and due its volatility, a major portion of the fusel oil ends up in the distillate and can only be concentrated partially in the afterrun. Because of its poor solubility in water the fusel oils lead to precipitations during the reduction of spirit proof and can cause a bitter harsh aftertaste.

Terpenes are accompanying substances of natural oils. They primarily consist of chained or ring-shaped hydrocarbons and their oxygen derivatives. In plants they have the task to enclose the natural oils and thus prevent their early evaporation. One of the best known terpenes is limonene, which is the distinctive citrus aroma that is present as an oily compound in all citrus peels. Through the influence of sunlight, oxygen and light terpenes are easily converted into resinous products which possess an unpleasant and rancid smell. They are practically insoluble in low-proof alcohol and therefore always cause cloudiness. A special property of terpenes is the fact that in the cold they lead to precipitations which disappear again during heating.

Natural oils and terpenes are easily distinguished from each other. The former show the formation of oil droplets which conglomerate on the surface whereas terpenes can be recognized by their bluish-milky opalescence.

Raw brandies/spirits inclined towards the cloudiness described above are reduced using de-hardened water to a drinkable level and stored in a cool place for a week. With special fining agents whose type and amount has to be determined in by experiments the precipitations can be separated. The following list contains some proven fining agents:

Fining Agent	**Dosage (Guideline)**
Magnesium oxide	100-1000 g/hl

Kieselgur*	200-300 g/hl
Bentonite	150 g/hl

The fining process is done in such a way that the ingredients are mixed with a few liters of brandy and added before the filtration to the cool main lot. After the mixing the clear filtration can be done.

Discoloration

Besides the discoloration caused by heavy metals which often is a pre-stage of turbidity sometimes undesired discoloration can occur due to the storage in wooden barrels. These are best eliminated through additional distillation after a preceding reduction of the distillates with clean well-water to 20-30 % vol.. A carbon fining with 10-20 g color carbon, e.g. Clarocarbon F or Granucol FA, should only be done if preliminary experiments show that the required amount of carbon for the decolorization does not cause any significant aroma loss. A certain impairment is, however, hardly avoidable even if the contact with the fining agents is limited to approx. 1 day.

Aroma and Flavor Mistakes

Microbial Mistakes

Odor and flavor mistakes are often encountered in distillates and can be traced back to faulty fermentations, i.e. an undesired micobial activity. Products inducts inlcuding acetic acid, butyric acid or acrolein reduce the quality and can spoil a distillate completely if present in larger amounts and require it's use only as a neutral spirit.

Film-forming yeast can be found in any mash. Since they need oxygen they reproduce only after the fermentation, they can be recognized as a connected skin film on the mash surface. The main disadvantage is that they decompose a number of organic substances, among them also the ethyl alcohol such that the yield is reduced. Single types of film-forming yeasts are also capable of converting sugar and acids into the rancid-smelling butyric acid. Remedy: Use a fermentation top, keep containers full and airtight after fermentation.

Wild yeasts are also found in every mash. Besides their poor fermentation capabilities (which is entirely suppressed at 5-6 % vol. alcohol) they produce higher amounts of volatile acids; they are moreover incapable of fermenting cane sugar (sucrose) because they lack the necessary enzyme. Remedy: Pure yeast fermentation and heavy innoculation.

* to be moistened before usage

Mold can be recognized through the formation of a white, green or black spot on the mash surface. They can be encountered even more often in damp basements and empty, poorly cleaned wooden barrels and hoses. In recent times some poisonous metabolic products of some types of mold have been observed, e.g., aflatoxins. Remedy: Use suitable raw material, thoroughly clean the mash container, disinfect if necessary and keep full after completed fermentation.

Acetobacters are well known as undesired inhabitants of fruit and grape wines. Whereas they can be kept at bay during the production by means of an adequate sulfuration, they find ideal nutritional grounds in fruit and berry mashes which are low in acids. The acetobacters convert the mash alcohol into acetic acid, which is the traditional vinegar producing process. Air (oxygen) and heat accelerate this process. Therefore, in practice, acetic mashes lead to alcohol losses. For example, a cherry mash containing 10 g/l volatile acid will reduce the alcohol content by nearly 1 % vol. in comparison to the equivalent healthy mash. Remedy: Exclusion of air (oxygen), full containers after completed fermentation, cool storage of the mash between fermentation end and distillation, acidification.

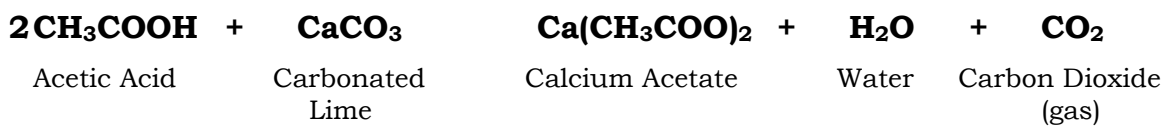
Lactic acid bacteria take part in various spontaneous processes occurring in nature. Whereas their activity is desired for the fermentation of sauerkraut, the production of silages or the production of specialty cheeses due to the formation of specific secondary products, certain types can cause extensive damage in the distillation business. During the fermentation glucose and other types of sugars are decomposed into lactic acid, but also into other undesired components such as acetic acid and malic acid. According to *Schwarz* and *Malsch* up to 17 g lactic acid, 5.6 g acetic acid and 30 g malic acid per liter have been found in cherry mashes. Besides the inevitable alcohol loss the mashes affected by lactic acid cause a sensitive quality loss for their distillates. A complicating fact for the fight against mashes touched by lactic acid is that lactic acid bacteria - in contrast to acetobacters - do not require air oxygen such that even in entirely full containers which are moreover equipped with a fermentation top the decomposition can proceed. Heat and low acid content favor the activity of lactic acid bacteria also. The same applies to the butyric acid bacteria which primarily form butyric acid but only play a minor role due to their relative sensitivity to acids. Bacteria can transform glycerin into acrolein which irritates the mucous membrane. This substance first combines with tanning agents in the fruit to a bitter substance. For this reason it is recognized in the mash as a bitter agent and not as irritating substance.

In summary, undesired bacteria activity can be counteracted with the following measures:
- use clean and washed raw materials (no hail-damaged fruit or drip juice)
- acidify mashes
- use fermentation lids
- fill containers after completion of the fermentation
- store containers in a cool place.

Acetic Effects

Distillates with a "pure" acetic touch are hardly encountered in practice since acetic acid (volatile acid) usually continues the reaction with alcohol to a partial ester formation. For a limited extent the ester formation is desired and even essential for the achievement of a well-balanced aroma. Distillates with an excessive amount of volatile acid and ester can be recognized by their pungent, solvent-type smell ("nail polish remover") and their pungent, sour taste. In easy cases (only slightly higher amounts of volatile acids) the distillate can be subjected after the strength reduction to a fining with magnesium oxide or basic magnesium carbonate in the amount of 300-500 g/hl. After 6 hours (occasional stirring is recommended) it is removed from the turbid residue.

Mashes with an acetic touch as often encountered in cherries are best subjected to a neutralization before distillation. The easiest method is to add carbonated lime (calcium carbonate) to the mash. This is mixed with water to a thin mush and then added to the mash. Released carbon dioxide escapes under strong effervescence and foaming until acids are present in the mash during this process. The neutralization of acetic acid is mentioned as example.



An over neutralization is usually not a problem. As a rule of thumb it can be said that for the neutralization of 10 g of total acid/l (calculated for malic acid) 700 g of carbonated lime are required per 100 l mash. In doubt, a determination of the titrateable total amount of acid can be done. If the equipment for the exact determination of the total amount of acid is not available it is possible to add carbonated lime to the mash until effervescence is observed. Care should be taken that the neutralization container is filled to only approx. 70 % in order to avoid losses through the effervescence. Too strong of an effervescence can be

suppressed through the addition of silicon anti-foam (approx. 3 ml/hl mash).

In another neutralization method the acids present are neutralized with 90 % with slaked lime (calcium hydroxide) (pH 5.6-5.8). Because this is a "stronger" agent special care has to be taken in order to avoid an over neutralization. Distillation should proceed immediately after the neutralization (danger of formation of acrolein!).

Increased Ester Content

The cause for increased ester content is always a tinged mash whose neutralization before the distillation has been omitted. In this way an excessive amount of volatile acid (acetic acid) ends up in the distillate which is partially converted with ethyl alcohol which is present in a surplus anyway. The ethyl acetate is therefore not the direct product of bacterial activity. For the treatment of these faulty distillates the point that esterifications take place in the alkaline range, i.e. with excessive amount of bases, and are thus reversible, is used. This means that the produced ester is transformed back into the original constituents (alcohol and acid). After a partial neutralization of the acid the distillation can be initiated. An operational procedure for the treatment of 50-65 % kirsch is given at this point because excessive amounts of ester are found often in cherry brandies. Under consideration of the equivalent ester content this procedure can be transferred also to other distillates.

Principle Procedure

Depending on the ester content 20% or more of the faulty distillate are adjusted with a base to pH 5.6-5.8, distilled separately and afterwards mixed with the main stock. After the dilution the main stock is entirely neutralized and mixed with an excess amount of sodium bicarbonate base. Through heating to 75 °C for 2 hours the ester splitting is achieved. After acidification to a pH of 5.6-5.8 the distillation can proceed normally.

Butyric Acid Tinge

Pulp and mashes from Bartlett pears with a tinge occur in warm weather and with high pH-values (low acid content). The brandies thus obtained possess smell and taste of rancid butter which can be attributed to butyric acid, valeric acid, caproic acid or their esters. The recovery of those distillates is often associated with great difficulties. A preventive mash acidification can provide sufficient protection.

Distillates with a significant butyric acid flaw are to be mixed with 500 g slaked lime (calcium hydroxide) per hl, diluted to approx. 20 % vol. with well water and boiled for 1 hour in the still at the reflux pipe (i.e. without withdrawing distillate). The cooling water in the intensification unit should be running at maximum; in addition the still top should be

watered. After cooling down the pH is adjusted to 6.5 with phosphoric acid (15 %) after which the distillation can proceed normally under separation of the forerun (heads) and the after run. According to experience the resulting distillates should be free of undesired components, but are neutral with regard to aroma and flavor such that during blending they have to be mixed.

Lactic Acid Tinge

Even though the lactic acid produced by undesired micro-organisms remains in the mash or juice while distilling the brandies are unfavorably affected. Volatile side products of the lactic acid such as e.g. acetic acid are formed simultaneously as well as volatile esters. A possible treatment would the ester decomposition with proceeding distillation through which also here a more or less neutral distillate would result which had to be blended in a suitable way.

Acrolein Tinge

If bitter mashes or juices are distilled, the bitter tanning agent/acrolein complex is decomposed again into the tanning agent and acrolein where the latter appears in all distillation fractions despite its low boiling point (53 °C) and can only be incompletely separated as forerun (heads). The aggressive, mucous membrane-irritating effect of this tear gas-like substance forced many a distiller to leave the room. This mistake is caused by bitter bacteria and can occur in most brandies. Acrolein-tinged Bartlett pear brandies, must fruit brandies and berry brandies are well-known examples which can be traced back to unclean and soil-covered raw material. In most cases the bitter bacteria are accompanied by a variety of other undesired micro-organisms such that other brandy flaws occur.

Before distillation of suspicious mashes it is recommended to investigate through trial experiments (test distillation, aroma check) whether an acrolein-tinged distillate is to be expected. If necessary the service of a specialized laboratory may be consulted. According to *Rüdiger* the over-distillation of acrolein can be reduced significantly through the addition of 1 kg calcium hydroxide/hl mash. Unfortunately, the distillate will be affected by this massive intervention (basic flavor); even a proceeding carbon treatment does not yield satisfactory results. The best way is to process acrolein-suspicious mashes after the fermentation under the separation of an especially large forerun (heads) to coarse spirits. After immediate reduction to approx. 25 % vol. and addition of a little sodium bicarbonate base up to a pH of 6.5 the fine spirit distillation can be initiated. The distillate adjusted to drinkable strength is to be stored for 6 months and can only be clarified but not distilled anymore. Acrolein has the tendency to polymerize during the course of storage such that its

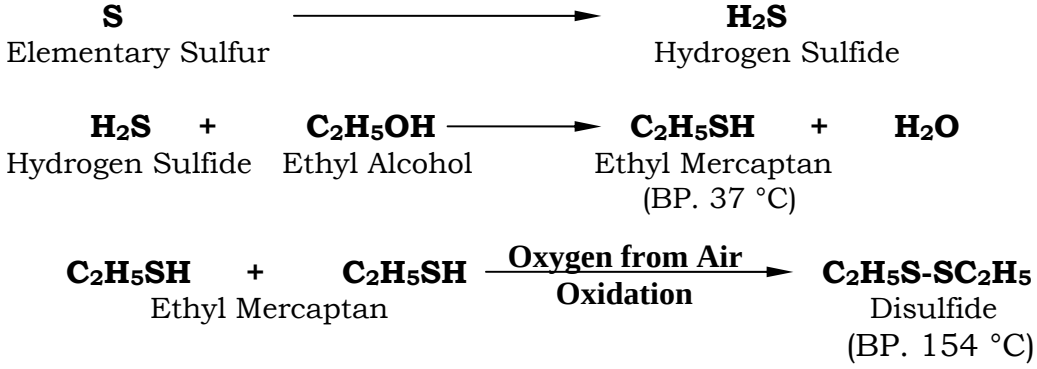
undesired irritating effect gradually disappears. It should be emphasized that once acrolein is present in the distillate it can hardly be removed entirely without affecting the quality.

A possible treatment for acrolein-tinged fine spirits is to add 400 g slaked lime (calcium hydroxide) per hl and to dilute with water to 20-30 % vol. After 24 hours a filtration is done, phosphoric acid (15 %) is added (see 3.1.2) to a pH of 6.5 and the distillation is initiated under separation of forerun (heads) and after run.

Rank-Tasting Wine

Odors and flavors like rotten eggs is often encountered with lees brandies, yeast brandies, and pulp brandies. The reason for this quality reduction is the production of hydrogen sulfide (H_2S) during the fermentation. This unpleasant smelling gas is produced mainly through the reduction of elementary sulfur or the decomposition of yeast proteins (a long storage period favors the H_2S-formation). If wooden barrels are used care has to be taken that non-dripping sulfur bars are used for the sulfuration; the barrels have to be dry. Under no circumstances should elementary sulfur be allowed to drip or to condense at the barrel walls due to incomplete burning.

During the course of the distillation the highly volatile hydrogen sulfide ends up in the distillate where it converts with ethyl alcohol to ethyl mercaptan which develops an even more unpleasant smell and influences the bouquet in even small amounts. Through ventilation of the distillates the ethyl mercaptan is converted to the likewise unpleasantly smelling, non-volatile disulfide. The formation of hydrogen sulfide combinations and mercaptan combinations can be stated as follows:



The best approach for an improvement could be achieved using a silver-chloride-containing agent (Ercofid, Sulfidex) in the amount of approx. 100 g/hl. The contact time with the insoluble powder is 3-10 days; the brandy has to be stirred every once in a while. After the treatment the distillate has to be clarified through filtration. The occurrence of

mercaptan can be avoided if the distillation of the mashes is done in devices entirely made of copper. As an alternative or if mashes or juices with a high hydrogen sulfide content are present it is recommended to pour over 1 liter copper sulfate (10%) per 400-liter-still. The fact that hydrogen sulfide is converted to non-volatile copper sulfide can be attributed to the presence of copper or copper ions.

Non-Microbial Mistakes

Metallic Flavor

The causes for metallic tastes in distillates have been described during the discussion of turbidity. At this point it is mentioned again that the recovery requires additional distillation or a treatment with ion-exchange. In cases of doubt a determination of the presence of copper or iron can be done. The undesired presence of aluminum or zinc may also lead to impairments with respect to taste (5 mg aluminum/l already cause a bitter taste).

Pit Flavor

A pit flavor can be found in many distillates. It may even cover the actual bouquet. The cause is an excessive damage of the stones. During this crushing of stones amygdalin is released which is enzymatically transformed into glucose, benzaldehyde and the poisonous hydrogen cyanide. The two latter components are volatile and are the aroma and flavor of bitter almonds. An immediate distillation of the fermented mash helps to suppress the bitter almond taste. Slightly higher amounts of benzaldehyde can be remedied through the addition of little amounts of sulfuric acid (50 ml (5%) per 100 l distillate, formation of an odor-neutral addition product). Addition of silver nitrate in the amount of 10 g per 100 l distillate causes hydrogen cyanide to precipitate as insoluble silver cyanide. After filtration of the precipitation the distillate can be distilled again.

Herbal Taste

This mistake is attributed to the processing of stems and leaves or too strong a pulping (formation of hexanol). It primarily occurs in cherry and juniper distillates. A treatment with activated carbon (20-100 g per hl; carry out preliminary tests!) a partial improvement can be obtained. The contact with the carbon should be limited to 24 hours.

Burnt Taste

With direct heating of stills local overheating (burning) can occur especially for highly viscous mashes as well as pulps. The decomposition products of sugar thus created (e.g. furfural) give a burnt, bitter taste to

the distillate which can hardly be removed. An activated-carbon treatment can still lead to a partial improvement of the product.

Odor and Taste of Sulfuric Acid

The odor and taste of sulfuric acid occurs primarily with the distillation of juices and wines treated strongly with SO_2. SO_2-containing distillates can be entirely recovered after repeated distillation with preceding neutralization. The distillate is first reduced to 20-30 % vol. and then adjusted to a pH of 5.6-5.8 using sodium bicarbonate base (15 %). Strongly sulfured juices are treated in a similar way. With these the pH is to be adjusted to 5.6-5.8 immediately before distillation.

Mistakes in the Forerun (heads) and Afterrun (tails)

Tastes from the forerun (heads) or a taste like fusel oil in the afterrun (tails) can be traced back to an inappropriate operation of the distillation device: regardless of the condition of the mashes to be processed the same amounts of forerun (heads) and afterrun (tails) are to be cut. Experienced distillers, however, know that every preparation in the still has its specific characteristics. Thus, for exceptional mashes the amount of the forerun (heads) can be reduced or even entirely omitted whereas for pungent-smelling mashes (acrolein, aldehydes, ethyl acetate etc.) the switching to the middle run (hearts) occurs at a later point. Only an organoleptic surveillance will lead to flawless distillates. The safest way to recover those faulty distillates is a repeated distillation after preceding reduction to a drinkable strength during which the moment for the switch to middle run (hearts) or after run has to be determined through simultaneous tasting of the resulting distillate.

Other Mistakes and Drawbacks

Besides the mistakes already mentioned there are some other ones which are, however, generally not frequently encountered in the practice of distillation. Their causes have been determined in the rarest cases; a suitable method for improvement can likewise not be recommended in all cases. Extensive finings with carbon or magnesium oxide (1-2 kg/hl) are also not always successful, not even if losses in the bouquet are accepted. If preliminary fining experiments or a repeated distillation of those faulty distillates do not lead to the desired improvement only the collaboration with a specialty laboratory could lead to a solution. The transport or storage of mashes and brandies in unsuited or unclean containers cause some degree of touch which reminds in odor and flavor in components of tar, petroleum, plastic or mold. In this context it should be remembered that not every container material which may be suited for the storage of mashes is likewise suited for the storage of high-proof distillates. The contact with hoses not approved for food (transport of spirits in bars) also causes considerable damage (extreme bitter

aftertaste). Distillates low in aroma are not only the result of the use of unripe fruit; an inappropriate fermentation process, acid contents and/or enzyme doses which are too high, and intense cooling can lead to those drawbacks.

PROCESS CONTROL

General Remarks

The monitoring of the production process is also very important in small-scale enterprises. Besides the judgment through tasting that gives the distiller information about quality, analytical examination of mashes and distillates should also be considered. In light of the fact that very few small distilleries have adequate specialty knowledge or laboratories at their disposal, analytical process control is usually kept in limits. Specialized dealers provide measurement equipment and testing utensils which can be used to comply with the most important regulations. Among them are

- Determination of TDSs in mashes and musts
- Determination of alcohol content in mashes, musts and distillates
- Determination of the pH-values of mashes, musts and distillates

With extra expenditure the interested distiller can carry out additional necessary analyses according to the specific task at hand, for example,

- Determination of titratable total acid content in mashes, musts and distillates
- Determination of sulfuric acid content in spirits and distillates
- Determination of esters in distillates
- Proof of heavy metals (iron, copper, zinc) in distillates

These tests can be done also in specialized laboratories. These laboratories are moreover in the position to detect additional constituents like aldehydes, acroleins, methanol, fusel oil etc. using more sophisticated methods (e.g. HPLC, gas chromatography (GC), GC with mass spectrometric detection (GC/MS)).

Once a measurement result is available it is crucial to interpret the results correctly. The TDS content of the unfermented musts and mash filtrates allows estimates of the sugar content as well as the expectable alcohol yield. Estimates from experience are of great use for the assessment of the raw materials delivered.

Sampling and Sample Preparation

Analytical tests are always performed on a small fraction of the lot to be tested. Whereas, for example, the TDS determination requires a

sampling volume of approximately 200 ml a few drops suffice for the determination using a refractometer. For this reason care is to be taken that the sampled probe truly constitutes an average representation. There is usually no problems to be expected with distillates (thorough mixing is required, though, after addition of blend water). Mashes have to be more carefully sampled to obtain a ratio of juice and solids representative of the fermentation container which it was taken from.

Due its solid content mashes cannot be examined directly because the measurements would yield a false representation or are even completely impossible. The sampled probe (approx. 0.5-1 liter) has to be filtered first and entire fruits (e.g. cherries, plums) may still have to be crushed. The filtrate ought to be as clear as possible; the first turbid portions should be returned into the filter. Eventually the filtration has to be repeated. The resulting almost clear filtrate can be used for the various tests (see following sections).

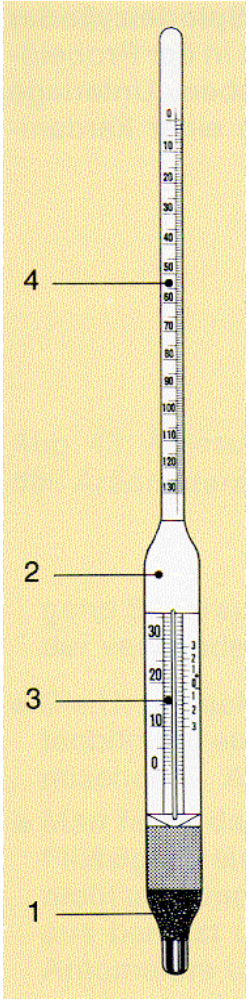
Funnel filters have proven to be reliable for the filtration of mashes, for example the so-called Fix-Filters which are equipped with folded filter made from paper and are also used for the filtration of brandies can hold about 2 l of substance.

Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) designates all soluble substances which do not evaporate. Among them are sugar, acids, mineral agents, and protein-like substances. The content of the TDSs poses an indispensable basis for judgments of unfermented as well as fermented mashes and musts. It can easily be determined using an hydrometer or refractometer.

Hydrometry

A hydrometer consists of a hollow glass body with a floating container at the bottom which is equipped with a small tube containing a measuring scale (see Figure 22).



More precise hydrometers are equipped with an additional thermometer in the lower part. In order to conduct a measurement the hydrometer has to be immersed into the liquid which is to be sampled. According to the TDS content it will sink more or less deep into the liquid because a body apparently looses as much weight while immersed in a liquid as the displaced fluid (Archimedes principle). In a liquid low in TDS, i.e. a lower specific gravity liquid, the hydrometer sinks more deeply than in a liquid rich in TDS. Because the volume expansion of liquid is closely associated with the temperature the hydrometric measurement has to be related to a norm temperature (or reference temperature).

Figure 22. Hydrometer: 1: Ballast, 2: Floating Body, 3: Temperature Scale, 4: Reading Scale (from *Tanner and Brunner*).

A hydrometer cylinder of sufficient height and width is also required for the hydrometry. The hydrometer should be floating freely within the solution.

Points to remember and working instructions

- The hydrometer only yield good results if they are in good condition, clean and free of grease. The instrument ought to be cleaned thoroughly with water after each use.
- The hydrometer ought to be protected against heat and cold, shock and drop. It is also crucial not to drop the hydrometer onto the bottom of the cylinder during immersing.
- The hydrometer cylinders should be kept clean (it is crucial to avoid oil and grease films on the insides). They should be washed thoroughly after use and turned upside down for drying (drying rack).

- The diameter of the hydrometer cylinder has to be much larger than the floating body of the hydrometer so that the instrument has sufficient space.

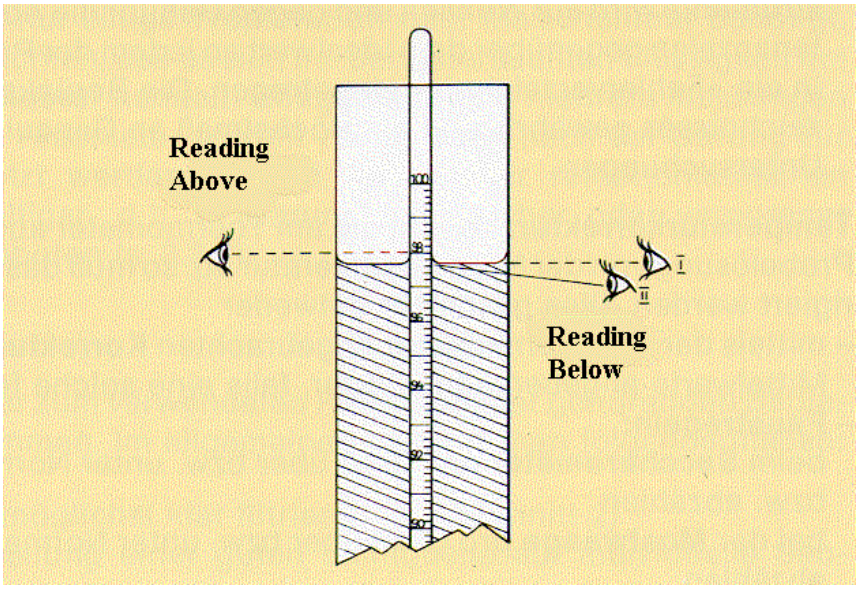


Fig. 23: Reading the display (from Tanner and Brunner)

- The liquid to be examined ought to be free of solids and should not show layer formation. For this reason the liquid should be filtered and well mixed.
- The instrument should be held at the upper portion and inserted carefully into the liquid until it swims freely. Do not let the hydrometer oscillate up and down in the liquid since the top portion might get covered by a liquid film which inadmissibly increases the weight of the hydrometer.
- Air bubbles adhering to the hydrometer influence the accuracy of the measurement. If noticed the hydrometer should be pulled out off the liquid and carefully be reinserted until no air bubbles are visible. A slight rotating motion helps to remove air bubbles.
- The temperature of the liquid to be tested often deviates from the temperature of the hydrometer, especially if the probed sample is retrieved from cold storage rooms into warmer laboratory areas. It is crucial to read the display of the hydrometer after approx. 1-2 minutes after immersing of the instrument. Completely exact measurements are achieved if both the probed sample and the hydrometer achieve room temperature.
- The hydrometer display has to be read correctly. Hydrometers without printed scales are always calibrated for a reading “Reading below”.

Instruments calibrated for “Reading below” have to be designated with the label “Reading below” printed onto the instrument. Figure 23 demonstrates the correct reading of the hydrometer. Two possibilities for “Reading below” are indicated.

- The calibration of a hydrometer represents the official guarantee that deviations within the printed scale can not be larger than one graduation mark. Every hydrometer has its own specific characteristics. The deviation of the instruments with respect to the ideal

Temperature correction: If the temperature of the sample solution read from the thermometer deviates from the norm temperature the result has to be corrected. This can be done using the correction scale attached to the thermometer (which only indicates mean values).

Refractometry

The refractometry is an optical measurement method during which the dependence of the refractive index on the concentration is used to determine the TDS content. Hand-held refractometers (Figure 24) used in practise have a reading scale which uses watery sugar solutions (g sucrose per 100 g solution) as reference very much like the Saccharometer. Measurement devices with a double-scale (sugar-%/must weight) are also widespread. Since the refractive index is moreover temperature dependent the values read off the refractometer scale have to be corrected to incorporate deviations from the NT (20 °C) (see working instructions).

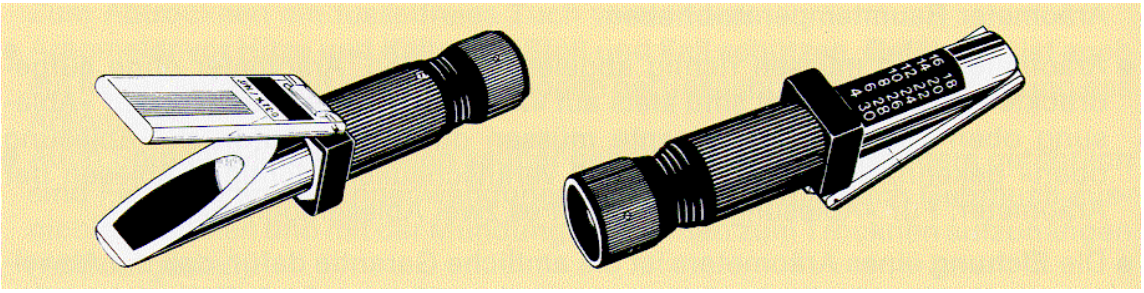


Fig. 24: Hand-held Refractometer (from *Tanner and Brunner*)

For the measurement only a few drops of juice or mash filtrate are required. Therefore, care needs to be taken that the examined liquid represents a good average sample. If necessary several measurements have to be done. Whereas before and after the fermentation hydrometers can be used for the measurements of TDSs the refractometric investigation of alcohol-containing, i.e. fermenting or fermented liquids requires caution.

Operation Procedure

The measurement is done according to the operation manual of the refractometer. In general, the following procedure applies:

- The liquid to be examined ought to be filtered
- Reading scale should be adjusted to the individual vision using sufficiently good light sources
- Open the lid, put 2-3 drops of distilled water onto the measurement surface of the prism, close lid again
- Look at the light source, check zero-base point with the interface bright/dark, correct if necessary
- Open the lid, clean the prism surface carefully with a damp cloth
- Put 2-3 drops of the sample solution onto the surface, close the lid again
- Look at the light source, take readings (interface bright/dark).

Remarks

1. In order to obtain an interface rich in contrast weakly colored solutions are to be measured using transmitted light whereas strongly colored solutions are measured using reflected light. This is done depending on the individual instrument by rotating the refractometer along its optical axis by 180 °C or through the use of special openings for light entrance.
2. After every measurement the measurement surface of the prism and the lower surface of the lid should be cleaned and dried thoroughly with a damp, non-scratching cloth. In order to avoid scratches which could render the instrument useless any contact of the glass parts with hard objects should be avoided.
3. The refractometer should not be cleaned under running water or immersed into water because penetrating water could damage the instrument.
4. The refractometer should be stored in dry condition and well cleaned at room temperature.

Temperature Correction: as rule of thumb it should be remembered that for measurements which deviate from the norm temperature 0.07 % has to be added and 0.06 % has to be subtracted per degree above or below 20 °C, respectively. More exact corrections can be done using special corrections tables in which moreover the different concentrations are considered. An excerpt of such a table which covers the range commonly encountered in fruit distillation is given in Table 5:

Table 5: Temperature correction for refractometric TDS determination

Temperature	TDS Concentration Range			
+ °C	5 %	10 %	15 %	20 %
5	-0.75	-0.80	-0.85	-0.90
6	-0.71	-0.76	-0.80	-0.85
7	-0.67	-0.72	-0.75	-0.79
8	-0.63	-0.67	-0.71	-0.74
9	-0.58	-0.62	-0.66	-0.68
10	-0.54	-0.58	-0.61	-0.64
11	-0.49	-0.53	-0.55	-0.58
12	-0.45	-0.48	-.050	-0.52
13	-0.40	-.042	-0.44	-0.46
14	-0.35	-0.37	-0.39	-0.40
15	-0.29	-0.31	-0.33	-0.34
16	-0.24	-0.25	-0.26	-0.27
17	-0.18	-0.19	-0.20	-0.21
18	-0.13	-0.13	-0.14	-0.14
19	-0.06	-0.06	-0.07	-0.07
20	**0**	**0**	**0**	**0**
21	+0.07	+0.07	+0.07	+0.07
22	+0.13	+0.14	+0.14	+0.15
23	+0.20	+0.21	+0.22	+0.22
24	+0.27	+0.28	+0.29	+0.30
25	+0.35	+0.36	+0.37	+0.38
26	+0.42	+0.43	+0.44	+0.45
27	+0.50	+0.52	+0.53	+0.54
28	+0.57	+0.60	+0.61	+0.62
29	+0.66	+0.68	+0.69	+0.71
30	+0.74	+0.77	+0.78	+0.79

Interpretation of the Measurements

Unfermented Juices and Mashes

The sugar content of distillery raw materials naturally fluctuate caused by the degree of ripeness as well as factors such as type, climate, vintage and soil conditions. The same applies even more strongly to the TDS contents because the unfermentable TDS portion does not constitute a fixed number. It is, however, possible to indicate fluctuation ranges within which the TDS contents normally reside (Table 5). This facilitates a first judgment for the distiller; in addition he will be able to consult his own experience. Moreover, the expected alcohol content can be determined from the TDS content of unfermented mashes and musts.

Table 5: TDS Contents of unfermented mashes (according to *Pieper, Bruchmann* and *Kolb*).

Raw material	Sugar-%

Apples, Pears	12-17
Bartlett Pears	10-12
Cherries	13-22
Plums ('Zwetschgen')	10-20
Plums	10-15
Raspberries, Blueberries, Blackberries	8-10
Elderberries	8-11

Fermented Juices and Mashes

Due to the conversion of the sugars into the main products alcohol and carbon dioxide the TDS content decreases during the course of the fermentation. The measurable TDS content at the end of the fermentation, also called degree of fermentation, is determined through the content of unfermentable mash constituents. For example, the unfermentable sugar alcohol sorbitol does not increase the TDS content of stone fruit mashes significantly. In cherries with a sorbitol content of approx. 40 g/l this amounts to approx.

Table 6: TDS Contents of fermented Mashes (according to *Pieper*, *Bruchmann & Kolb*, and *Tanner & Brunner*). The values refer to the mash filtrate.

Raw material	TDS %*	
Apples	1-3	(2-6)
Pears	1.5-4	(3-8)
Bartlett Pears	2.5-4	(4-8)
Cherries	3-6	(6-10)
Plums ('Zwetschgen')	2-5	(5-8)
Plums	2-3	
Raspberries, Blueberries, Blackberries	1-2	
Elderberries	3-5	

2 %. With 0.5-1 % the fruit acids also contribute to the degree of fermentation. In Table 6 the fermentation degrees of the most important distillery raw materials are summarized. Larger deviations from these values can be attributed to fermentation hold-ups. In those cases it is recommended to initiate a control for completed fermentation. A determination of the sugar is also a principal possibility. It should be taken into account though that not TDS determined chemically reflects sugar actually present because further unfermentable substances such as, for example, galacturonic acid are registered. More exact results can only be obtained through more sophisticated methods which are suitable for practical purposes.

* Data in brackets are values determined by refractometry. They are, as experience shows, higher than those determined hydrometricly and also less reliable since they strongly depend on the alcohol content.

Alcohol

Beside the TDS determination it is the determination of the alcohol content which assumes a central position for process control. This applies to distillates and distillate fractions as well as for fermented mashes and musts. Among the different methods for determination the hydrometry and refractometry are best suited. If carried out properly they yield sufficiently accurate results despite their simplicity.

The declaration of the alcohol content in practice is mostly done in "volume percents" (common abbreviations % vol. or vol. %), i.e. amount of liter of pure alcohol in 100 l test solution[*] (mash filtrate, must, distillate). Because this value depends on the temperature a reference temperature has to be set. Corresponding measurement devices can not be calibrated anymore. The conversion of volume percent into other volume specifications such as mass percent[**] (abbreviation % mass) or gram per liter (abbreviation g/l) can be done using tables (Gauging Manual).

Hydrometry

Determination in TDS-Free Sample Solution

The previous explanations regarding hydrometry analogously apply here. A direct hydrometric alcohol determination can, however, only be done in TDS-free sample solutions (distillates, distillate fractions). Strictly speaking solutions containing only water and alcohol yield exact results; the influence of commonly encountered accompanying substances such as methanol, esters and higher alcohol are neglected in practice. TDS-containing sample solutions (mashes, must, liqueurs) have to be distilled prior to determination.

Analogously to the TDS determination, an accurate alcohol densitometer has to be equipped with a thermometer so that a temperature correction can be done. Of course, an densitometer only covers part of the volume percent scale (densitometer with a measurement range of 0-100 % vol. and a correspondingly coarse scale, i.e. gradation of 1-2 % vol. are to be used for approximate measurements only). The adjustment of the brandies to a drinkable strength requires precision densitometer.

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[*] Strictly speaking the alcohol **concentration** should refer to a total **volume**.

[**] The designation "mass percent" replaces the earlier designation "weight percent" (wght. %) commonly used.

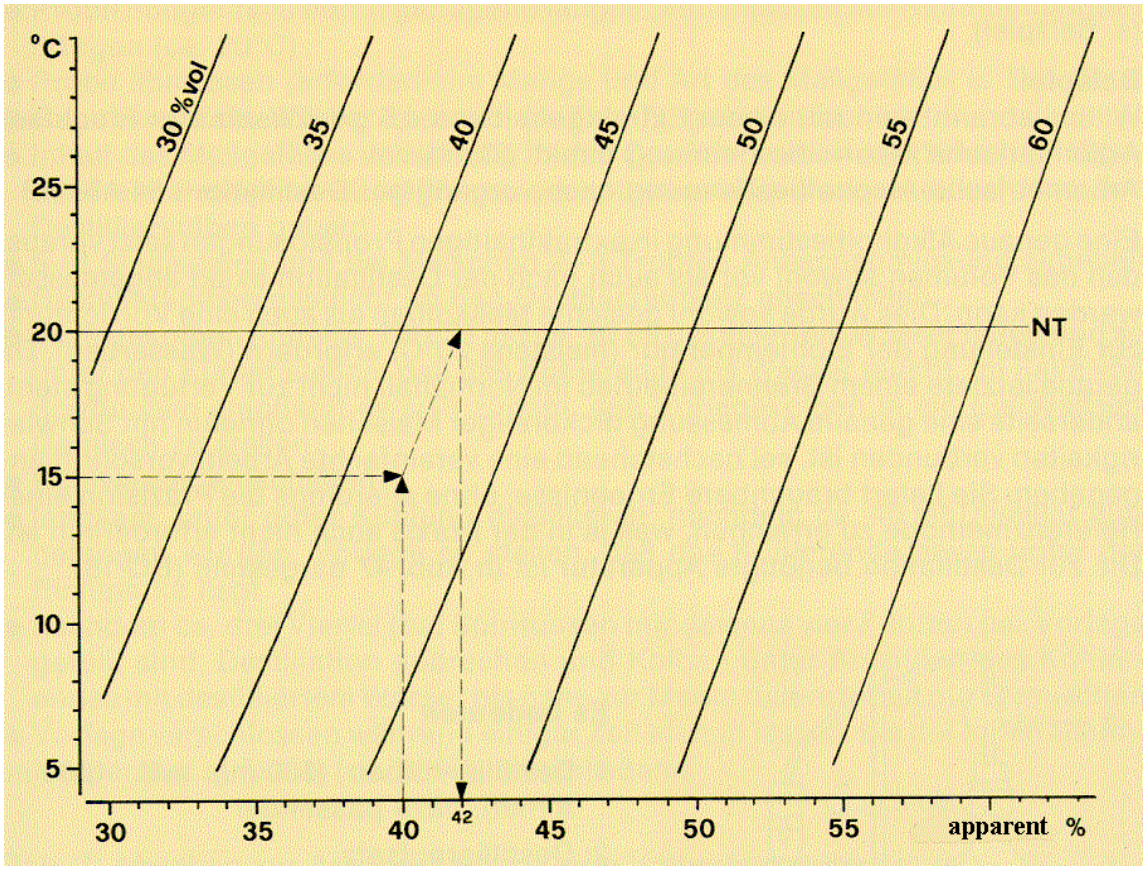

Fig. 26: Dependence of the apparent Alcohol Concentration on the Measurement Temperature (from *Tanner and Brunner*)

For an exact temperature correction the use of temperature correction tables is required. Figure 26 gives a sense of the amount of correction.

Determination in TDS-Containing Sample Solution

In TDS-containing sample solutions the hydrometric alcohol determination is falsified because TDS substances increase the density. This leads to a corresponding lower immersion depth, i.e. to the indication of a lower alcohol content.

For this reason a distillation has to be done before the hydrometric determination. The resulting distillate has to be replenished with distilled water to the original volume. This procedure has to be applied not only for fermented musts and mashes (calculation of alcohol yield) but also for TDS-containing spirits (see example).

An exact alcohol determination in TDS-containing sample solutions requires that the volume can be measured exactly before as well as after the distillation. This requires calibrated graduated flasks as well as an apparatus (water bath) to adjust the calibration temperature (most often 20 °C). Because on the one hand this apparatus is usually not available

in most distilleries and on the other hand the exact measurement of thick-mushy mashes is commonly associated with difficulties anyway the following work instruction provides facilitated working directions. These instructions yield practicable results without the precision of a reference method. The apparatus for the distillation is illustrated in Fig 27.

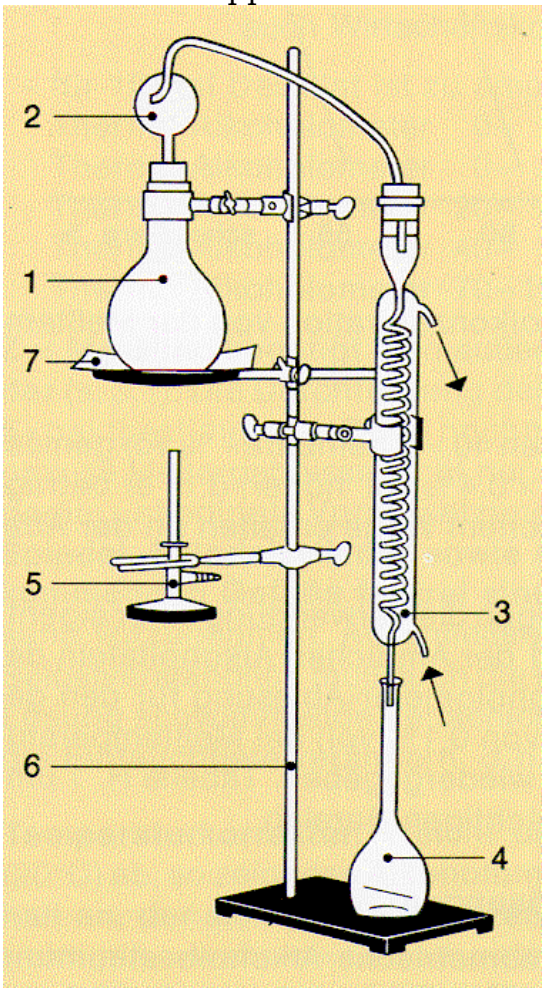

Fig. 27: Distillation Apparatus (from *Tanner and Brunner*)

Legend

1: Still (500 ml, evtl. 1000 ml volume), in addition a suitable
2: Still top
3: Coil cooler (length approx. 25 cm), with inlet and outlet for cooling water
4: Receiver (measurement flask with 200 or 250 ml volume)
5: Gas burner
6: Tripod
7: Flame resistant wire net

Additional material:

Graduated cylinder (Volume 500 ml)
Spray bottle for distilled water
Boiling chips
Silicon anti-foam solution
Densitometer (measurement range according to the sample)
Densitometer, accordingly

Working Instruction

- Obtain an average sample solution
- Let the sample adjust to room temperature, if necessary by letting it stand for a sufficiently long period
- Measure sample (required amount and type of measurement container see Table 8)
- Add water if necessary, mix well
- Pour content of the measurement container into the still (flush measurement container 3 times with 20 ml water and add water every time to the still content)
- Add 5-8 boiling chips and for mashes 2-3 drops anti-foam solution
- Connect still airtight with the still top
- Fill receiving flask (for volume see Table 7) with approx. 10 ml distilled water and place under the cooler such that the cooler end reaches into the water. For spirits it is recommended to put the receiving flask in an ice/water mixture
- Switch on the cooling water
- Distill slowly with good cooling: after approx. 40 ml of distillate have been collected place the receiver in such a way that the cooler end reaches slightly below the calibration mark
- After approx. 3/4 (for spirits at least 4/5) of the receiver is filled stop the distillation and fill the receiver up to the calibration mark with distilled water while simultaneously rinsing the cooler end with this water; mix the content well
- Close receiver and leave standing for a while until the content assumes room temperature (approx. 20 °C), afterwards

Table 7: Supplemental Information for the working Instruction (all volumes in ml)

Sample	Amount to be measured	Measurement Container (Volume)	Water Addition (w/o flushing w.)	Receiver Volume	Yield Factor*
Spirits (TDS-containing)	200	Measurement Flask (200)	-	200	-
Must	300	Graduated Cylinder (500)	-	200	0.67
Thin Mashes	200	Graduated Cylinder (500)	50	200	-
Viscous Mash	200	Graduated Cylinder (500)	150	200	-
Thick mushy Mash	200	Graduated Cylinder (500)	250	250	1.25

* is only required if the sample volume does not coincide with the receiver volume.

- Fill the receiver again up to the calibration mark with distilled water and mix again well
- Pour the distillate into the densitometer and carry out the hydrometric alcohol determination.

Calculation of the Alcohol Yield of Mashes and Musts

a) **Measured sample volume equals the receiver volume:** the determined true alcohol content of the distillate (in % vol.) is equivalent to the alcohol yield in l of pure alcohol per 100 l must or mash.

b) **Measured sample volume does not equal the receiver volume:** the determined true alcohol content multiplied by the yield factor results in the alcohol yield in l of pure alcohol per 100 l must or mash (Table 8).

Table 8. Average Brandy Yield from 100 kg Raw Materials[1](from the statistical statements of the Federal Alcohol Administration 1981/82)

Raw Material	Liter 100 % vol.	Raw Material	Liter 100 % vol.
Apples	4.5-5.4	Cherries	5.6-6.5
Pears	4.1-4.7	'Zwetschgen',	4.8-5.7
Bartlett Pears	3.6-4.1	Greengage	±5.5
Juice, Must	5.0-5.8	Yellow Plum	6.3-7.6
Pomaceous Pulp	3.0-3.5	Apricots	3.6-4.1
Yeast, Must Lees and Must Lees	4.1-4.9	Peaches	±3
Grapes	±9	Juniper (dried)	±12
Wine	9-12	Raspberries	±3
Grape Pulp	3.3-3.8	Blackberries	±3
'Wineresten'	8.1-9.7	Gentian Root Mash	2.2-2.9
Wine Yeasts	5.5-6.6	Pure Gentian Roots	4-4.6[2]

[1] The yield can be higher or smaller than the presented data depending on the year of harvest, quality and origin of the raw material.

[2] Without addition of water.

pH

The pH is as an indicator for the acid character of watery solutions is of importance for the fruit distillation for two reasons. On the one hand the activity of micro organisms such as yeasts and bacteria is pH-dependent and can therefore be promoted or prevented through a change in the pH. On the other hand there is a relationship between the pH-value and the ratio of free/bound acids of a solution. Consider, for example, diluted acetic acid: the solution reacts acidic, i.e. its pH-value is lower as the one of a neutral solution (pH=7, see Fig. 28). It moreover shows the typical aroma of vinegar indicating that acetic acid exists in free form. If the pH-value is increased through the addition of a base the amount of bound acid in the solution also increases. As can be taken from Table 9 acetic acid is bound to more than 99 % at a pH of 7 (neutral point), a fact easily recognized by the vanishing vinegar aroma.

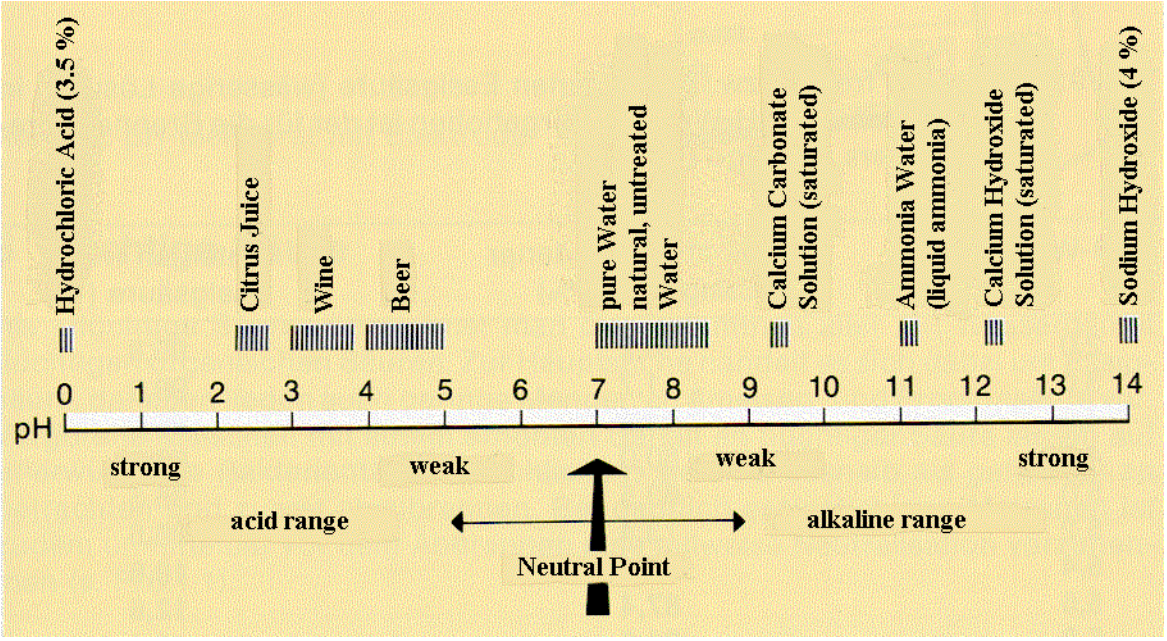

Figure 28. pH-Scale with Examples (from *Tanner and Brunner*)

In practice the distiller has the possibility to treat the mashes or distillates with an increased level in volatile acids (acetic acid, sulfuric acid) before the first or renewed distillation. Thus, the acids are converted into their non-volatile form and can not get into the distillate. A complete neutralization is neither necessary nor recommended because a certain acid content is normally present in brandies (see Table 9). Table 9 shows the dependence of the free and bound amounts of acetic acid on the pH-value.

Determination with Indicators

Indicators are coloring agents which change their color according to the pH-value of the solution in which they are contained. The simplest way is the pH measurement by means of indicator paper or indicator stick made of plastic. These are equipped with an indicator mixture and are to be immersed briefly into the liquid to be examined. Depending on the color they assume as well as some reference colors the pH-value of the solution can be approximated. Indicator sticks with gradations of 0.2-0.3 pH-units are quite sufficient (measurement range 2.5-4.5 or 4.0-7.0). Universal indicator sticks for the entire pH-range of 0-14 (gradation 1 pH unit) are useful in many cases.

Important: Indicator sticks or indicator paper (commercially available in packs of 100 pieces, tear-off booklet or rolls) are meant for a one time use. They must be stored in a dry place and protected against vapors.

Table 9: Amounts of free and bound acetic acid (watery solution) in dependence on the pH-value (the important range for distillery practice is emphasized).

pH-Value	Amount of bound Acetic Acid (%)	Amount of free Acetic Acid (%)
2.0	0.2	99.8
3.0	1.7	98.3
4.0	14.8	85.2
4.76	50.0	50.0
5.0	63.5	36.5
5.2	73.4	26.6
5.4	**81.4**	**18.6**
5.6	**87.4**	**12.6**
5.8	**91.6**	**8.4**
6.0	94.6	5.4
6.5	98.2	1.8
7.0	99.4	0.6
8.0	99.9	0.1

Electrometrical Determination

A more exact determination of the pH-value if compared to indicators can only be done with special equipment consisting of a measuring instrument and an electrode which is immersed into the sample solution. If such an instrument is available one has to follow the instructions set up by the manufacturer. In principle the determination is done as follows:

a) Calibration: This is done using 2 buffer solutions, one of which should be in the neutral range while the other ought to be in the measurement range (e.g. pH 4-5). The calibration has to be done daily before the first measurement.

b) Measurement: Immerse the electrode into the sample solution, choose the appropriate measurement range and read the pH-value when constant.

Important: For storage purposes the electrode has to be immersed in an electrolyte-solution as prescribed by the manufacturer. One also has to take care of the minimum filling level of the solution for the reference electrodes.