

Chapter 17

From pot stills to continuous stills: flavor modification by distillation

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Introduction

Since at least the early 8th century men have been increasing the strength of their fermentations. The first attempts were freezing the mash and removing the ice. Later distillation was developed. Distillation is the separation of components by taking advantage of their relative volatilities. When a liquid is boiled its vapor will be richer in its more volatile components. When this vapor is condensed, the resulting liquid will have a higher concentration of the more volatile component. This process can then be repeated.

Pot distillation

Until the advent of practical continuous distillation by Stein in 1827 and Aeneas Coffey in 1830, all distillations were carried out using pot stills. Although simple, pot stills continue to be used to produce the finest Scotch malt whisky, cognac and Irish whiskey. They have evolved from simple small retorts to unique complex pieces of technology (Nicol, 1989). Development took place in Scotland during the nineteenth century as each distiller tried to differentiate himself from the distiller next door. Once set, however, the still design, even to dents, and production methods are not changed (Bathgate, 2003). Pot stills are also used in production of extracted flavor drinks such as gin. While the apparatus is simple it takes skill to

produce fine beverages with this type of distillation. The pot still is made of copper. Originally copper may have been chosen because the metal was durable and easy to work and a good conductor of heat. It has proved to be an important part of the distillation process. It is more recently that another attribute, its ability to influence the flavor of the distillate, has been fully appreciated (Nicol, 1989). Copper aids in the removal of undesirable components, especially sulfur, which imparts an off flavor to the distillate.

There are basically two ways to run a pot still. In the first the wash is added to the pot, and then steam is applied to the coils to start the liquid boiling. The collection of the alcohol enhanced condensate is continued until the alcohol remaining in the pot is not economical to remove. To prevent solids burning on the coils, it is important that the liquid is always kept above the steam coils. The spirit derived from this type of distillation is normally very rough as it contains most of the congeners from the fermentation and it is often redistilled to remove some of these congeners. The other way to operate a pot still is to take three fractions from the distillation. The first spirit off, called the foreshot or heads cut, is removed and stored separately. The mid-run is the next spirit off, and it is kept for further distillation. The last spirit off, called the tails cut, contains the heavy fusel

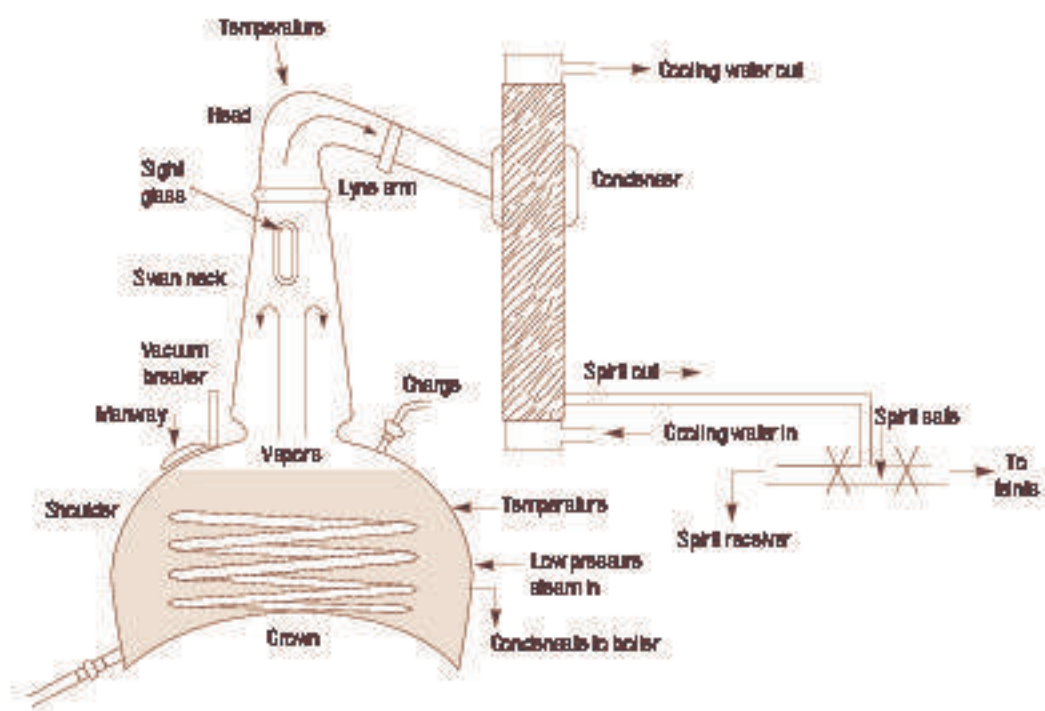


Figure 1. Schematic of a still with MCH.

oils and is removed at the end of the distillation. Distillation is continued (steam is normally increased at this time to speed the process time) until all practical alcohol has been removed (pot temperature approximately 98°C) the distillation is complete and the spent wash is discharged from the base of the still. The mid-cut from the first distillation, called low wines, (20-25% alcohol) is distilled again in similar fashion. Irish pot distilled whiskey is distilled three times, cognac twice. The result is spirit containing 65-75% alcohol that has the characteristics that the distiller deems right for aging. This sounds like a very simple process, but there are many factors that can influence the characteristics of pot distilled spirit.

WASH

The wash must be from a fermentation that is complete, free from infection and in which the yeast has not been stressed or produced excess fusel oils. The ingredients used to make up the wash will add their own individual characteristics to the final distillate. Water should be soft, clear

and free from off odors or tastes. Wine used in brandy production should be as low as possible in sulfur compounds. While it is obvious that different sugar sources, molasses, fruit or grain will produce different spirits, more subtle influences such as fermentation temperature will also affect the final product.

HEADSCUT

The wash strength and the cutoff points for the heads and tails cuts are only changed after very serious consideration as such changes will probably alter the flavor profile of the resulting spirit. The amount of heads removed at the start of distillation will affect the volatile top note of the distillate and remove the 'low boilers' (compounds with low boiling points) such as methanol and acetone from the product. The first cut has a role often overlooked, which is to remove the heavy oils and fatty acids in the swan neck, lyne arm and condenser left over from the previous distillation. The historic way to change from the heads cut to the mid-cut in Scotland is to perform a haze test, when it no longer turns

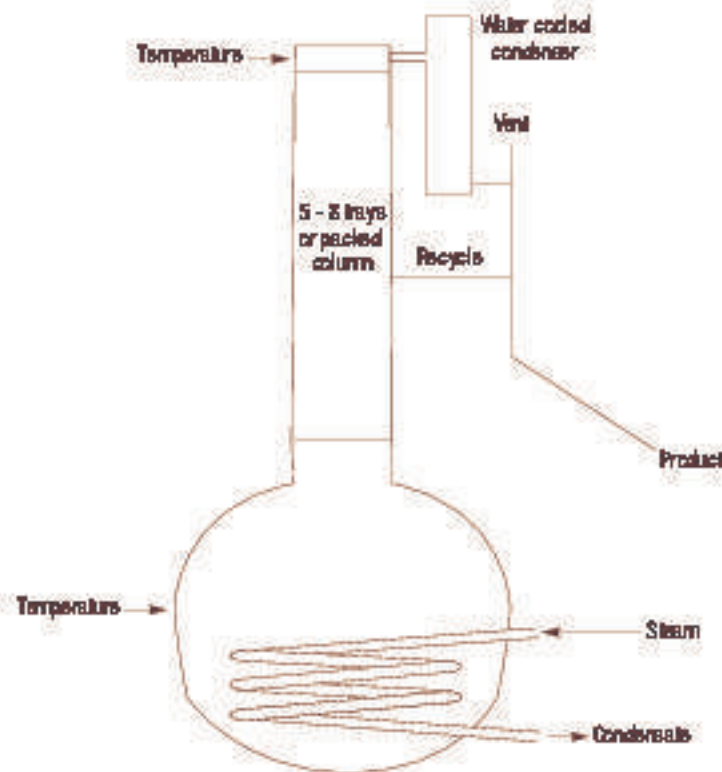


Figure 2. Schematic of a pot still with a distillation head.

cloudy when mixed with water. These days the change is based on time or volume measurement.

TAILSCUT

While some of the heavier alcohols are needed to give the spirit some body, too much results in an oily, unpleasant character and may cause haze problems when diluted to bottling strength.

STILL DESIGN

The design of a still will affect the characteristics of the product. Length and configuration of the swan neck will influence the amount of reflux. Another variation on the pot still is to put a head, either packed or with cross flow trays, in the vapor path (Figure 2). This allows a cleaner, more consistent product. It is popular in small distilleries that cannot afford or justify a continuous still. There are also some very large pot stills used by major beverage alcohol producers for flavor production.

DISTILLATION RATE

The amount of steam applied to a pot distillation will affect the final spirit quality. When the desired final result is obtained, the staging and amount of the steam addition should be kept constant. Too much steam can result in foaming, liquid carryover, and very little internal reflux. A light steam load can give the product a 'stewed' character. The large internal reflux will produce a spirit lighter in character, but will result in more time for chemical combinations to occur during distillation. The resulting energy losses raise the distillation cost.

CONTROL AND AUTOMATION

Traditionally, the changes from heads to mid-cut and then to tails have been accomplished by measuring spirit density after the condenser as it flows through the 'safe'. The safe is a device designed to let the distiller control the process without actually removing a sample. Use of a spirit safe allowed distillation to proceed without the presence of customs and revenue personnel

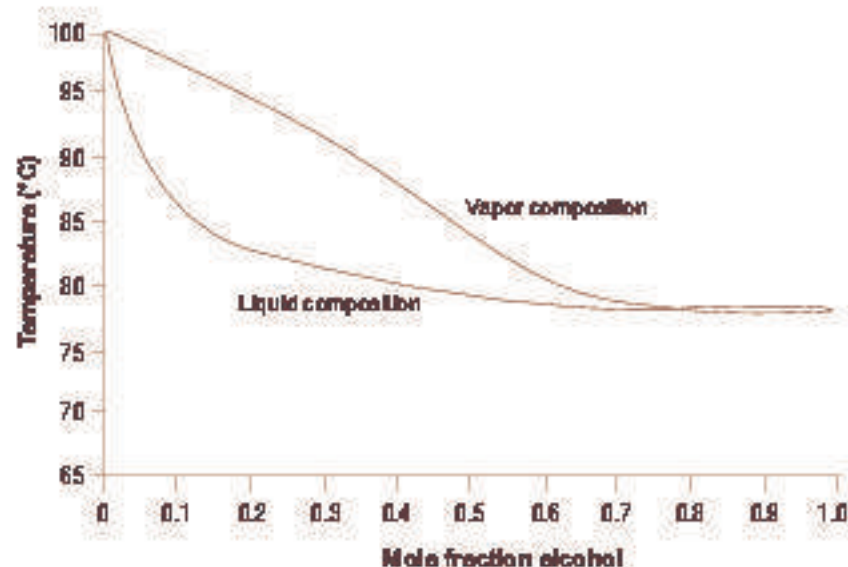


Figure 3. Relationship of temperature and mole fraction of alcohol.

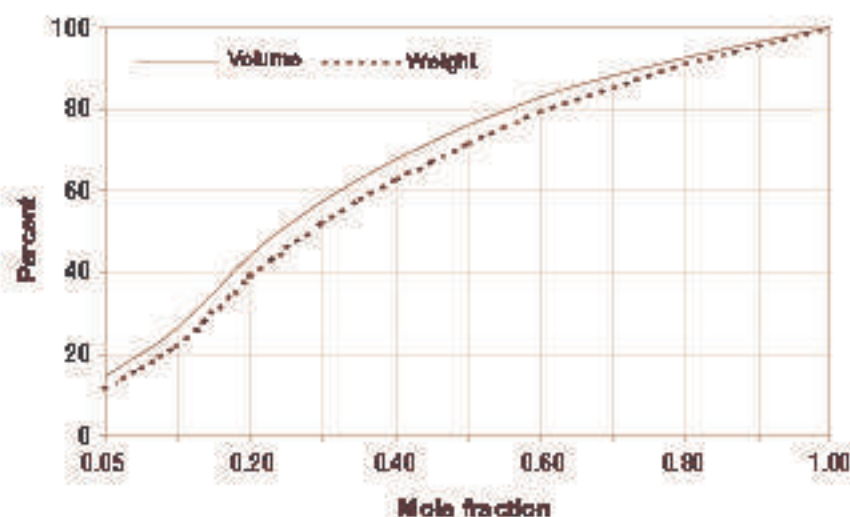


Figure 4. Converting between mole fraction and percent alcohol.

who are very sensitive about the removal of spirit on which the excise duty has not been paid.

Today many pot stills are automated. As can be seen in Figures 3 and 4, if we know the temperature of either the liquid or vapor phase we can know the composition. This is generally the way that pot distillations are automated. Since the feedstock can vary in strength and flow can be erratic at the start of a distillation, it may be better to take the heads cut on a volume basis.

At the start of distillation the flow is valved to a container. When a level probe is activated by the distillate, flow switches to the product receiver. A valve opens, dumping the container into the feints tank. When the temperature indicates that the mid-cut is finished, the flow is returned to the feints tank until practically all alcohol has been removed. This temperature is about 98°C. Above that temperature, the steam cost is worth more than the alcohol.

Production of flavored beverages

There are several products which extract flavor by redistillation in a pot still, gin being the most common. While gin may be made by adding flavors to neutral spirit, the best gins are distilled with botanicals to extract the subtle characteristics of these flavored ingredients. The following is an excerpt from the EU regulations on gin:

"The drink may be called 'distilled gin', if it is produced solely by redistilling organoleptically suitable ethyl alcohol of agricultural origin of an appropriate quality, with an initial alcoholic strength of at least 96% vol, in stills traditionally used for gin, in the presence of juniper berries and of other natural botanicals, provided that the juniper taste is predominant. The term 'distilled gin' may also apply to a mixture of the product of such distillation and ethyl alcohol of agricultural origin with the same composition, purity and alcoholic strength. Natural and/or nature-identical flavoring substances and/or flavoring preparations as specified at (a) may also be used to flavor distilled gin. 'London Gin' is a type of distilled gin.

Gin obtained simply by adding essences or flavoring to ethyl alcohol of agricultural origin shall not qualify for the description 'distilled gin'."

DISTILLED GIN PRODUCTION

A measured amount of good quality neutral spirit is added to the pot still; and sufficient water with no odor or taste is added to bring the contents to about 60% alcohol by volume. Botanicals are included in weighed amounts. While juniper berries must be included, other botanicals are also used to enhance the flavor profile. Common botanicals used are coriander seed, cassia bark, citrus peel, angelia root, orris root and fennel seed. There are several ways to extract the flavor from the botanicals during distillation. They may be suspended in muslin bags in the swan neck, spread out on a rack above the alcohol level or placed into the alcohol mixture. A standard pot still distillation is then carried out. Steam is added, and the flavor and aroma of the botanicals is carried with the spirit into the receiver. A heads and tails cut is taken as normal. Usually the cut to tails occurs when the vapor reaches 55% by volume.

Continuous distillation

THE COFFEY STILL

The first continuous still was designed and patented by Robert Stein in 1828. It was installed in the Kirkliston distillery near Edinburgh. It was very complex and not a commercial success. In 1830 Aeneas Coffey, an Irish excise officer, developed the more efficient Patent still in Dublin. This design was simpler, more efficient and well suited for distilling whole grain wort first (Bathgate, 2003). The design took the distilling world by storm and was an immediate success (Table 1, Figure 5) (Robson, 2001). This still had metal trays and wooden walls on the column. A few of these early stills are still functional.

Table 1. Coffey stills in operation 1820-1860.

Year	England	Scotland	Ireland	Total
1820	0	1	2	3
1840	4	2	13	19
1860	8	12	8	28

Variations on Coffey's design are still in use in the Caribbean rum and the Scotch whisky industries. In several of the rum plants they will vary the flavor of the final product by adjusting the fusel oil and heads draw by a fixed ratio.

Neutral spirit and brown spirits are two main product types from continuous distillation. Neutral spirit can be made from any feedstock but is usually made from grain or molasses. This spirit has very low odor and taste, and is used for non-aged products (known as white spirits) such as gin and vodka. It may also be used to blend with a highly flavored product and aged in wood barrels. This blended product usually has a lighter flavor than its pot or single column still counterpart.

Brown spirits, so called because they develop a color during maturation in wood barrels, have a much stronger flavor. These spirits are distilled to leave some congeners in the final product. This spirit more resembles pot distillation and gives us bourbon, Arramagac, some fine rums and Canadian whisky.

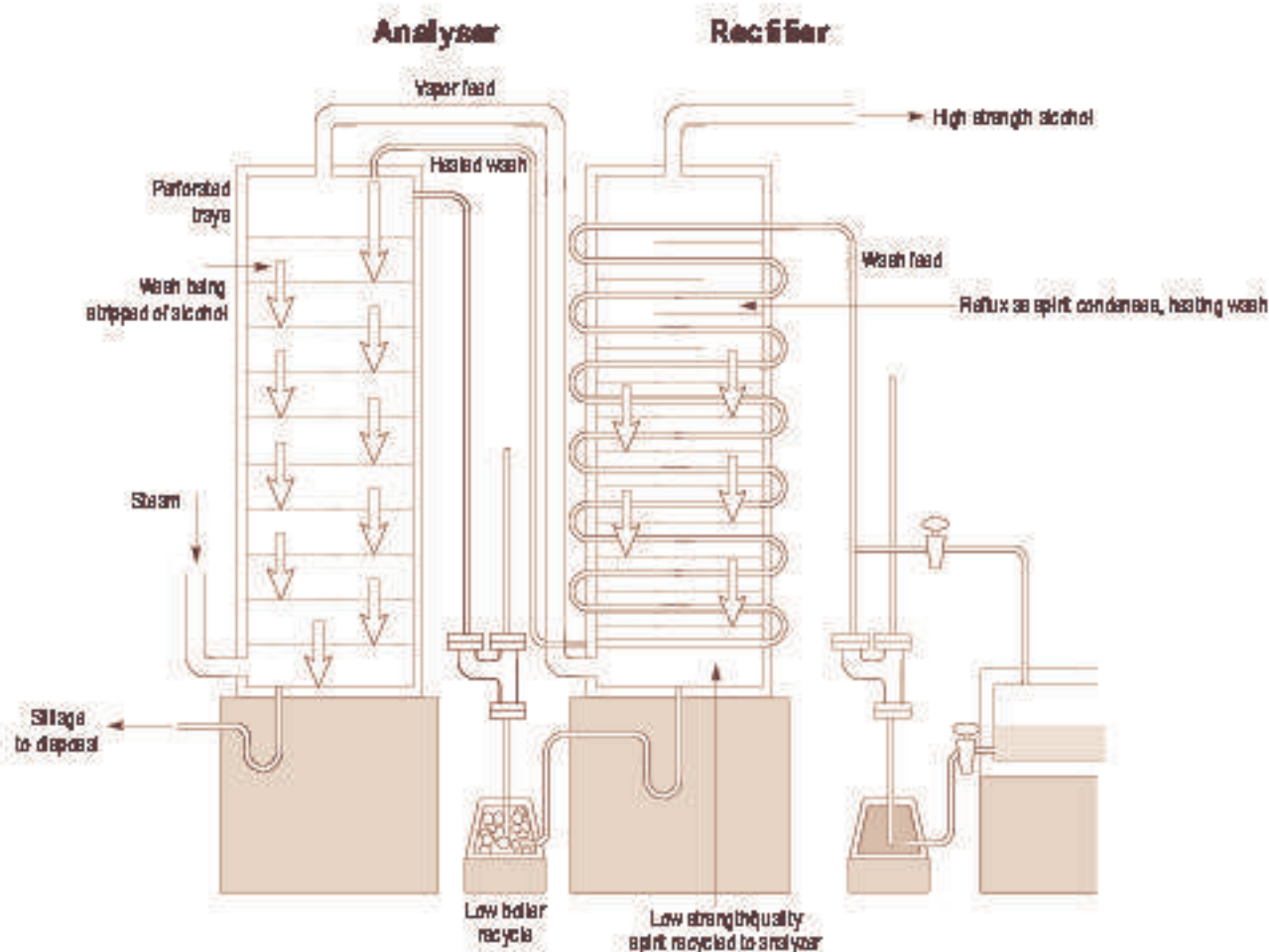


Figure 5. Schematic of a Coffey still, circa 1840.

FLAVORED SPIRIT PRODUCTION ON A CONTINUOUS STILL

As with the pot distillation, it is important that the fermented beer or wash is sound. Off odors or taste from poor quality feedstock or contaminated fermentations can carry over into the final product. In the production of Canadian whisky and bourbon, the beer is distilled in a single column that is really a stripping and condensing column stacked together. Some plants use a doubler or thumper (a sort of continuous pot still) after this column.

Operation of a Canadian whisky flavor still

A Canadian whisky flavor still is illustrated in Figure 6. The beer (normally 8 to 10% alcohol by volume, but it can be as high as 15%) is pumped from fermentation through a preheater

where it is heated with the overhead vapors from the column. It passes through a tank that vents the liberated carbon dioxide (CO_2) to the atmosphere and then into the column.

Steam enters at the base of the column, either through a reboiler or by direct injection. The column below the feed tray (stripper section) removes the alcohol. The stillage passing out the base should be less than 0.07% alcohol. Since it is a whole mash, it is important that the stripping section uses trays that are not easily fouled by the grain solids or mineral buildup.

The alcohol vapors pass through a solids separation tray into the concentrating section. This section concentrates the alcohol from 55 to 80% by volume. The draw strength has a great effect on the flavor profile of the spirit. Spirit strength is controlled by a temperature reading at the top of the column. This controls either the

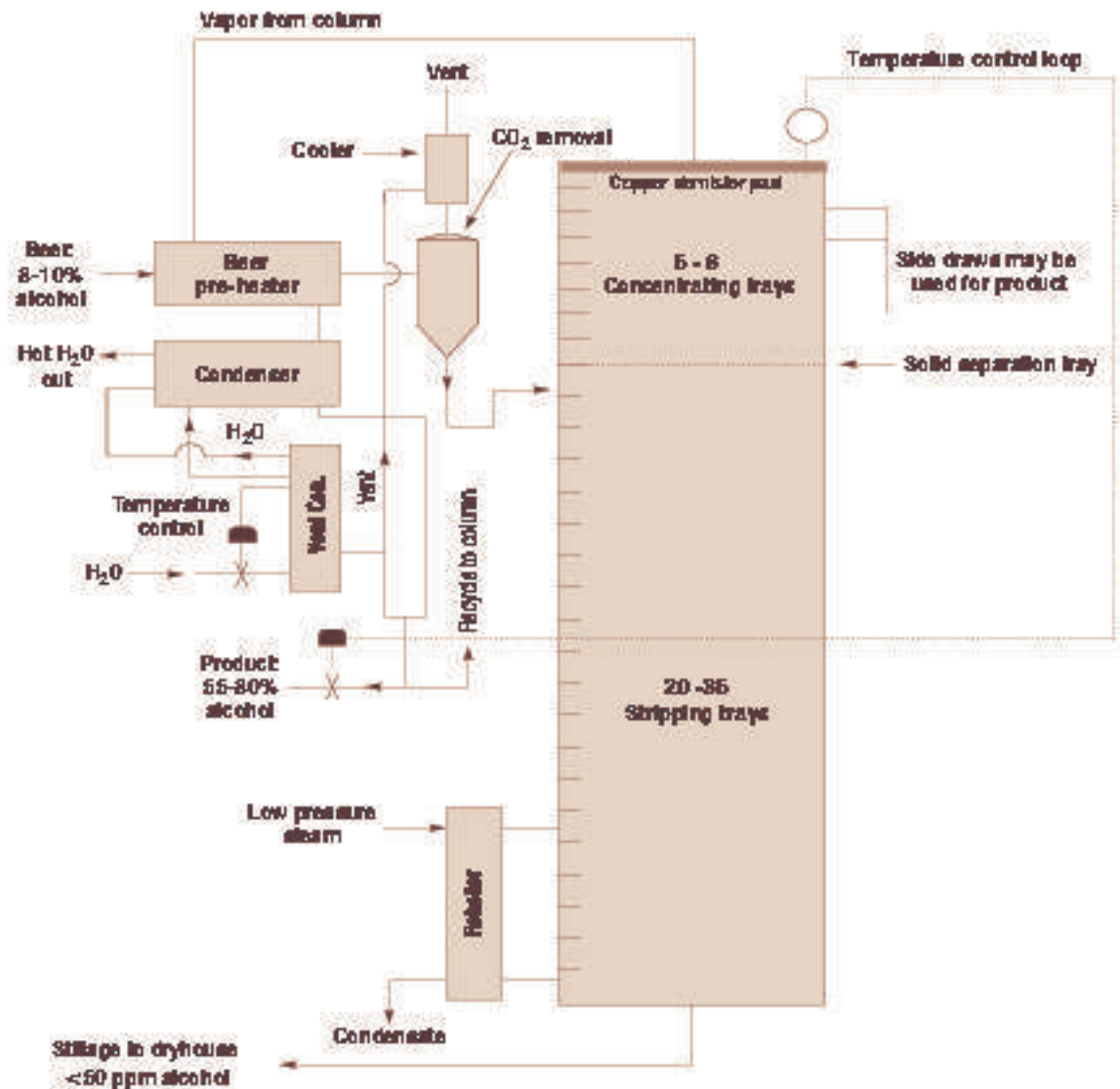


Figure 5. Typical Catalina whiskey flavor still.

amount of reflux or product draw. If temperature is below set point, then spirit is too strong and recycle is reduced. If too high, then spirit is too weak and recycle is increased.

Spirit straight from the still is raw. It is aged for a minimum of three years in small oak barrels.

Production of light and neutral spirit

The product of neutral spirit in a continuous still requires the removal of all components that have odor or taste components over a set threshold. Some products such as light rum require some

flavor in the final product, while the specifications for good quality vodka demand no odor or taste. Specifications will also indicate the amount of congeners allowed to be present. These can be less than 1 ppm. Depending on the degree of neutrality required, the rectifying section in a beverage plant can consist of two, three or four columns.

SPIRIT PREPARATION FOR THE RECTIFYING SYSTEM

Many whisky plants in North America also

produce a neutral spirit. These plants generally use the flavor column, or one of similar design, as the base alcohol to feed the rectifying system. The strength of this product is usually 70-80%. Due to this low strength, the fusel oils have not been removed. Some heads will be vented or sent to a heads column.

In plants designed to just produce neutral spirit, the spirit is often taken to a higher strength (over 95%). This allows the removal of some fusel oils and heads, similar to the rectification column, before it is sent to the rectifying system. Another possibility is the use of a Barbet head on the column to concentrate and remove the heads (Figure 7).

Extractive distillation or hydrofining

The most common way to remove fusel oils is known as extractive distillation, or hydrofining. The operating principle behind this column is addition of water to the spirit. Ethanol is very soluble in water while the fusel oils are not (Figure 8). The alcohol is added to the column about 2/3 of the way up. The water soluble components (ethanol and methanol) will combine with the water, forming a solution with a higher vapor pressure and hence move down the column. The components that are less water soluble will rise to the top of the column where they are removed. This column requires three components (alcohol feed, steam and water) to be properly balanced. Generally at least eight parts of water for each part of alcohol must be used. In practice much higher ratios (10 to 15) are normally used for good separation.

In order to balance the steam, one must first understand what is happening in the column. The water coming from the top of the column will push the ethanol down the column, while steam coming from the base of the column will try to push it up the column. The result is that the alcohol has a peak in concentration, known as the *pinch point*, about 16 trays from the base of the column. Keeping this pinch in the correct position and strength is a key to the proper balancing of this column. The concentrated fusel oil removed from the top of the column can be sent to a fusel oil washer. Strength at the top of the column will be in the 60 to 68% range. As can be seen in Figure 9, propanol is the most

difficult component to remove and is therefore a good indication of how well the column is working. This cleaner low strength spirit is sent to the rectifying column.

Rectification

The rectifying column takes the low strength spirit, removes the last traces of impurities, fusel oils and heads, and takes the strength up to the azeotropic point. One difference in the rectifying column is the large number of trays: over 60 trays is common. This enables a large amount of internal reflux inside the column, which helps concentrate the congeners for better removal (Figure 9). Fusel oils concentrate on the tray where alcohol concentration is 65%; propanol concentrates on the tray with 80% alcohol. It is important that the column is kept stable and that the draws are sufficient to prevent the column becoming loaded with impurities. The cleaner product is removed about five trays from the top of the column. While they concentrate at the top of the column where they are removed, it should be noted that the heads must pass the product draw tray to reach the top of the column. It is therefore not possible to remove all the heads from the product in the rectifying column. To improve alcohol recovery and to increase purity levels, other columns are usually added to the system for demethylization, heads and fusel oil separation. In a well-designed and run extractive distillation system, components other than ethanol will be less than 1 ppm.

FUSEL OIL AND HEADS COLUMNS

These columns take the fusel oil and heads draws from various parts of the process, concentrate them for removal and return cleaned spirit to the process. They are generally small columns with low feed rates that have trays or are packed.

DEMETHYLIZING COLUMN

Certain feedstocks such as fruit and potatoes can end up with very high concentrations of methanol that need to be reduced, or perhaps a product very low in methanol is required. One way to do this, especially if methanol cannot be

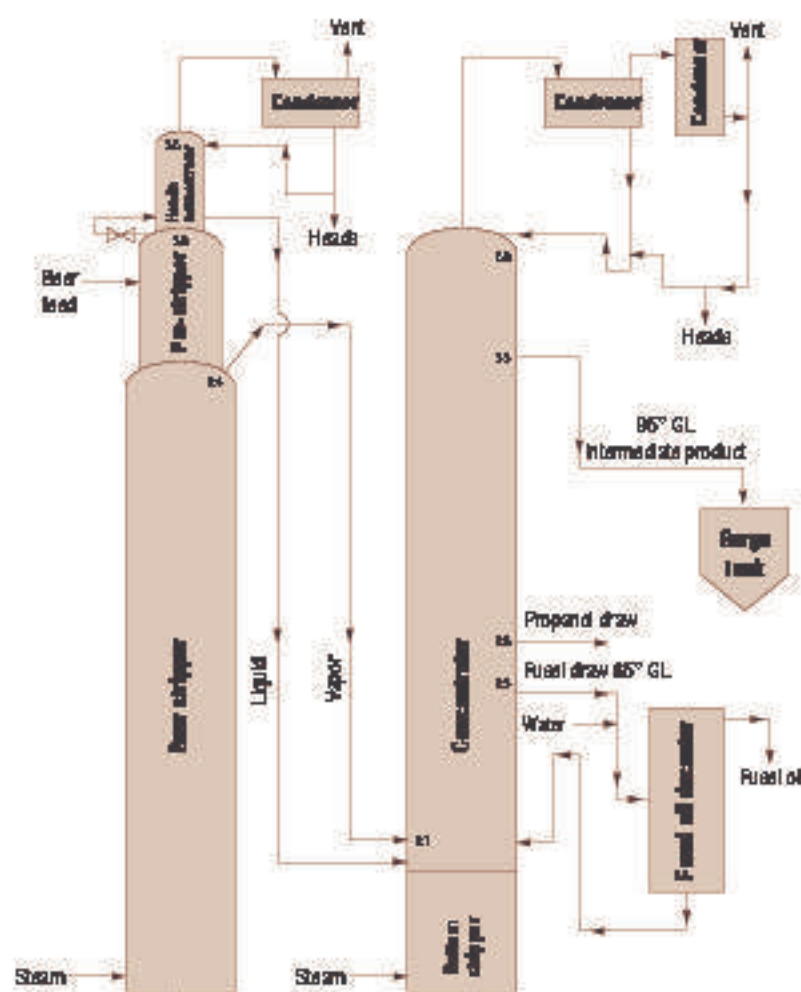


Figure 7. Concentrating neutral spirit: Beer feed, head, on the column to concentrate and remove the heads.

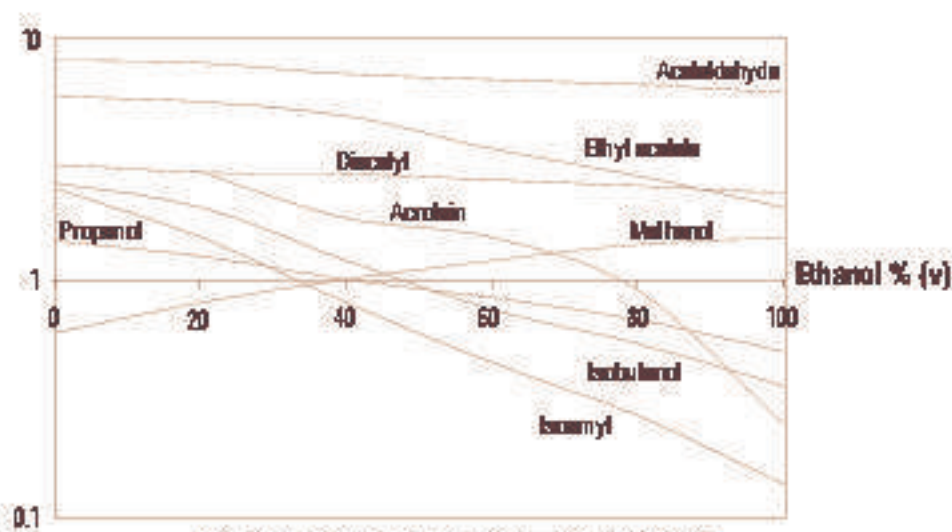


Figure 8. Relative volatility of congeners and ethanol.

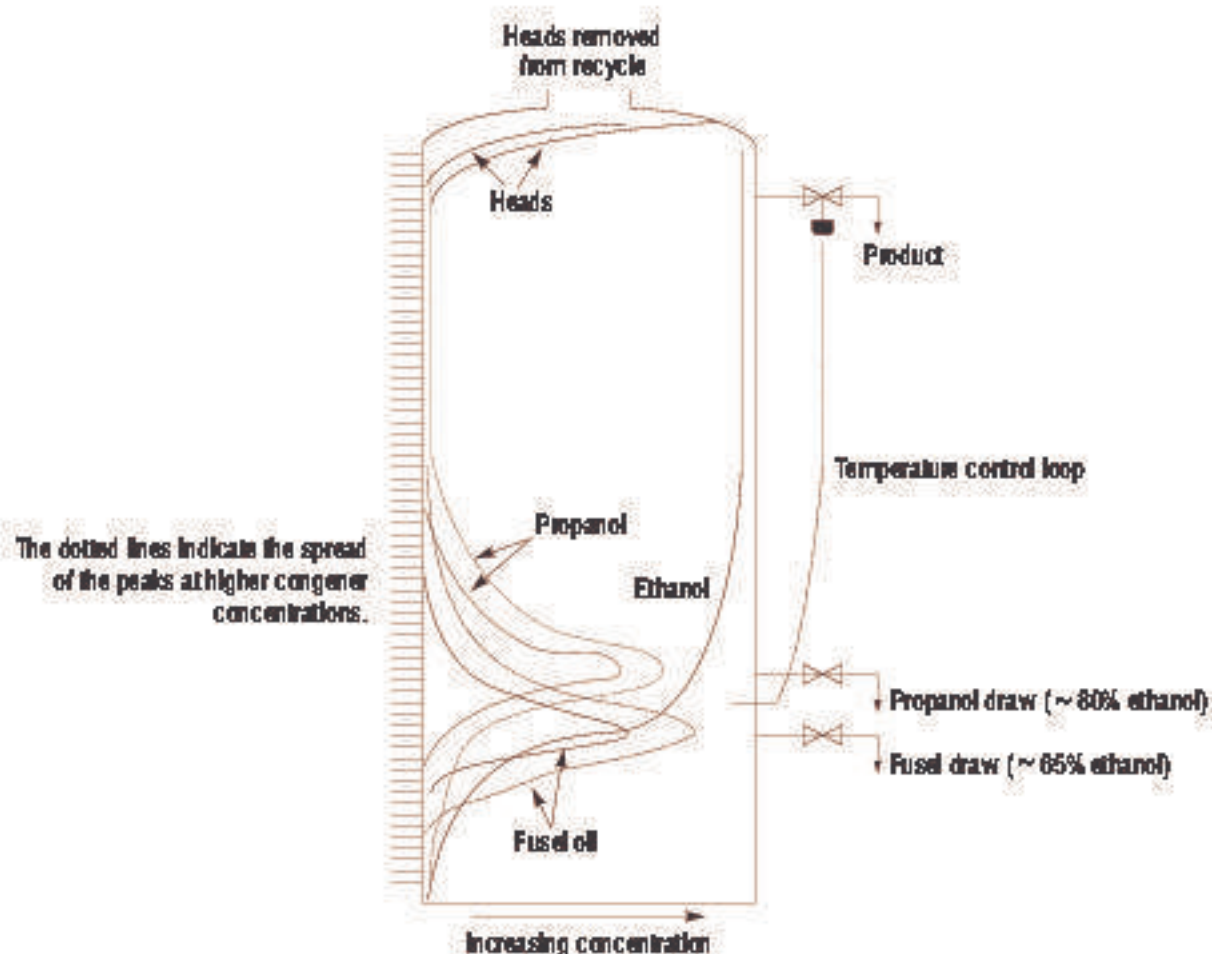


Figure 9. Fusel oil and heads removal in the rectifying column.

removed at the beginning of the process, is to remove it after the rectifying column. Steam to this column is via a reboiler so as not to add water to the system. The alcohol is added to the column about 1/3 to 1/2 of the way up. The lighter methanol and any other heads present are driven up the column and removed. The purified ethanol is removed at the base (Figure 10).

PACKED COLUMNS

Packed columns are known as continuous contact columns. They have an advantage of continuous vapor-liquid contact. Because of this, they may be an advantage when a small column needs an increase in capacity. However, they are only used on clear, non-fouling tasks and as the

column size increases they become increasingly complex and not cost effective.

Energy efficiency

Distillation uses a lot of energy, however with good design the energy requirements can be reduced or recovered for other operations.

REBOILERS

Reboilers are simply heat exchangers that take a hot stream and use it to generate steam for another part of the process. This is illustrated in the flavor column (Figure 10). The advantage of this is that the condensate can be returned to

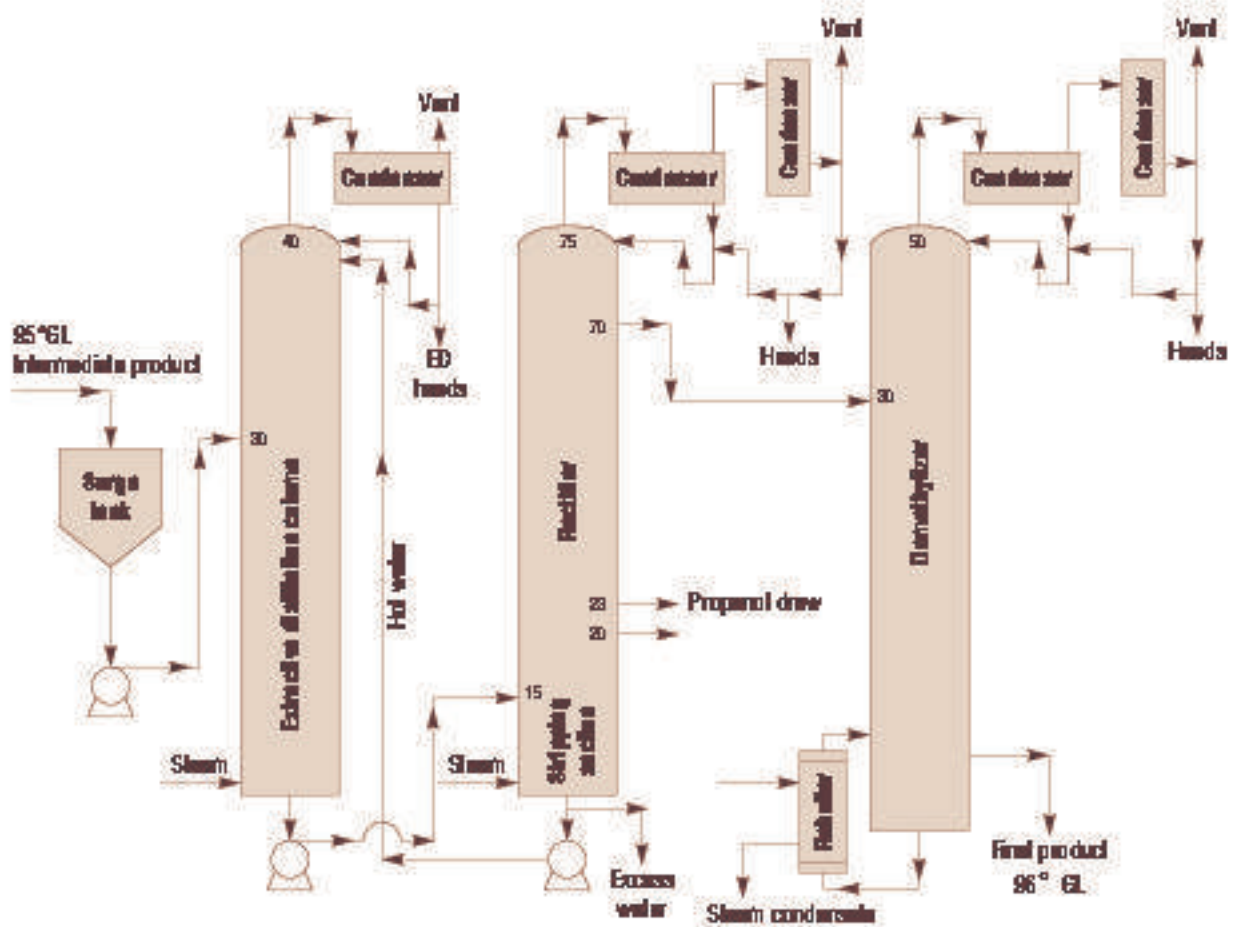


Figure 16. Three column rectification systems used in neutral spirit production.

the boiler instead of creating extra liquid that must be disposed of in the stillage.

PRESSURE DISTILLATION

One or more columns are run under pressure. Instead of the heads being condensed by cooling water, they are passed through a reboiler that produces steam for another column. This reduces the total distillation steam required.

VACUUM DISTILLATION

In this configuration, one column (usually the stripping column) is run under vacuum. This means heads from an atmospheric column can power the reboiler on the vacuum column. This is becoming common in distilleries using

molasses as a feedstock. The lower temperatures in the stripping section reduce calcium fouling of the trays.

THERMOCOMPRESSORS

Thermocompressors are simple, low maintenance devices that can save a considerable amount of energy. High pressure steam is passed through a venturi-type nozzle. This draws a vacuum in the vessel containing the hot liquid causing it to boil. This steam combines with the now-low-pressure steam for use. About 25% (depending on design) of the steam out of the thermocompressor is recovered heat from the liquid. Mechanical recompression is another possible option, but it is costly to install and run so the savings must make it cost effective.

HEAT RECOVERY

The condensers should be viewed as a source of heat. This could be used for feed preheating, heating boiler water feed or any other process that requires hot water such as cooking or CIP systems.

INSULATION

The heat savings obtained by simply insulating columns and other hot vessels to retain heat is often overlooked, but usually gives an excellent return on investment.

Quality assurance

In order to be sure the correct quality product reaches the receiver, a system of predictive quality control must be implemented. This can include such things as a check on the fermenter for odor and taste before it is pumped to the still. Samples of the fusel oil and propanol draws on the rectifying column can be obtained to see if there is a buildup before it gets into the final product. Whatever works in a particular system, the trick is to detect potential problems before they become full-blown problems that affect final spirit quality.

While many countries including the EU have specifications for neutral spirit (the US does not) the companies using the spirit usually have their own much tighter specifications that must be met by the producer.

In these days of large corporations and improved technology there is an increasing trend to use instruments, especially the gas chromatograph, to set standards for beverage alcohol. While these procedures can be of great use in doing predictive testing of the distillation system, they cannot duplicate the human senses when it comes to assessing a product. To do this, it is important that a distillery has a trained staff, proper facilities and procedures for organoleptic testing. Remember that the final customer will not have a gas chromatograph on the bar, but he or she will have a nose and taste buds. The customer is the final test of product quality.

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Chapter 18

From liqueurs to 'malternatives': the art of flavoring and compounding alcohol

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Introduction

Using flavor in alcoholic beverages expands the variety of consistent, high quality products available to the consumer. From high proof spirits that have a twist of fruit flavor or spice, to medium strength cordials, to low alcohol premixed cocktails and 'malternatives', the inclusion of flavors gives the beverage producer limitless flexibility in creating products to satisfy the constantly changing beverage alcohol market.

Historically, flavors were added to alcohol to cover up poor quality and bad taste. Gin was first used for medicinal purposes in the 17th century. Juniper berries were added prior to distillation to improve the taste. It was common practice to use poor quality corn and barley and to add a flavor to make the product more palatable. In the 18th century, production of flavored vodkas became popular. This was done to improve marketability of poor quality spirits.

Today, flavors are often added to give a marketing edge to a competitive industry. According to Adams Handbook Advance, "The US distilled spirits industry was up for the 5th consecutive year in 2002". The number of flavored alternatives is credited with this increase.

Flavor perception

Our tongues sense the four basic tastes of

sweetness, sourness, saltiness and bitterness. Additionally our mouths detect textures referred to as 'mouthfeel'. In beverages these include viscosity and slickness often described as oiliness. Other sensations are drying and trigeminal sensations or salivation stimulation. Some tastes, especially bitterness, tend to linger or are perceived less quickly.

Most of what we describe as flavor perception is actually aroma. Aroma perception occurs in the nose and can occur without tasting. Thousands of aromas are distinguishable. In order for a chemical to be smelled, it must become airborne so that it can reach the air in the nose and be detected. Holding a beverage in the mouth warms it and more of the aromatic compounds are released. Most aroma chemicals are not soluble in water. Alcoholic beverages have an advantage in that rich, intense flavors are produced because alcohol is a natural solvent that is exceptionally volatile. The aroma compounds release more readily from an alcoholic beverage than from a soft drink.

Aesthetics of flavored beverages

Because people 'drink with their eyes', the appearance of these lower proof products is important. Approved artificial colors and caramel can produce virtually any shade of

color. Adding a homogenized clouding flavor can simulate the inclusion of juice. The complexity of the interaction of these taste, smell and visual sensations is what provides nuance and character to a beverage.

Types of flavored beverages

HIGH PROOF SPIRITS

Although originally considered an inferior substitute for the distiller's art or a mask for product deficiencies, flavor-added spirits are now considered to be the equal of unflavored spirit. As previously mentioned, one of the earliest examples of added flavor in high proof spirits was improvement of inferior spirit flavor by adding juniper berries during distillation. These were the earliest gins. Now, many gin products are made by adding flavor from the refined oil of juniper berries, along with other essential oils, directly to high proof neutral spirits. Refined essential oils are much more consistent than raw botanicals, which can be affected by varying growing conditions.

Blended American and Canadian whiskies use flavors to provide a fuller, more balanced flavor profile while reducing the ingredient costs of more expensive spirits. American whisky blends are made by combining a straight bourbon whisky with neutral alcohol. A well-designed flavor can mimic the flavor compounds lost from the neutral spirit. Vanilla can be added to replace that which would have been extracted from the oak barrel. Higher alcohols and other congeners can be added back in amounts and proportions that are more desirable than the original product. Oak flavor from oak wood is not permitted for flavoring American blended whiskies.

Producers in the crowded vodka and rum market have found that flavor and a little sugar can add an 'extra' that sets a product apart. Citrus extracts and pepper or spice flavors are quite popular in flavored vodkas, which have found a new niche in trendy martini cocktails. Spiced rums, which are high in vanilla flavor, and tropical rums, reminiscent of piña colodas, have also become the base of many popular drinks.

CORDIALS AND LIQUEURS

Cordials, and other medium strength sweetened

beverages, are an extremely important segment of the alcoholic beverage market. Coffee, chocolate, vanilla, almond, cherry, peach, orange, cinnamon, hazelnut, anise and even gold leaf are just the beginnings of a list for popular flavors used in this broad category. Sweetened to between 12 and 40% sugar, these products can be consumed by themselves, but are frequently used as ingredients in cocktails, in cooking or even as toppings for deserts.

PREMIX COCKTAILS

Shelf-stable cream-type beverages can be produced using non-dairy cream substitutes. This allows for a whole array of milkshake type products, with names such as mudslides, creamsicles and grasshoppers. Margaritas and similar premixed cocktails give the consumer the convenience of a complete spirits drink without the inconvenience of buying multiple ingredients and the hassle of complex and time consuming preparation.

MALTERNATIVES

'Malternatives' and 'Alcopops' are beverages that contain alcohol at the same level as beer. Malternatives, which are produced in the US, use as a base a malt product with an intentionally low flavor. Flavor and sweetener are added to produce a drink similar to a cocktail from a distilled spirit. Many are marketed using the brand name of a spirit product, e.g. SMIRNOFF ICE®, BACARDI SILVER™, etc. This category has been the most successful of recently introduced product lines. Among the marketing advantages these products have is unlimited flexibility for product design. Virtually any type of cocktail can be developed in this base product. These products can be sold at the same retail outlets as standard beer products, which is a tremendous advantage over spirit-based beverages. Crossover advertising can benefit the spirit product, as well. Distilled spirits have traditionally not been advertised on television in the US, however malternatives with the same brand name can be advertised (e.g. Schmirnoff Ice). The production costs are much lower because of the differential between beer (\$18.00 per 31 gallon barrel regardless of alcohol level), wine and flavoring (\$2.00 per gallon of alcohol)

and distilled spirits excise taxes (\$27.00 per gallon).

Alcopops are similar products that are actually made with spirits set to a comparable alcohol level. Smirnoff Ice sold outside the US will contain vodka as the alcohol source in place of a malt base.

Types of flavors

ARTIFICIAL VS NATURAL

For the purposes of the Codex Alimentarius *"Natural flavors and 'natural flavoring substances' are preparations and single substances, respectively, acceptable for human consumption, obtained exclusively by physical processes from vegetable and sometimes animal raw materials either in their natural state or as traditionally processed for human consumption."* 'Natural' does not mean coming from the plant that characteristically produces the flavor. The classic example is benzaldehyde derived from peach pits and used in almond or cherry flavors. 'Natural' does not mean more healthful, safer or higher in quality than artificial. It is merely a description of the source.

'Nature-identical flavoring substances' are *"substances chemically isolated from aromatic raw materials or obtained synthetically. They are chemically identical to substances present in natural products intended for human consumption, either processed or not, as defined above."*

Another group of ingredients called 'nature-identical' is comprised of *"substances that are chemically identical to flavoring substances naturally present in vegetable or animal raw materials that are not normally considered as human food."*

The same ingredient can be available in both natural and nature-identical forms (i.e. natural vanilla versus vanilla that is nature-identical). The natural version is typically considerably more expensive and less concentrated. However, there can be valuable reasons for selecting the natural form for a beverage flavor.

'Artificial flavoring substances' are *"those substances which have not yet been identified in natural products intended for human consumption, either processed or not."*

In addition to these classifications the US Bureau of Alcohol, Tobacco and Firearms (BATF) has placed restrictions on the inclusion and labeling of certain ingredients. Artificial flavor substances can be included in an alcoholic beverage product without being labeled artificially flavored if the BATF-approved flavor contains 0.1% or less of an artificial ingredient. There are also restrictions on the level of certain ingredients, whether or not they are artificial.

KOSHER

Foods, beverages, raw materials and processing aids are kosher if they are produced in accordance with the Jewish dietary laws. There are several rabbinical services that will, for a fee, certify processes, equipment and ingredients as kosher and allow their seal to be placed on product packaging. Although these certifications are useful for marketing purposes, Kosher does not mean more healthful, safer or superior in quality to non-Kosher.

BOTANICALS

These are the starting point for most natural flavors. Botanicals are parts of a plant that contain aromatic chemicals that are desirable as flavoring agents. All parts of plants have been used for flavor. A few examples are juniper berries, hop flowers, leaves and stems, rose petals and hips, cinnamon leaf and bark, whole peppers and pepper corns, clove buds, angelica root and citrus rinds. Non-plant derived natural flavoring agents include beeswax, castoreum and fermentation congeners.

EXTRACTS

It is frequently useful to remove the aromatic compounds from the whole plant material prior to use. Essential oils, absolutes and concretes are the fragrant chemicals found in the plant material. There are various extraction techniques. Expressed oils are squeezed out in presses. Carbon dioxide, propylene glycol, steam and ethanol are commonly used for extraction of essential oils. Further purification can be achieved by distillation into various fractions based on boiling points.

Flavor delivery systems

Most aroma chemicals are hydrophobic, not soluble in water. In order to use them in a beverage they must be made soluble. The three commonly used delivery systems for putting hydrophobic flavors into beverages are solutions, emulsions and extracts. Solutions are simple mixtures made by dissolving flavor ingredients in solvents that can be mixed into water. Typical solvents are ethanol and propylene glycol. Extracts or hydro-alcoholic extracts take advantage of the different solubility limits of the different compounds in essential oils, especially citrus oils. Citrus extracts are made by dissolving a citrus oil or blend of oils in high proof alcohol and then combining or 'shocking' with water. The less soluble compounds will come out of solution and rise to the top and can be decanted. Fortunately, with citrus oils the compounds that are soluble in the alcohol/water portion are the more organoleptically pleasing compounds. The insoluble terpenes, which have been removed, are typically astringent and bitter. The remaining extracted portion is water-soluble.

Emulsions are made by homogenizing the flavor ingredients in a solution of a gum. A gum is a high molecular weight carbohydrate polymer. The oil droplets are trapped in the gum matrix and will not re-coalesce when mixed into the beverage. Another use of emulsions is as a clouding agent. If a clouded product is desired, such as to simulate limejuice in a margarita premix, a homogenized ester gum flavor can produce the desired effect. Clouding agents can also be used to add variation to a product line, such as with Gatorade's Frost line of products.

Tax benefits of flavored beverages in the US

The alcohol portion of a flavored beverage is usually provided by neutral spirits, but whisky or other spirit can be used. Alcohol used in the flavor contributes to the total alcohol as well. Many of these products take advantage of the so-called 'wine option'. This is a tax savings available by using a neutral wine, which can be included at up to 49% of the alcohol in the product after the alcohol from the flavor is taken

into account (example formulations in Tables 1 and 2).

A significant, but frequently overlooked, method of cost reduction available in the distilled spirits industry is the use of flavors to reduce the level of taxable alcohol. Alcohol used in flavors is taxed at a substantially lower rate than distilled alcohol used in beverages. When a flavor is added to a spirits beverage, the alcohol it contains is included in the total proof. However, alcohol contained in the added flavor, when kept under 2.5% of the total proof of the finished beverage, is not taxed as beverage spirits alcohol. Because the tax burden on beverage spirits is so high relative to non-beverage alcohol (\$13.50 per proof gallon or \$27.00 per gallon of pure alcohol for beverage distilled spirits as of this writing), it is possible to add a flavor that costs less than the tax. Flavor producers are able to formulate alcohol-containing flavors that will not alter the flavor profile of the finished product, thus allowing the full savings available from this tax benefit. Flavoring substances must be compounds judged by BATF to be 'unfit' for human consumption at full strength, but can be developed such that when diluted and/or combined with other flavors, the desired flavor profile is achieved. A judicious use of flavors containing alcohol can reduce costs in alcoholic beverages containing distilled spirits (See Tables 3-5).

Building a beverage

Creating a new alcoholic beverage requires decisions at every step. One first must decide on the alcohol level and source. In addition to beverage type, tax rates and marketing regulations affect this decision. For example, there might be a marketing benefit to using rum to make a premixed cocktail, but the cost might be prohibitive. A combination of rum and neutral spirits might be the compromise. Malt and other than standard wine can only be used in products that are relatively low in alcohol level, i.e. cordials and malternatives. They also have characteristic flavor and so must be used in heavily flavored products.

Next, the flavor is selected. This is typically the bottleneck of the project. Choosing the perfect flavor, or combinations of flavors to give

Table 1. Vodka with full 'drawback'¹.

	Vodka @ 80 proof (full drawback)		Vodka @ 80 proof	
	Wine gallon	Proof gallon	Wine gallon	Proof gallon
Vodka (@ 190 proof)	41.05263	78	42.10526	80
Neutral blender (@ 180 proof)	1.11111	2	0.0	0
Water	95	0	95	0
Total	100.00	80	100.00	80
Taxes				
Tax paid at \$13.50/proof gallon for distilled spirits		\$1053.00		\$1080.00
Tax paid at \$1.00/proof gallon for approved neutral blender		\$1.11		\$0.00
Total		\$1054.11		\$1080.00

Tax difference = \$1080.00 - \$1054.11 = \$25.89/100 wine gallons (Distilled goods)

One case of 12 x 750 ml bottles = 2.38 wine gallons

2.38 wine gallons/case x \$0.2589 tax reduction/wine gallon = \$0.61 tax savings per case.

¹Full drawback is the term describing the taxbreak advantage taken of the lack of excise tax on alcohol in flavors (i.e. 2.5% of total alcohol). In a flavored 80 proof vodka, 2 proof degrees or 1/40th of the alcohol is not-taxable.

Table 2. Margarita premixed cocktails.

	25 proof		25 proof with wine option and drawback	
	Wine gallons	Proof gallons	Wine gallons	Proof gallons
High proof tequila (@ 190 proof)	16.63	24.945	8.287	12.431
C.T.S. wine @ 21% alc. ²			28.428	11.944
High fructose corn syrup (72°Brix)	15.00		15.00	
Neutral blender @ 180 proof			0.317	0.57
Orange Extract ¹ @ 50% alc	0.01	0.005	0.01	0.005
Lime Extract ¹ @ 50% alc	0.1	0.05	0.1	0.05
Neutral Cloud Flavor ¹	0.05		0.05	
Citric acid, lbs	4.2		4.2	
FD&C Yellow 5, lbs	0.1		0.1	
FD&C Yellow 6, lbs	0.02		0.2	
Water	Q3		Q3	
Total	100	25	100.0	25

¹Alltech Inc.

²Absolute alcohol by volume

the intended effect, can take time. Any changes in the other parameters can put you back to the drawing board with the flavor.

Sweetness level is based on the beverage type and flavor. As little as 1% sugar can smooth the roughness of a high proof spirit. Premixes blended with ice need the sugar level sufficiently high to prevent the product becoming watered down after dilution. Fruit flavored beverages may have different sweetness levels depending on the fruit flavor. Sugar also adds viscosity to a beverage. Some products such as egg-nogs can be made more viscous by adding gums such as xanthan.

Acids (usually citric and sometimes with sodium citrate) are used in most cocktails to

provide tartness and simulate juice content. The correct acid/sugar ratio is important for giving the right taste and mouth feel to a drink. Coffee and vanilla beverages require little or no acid addition. Cream drinks are incompatible with acid, so the flavor selected for these products should not need tartness to enhance flavor. Malt, which is fermented in an acidic pH range, is also not suitable for cream drinks.

After the flavor profile is completed the aesthetic issues of color and cloud are addressed. Many citrus flavored drinks are clouded to simulate juice content. Others such as a melon cordial would be shiny with only some color added. Deep color suggests richness and enhances the flavor experience.

Table 3. Irish cream cordial with full drawback @ 50 proof.

	Wine gallon	Proof gallon
Irish whiskey @ 65% alc. ¹	37.5	48.75
Neutral blender TM @ 90% alc	1.989	1.25
High fructose corn syrup @ 72° brix	12.0	
Non-dairy cream substitute, 1lb	200	
Water (to integrate with cream substitute)	25.00	
Non-alcoholic vanilla flavor TM	0.1	
Caramel color, white gallons	0.01	
Water	QS	
Total	100	50

¹ Absolute alcohol by volume² Alltech Inc.

Table 4. Strawberry cordial alternative @ 6% a.s.v.

	Wine gallon	Proof gallons
Beer @ 10% alc. ¹	30.0	6.0
Strawberry Flavor TM @ 60% alc	5.0	6.0
High fructose corn syrup @ 72° brix	12.0	
Citric acid, 1lb	2.5	
FD&C Red 40, 1lb	0.5	
Neutral Cloud Flavor TM	0.1	
Water	QS	
Carbonate to 3.5 volumes	100.0	12.0

¹ Absolute alcohol by volume² Alltech Inc.

Table 5. Conversion tables for computation of taxable quantity of spirits.

Bottle size	Equivalent fluid ounces	Bottles per case	Liters per case	US gallons per case	Corresponds to
1.75 L	59.2	6	10.50	2.773806	1/2 gallon
1.00 L	33.8	12	12.00	3.170064	1 quart
750 mL	25.4	12	9.00	2.377548	4/5 quart
375 mL	12.7	24	9.00	2.377548	4/5 pint
200 mL	6.8	48	9.60	2.536051	1/2 pint
100 mL	3.4	60	6.00	1.585032	1/4 pint
50 mL	1.7	120	6.00	1.585032	1, 1.6 & 2 oz

OECD conversion factor: 1 L = 0.264172 US gallon

TTB, 2003

Table 6. Conversion tables for computation of taxable quantity of wine.

Bottle size	Equivalent fluid ounces	Bottles per case	Liters per case	US gallons per case	Corresponds to
3.0 L	101	4	12.00	3.170064	4/5 gallon
1.5 L	50.7	6	9.00	2.377548	2/5 gallon
1.0 L	33.8	12	12.00	3.170064	1 quart
750 mL	25.4	12	9.00	2.377548	4/5 quart
500 mL	16.9	24	12.00	3.170064	1 pint
375 mL	12.7	24	9.00	2.377548	4/5 pint
187 mL	6.3	48	8.976	2.37119	2/5 pint
100 mL	3.4	60	6.00	1.585032	2, 3 & 4 oz
50 mL	1.7	120	6.00	1.585032	1, 1.6 & 2 oz

OECD conversion factor: 1 L = 0.264172 US Gallon

TTB, 2003

Table 7. Tax and fee rates.

Product	Tax	Tax per package (usually to nearest cent)
Beer	Barrel (31 gallons)	12 oz. can
Regular rate	\$18	\$0.05
Reduced rate	\$7 on first 60,000 barrels for brewer who produces less than 2 million barrels	\$0.02
Wine	Wine gallon	750 ml bottle
14% & under	\$1.07 ¹	\$0.21
Over 14 to 21%	\$1.57 ¹	\$0.31
Over 21 to 24%	\$3.15 ¹	\$0.62
Naturally sparkling	\$3.40	\$0.67
Artificially carbonated	\$3.30 ¹	\$0.65
Hard cider	\$0.226 ¹	\$0.04
¹ \$0.50 credit, or for hard cider \$0.056, for first 100,000 gallons removed by a small winery producing not more than 150,000 wine gallons per year. Decreasing credit rates for winery producing up to 250,000 wine gallons per year.		
Distilled spirits	Proof gallon	750 ml bottle
All	\$13.50 less any credit for wine and flavor content.	\$2.14 (at 80 proof)

This was last updated on November 23, 1999 (www.ttb.gov)

Conclusions

The beverage alcohol industry is increasingly competitive. Producers are in a continuous struggle to increase profits and market share and consumers are looking for the latest trend and more convenience. The art and practice of flavoring beverage alcohol provides short product development times for a wide variety of products, improves consistency and quality of products and can reduce tax liability and improve profits.

References

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Chapter 19

Production of American whiskies: bourbon, corn, rye and Tennessee

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Introduction: definitions of bourbon, corn, rye, wheat, and Tennessee whiskies

The US Bureau of Alcohol, Tobacco and Firearms (BATF) has set specific guidelines to define all types of alcoholic beverages produced in the United States. The general definition of whisky is 'a spirit aged in wood, obtained from the distillation of a fermented mash of grain'. This spirit can be produced from any grain or combination of grains; but corn, rye and malted barley are the principle grains used. Whisky is an alcohol distillate from a fermented mash produced at less than 190° proof in such a manner that the distillate possesses the taste, aroma and characteristics generally attributed to whisky; stored in an oak container, and bottled at not less than 80° proof. Also, whisky may contain mixtures of other distillates for which no specific standards of identity are noted.

Bourbon, rye and wheat whiskies are produced (distilled) at a proof no higher than 160° from a fermented mash of not less than 51% corn, rye or wheat and aged in new, charred oak barrels at a proof no greater than 125°. Also, these whiskies may include mixtures of whiskies of the same type. Corn whisky differs in that it may be aged in used or uncharred new oak barrels. Also, corn whisky may include a

mixture of other whiskies. Tennessee whisky has the same definition as the other four whisky types, but to be labeled 'Tennessee' it must be produced and aged in wood in the state of Tennessee.

All whiskies conforming to Section 5.22 of the BATF regulations must be aged a minimum of two years. To be designated a 'straight' whisky, it must conform to all regulations for its type and be aged not less than two years. 'Light' whisky is another type of whisky produced in the US. It is distilled at more than 160° but less than 190° proof and aged at least two years in used or uncharred new oak barrels.

In the US regulations, neutral spirits, vodka, Scotch whisky, Irish whiskey, and Canadian whisky are further defined. Neutral spirits are distilled spirits produced from any material distilled at or above 190° proof and bottled at not less than 80° proof. Vodka is a neutral spirit distilled and treated with charcoal or other materials to be without distinctive character, aroma, taste or color. Scotch, Irish and Canadian whiskies are defined as 'distinctive products of Scotland, Ireland, and Canada, respectively, and produced and distilled under the laws of those countries'.

History of North American whisky production

Whisky production began in the US in 1733 when the British government passed the Molasses Act. Until that time, the colonists produced distilled spirits from molasses. The Molasses Act imposed a duty on molasses of non-British origin. Since the American colonists imported most of their molasses from the French and Spanish islands, they were greatly concerned. Since non-British molasses was cheaper and more abundant, smuggling and ignoring the Molasses Act (and the later Sugar Act) was the basis for much of the 'Spirit of '76'.

Pre-revolution grain whisky production was small, although history notes that settlers in western Maryland and Pennsylvania produced rye whisky from their abundant rye grain crops and that rye whisky began to replace the popular molasses-based rum. After the Revolution, the Embargo Act cut off the supply of molasses, and with abolition of the slave trade by the new Congress, both molasses and slaves were smuggled into the US. These events increased the cost of molasses and accelerated the decline of rum.

THE WESTWARD MIGRATION

Early settlers crossing the Allegheny Mountains included many Scots and Irish immigrants who were grain farmers and distillers with knowledge of pot still operation from their homelands. They produced the rye whisky that became the first 'American' whisky. When Alexander Hamilton needed money to pay the debts incurred during the American Revolution, he pushed an excise tax levied on distilled spirits through Congress. As news of the tax spread, the uproar and public outrage was so intense that President Washington sent 13,000 troops into western Pennsylvania to quell the 'Whisky Rebellion'. As the troops entered from the east, many farmer-distillers packed their stills and headed west to Kentucky to avoid both the tax and the army.

The farmers found Kentucky soils not as suitable for rye and wheat crops as soils in Pennsylvania and Maryland. They discovered that corn was much easier to cultivate. The first

writing that expounded on corn growing in Kentucky comes from the Jesuit Hieronymus Lalemont. He noted 'to mention the Indian Corn only, it puts forth a stalk of such extraordinary thickness and height that one could take it for a tree, while it bears ears two feet long with grains that resemble in size our large Muscatel grapes' (Carson, 1963).

Whisky production grew rapidly in the early frontier areas as the settlers found in whisky a means of moving grain to market. A pack horse could carry only four bushels of corn, rye or wheat; but that same horse could carry 24 bushels of grain that had been mashed and distilled into two kegs of whisky. Also, the price of whisky was more than double the price the farmer could get for grain.

BOURBON'S 'ACCIDENTAL' HISTORY

As settlements moved westward, the demand for spirits increased. Riverboats had become a means for shipping barrelled whiskies to their destinations. A version of 'bourbon history' recounts how a Baptist minister, Elijah Craig, burned or 'charred' the inside of fish barrels to rid them of the fishy smell so he could fill the barrels with whisky to be shipped by raft down the Mississippi River to New Orleans. The whisky from the charred oak barrels 'aged' during shipping and storage. This aging improved the character of the whisky, gave it color and smoothed the taste (Carson, 1963).

Another version of this history tells of a careless cooper who accidentally let the staves catch fire (char) when heating them for pliability to make into barrels. Not wanting to lose money, he did not tell his distiller customer about the charred staves in the barrels. Months later, after the distiller filled the barrels and shipped the whisky downriver, the distiller heard pleasing compliments about his whisky. After discovering the cooper's 'mistake', the distiller asked him to repeat the charring process for all of his barrels.

Contrary to popular belief, none of this 'history' occurred in Bourbon County, Kentucky, and no one really knows how bourbon whisky was first made. The only historical evidence indicating Bourbon County as the source of bourbon whisky comes from a

1787 indictment of James Garrad (later a Kentucky governor) and two others by a Bourbon County grand jury for retailing liquor without a license. The only certainty in any of the lore is that Kentucky has a county named Bourbon and produces a whisky by the same name (Cornelley and Coulter, 1922).

ESSENTIAL TRADITIONS

Despite uncertainty about origins of the bourbon name, a tradition of good whisky making was handed down from fathers to sons for generations. Formulas, mash bills, yeasting methods and skills for operating the stills were passed along, even though many farmer-distillers could not read or write. They did not know acrolein from fusel oil, but they did have the special knack for making the 'cuts'. They knew good, clean yellow corn and plump rye. They faithfully guarded their yeast and yeast methods though many could not have said whether yeast belonged to the animal or vegetable kingdoms. Two exceptional bourbon whiskies of the 19th century were Old Taylor and Old Crow. Old Overholt was reportedly the best of the rye whiskies.

During the 19th century, the pot still evolved into the continuous column 'beer still' with a doubler or thumper. The continuous still operations allowed distillers to move to larger fermenters, more and larger cookers and automated grain handling. As the distillery operations grew and became increasingly automated, some of the smaller distilleries fell by the wayside or promoted their brands as better as a result of their 'old time, small distillery tradition and quality'. They touted this tradition and sold it as part of the product. The well known Maker's Mark bourbon is a prime example of tradition and sound practice bottled and successfully marketed to modern consumers.

As grain whisky and bourbon production grew in the 19th century, the US government increased the excise tax and the number of regulations. Costs passed on to the consumers dampened their enthusiasm for drink; but government regulation incensed leaders of the Temperance Movement because the tax and regulations drew attention to the production and sales of liquor. Most whisky at that time was

sold 'from the barrel', and quality standards were almost nonexistent. It was not until the end of the century that consumers could purchase whisky sold in a corked and sealed bottle. Old Forester was the first product with 'guaranteed quality' put on the label. Old Heritage was the first bourbon with a strip stamp over the cork, thereby becoming the first 'bottled-in-bond' bourbon.

THE PROHIBITION ERA

All of the improvements in the 'character' of whisky production and consumption were to no avail when at 12:01 a.m. on Saturday, January 17, 1920 all beverages containing more than 0.5% alcohol were outlawed in the US (Tennessee, the state with the first registered distillery in the country, Jack Daniel Distillery, became the third state to vote to go dry in 1910, ten long years before the passing of the Volstead (Alcohol Prohibition) Act). The 18th amendment to the Constitution, which prohibited the production and sale of alcoholic beverages, sounded a death knell for many distilleries. A drive through the countryside revealed closed distilleries choked with weeds with facilities in ruins. Brown-Forman Distillery in Louisville, Kentucky, was one of the few that survived because it produced its Old Forester Bourbon 'for medicinal purposes only'. Other distilleries lay in wait for 'the experiment' of prohibition to end.

Passage of the 21st amendment ended Prohibition after 13 years. At midnight on April 7, 1933 wines and beer were again legally sold; and on December 5 of that year at 5:32 p.m. bourbon was again on the market. The American distilled spirits industry surged into production, building larger, more modern distilleries. The resumed legal production and sales were reinforced by the federal government when it passed the Federal Alcohol Control Act, which eliminated the sale of bulk whiskies to the wholesale and retail trades. This Act also formed the Alcohol and Tobacco Tax Division of the Internal Revenue Service. Though creating bureaucracy and taxation, the new Act also set regulations and definitions for producing spirits in the United States.

DISTILLATION'S NEW ERA

The new regulations defined the production of bourbon, rye, corn and blended whiskies as well as gin, brandies, rums, cordials and vodka according to their spirit type. The Act also noted the use of geographical designations with an origin defined for Scotch, Canadian, and Irish whiskies. This evolution of the industry led to the organization of companies that had goals of producing top quality spirits within the new regulations. New companies such as National Distillers and Schenley joined the American distilleries that survived prohibition, Brown-Forman and Jim Beam, along with the Canadian distillers, Seagrams and Hiram Walker. These distillers based their production methods on precisely defined procedures from yeasting to maturation.

During World War II, North American distilleries ceased whisky production and began manufacturing industrial alcohol for the war effort. Distillers gained the resources for further technical improvements; and at the War's end, the industry in the United States was technically ready to produce better bourbons, ryes, and Tennessee whiskies than ever before.

While the basis for modern American whisky production was developed during World War II, today's modern American distillery operates with recent innovations. Even with all of the modern technology, the US distiller still carefully controls his yeasts, mash bills, distillation methods and maturation criteria, essential factors for good quality products initiated by the early pioneer distillers.

Production and maturation operations

In the production of American whiskies, six factors determine the character and flavor for each type of whisky:

- 1) Grain proportions in the mash bill
- 2) Mashing technique
- 3) Strain of yeast
- 4) Fermentation environment
- 5) Type and operation parameters of distillation equipment

- 6) Type of barrel used and the maturation process

These factors were recognized and carefully controlled in the distilling operations of the early settlers (Lyons, 1981). Families and companies that ensured consistency and control over these factors remain in business today. Those who failed to strictly adhere to a regimen controlling each factor have fallen by the wayside.

A MATTER OF DISTINCTION

Popular bourbon producers use specific process differences to make their products distinct. The Jack Daniel Distillery continues to produce its whisky with the same processes used more than 100 years ago. Their strict adherence to tradition along with a down-home, folksy image have proven successful marketing tools for the whisky. At Maker's Mark, grain selection and proportions are used to produce a superior whisky. They use wheat instead of rye in the mash bill. The wheat and good, consistent control of all factors, especially the barrels, make Maker's Mark the smoothest of the bourbons. Their claim of 'handmade' is justified because of their intense attention to production parameters.

All American whiskies maintain standards for the six production factors; and the variations among distilleries in adherence to standards for these factors determine flavor and cost differences. All American distillers start with a careful grain purchasing program. Though price is a criterion, they all use No. 1 or No. 2 yellow corn, No. 1 plump northern rye, and choice northern malted barley. Any off odors or below-grade grain are rejected at the distillery. Very stringent grain standards are a common feature of all American distilleries (Table 1).

MASHBILL

The mash bill may vary, with a typical bourbon having a mash bill of 70% corn, 15% rye and 15% malt. A typical Tennessee whisky may have 80% corn, 10% rye and 10% malt while a typical rye whisky will have a mash bill of 51% rye, 39% corn and 10% malt. All grains are

Table 1. Specifications and analyses of corn, rye, wheat and malt.

	Specification	Typical analysis
Corn (No. 2 re-cleaned)		
Grain color	No rotting, sour or off color	'Moist spec'
Moisture, %	14.0 (maximum)	12-14
Cracked grains and foreign material, %	2.0 (maximum)	1-2
Damaged kernels, %	3.0 (maximum)	0-1.5
Heat-damaged kernels, %	0.2 (maximum)	0-0.1
Bushel weight, lb	55.0 (minimum)	55-60
Rye (No. 1 plump)		
Color	None	'Moist spec'
Moisture, %	14.0 (maximum)	10-14
Thins, %	2.0 (maximum)	1-2
Damage, %	2.0 (maximum)	1-2
Bushel weight, lb	56.0 (minimum)	56-60
Malt		
Bushel weight, lb	35.0 (minimum)	35-38
Moisture, %	6.0 (maximum)	4-6
α -amylase	60.0 (minimum)	60-64
Diastase power	22.0 (minimum)	22-26
Bacteria count, CFU/g	1,000,000.0 (maximum)	400-500,000
Wheat		
Color	None	'Moist spec'
Moisture, %	14.0 (maximum)	10-14
Thins, %	2.0 (maximum)	1-2
Damage, %	2.0 (maximum)	1-2
Bushel weight, lb	56.0 (minimum)	56-60

ground, with the hammer mill being the most common type of processing; however some roller and attrition mills are still in use. The milling (Figure 1) is checked for grind by a sieve analysis. A typical sieve analysis for grains in a bourbon mash bill is shown in Table 2.

Table 2. Typical sieve analysis for grains in a bourbon mash bill.

US Sieve #	Corn	Rye	Malt	Wheat
16	15	22	2	20
20	21	25	8	26
30	17	13	14	12
40	13	9	16	8
50	10	7	13	6
60	3	2	8	2
Through 60	21	22	34	22

Mashing

Mashing techniques vary considerably, but the major difference is whether pressure or

atmospheric batch cooking is used. Bourbon, rye, wheat, Tennessee and corn whisky are mashed using batch cookers. Only the 'blend' or 'light' whisky producers use continuous cookers. Pressure cooking is usually done at 124°C while atmospheric cooks are done at 100°C. Cooking time varies from 15 minutes to 1 hr. Conversion time and temperature are very consistent among distilleries. Malt is never subjected to temperatures greater than 64°C, and conversion time is usually less than 25 minutes to minimize contamination. All distillers use backset (centrifuged or screened stillage from the base of the still), but the quantity of backset will vary based upon the beer gallowage (gallons of water per 56 lb distillers bushel of grain) to be used. American whiskies have beer gallowages in the 30-40 gallon range. High energy costs for by-product recovery have encouraged some distillers to use lower beer gallowage ratios for spirits. However, bourbon and Tennessee whisky producers continue to use 30-40 gallon beers. The cooling of cooked mash

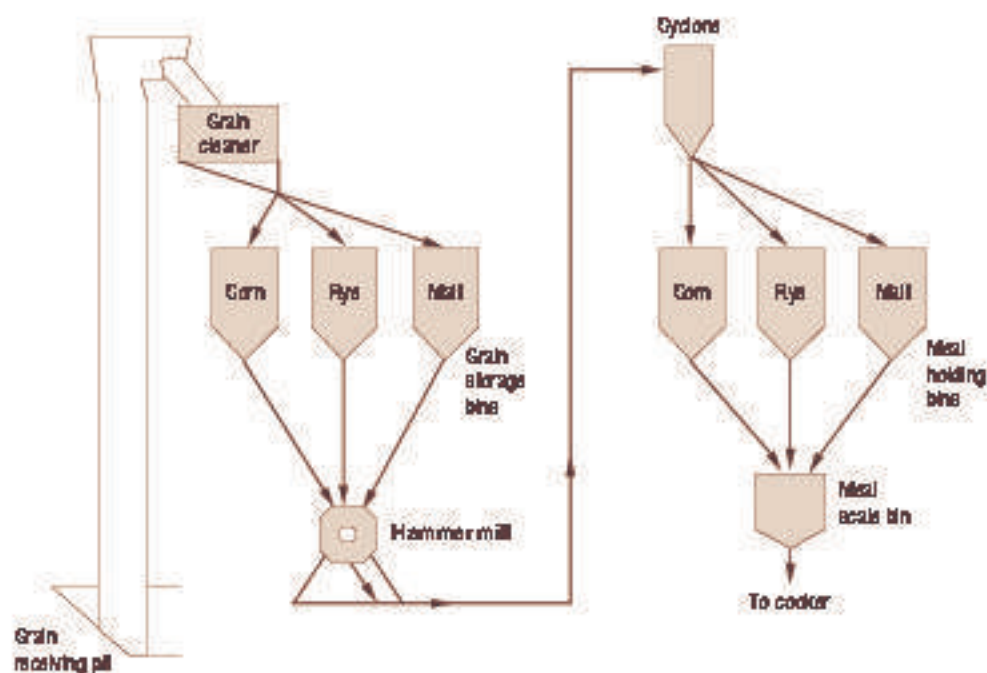


Figure 1. Typical grain-handling and milling facility.

to fermentation temperature is achieved using vacuum (barometric condensers) or cooling coils.

YEASTING

All whisky producers use *Saccharomyces cerevisiae*, however the yeasting techniques vary tremendously between the 'modern' and 'traditional' distillers. The modern distillers have elaborate yeast laboratories and will propagate a new yeast from an agar slant every week. They are very aseptic and accurate, assuring continuity of the same flavor. The 'traditional' distillers use yeast stored in jugs; and though they backstock weekly, the potential for gradual yeast culture changes and contamination can lead to flavor variances. These distillers take extra effort and care to ensure that their yeasting does not cause ester, aldehyde or fusel oil variances in the distillate.

The most common grains used for yeasting are small grains, rye and malted barley. These grains are cooked in a separate cooker to about 63°C, and the pH is adjusted to 3.8 with lactic acid bacteria grown in the yeast mash. Lactic

acid production is then stopped by increasing the temperature to 100°C for 30 minutes to kill the bacteria. This aseptic, sterile mash is then ready for the yeast from the dera tub grown in the laboratory (Figure 2). The yeast fermentation temperature is controlled at 27-30°C; and the yeast propagates until the Balling drops to half the original 22° Balling reading. This yeast mash will have a yeast concentration of 400 million cells/ml. Both modern and traditional distillers regularly have clean, sterile yeasts free of bacterial contamination that may cause side fermentations and unusual congeners in the distillate. The 'lactic souring' and the alcohol content of the finished yeast mash (8%), along with sterile dera and yeast tank methods contribute to the excellent reputation American whiskies have for fermentation congener consistency. The advantage of using small grains are: preservation of enzymes for secondary conversion, low steam requirements and shorter processing time. Also, because of its nutrient value, barley malt is the most important constituent of yeast mashes. Corn is not used in a yeast mash because it does not contain the growth factors required for yeast and lactic bacteria growth.

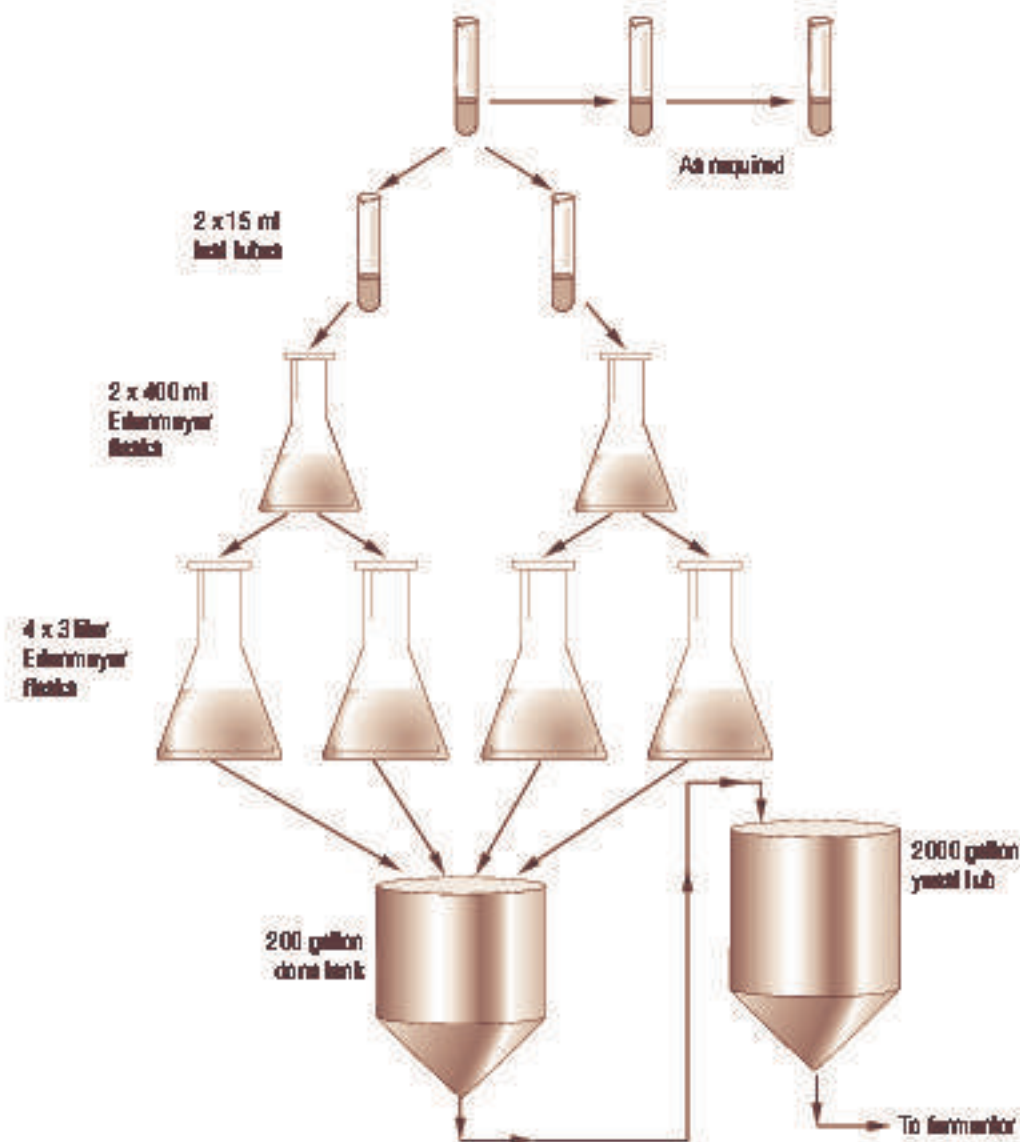


Figure 2. Stages in yeast production.

FERMENTATION

Fermentation is the simplest part of the production process, but requires more control with efficient equipment in order to have stable, consistent results. After the two or three cooks required are completed, cooled, and transferred to the fermenter, the fermenter is 'set'. Setting the fermenter means filling the fermenter with cooked mash, inoculated yeast and backset. The yeast mash is pumped in as soon as the first cook is added to the fermenter. The addition of backset and/or water is done at the end of filling

to bring the fermenter to the desired final beer gallowage. Most distillers use a 30-36 gallon mash, and the water/backset ratio determines the set pH. Set pH values of 4.8-5.2 are considered to be the best starting point. The modern distillers have closed-top fermenters with cooling coils or external heat exchangers to control fermentation temperature. They usually set fermenters at 27-29°C and control at 30-31°C. Traditional distillers will have metal or wood open-top fermenters without any device to control fermentation temperature. They usually set their fermenters as cool as they can (18-21°C)

and let the fermenters work up to 31-32°C. All of this is controlled by mash cooker cooling, addition of cold water and weather factors. Contamination is controlled by cleaning fermenters, ensuring no mash pockets in pipes and regular steaming of fermenters.

Both traditional and modern distillers ferment their beers for at least 72 hrs, and some for as long as 96-120 hrs. Three and five day fermentations are the norm. During these periods the Balling will drop to 0.0 and the pH from 5.0 to 3.8 while the alcohol concentration rises to 8-10%. All the changes that happen during fermentation are checked daily by performing 'beer chemistry'. Balling, pH, acids, and fermenter temperature are monitored and recorded daily. The pH is the main indicator of contamination and potential fermentation problems and is regularly measured by traditional and modern distillers (Table 3).

DISTILLATION

Upon completion of the fermentation process, the beer with 8.0-10.0% alcohol is transferred

from the fermenter to the beer well. The beer well is a holding tank for the fermented beer, such that a continuous feed to the beer still can be maintained. Beer wells are usually 1-1.5 times the size of a fermenter. They also have continuous agitation to prevent solid grain particles from settling to the bottom of the vessel. All American whisky producers use a continuous still (Figure 3), though some have a second distillation 'doubler' or 'thumper' (Figure 4). The basic difference between a doubler and a thumper is whether the unit is operated with a liquid level (doubler) or essentially dry (thumper). Both the doubler and the thumper provide a second distillation.

The beer is pumped into the upper section of the first continuous column, the beer still, six to ten plates from the top. Live steam is introduced at the bottom. Beer stripping plates 1-18 have perforations, a downcomer from above and a dish on the plate below to hold the beer liquid at a set level so the plates are never dry, as the beer moves back and forth across each plate. The steam passing up and through the perforations, controlled by pressure or flow rate, strips the lighter, more volatile alcohol from the

Table 3. Typical analysis of beers from bourbon, rye and corn whisky production.

	Bourbon	Rye	Corn
<i>Set sample</i>			
Balling	13.4	13.4	12.3
Titratable acidity	4.5	3.6	2.8
pH	4.5	5.0	5.2
Temperature, °C	27.0	24.0	27.0
<i>24 hr sample</i>			
Balling	2.6	4.0	3.6
Titratable acidity	5.1	4.6	4.2
pH	4.2	4.4	4.3
Temperature, °C	30.0	31.0	29.0
<i>48 hr sample</i>			
Balling	2.4	3.6	1.0
Titratable acidity	7.8	7.5	6.1
pH	3.8	3.9	3.8
Temperature, (°C)	30.0	30.0	30.0
<i>Drop sample</i>			
Balling	0.4	1.5	-0.4
Titratable acidity	8.2	7.9	7.1
pH	3.8	3.9	3.8
Temperature, °C	30.0	30.0	30.0
Alcohol, % by volume	6.73	5.8	6.8
Residual carbohydrates, %	8.0	8.4	4.2
Residual carbohydrates, % residual	0.73	0.6	0.46

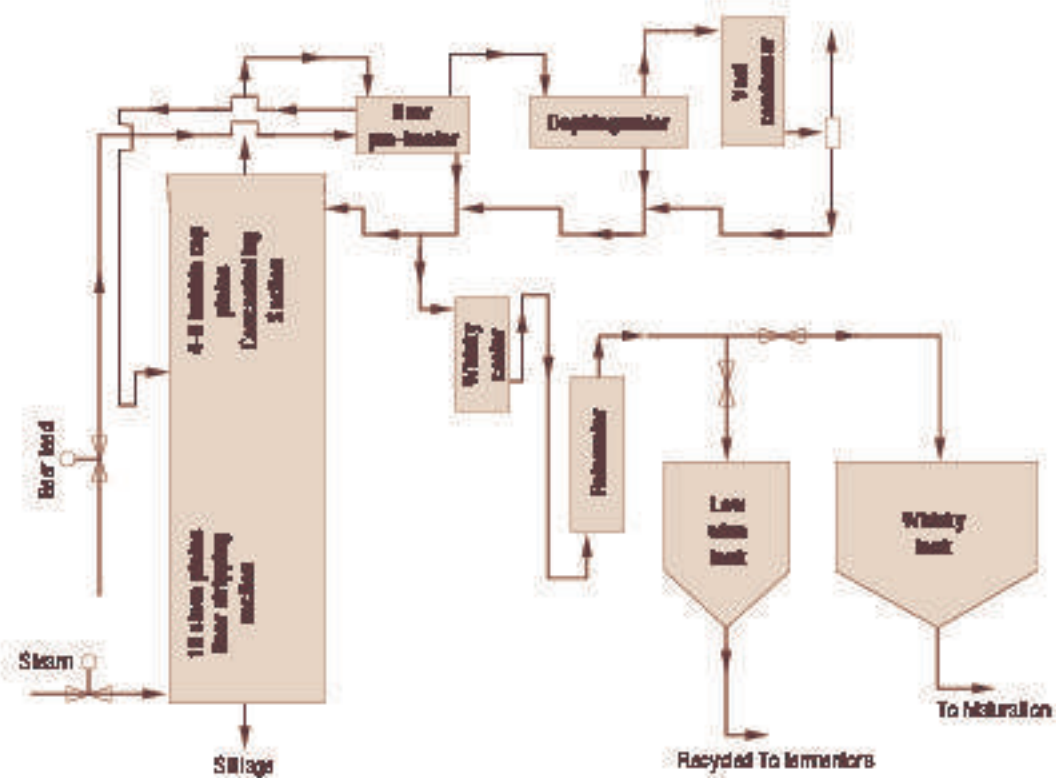


Figure 3. Bourbon whiskey still.

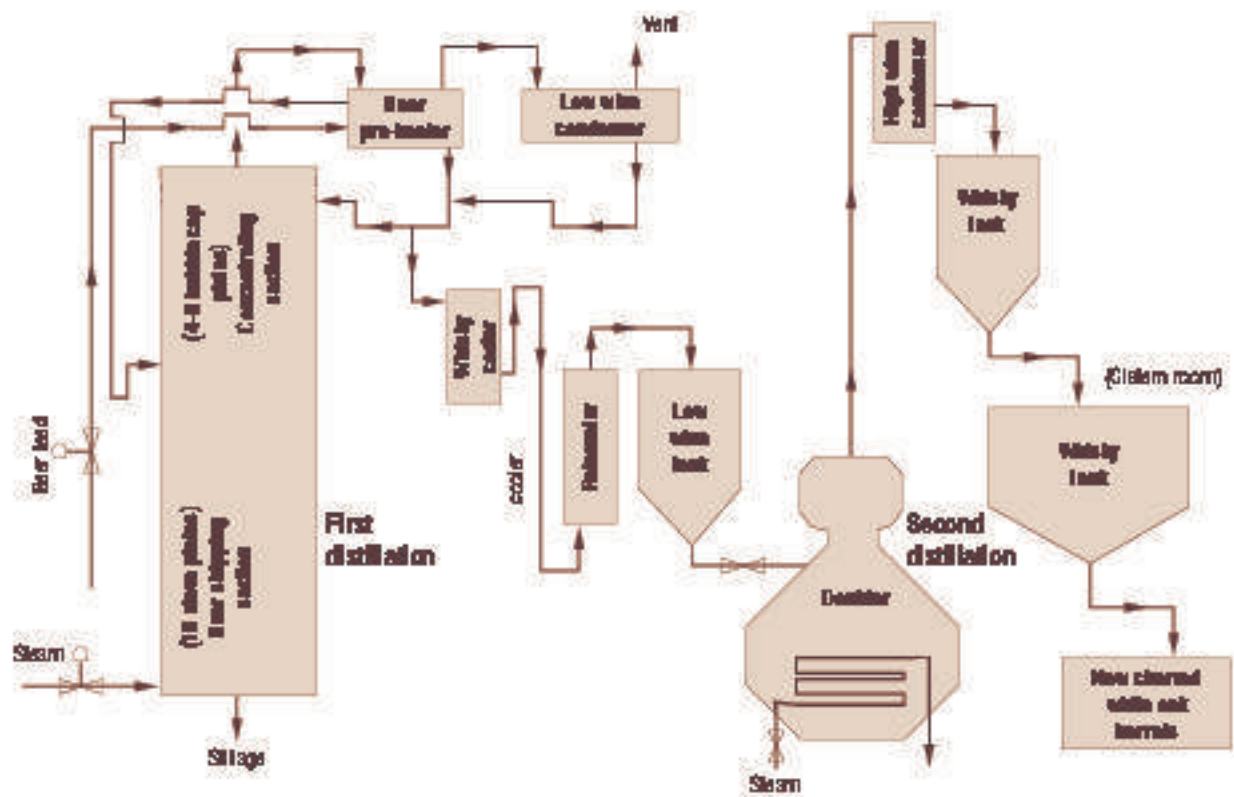


Figure 4. Bourbon whiskey distillation system, including double.

water/grain mixture on the plates. When this alcohol gets to the top 4-8 bubble cap plates it is concentrated to about 100° proof (50° GL). As the vapors continue up into the beer preheater (a heat exchanger to heat beer going into the column), some alcohol is condensed and refluxed to the top of the beer column. The rest flows to the doubler or thumper as vapor. From either of these pot still-type chambers, the vapor goes to the condenser where the product is drawn off at 130-140° proof (65-70° GL). Bourbon cannot be distilled above 160° proof (80° GL). If it comes off at more than 160° proof, it must be called 'light' whisky. The stillage from the base of the beer still is pumped to the dryer house to be processed. The 'high wine' from the stills is pumped to the cistern room where it is held, tested and reduced to barrelling proof (Table 4).

BY-PRODUCT RECOVERY

The by-product recovery does not usually receive the same care that the other processes demand. The only essential for this process is ensuring that the backset stays hot, around 99°C, so that it is absolutely sterile when used in the mash tubs, yeast tubs and fermentors. (Most distillers use 20-30% backset in their total process.) Furthermore, the hotter the backset remains, the greater the savings in energy costs during the cooking process. The stillage from the base of the beer still has about 7-10% total solids. When used for backset it is screened or

centrifuged to prevent solids accumulation in the cooker and fermentors. Nearly all distillers have a dryer house, though a couple of traditional distillers continue to sell their 'slop' to nearby farmers. For a while some, like the Jack Daniel Distillery, fed the stillage to cattle in wet-feeding operations; but environmental restrictions have generally eliminated such practices. Also, modern dryer house operations have become very profitable and the profit helps lower the cost of making whisky.

COOPERAGE AND MATURATION

Cooperage and maturation are the processing factors that distinguish bourbon and American whisky from the other whiskies of the world. Only bourbon whisky regulations require that it be matured in a new charred, white oak barrel. Other whiskies of the world may require the use of small wooden barrels, but no other whisky but bourbon goes through the care and expense of requiring small white oak barrels to be freshly charred.

The making of the bourbon whisky barrel is a very traditional, but exact science and craft. Staves and heading are quarter-sawed from mature, white oak timber. Actually, some physical variance exists within a single tree, but no more than between trees. After being quarter-sawed with the medullary rays not less than 45 degrees to the stave surface, the staves and heading are air-dried in a stave yard. The more traditional distilleries require wood to be air-

Table 4. Typical operating data for whisky distillations.

	Bourbon	Rye
Product proof	130°	130°
SGU pressure (inches of water)	48	42
Steam rate, lb/hr	12,000	12,000
Beer feed rate, gallons/minute	120	117
Reflux rate from beer preheater, gallons/hr	350	300
Reflux rate from dephlegmator, gallons/hr	700	750
Reflux rate from vent condenser, gallons/hr	30	65
Draw-off of product, gallons/minute	12.5	10.0
SGU losses, %	0.0004	0.00025
Water temperature to vent condenser, °C	21	21
Water temperature from dephlegmator, °C	79	79
Beer to SGU, %	0.05	0.05

dried at least one year. The modern distillery usually has no air-drying specifications and allows its barrels to be produced from wood that has been air-dried for six months or less. All of the wood is kiln-dried at the cooperage, with staves and heading dried to 12 and 10% moisture, respectively. The kiln-drying is essential to prepare the wood for the planing, milling, edging and joining operations that cannot be done on wet wood. More important, however, is that proper drying (air-drying a year followed by kiln-drying), makes the wood chemistry satisfactory for flavoring the whisky during maturation.

As the whisky goes through maturation (3-4 years for the modern distillers and 4-8 years for the traditional distillers), two distinct types of reactions occur: reactions between the distillate components (regardless of the barrel); and reactions that occur when the distillate extracts chemical compounds from the wood. A major factor differing among the distillers is the warehouse environment. Most modern distillers heat their warehouses in winter. One particular distiller even controls the heat cycles to ensure constant aging. The traditional distillery seldom has heated warehouses and depends strictly on Mother Nature to determine the number and range of its heating and cooling cycles.

Whether the heat cycle is natural or forced, the greatest rate of change or formation of congeners occurs in the first 12-16 months. Only ester formation occurs at a fairly constant rate. Proof increases at a fairly constant rate of 4-5% each year of aging. Other specific changes occurring when the distillate reacts with the charred wood are: a) aldehyde formation, specifically acetaldehyde, which comes from the alcohol via oxidation, b) acetic acid formation with greatest activity in the first year of maturation, and c) ester formation (ethyl acetate)

from the alcohol via oxidation. The components coming from the wood are tannins, sugars, glycerol and fructose. The hemicellulose in the wood appears to be the source of the sugars found in aged American whiskies.

The depth of charring and 'toast level' in the barrel determines the color of the whisky. Color formation is almost instantaneous when the distillate is put into the charred barrel, with 25-30% of the color formed in the first six months. Some color development occurs each year of maturation until the whisky is dumped from the barrel. The final product is then filtered, its proof reduced with demineralized water and bottled. Compared to the sweet rums, 'breathless vodka', fruity gins, light Canadians and Scotches, the American whiskies have flavor and bravado with a balance that is pleasant to the taste. American whisky produced and matured as described has a big, pungent aroma that leaves no doubt that it is bourbon or Tennessee whisky.

Though the modern and traditional distillers have different levels of technology, they both use the same basic processes for making bourbon or other American whiskies. Individual plant nuances produce different flavors, but they all have an American whisky bouquet and taste.

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Contamination and hygiene



Chapter 20

Bacterial contamination and control in ethanol production

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Introduction

Bacterial contamination is a major cause of reduction in ethanol yield during fermentation of starch-based or sugar-based feedstocks by *Saccharomyces cerevisiae*. The sugar consumed by bacteria is diverted away from alcohol production and is converted into by-products. In addition to reducing the yield, the presence of bacterial metabolites in the fermentation medium is inhibitory to yeast growth and metabolism. In distilleries, cleaning and sanitizing are much less rigorous compared to breweries, and mashes are subjected to less heat and are not sterile. Contaminants can arise from tankage, transfer lines, heat exchangers, raw materials, active dry yeast, poorly stored backset, or yeast slurry used as inoculum. Microbial numbers can be significantly reduced by cleaning and sanitizing the equipment, by maintaining backset at a temperature over 70°C, by pasteurizing or chemically sterilizing the substrates, and by adding antibiotics to fermentors (Ralph, 1981). In a distillery, it is necessary to recognize the potential sources of contamination and know the most commonly encountered contaminants so that appropriate measures can be taken to minimize serious losses.

Commonly encountered contaminants

The bacterial contaminants encountered during alcohol production include both Gram-positive and Gram-negative species. Figure 1 summarizes the types of bacteria that can occur in a distillery and their characteristics. Among the bacterial contaminants encountered, lactic acid bacteria are the most troublesome because of their tolerance to high temperature and low pH and their ability to grow rapidly and survive under ethanol production conditions. Therefore, discussion in this chapter will primarily focus on the effects of lactobacilli, the predominant organism in distilleries and fuel ethanol plants and their control.

ACETIC ACID-PRODUCING BACTERIA

While Gram-positive lactobacilli comprise the most important single group of bacterial contaminants, certain Gram-negative bacteria such as acetic acid bacteria cannot be ignored. The genera *Acetobacter* and *Gluconobacter* comprise bacteria that produce acetic acid as the dominant end product of metabolism. *Acetobacter* oxidizes acetic acid to CO₂ and water whereas *Gluconobacter* just produces

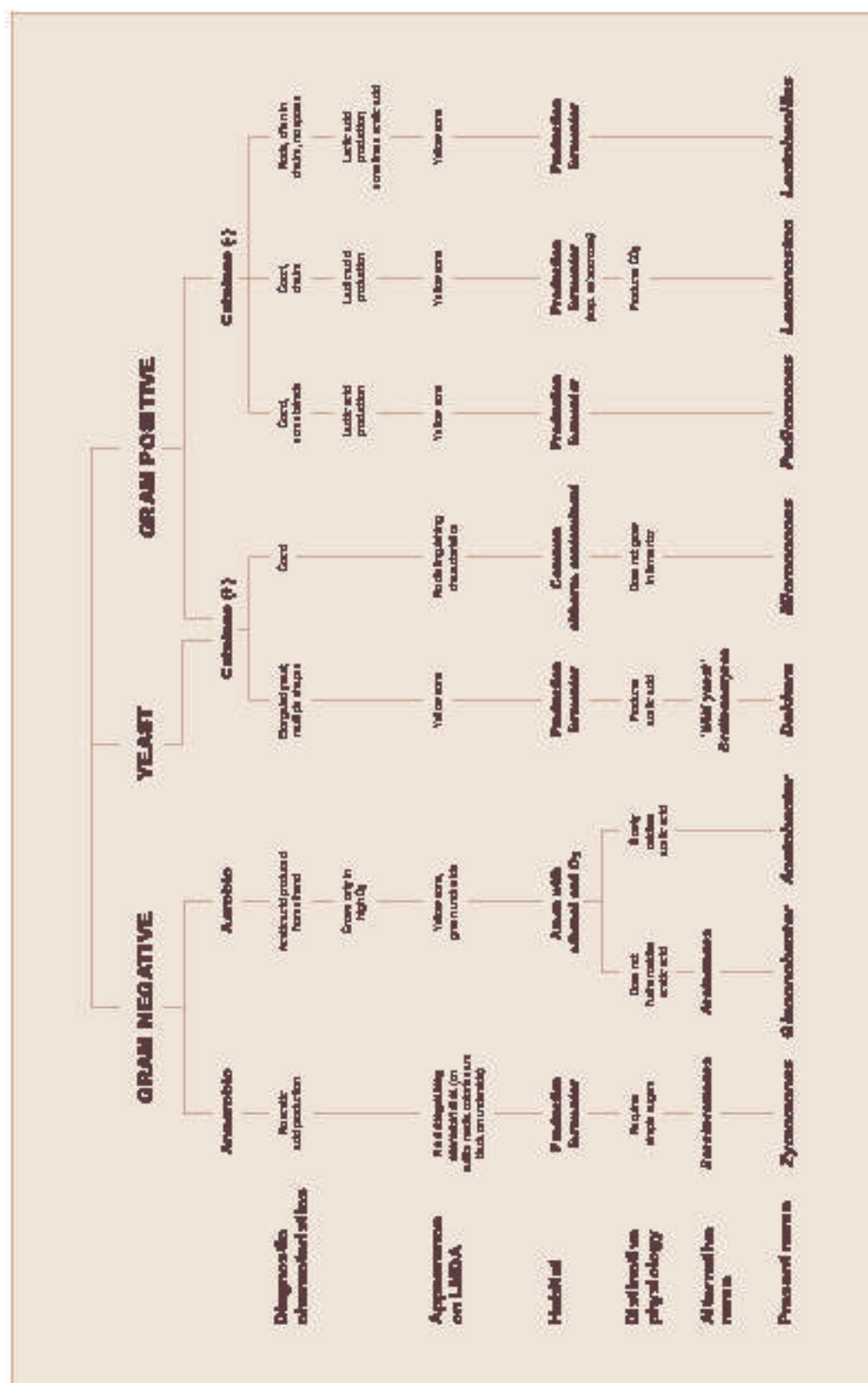


Figure 1. Classification and characteristic tests of bacteria (adapted from a laboratory manual).

acetic acid from sugar substrates and does not further oxidize the acetic acid produced.

Acetic acid bacteria are rod-shaped cells and are unable to survive and grow in the absence of oxygen. Therefore, these organisms are not a threat in the fermenter where the conditions are anaerobic. However, acetic acid bacteria can occur in the yeast propagator or yeast conditioning tank, which is subjected to high agitation and aeration to promote yeast growth. Once the inoculum is pumped to the fermenter and an anaerobic system is established, acetic acid bacteria will usually die; however sufficient acetic acid to slow or inhibit yeast growth may already be present. It is easier to control these bacteria in batch propagation systems where the tank is emptied, cleaned and sanitized between batches.

LACTIC ACID BACTERIA

Lactic acid bacteria (LAB) are Gram-positive, catalase negative, microaerophilic or aerotolerant anaerobes. They are either rod-shaped or cocci-shaped cells that produce lactic acid as a major end product of carbohydrate metabolism. LAB have complex nutritional requirements (Kandler and Weiss, 1986). These bacteria can grow in a wide range of temperatures,

from 2 to 53°C, with an optimum temperature generally between 30 and 40°C. Optimal pH for growth is 5.5–6.0. Growth generally occurs at pH 5.0 or less, but growth rate is significantly reduced. Under optimal growth conditions, the doubling time for lactic bacteria is much quicker than that of yeast.

Metabolically, LAB possess efficient carbohydrate fermentation pathways. The main fermentation pathways for glucose are the Embden-Meyerhof pathway, converting 1 mole of glucose to 2 moles of lactic acid (homolactic fermentation) and the 6-phosphogluconate pathway, resulting in 1 mole of CO₂, 1 mole ethanol (or acetic acid) and 1 mole lactic acid (heterolactic fermentation). The homofermentative LAB produce virtually a single fermentation product, lactic acid, whereas the other LAB, called heterofermentative, produce other products, mainly ethanol (or acetic acid) and CO₂ as well as lactic acid. The abbreviated pathways for the fermentation of glucose by homo- and heterofermentative organisms are shown in Figure 2. The differences observed in the fermentation products are determined by the presence or absence of the enzyme aldolase, one of the key enzymes in glycolysis.

Lacking the aldolase enzyme, heterofermenters instead oxidize glucose-6-phosphate to 6-phosphogluconate and then decarboxylate

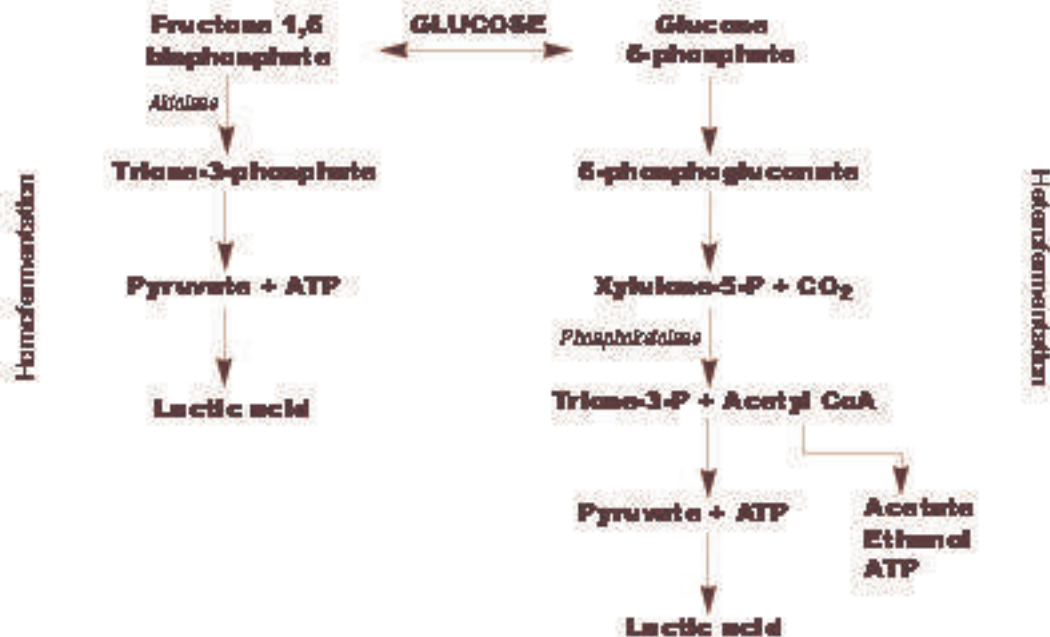


Figure 2. The fermentation of glucose in homofermentative and heterofermentative lactic acid bacteria.

this to pentose phosphate, which is then broken down to triose phosphate and acetylphosphate by means of the enzyme phosphoketolase. Whereas the hetero-fermentative lactobacilli possess ketolase but no aldolase, homo-fermentative species possess aldolase but no phosphoketolase. Obligate homofermenters are thus unable to ferment pentoses, which are broken down by the heterofermenters via phosphoketolase, yielding equimolar amounts of lactic acid and acetic acid. However, one group of homofermentative lactobacilli possesses an inducible phospho-ketolase with pentoses acting as inducers. They are thus able to ferment pentoses upon adaptation to lactic acid and acetic acid, while hexoses are homofermentatively metabolized. Therefore, these lactic bacteria are called **facultative heterofermenters**. Table 1 shows some examples of the different classes of lactic acid bacteria. Isolates of LAB from distilleries are well-adapted to the conditions existing in such fermentations (Bryan-Jones, 1975). In fact, enumeration of bacteria in many distilleries is often limited to the detection of lactic acid bacteria because aerobes and facultative anaerobes with little pH tolerance are not considered serious threats to product quality or production efficiency.

Lactobacilli effects on ethanol production by yeast

Yeasts and LAB are often encountered together in natural ecosystems and may be in competition for the same nutrients (Alexander, 1971). The genus *Lactobacillus* is of major concern to distilleries and fuel ethanol plants. Chin and Ingledew (1994) reported that *Lactobacillus fermentum* inoculated at approximately 10^3 CFU/ml did not seriously affect ethanol productivity in the fermentation of diluted (14°Plato) wheat mash. Only moderate growth (2 to 8-fold

increases) of the bacteria occurred. Other scientists, however, have reported that when bacterial numbers exceeded 10^5 CFU/ml at 30 hrs of fermentation, alcohol loss was approximately 5% (Barbour and Priest, 1988; Dolan, 1979). According to Makanjuola *et al.* (1992), reduced ethanol yields, lower yeast numbers, reduced carbohydrate utilization, and an increase in acidity were all caused by the build up of lactic acid produced by lactobacilli. They found that a bacterial count of 4.5×10^5 CFU/ml at 30 hrs resulted in a 17% reduction in ethanol yield due to a stuck fermentation.

Initial bacterial contamination of mash with approximately 10^7 CFU/ml led to as much as 0.6-1% v/v reduction in ethanol depending on the strain of bacteria (Narendranath *et al.*, 1997). These authors were the first to report that both final lactic acid concentrations and decreases in ethanol yields at the end of fermentation were directly correlated with initial numbers of viable bacteria in mash (Figure 3). Apart from the diversion of glucose for growth, the production of end products such as lactic and acetic acid, and a suspected competition with yeast cells for essential growth factors in the fermenting medium are the major reasons for the reductions in yeast growth and final ethanol yield when lactic bacteria are present.

EFFECTS OF BACTERIAL END PRODUCTS ON YEAST GROWTH

The end products of metabolism of lactobacilli, lactic acid and acetic acid, are inhibitory to yeast growth and metabolism. The concentrations of acetic acid (a minor end product of heterofermentative lactic acid bacteria and wild yeasts or a major end product of aerobic bacteria such as *Acetobacter* spp.) and lactic acid inhibitory to the growth of *S. cerevisiae* were 0.5-9 g/L and 10-40 g/L, respectively, and an

Table 1. Three classes of lactic acid bacteria.

Type	Examples
Obligately homofermentative	<i>Lactobacillus de Brouckii</i> , <i>L. acidophilus</i> , <i>Pediococcus damnosus</i>
Obligately heterofermentative	<i>L. brevis</i> , <i>L. buchneri</i> , <i>L. fermentum</i>
Facultatively heterofermentative	<i>L. plantarum</i> , <i>L. casei</i> , <i>L. pentosus</i> , <i>L. sake</i>

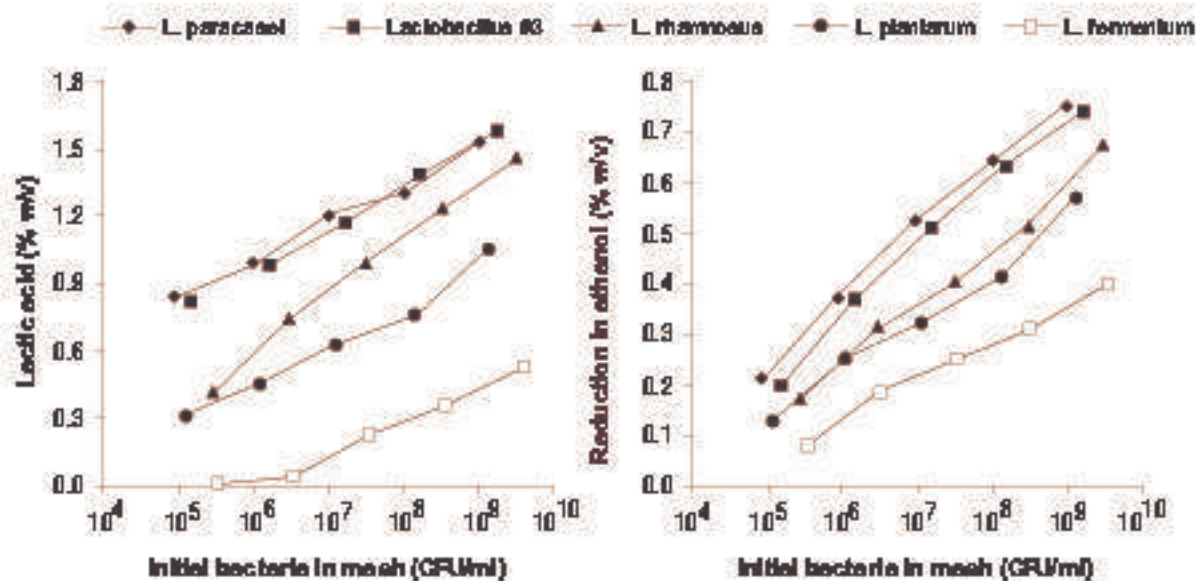


Figure 3. Effect of the initial number of lactobacilli on the final lactic acid concentration and on the reduction in final ethanol concentration compared to the control with no bacterial inoculation. (Adapted from Narendranath *et al.*, 1997).

80% reduction in yeast cell mass occurred at concentrations of 7.5 g and 38 g/L, respectively (Maiorella *et al.*, 1983). The effects of these acids on the specific growth rate of yeast are detailed in the chapter on continuous fermentation in this volume. The minimum inhibitory concentration (MIC) of acetic acid for yeast growth is 0.6% w/v (100 mM) and that of lactic acid is 2.5% w/v (278 mM). However, acetic acid at concentrations as low as 0.05–0.1% w/v and lactic acid at concentrations of 0.2–0.8% w/v begin to stress yeast as seen by decreased growth rates and decreased rates of glucose consumption (Narendranath *et al.*, 2001a).

The inhibitory effect of weak organic acids such as acetic acid and lactic acid on yeast growth depends on the pH of the medium, the dissociation constant of the acid, and its molar concentration. In solution, a weak acid exists in a pH-dependent equilibrium between dissociated and undissociated states, as described by the Henderson-Hasselbach equation ($\text{pH} = \text{pK}_a + \log[\text{A}^-]/[\text{HA}]$ where A^- and HA are the dissociated and undissociated species, respectively). This equation indicates that at a pH above its pK_a value, more than 50% of the acid is dissociated and that the concentration of undissociated acid increases logarithmically as the pH declines. Since organic acids are

generally more toxic to microorganisms at low pH, it is assumed that the antimicrobial activity of these acids is the result of an increased proportion of undissociated molecules (Salmond *et al.*, 1984). Therefore, acetic acid ($\text{pK}_a = 4.74$) with a higher pK_a value is more toxic to yeast than lactic acid ($\text{pK}_a = 3.86$) at any given pH of the medium. Acetic acid has between two and four times more molecules in the undissociated form over a pH range between 4.0 and 4.6 compared to lactic acid (Lindgren and Dobrogosz, 1990). Undissociated weak acids diffuse passively into the microbial cell until equilibrium is established across the membrane. As molecules enter the cytoplasm, they dissociate at the higher intracellular pH. The protons liberated are either pumped out of the cell in exchange for cations or are neutralized by the buffering capacity of the cytoplasm (Booth and Kroll, 1989). Figure 4 illustrates how the anions (A^-) and undissociated acids (HA) are distributed inside and outside the yeast cell for a given concentration of acetic acid and lactic acid at a particular pH of the medium. However, Narendranath *et al.* (2001b) found that acetic and lactic acids inhibit yeast growth by different mechanisms.

Therefore, the two major reasons for reduction in ethanol yield due to lactobacilli contamination

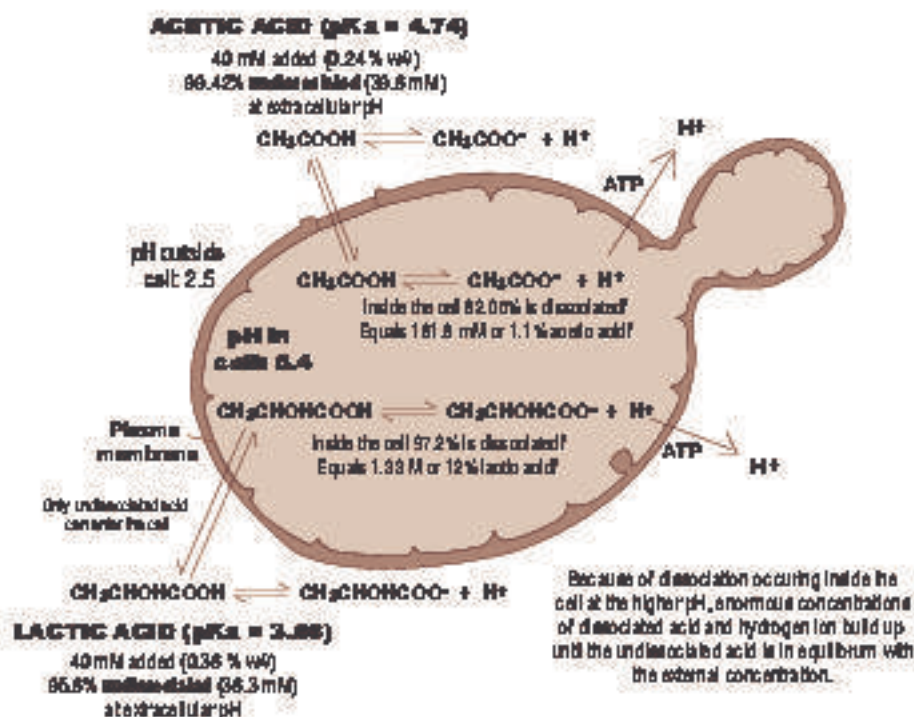


Figure 4. Illustration of the concentrations of acetic and undissociated acids that would be present in the medium and inside the cell (based on the pH_{ext} and pH_{in}) when 40 mM of either acetic acid or lactic acid is present. The concentrations were calculated based on the Henderson-Hasselbalch equation. The concentrations differ based on the initial concentration of the acids in the medium and the pH_{ext} and pH_{in} values. The concentrations indicated do not remain steady because there is constant pumping out of the excess protons (by H^+ -ATPase) to raise the intracellular pH, resulting in further penetration of weak acid molecules into the cell that re-acidify the cytoplasm. In most situations, the pH of the medium also falls, affecting results. The concentrations of acids could reach 181.8 mM for acetate and 1.33 M for lactate under the stated conditions when 40 mM acid is added to the medium (adapted from Narendranath *et al.*, 2001b).

are: 1) Glucose that could be available for yeast to produce ethanol is taken up by these bacteria, and 2) the end products of metabolism, acetic acid and lactic acid, inhibit yeast growth and concomitantly ethanol production.

As little as 1% decrease in ethanol yield is highly significant to distillers of fuel alcohol (Makanjuola *et al.*, 1992). In large plants with outputs of 400 million to 1100 million liters of ethanol per year, such a decrease would reduce income by 1 to \$3 million USD annually.

Management of lactobacilli in distilleries

Despite cleaning and sanitation procedures (covered in detail in elsewhere in this volume), bacteria may find their way into distillery

processes. These bacteria must be removed as quickly as possible. The methods used in the ethanol industry to control contaminant bacteria include stringent cleaning and sanitation, acid washing of yeast destined for reuse (in case of breweries), adjustment of mash pH, and the use of antibiotics during fermentation. The method(s) used depends to a large degree on the end use of the alcohol.

USE OF ANTIBIOTICS

To control lactobacilli during fermentation, antibiotics are used in fuel ethanol plants. Antibiotics are compounds produced by microorganisms, which at low concentrations inhibit the growth of other microorganisms.

There are different kinds of antibiotics and they can be grouped according to their mechanism of action against bacteria.

Penicillin G has been widely studied (Day *et al.*, 1954) and used in the alcohol production industry during fermentation since the 1950s. Penicillin G is primarily active against Gram-positive bacteria. The extensive use of this antibiotic, which acts by inhibiting bacterial cell wall synthesis, has led to the emergence of resistant microflora. For this reason and due to the instability of penicillin G pH levels below 5, various other antimicrobials have been introduced or investigated for application including virginiamycin (Hynes *et al.*, 1997), streptomycin, tetracycline (Aguarone, 1960; Day *et al.*, 1954) and monensin (Stroppa *et al.*, 2000). Tetracycline is a broad spectrum antibiotic, where as penicillin V, monensin, and virginiamycin are more active against Gram-positive bacteria. The other antibiotics that have been tried such as streptomycin and polymyxin are more active against Gram-negative bacteria. The typical usage rate for these antibiotics in the fermentation is 2–5 ppm. The mechanisms of action and the spectrum of these antibiotics are summarized in Table 2.

Although many antibiotics have been tested at a laboratory scale, the most widely used in the ethanol industry are penicillin G and virginiamycin. Antibiotic residues and establishment of antibiotic-resistant bacterial

strains is a global issue, and one that ethanol producers must understand because of DDGS use in food animal diets. Penicillin G is inactivated during the alcohol fermentation (Islam *et al.*, 1999). Inactivation of penicillin G is significant at 35°C. At pH 4.8, the biological half-life of penicillin G is 24 hrs at 25°C and 4 hrs at 35°C, whereas at pH 3.8, it is <4 hrs for both temperatures. Moreover, any penicillin G still active at the end of fermentation is definitely destroyed in the still since penicillin G decomposes rapidly at temperatures over 52°C (Kheirulomoom *et al.*, 1999). In contrast, virginiamycin is not significantly altered during alcohol fermentation after 72 hrs at 35°C (Islam *et al.*, 1999). Research has shown that using over 2 ppm virginiamycin to control bacteria suppresses the rate of fermentation. Upon distillation (100°C for 30 min) virginiamycin activity is reduced to 2.6% of the original (Hamdy *et al.*, 1996). Residues can therefore be present in DDGS, which is a potential problem in markets where this antibiotic has been banned in animal feeds.

SYNERGY: ANTIBIOTIC COMBINATIONS

Using single antibiotics such as penicillin G or virginiamycin repeatedly can lead to development of resistance in microorganisms. Figure 5 shows the development of resistant

Table 2. List of some of the antibiotics used in the ethanol industry, their modes of action and activity spectrum.

Antibiotic	Mechanism	Bactericidal/static	Spectrum
1a. Penicillin G	Inhibits cell wall synthesis	Bactericidal	Gram(+) bacteria
1b. Penicillin V*			
2. Bacitracin	Affects cell wall	Bactericidal	Gram(+) bacteria
3. Tetracycline	Protein synthesis inhibitor	Bacteriostatic	Gram(+) & Gram(-) bacteria
4. Streptomycin	Protein synthesis inhibitor	Bactericidal	Gram(+) & aerobic Gram(-) bacteria
5. Erythromycin	Protein synthesis inhibitor	Bacteriostatic, cidal at high doses	Gram(+) & Gram(-) bacteria
6. Polymyxin	Affects cell membrane	Bactericidal	Gram(-) bacteria
7. Virginiamycin	Protein synthesis inhibitor	Bactericidal	Gram(+) bacteria
8. Monensin	Affects cell membrane	Bactericidal	Gram(+) bacteria
9. Chloramphenicol	Protein synthesis inhibitor	Bactericidal (or) static	Gram(+) & Gram(-) bacteria. Good against anaerobes. Heat stable?

* Has the same properties as penicillin G but is more stable at acidic pH.

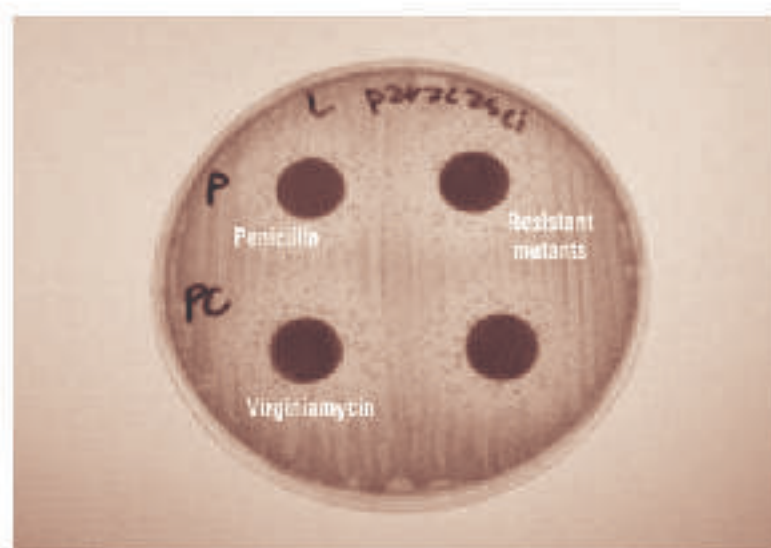


Figure 5. A typical disc assay performed to test the antimicrobial activity of penicillin G and virginiamycin against *Lactobacillus paracasei*. Note the growth of resistant mutants in the zone of inhibition.

mutants to single antibiotics such as penicillin or virginiamycin. One of the strategies to reduce the risk of resistance is to use a combination of antimicrobials, including non-antibiotic substances, thereby taking advantage of synergism in activity as well. Lactoside™, a proprietary blend of antimicrobials, reduced risk of resistance while increasing spectrum of activity and pH range. Following five years of use, no build up of resistance has been reported.

The advantage of balanced mixtures of antibiotics has been demonstrated in several practical situations. A recent experiment examined corn mash (30% dry solids; pH 5.6) contaminated with an aggressive *Lactobacillus paracasei* strain. Yeast was inoculated at 30 million cells/ml just prior to yeast inoculation, test fermentors were contaminated (inoculated) with *L. paracasei* at $\sim 10^7$ CFU/ml (in the treatments with bacteria). The antibiotics used, penicillin G, virginiamycin, and Lactoside™, were added from 10,000 ppm stock solutions. Virginiamycin was made up in HPLC-grade methanol. The temperature was maintained at 31.1°C (88°F) throughout the fermentation. Samples were withdrawn for analysis from each fermentor at 8, 24, 32, 48, 56, and 72 hrs. Viable cell counts were monitored by the spread plate technique. For enumeration of bacteria, the MRS agar plates (with 10 ppm cycloheximide) were incubated in anaerobic jars at 30°C. The plating was done in duplicate for each dilution. Results

indicated that Lactoside™ significantly reduced the viable numbers of bacteria. Virginiamycin was the least effective antibiotic at the dosage used in controlling *L. paracasei* (Figure 6).

In experiments performed to determine the minimum inhibitory concentrations (MIC) for various antibiotics against lactobacilli at various stages of their growth, Lactoside™ at low concentrations killed *L. plantarum* at early, mid and late log phases of growth (Table 3).

Table 3. Minimum inhibitory concentrations for different antibiotics and Lactoside™ (expressed in ppm) for *L. plantarum* at different stages of its growth.

Antibiotic	MICs when antibiotic added at various stages of growth			
	0 hrs	Early log	Mid log	Late log
Penicillin G	0.2	12.8	>12.8	>12.8
Penicillin V	0.2	12.8	>12.8	12.8
Virginiamycin	0.2	>12.8	>12.8	>12.8
Lactoside™	0.2	0.2	0.2	0.8
Oxytetracycline	>6.4	>6.4	>6.4	>6.4
Erythromycin	12.8	>12.8	>12.8	>12.8
Streptomycin	>12.8	>12.8	>12.8	>12.8

Similar results were obtained with four other species of lactobacilli. Figure 7 shows the regions of a typical growth curve for a microbe where the various antibiotics when used at low concentrations would be effective in killing the microbe. This information is important for a

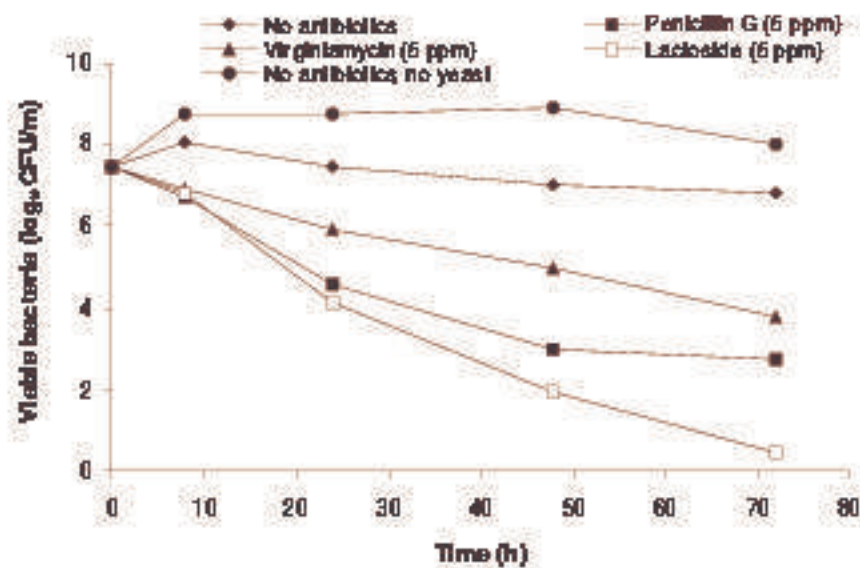


Figure 6. Survival of *L. paracasei* in the fermentation of corn mash (30% DS, pH 5.6) at 31.1°C (88°F) in the presence or absence of various antibiotics. Values are means of duplicate fermentations that had a CV of <8%.

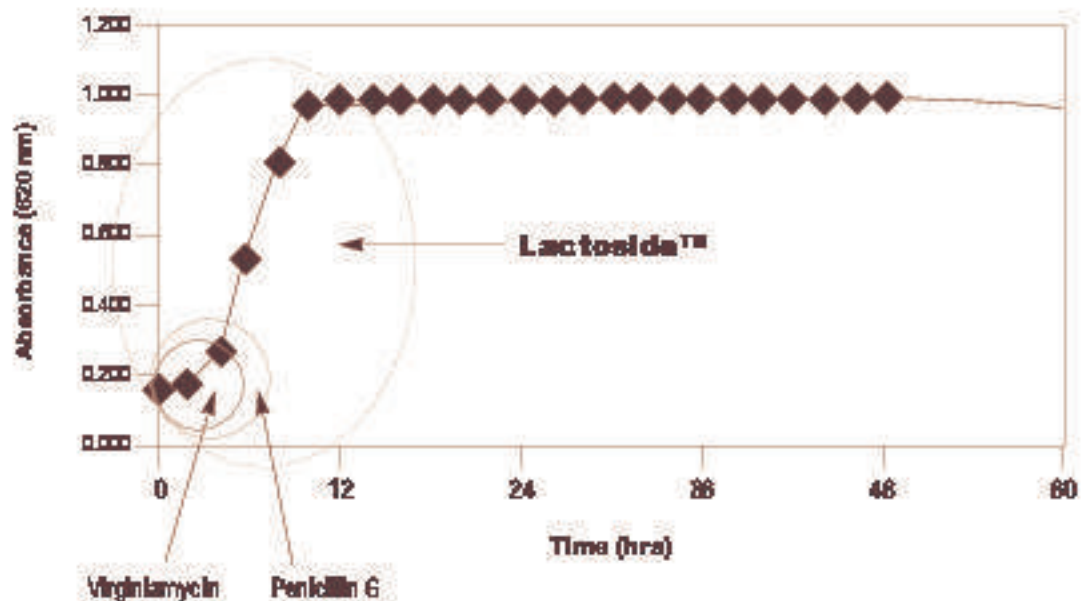


Figure 7. A typical growth curve of a microorganism showing at what stages antibiotics are effective at low concentrations.

distillery since contamination can be detected as early as 6–10 hrs from the start of filling a fermentor. By this time, the contaminants are approaching the mid-log phase of growth. Therefore, an antibiotic or antimicrobial effective at a low concentration at this stage would be an ideal choice.

The ideal antimicrobial should, however, possess all the following characteristics:

1. Broad-spectrum activity: effective against both Gram-positive and Gram-negative bacteria.
2. Effective over a wide pH range.

3. Control the bacteria at various growth stages.
4. Effective at low concentrations.
5. Bactericidal rather than bacteriostatic.
6. Able to be combined with other antibiotics or antimicrobials to avoid resistance development in bacteria.

FORMULATION OF ANTIBIOTIC COMBINATIONS

Factorial experiments are conducted to test interaction effects (either synergistic or antagonistic) among antibiotics used in combination to control growth of a test lactic acid bacteria. These experiments are conducted in corn mash rather than laboratory media so that the results can be translated to the field. From these experiments, the individual effects of the antibiotics can also be determined. Lactic acid is the parameter measured since lactic acid produced is directly proportional to the viable cell numbers of bacteria present in mash (Narendranath *et al.*, 1997). The results of the interactions are plotted in 3-D graphs with the two test antibiotics on x- and y-axes, and lactic acid on the z-axis. The graphs are created based on the response surface regression analysis of the data using the SAS program. Figure 8 shows the model created by using the equation based on the data obtained in an experiment. This equation can then be used to make formulations

with correct proportions of each antibiotic. Experimental designs are available to generate such equations for studying the combination of more than two antibiotics.

It is becoming a common practice in some industrial operations to either under- or overdose antibiotics for controlling contaminating bacteria. Under-dosing antibiotics leads to the development of resistance in microorganisms. Overdosing antibiotics can affect fermentation rate by yeast (Hamdy *et al.*, 1996) and increase the chances that all the antibiotic will not be inactivated by the distillation process. Therefore, it is always advisable to use the antibiotics at the dosage recommended by the supplier/manufacturer.

LOWERING MASH pH CAUSES ETHANOL LOSS

Since the growth rate of lactic acid bacteria is reduced significantly at pH levels <5.0 (Kandler and Weiss, 1986), most ethanol plants tend to reduce the pH of the mash with sulfuric acid to <4.5 at the start of fermentation. Some continuous fermentation plants even start fermentations at pH of 4.0 or less. Lowering mash pH may reduce the growth rate of contaminant bacteria but it significantly reduces ethanol yield. In an experiment using mashes of various dissolved solids concentrations adjusted to pH values from 4 to 5.5, significantly higher ethanol was obtained when the initial

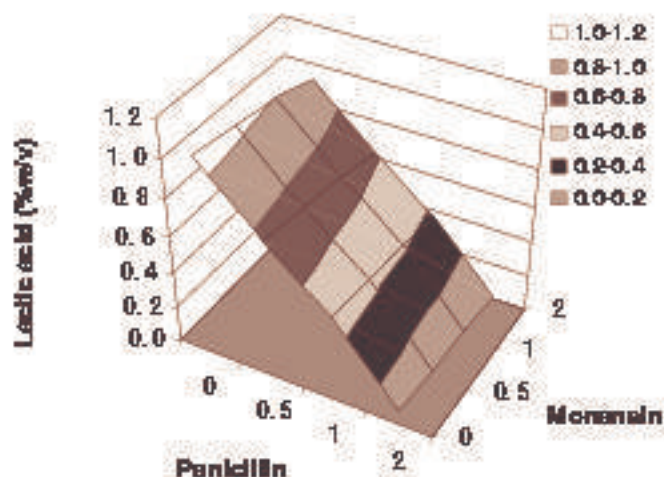


Figure 8. Lactic acid produced by *L. plantarum* in corn mash (pH 5.5, D.S. 24%) at 30°C as affected by various concentrations (ppm) of penicillin and monensin in combination in a 4 × 4 factorial experiment. Model was fitted based ($P < 0.001$) with $R^2 = 0.9993$.

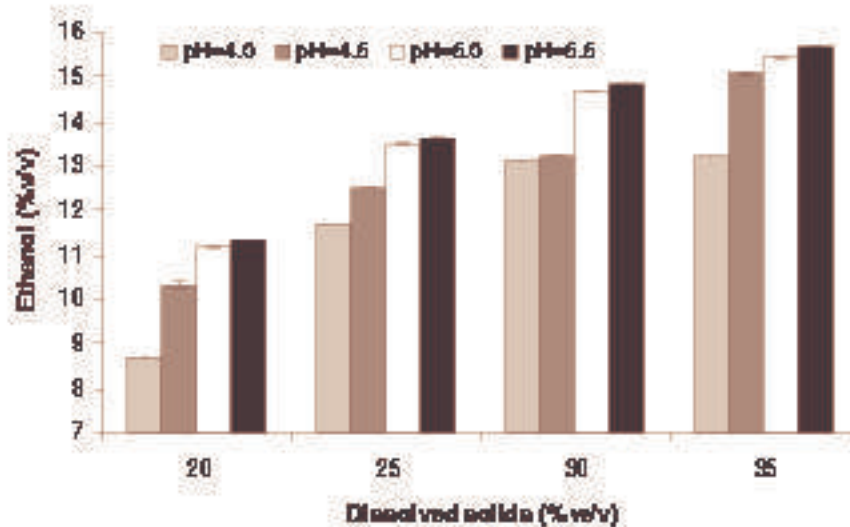


Figure 9. Ethanol produced by *S. cerevisiae* in 48 hrs at 30°C at different concentrations of dissolved solids in the mash at four pH levels. Coefficient of variation among the duplicates was <2%.

mash pH was 5.5 (Figure 9). Moreover, yeast can tolerate higher acetic acid (0.1–0.2%w/v) and lactic acid (up to 3%w/v) when the starting pH is 5.5, since at this pH these acids are primarily in the dissociated form. By the end of fermentation, however, the pH drops 1 unit to 4.5 under normal 'contaminant-free' conditions. Similar observations were also made with wheat and mile mashes.

The occurrence of bacterial contaminants in an industrial-scale ethanol production process is unavoidable, especially when the pH of the mash at set (start of fermentation) is between 5.0 and 5.5. Therefore, a good cleaning and sanitation regime combined with an effective antimicrobial program will reduce bacterial numbers and significantly increase ethanol yield, which ultimately results in increased profit for ethanol producers.

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Chapter 21

Managing the Four Ts of cleaning and sanitizing: time, temperature, titration and turbulence

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Introduction

Cleaning and sanitizing is an integral part of the operation in many processing facilities including distilleries, ethanol plants and breweries. The cleaning and sanitizing effort represents a significant investment of time, labor and operating costs. At the same time there is usually a positive payback for this effort in terms of yields, efficiencies, safety and product quality.

In a clean plant that is running efficiently with no infection problems, there is always the temptation to reduce operating costs by trimming back cleaning times and chemical usages. This type of ongoing evaluation is a worthwhile part of plant management. We should always strive to clean and sanitize to the extent required by the process and the equipment but overkill in this area should be avoided. If a little bit is good, a lot is not necessarily better.

To achieve the proper degree of cleaning and sanitizing at an acceptable cost, there are a myriad of approaches and tools that can be used. Sometimes called the 'cleaner's bag of tricks', these tools can be grouped in four categories known as the 'Four Ts' of Cleaning and Sanitizing. The Four Ts are:

- **Time**
- **Temperature**

- **Titration**
- **Turbulence**

Time refers to the frequency of running the cleaning operation, for example weekly, daily, or after each batch. In a given cleaning cycle it also refers to the length of each step. For example a 5 min rinse, a 1 hr caustic wash, etc.

Temperature refers to the temperature of the cleaning solutions used in each step of the cleaning cycle. The first rinse may be at ambient temperature while the caustic wash may be specified between 150 and 160°F.

Titration refers to the chemistry of the cleaning solutions. This includes selecting the right cleaning chemical for the job being done. It also includes the concentration of chemicals used in the cleaning solutions.

Turbulence is the mechanical action in the cleaning program that will physically scrub soil from dirty surfaces. Turbulence encompasses the use of scrub brushes and high-pressure nozzles as well as pumping cleaning solutions at high velocities through dirty pipelines.

For any cleaning job, many combinations of time, temperature, titrations and turbulence can be used to achieve effective cleaning at a reasonable cost. There are also many combinations that will not work because of a deficiency in one or more of the Four Ts. For example, cleaning time may be too short or too infrequent. The detergent may be too weak, it may be at too low a temperature or it may not be the right choice for the soil type present (Figures 1 and 2).

If cleaning is inadequate, it is usually possible to correct it by increasing the intensity of one of

the Four Ts (Figure 3). If the turbulence created by the velocity of cleaning solution flowing in a pipeline is inadequate, it may be possible to compensate by cleaning for a longer time, by increasing the concentration of the cleaning chemicals or by raising the cleaning solution temperature.

Our challenge is to achieve an acceptable degree of cleaning and sanitizing in specific processes. We sometimes go through elaborate procedures but in the end still have infections. Why?

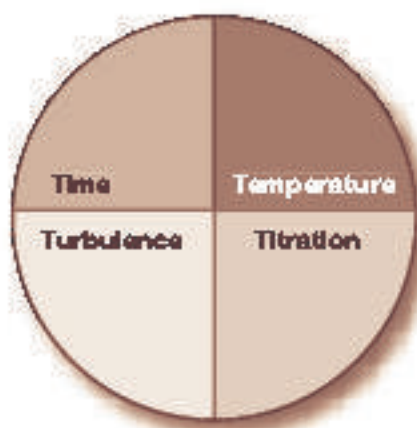


Figure 1. Soils contributions do work.

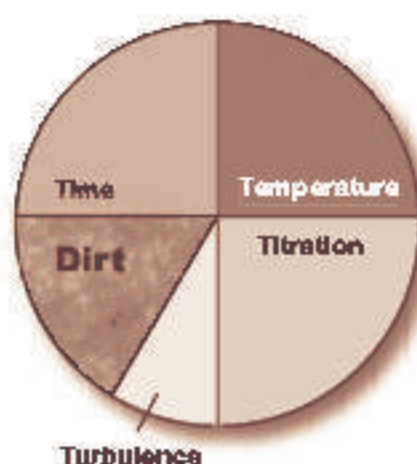


Figure 2. Soils contributions do not work; soil dirt remains.

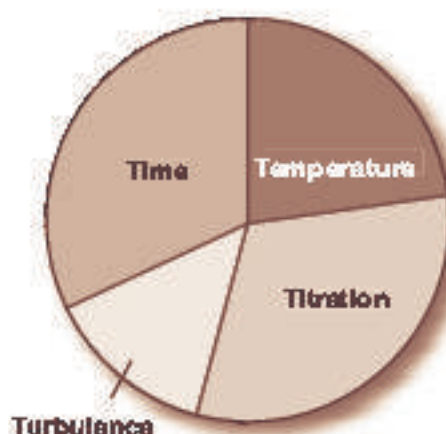


Figure 3. Deficiencies in one of the Four Ts can be corrected or compensated by changing another.

This paper examines the tools at our disposal for effective cleaning and sanitizing – our cleaning bag of tricks. Proper attention to the Four Ts in the toolkit and how they are combined is needed to make cleaning and sanitizing effective.

Definitions

Cleaning is reducing the amount of soil to an acceptable level. Cleaning is usually done with a combination of water and added detergents. Undercleaning means that we have not done the job properly. Gross overcleaning means wasted resources – time, chemicals and manpower. An acceptable level of cleaning in a pharmaceutical plant would probably be overcleaning in an ethanol distillery.

Sanitizing is reducing the population of viable organisms on a clean surface to an acceptable level. Again, 'acceptable' has different meanings in different operations. Within the ethanol industry it may even vary from plant to plant. Heat and/or sanitizing chemicals are used for this step.

Disinfection is the destruction of all vegetative microorganisms, but not necessarily spores.

Steritization is the complete destruction of all organisms including spores and viruses.

Soil is any unwanted material left on a surface that needs to be clean. Soils can be composed of sugars, salts, fats, proteins, microbes, scales and other mineral deposits. Knowing the nature of the soil is necessary when planning the cleaning procedure used to remove it. Soils left on surfaces harbor contaminating bacteria, reduce efficiency in heat exchangers and plug pipes and other passageways.

CIP is the acronym for cleaning-in-place. Pipelines, tanks, process equipment and accessories are cleaned by pumping cleaning solutions through them without disassembly or manual cleaning. CIP processes are usually automated.

COP is cleaning-out-of-place. COP involves manual disassembly and cleaning by hand.

Therefore, cleaning is defined as the removal of soil while sanitizing is the reduction of viable organisms remaining on the clean surface. An important concept in cleaning and sanitizing is that first we remove the dirt, then we sanitize. *Sanitizing dirt is not in the program!*

Time

If you don't get it clean the first time, wash it again. Spend more time cleaning and you will get better results. This sounds like a simple solution, but a dilemma arises because time spent cleaning could be time spent producing product.

Figure 4 illustrates this in the operation of a batch ethanol fermentor. In the fermentation cycle, a period of time is set aside for cleaning and sanitizing between batches. The ethanol concentration curve, however, shows that we can produce more ethanol in the fermentor if we omit all or part of the cleaning time. But what will the longer-term results be if we take shortcuts in cleaning? We must find a happy medium, which is the optimum amount of time taken from production to keep the process equipment clean. The other three Ts of cleaning and sanitizing can help us do this.

Time refers to the frequency of cleaning as well as the length of the cleaning cycle. We learn from experience that some parts of the process are very sensitive to infection and require frequent cleaning. An example is the yeast propagation system, which is thoroughly cleaned and sanitized after every use. Other parts such as the slurry tank or liquefaction tank are less critical and may be cleaned every 1-6 months.

Continuous fermentation systems present special problems compared to batch fermentors. A continuous fermentation train may be shut down only one or two times a year for cleaning. This shutdown requires a total stoppage of production, so it has significant cost implications. Because of the continuous flow through the fermentation train, there is some degree of flushing of the infecting organism. Frequently the culture yeast grows more slowly than the contaminant, and reduced ethanol yield requires some action. Antibiotics such as Lactoside™ and Allpen™ and antimicrobials may be added to the mash to kill bacteria without requiring a shutdown. For a wild yeast infection it is usually

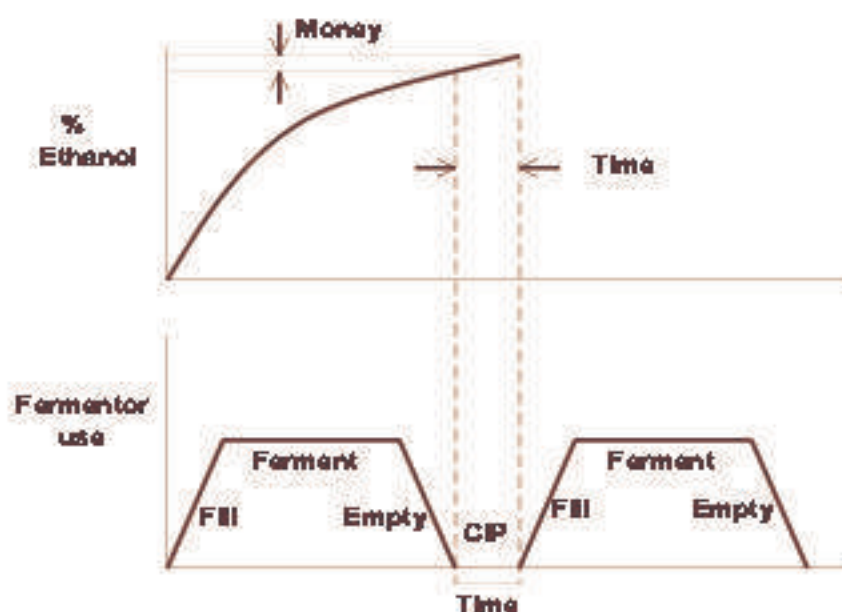


Figure 4. The dilemma between cleaning time vs. production: (time = money!)

necessary to shut down and clean because agents that kill the wild yeast will also kill the culture yeast.

Organizing a cleaning schedule for every piece of equipment in the plant is an important part of the CIP program. An example of such a schedule is shown in Table 1.

Temperature

Warm cleaning is more effective than cold cleaning. Within limits, this is usually true in cleaning and may or may not be true in sanitizing. Caustic soda (sodium hydroxide) cleaning solutions can be used at ambient temperatures but they are normally heated, as high as 82°C (180°F). Reactions proceed faster at higher temperatures and many soils are more soluble in hot water than in cold water. The cleaning process can therefore be faster and more effective if hot solutions are used.

Table 2 shows the results of a cleaning study comparing warm and cold detergent solutions to clean dirty beer lines. The amount of soil present was measured with an ATP-detecting luminometer. Starting from a 'soil overload' condition (>500,000), the cold solution left 300 times as much soil as the warm solution.

Table 2. Effect of temperature on amount of soil present before and after use of cold or warm cleaning solutions.

	Cold cleaning 23°C (74°F)	Warm cleaning 57°C (135°F)
Before cleaning	>500,000	>500,000
After cleaning	18,242	59

When raising the temperature of a cleaning solution it is important to check the chemical compatibility of the equipment material of construction with the hot cleaning solution. Some hot acid solutions, for example, may be too corrosive for metals such as mild steel or brass.

Most sanitizing solutions lose effectiveness when the temperature is raised above a threshold level. For example, cool or tepid water should be used for preparing solutions of Iotech™ and other iodophor sanitizers and they should be stored below 38°C (100°F). At higher temperatures the vapor pressure of the active ingredient causes it to vaporize.

Temperature can be an effective tool in the 'cleaning bag of tricks.' For example, if we want to reduce the time spent cleaning a product transfer line without sacrificing cleaning effectiveness, a

Table 1. Constant routine CIP schedule.

Monday		Tuesday		Wednesday		Thursday		Friday		Saturday		Sunday	
DAYTIME	Start time	DAYTIME	Start time	DAYTIME	Start time	DAYTIME	Start time	DAYTIME	Start time	DAYTIME	Start time	DAYTIME	Start time
Dishwash Spiral transfer		Dishwash Spiral transfer		Dishwash Spiral transfer		Dishwash Spiral transfer		Dishwash Spiral transfer		Dishwash Spiral transfer		Dishwash Spiral transfer	
NIGHT		NIGHT		NIGHT		NIGHT		NIGHT		NIGHT		NIGHT	
Batch 1302 A or B		Batch 1400		Batch 1402		Batch 1404		Batch 1302 A or B		Evaporator			
Batch 1303		Batch 1401		Batch 1403		Batch 1301 B		Batch 1302C					
Batch 1302C						Batch 1405		Batch 103					

wanner or hotter cleaning solution could be the answer.

Titration

Titration, the third T in the cleaning and sanitizing bag of tricks, refers to the chemistry of cleaning and sanitizing chemicals and solutions. It includes matching the type of chemical cleaner to the type of soil present and using that chemical at a strength that is both effective and affordable. It is therefore essential to have as much information as possible about the soil we are trying to remove (McCabe, 1999; Kretsch, 1994).

THE NATURE OF SOILS

Any of the compounds present in raw materials or in the water supply used for fermentation may become insoluble and be deposited on equipment surfaces as an unwanted soil. Methods used to remove these soils depend on the specific nature of the material involved.

Carbohydrates

The soluble sugars present during fermentation may be left on surfaces, especially the non-fermentable sugars. A much bigger problem is the higher molecular weight carbohydrates such as gums, which can form tough deposits on surfaces. Retrograded starch can form when starch is not sufficiently digested by α -amylase enzymes. Depending on the type of grains used, gums such as β -glucans or pentosans may become soluble in the mash and then be deposited later on. Dextrans produced by *Leuconostoc* bacteria from sucrose can be produced in plants fermenting sucrose-containing materials.

Proteins

Most of the protein present in grains is insoluble and passes through mashing and fermentation in the insoluble form. The soluble portion of the protein may become denatured by conditions such as temperature changes or pH shifts. As the protein becomes insoluble it may be deposited onto various surfaces. If tannins are

present, they may react with proteins in a reaction similar to the tanning of leather, forming tough, water-resistant deposits.

Oils

Oils are liquid fats and are intrinsically insoluble. Much of the oil present in grains is broken into microscopic droplets or emulsions that are suspended in the mash. As conditions change, the emulsions may coalesce forming larger deposits of insoluble oil.

Inorganic compounds

Various inorganic compounds may become insoluble during mashing or fermentation. Most commonly calcium in water reacts with the oxalate present in grains to form insoluble calcium oxalate, commonly called beerstone. Carbonates present in water may combine with calcium to form calcium carbonate scale. Magnesium hydroxide tends to co-precipitate as part of the carbonate scale. Occasionally water with high silicate content may generate a silica scale as the pH drops. Soluble silicate is converted by acid to insoluble silica (SiO_2).

Biological deposits

Many microorganisms tend to grow better on surfaces than when freely suspended in a liquid. The layer of microorganisms that forms together with other materials such as non-living soil and external polysaccharides produced by the microorganisms is called a *biofilm* (Czechowski and Banner, 1992). A biofilm may be observed as a slimy layer on tanks used to store water. Fortunately, most microorganisms found in fermentation do not have a pronounced tendency to form a biofilm, but films of yeast or bacteria growing inside a surface scale are frequently observed. These films are a potent source of contamination.

MATERIALS USED FOR CLEANING

Water

Water is a good solvent for many compounds, especially polar compounds. Materials such as simple sugars, soluble proteins and the soluble

products of fermentation are easily removed with water. Most compounds are more soluble in hot water than cold, so heating water helps make it a better cleaner. Exceptions are the water hardness compounds, particularly those of temporary hardness. These become less soluble at higher temperature leading to the deposition of calcium carbonate-based water scales. An important consideration in the use of hot water for cleaning is to prevent formation of scales by softening the water. Many cleaners contain water-softening ingredients.

Pure water has a relatively high surface tension, as shown by the fact that water tends to form round drops when placed on a surface. Water is described as not being good at wetting because the water forms droplets and does not wet the entire surface. Compounds that concentrate at the surface of water often decrease the surface tension of water droplets, making it easier for the water to spread out and cover more of the surface. These compounds are called wetting agents.

Alkali

An alkali is something that raises the pH of water. The pH depends on the concentration of hydroxide ions: the more hydroxide the higher the pH. The most common alkali used for cleaning is caustic soda (sodium hydroxide), which is an excellent source of hydroxide ions and is relatively inexpensive. Unfortunately, caustic soda has poor rinsability; it does not rinse away very easily after it is used for cleaning. Potassium hydroxide is also a strong alkali and it rinses more easily than sodium hydroxide, but it is significantly more expensive. Addition of surfactants to cleaning compounds with caustic soda will improve rinsability.

Other alkaline compounds include silicates, phosphates and carbonates. Sodium metasilicate is a commonly used alkali. It provides a high pH, although not as high as caustic. It tends to keep removed soil in suspension, providing good removal from the area cleaned. Silicate does not tend to corrode soft metals such as aluminum and copper, while caustic attacks these metals. Silicates are also less dangerous to handle.

Alkaline phosphates, especially trisodium phosphate, provide significant alkalinity, but less

than caustic or silicates. It is safe for use in hand cleaning applications. It helps to soften water by forming an easily removed precipitate with hardness compounds. It can be combined with sodium hypochlorite to form a co-crystal, which is a convenient, stable source of chlorine.

Sodium carbonate or washing soda is a mildly alkaline compound that helps soften water as well as provide alkalinity. Its main use is in a mixture with solid caustic soda where its anti-caking activity helps prevent handling problems.

When alkaline compounds raise the pH level, they increase the amount of negative hydroxide ions present. This has two main effects. Bonds between the amino acids of proteins can be hydrolyzed or broken by reaction with hydroxide. This makes the proteins smaller and more soluble so that they can be removed. Acid compounds can have their acidic hydrogen removed by neutralization with hydroxide. The compounds are converted to their negatively charged ionic form. The negative ions repel each other, leading to a breakup of large aggregates of soil to smaller ones. This breakdown is called *peptizing*. The negative ions are also more soluble in water, leading to their removal from the surface. Proteins, composed of amino acids, are very effectively cleaned by alkali. If the alkali is strong enough, carbohydrates can also be converted into negative ions leading to their easier removal.

Alkali will also break down fats and oils to their component glycerol and free fatty acids. This is the basis for making soap from fat and alkali, and the process is called *saponification*. Provided that hardness ions are not present to precipitate them and that the high pH keeps the fatty acids in the ionized form, fats and oils are effectively removed by alkali.

Most inorganic scales are not effectively removed by alkali.

Chelating agents and sequestrants

Chelation is the binding of ions, most importantly the hardness ions calcium and magnesium, so that the hardness does not cause precipitation and scale formation. Common chelating agents are EDTA (ethylene diamine tetraacetic acid) and NTA (nitrilo triacetic acid). Sequestrants, especially the polyphosphates, have a similar action. Sodium gluconate acts as

a chelator under strongly alkaline conditions and is often combined with caustic soda.

A strong chelating agent can also help dissolve inorganic scale that has already formed on surfaces. Chelators such as EDTA are relatively expensive and relatively large amounts are needed to remove scale where it has accumulated to significant depths. It is a good idea to measure the amount of free EDTA remaining in solution when it is being used for scale removal to make sure that not all of the compound has formed complexes with hardness ions.

Manufacturers of EDTA do not recommend using EDTA at high pH such as a mixture with caustic soda. The reason is because it loses its effectiveness at chelating magnesium at the high pH, but its chelation of calcium is not affected. Since cleaning difficulties are more associated with calcium than with magnesium, this caution can often be ignored.

Surfactants

Surfactants concentrate at the surface of water. They have both hydrophobic (water-fearing) and hydrophilic (water-loving) properties. Both properties can be satisfied at the same time at the surface where the hydrophilic portion can remain in the water and the hydrophobic portion can exit the water. The surface of the water is stabilized by surfactants. This means that water can more easily spread out and wet larger areas of surface. By increasing the wetting ability of cleaning solutions, surfactants allow the cleaner to spread out and clean more of the surface. By a similar mechanism it also helps the cleaner penetrate small crevices in the soil, increasing its effectiveness.

Surfactants may also congregate at the interface between water and small particles of soil. They can form a stabilizing sphere around the particle that keeps it in suspension and allows it to be efficiently swept away from the surface. Particles stabilized in this way are called *micelles*.

The oldest surfactant used for cleaning is soap. Soap is free fatty acid. As a rather insoluble acid, it only remains soluble if the pH is high (alkaline), stabilizing the acid in water. Soaps also form insoluble salts with the hardness ions, calcium and magnesium (bathtub ring) so they work poorly in hard water.

Newer synthetic detergents such as alkyl (from oil) benzene sulfonates overcome the problems

of soap. The sulfonic acid portion is more easily ionized, so the pH does not need to be so high. The acid also does not tend to form salts with water hardness, so these detergents can be used in hard water. The drawback with these synthetic compounds, called anionic detergents, is that they are so surface active that they form a heavy layer of foam when sprayed onto surfaces in clean-in-place applications. Their use is therefore limited in industrial cleaning.

Another class of synthetic detergents, non-ionic detergents, does not have a strong tendency to form foam. They therefore can be used in clean-in-place applications. Most of these are polyoxyethylene compounds.

Acids

Acids are used in cleaning especially where removal of inorganic scales is necessary. Calcium compounds do not dissolve well in alkali, but are often quite soluble in acid. Most commonly, phosphoric acid is used or a combination of phosphoric and nitric acids. Sulfamic acid is also occasionally used.

An acid cleaning can follow an initial cleaning with a caustic soda-based alkaline detergent, which removes the organic components of the soil. The acid is then used to remove inorganic residue.

Broader range detergents based on acid with additional ingredients to remove organic soils have been used in some applications, but their use is not widespread.

Bleach

Oxidizing bleaches are used to partially oxidize components of the soil. Bleach can oxidize subunits of long chain proteins or polysaccharides, producing smaller and more soluble fragments, which can be more easily removed. Bleaches are usually added to other components of a formulated detergent to enhance overall cleaning.

Chlorine is the most commonly used bleach. Sodium hypochlorite, produced by adding chlorine to a caustic solution, can be added in small amounts to alkaline cleaners, such as caustic soda. Chlorinated trisodium phosphate, a stable solid, is also commonly used.

Typically about 200 ppm of chlorine equivalent is present in the cleaning solution.

Chlorine can be corrosive to stainless steel if left in contact for long periods of time, so the equipment should be thoroughly rinsed immediately after cleaning. Chlorinated alkali cleaners are very effective at removing soils with high protein content and also beerstone scales. Probably the beerstone is stabilized by organic compounds between the calcium oxalate crystals, and the cleaner removes the organic part very efficiently, making it easier to remove the exposed crystals.

The chlorine in cleaners is diluted to a much lower concentration than in the original sodium hypochlorite; and diluted hypochlorite is much more stable than concentrated. Diluted cleaners have been used at temperatures as high as 80°C (176°F).

Hydrogen peroxide is also effective as a 'bleach' for cleaning. Stabilized peroxides such as sodium percarbonate and sodium perborate are available in powdered form. These are added to cleaner or blended with solid cleaning products.

SANITIZERS

The use of a sanitizer after effective cleaning can provide nearly sterile equipment. It should be emphasized that the cleaning must be extremely thorough in order to achieve this level of sanitation. Cleaning removes most dirt from surfaces and a part of this soil will be the microorganisms left behind after previous use. Most of the removal of microorganisms will occur during the cleaning step. Sanitizers remove most of the last organisms remaining behind.

Chlorine-releasing materials

The most commonly used 'chlorine' solution is actually a solution of sodium hypochlorite. Adding chlorine gas to a caustic solution produces sodium hypochlorite, and under the right conditions the chlorine is slowly released to do its sanitizing job. The sodium hypochlorite can exist in two forms, hypochlorite ion and hypochlorous acid. It is the hypochlorous acid that attacks microorganisms and provides the sanitizing effect. When the sodium hypochlorite is mixed with water, the pH of the solution decreases and hypochlorous acid begins to form.

The lower the pH, the more hypochlorous acid is formed and the more effective sanitation will be. Unfortunately, if the pH drops too low, free chlorine gas begins to be released, leading to a very dangerous situation. Therefore, for effective use, the pH should be below 8.2 but not lower than 7.0. There is a very narrow range where hypochlorite should be used.

Dual halogen sanitizers have been developed that extend the effective range of chlorine-based sanitizers. A source of bromine is added to hypochlorite, allowing hypobromite to be formed. The dual halogens are effective at about one pH unit higher than plain hypochlorite.

It may seem paradoxical that hypochlorite as a bleach can be used in high pH alkaline cleaning formulations, but that it should be used at nearly neutral pH as a sanitizer. The bleaching action is indiscriminate, while the antimicrobial action is more specific, appearing to depend on the ability of the non-ionized form to penetrate and exert killing action inside living cells.

Chlorine in the form of hypochlorite is the least expensive sanitizer available. It is effective against a wide range of microorganisms, including spores. Its action is not diminished in hard water. If residual soil is present, the hypochlorite will bleach or oxidize the soil and be lost. It is important that equipment be thoroughly cleaned before a chlorine sanitizer is used or it will be inactivated before it can exert its sanitizing effect. Chlorine is also corrosive to many metals. It may be used on stainless steel at low concentrations, but it must be thoroughly removed by rinsing after use.

Chlorine dioxide

Chlorine dioxide (ClO_2), is a relatively new sanitizer based on chlorine. Chlorine dioxide will kill organisms more quickly and at lower concentrations than hypochlorite. Typical use rates are 2 to 10 ppm, measured as available chlorine, versus 25 to 200 ppm for hypochlorite. When residual soil is present, chlorine dioxide reacts more slowly than does hypochlorite so the need for thorough cleaning before use is reduced. It also can be used over a wide pH range since it dissolves as a gas, not forming an acid or salt in water. It is less corrosive than hypochlorite. The biggest disadvantage of chlorine dioxide is that it is relatively expensive.

It is a gas and will not remain in water solution for long periods of time; it must be generated and used on the same day. Many methods of generation are available. Acid conversion of chlorite is used on a small scale, but is inefficient. Larger scale generators may use dangerous chemicals such as chlorine gas or hydrochloric acid. Electrolytic generators are a newer development that promise greater efficiency and safety.

Iodine-releasing materials

Iodine is a very efficient sanitizer when used at a concentration of about 25 ppm at colder temperatures, and at an acid pH. Iodine tinctures in water are not very stable and actively stain materials with which they come into contact. Industrial use of iodine is usually in the form of a complex with detergents and acid called an *iodophor*. When concentrated iodophor is diluted in water, the iodine is freed from its complex with detergent. The acid in the iodophor reduces the pH of the diluted solution to the acid range where iodine is most effective. The acid can also help dissolve mineral scale left behind after alkaline cleaning. Because of the detergents in the iodophor, the sanitizer tends to foam when used in spray applications. The recent development of iodine stabilized with chlorine, 'stabilized iodine', has eliminated foaming as a problem and requires about half as much iodine to do the same sanitizing job. Since stabilized iodine is relatively new, it has not been legally cleared for use as a food equipment sanitizer in all areas.

Iodine must be used at an acid pH to be most effective. If an iodophor is used at higher than recommended dilution, the pH of the mixed sanitizer should be checked to make sure that the pH of the diluted solution is not too high. Since iodine tends to stain, be certain that staining can be tolerated before using an iodine based compound. There is little tendency to corrode metal equipment unless the metal is not resistant to the acid contained in iodophors.

Anionic surfactants

The anionic surfactants are not very commonly used as sanitizers, but they do have properties that make them the choice for some special applications. They are surface-active compounds

and are active at low pH, so they must be combined with acid. While hypochlorites, iodophores and chlorine dioxide all dissipate or evaporate in a relatively short period of time, anionics are completely stable. They will last for weeks or months and are therefore the best choice for applications where equipment is to be stored in water or filled with water for longer than a few days. The practice of storing equipment soaking in plain water is extremely unsanitary and is a very common but bad practice. Bacteria will grow in the water, especially if some residue is left on the equipment. Slimy layers that often form on the equipment and storage containers are layers of billions of bacteria or a biofilm. Store the equipment with mild acid and an anionic surfactant and it will remain clean for months.

Being detergents, some of the anionic surfactants are also fairly good cleaning compounds and acid cleaning can also be accomplished with some of these compounds.

Peroacetic acid

Peroacetic acid is a complex of acetic acid with hydrogen peroxide. The peroxide is the sanitizer. It is effective at about 200 ppm of peroxide and at colder temperatures. It is expensive and is used mainly in special situations where residue of chloride or iodide from less expensive sanitizers or some of their reaction products cannot be tolerated, especially some food applications.

Quarternary ammonium compounds

Quarternary ammonium compounds, called 'quats', are stable, effective and long lasting, tending to leave a residue. They adsorb to surfaces and have a residual killing effect for relatively long periods of time. Usually the residue is not desirable in vessels such as fermenting tanks since the residue will also kill some yeast. If a lot of yeast are present, the number killed may not be too significant, so quats are occasionally used to sanitize these vessels. A better application is to use quats on areas where yeast should not be present. They are used on the outside of fermenting tanks and on floors where spills are likely to occur to keep down the growth of undesirable organisms such as molds on these surfaces.

Hot water

Hot water, over 180°F (82°C), is a very effective sanitizer because the heat can be transferred to areas that are not penetrated by chemical sanitizers. Cost of fuel to generate hot water is a factor that limits its use as a sanitizer.

Hot caustic

Caustic (NaOH) by itself is not a sanitizer. Bacteria are often found in high numbers in caustic solutions stored at room temperature. Hot caustic, though, will very effectively kill microorganisms. The temperature must be at least 110°F and temperatures above 130°F give good sanitizing in a matter of a few minutes. The exact effect depends on the time, temperature and caustic concentration used. Many areas have legal requirements for washing and sanitizing reusable containers with caustic solutions.

Turbulence

Turbulence refers to the scrubbing and scouring action of cleaning solutions as they flow through pipelines or onto the dirty surfaces inside tanks and other equipment. More turbulence improves cleaning. Sometimes the issue is more basic than the degree of turbulence: does the cleaning solution even contact the soil? Large diameter horizontal pipes will not completely fill with liquid if the flow rate is too low. 'Shadow areas' can also prevent cleaning solution from contacting the soil.

For pipelines, effective cleaning requires velocities of 1–1.5 to 3 m/s (5–10 ft/s). We are more used to thinking in terms of flow rates like cubic meters per hour or gallons per minute. This requirement means that bigger pipes need higher flow rates for cleaning. Table 3 shows the flow rates required for 5 ft/s (1.5 m/s) in pipes with diameters from 75 mm to 300 mm. It is important to note that when the pipe diameter is doubled, the required flow rate for cleaning must be *four* times as large. This has a large effect on the size of pumps needed for CIP.

Table 3. Turbulence in pipelines: flow rates required for effective cleaning as pipe diameter increases¹.

Pipe size		Flow rate for 5 ft/sec (1.5 m/sec)	
Inches	Millimeters	US gpm	Litres/min
3	75	102	386
4	100	182	689
6	150	410	1552
8	200	728	2755
12	300	1620	6130

¹Annex (1992).

A rule of thumb for cleaning process equipment (e.g., a heat exchanger) is that the cleaning solution flow rate should be 1.5 times the normal process flow rate to achieve good turbulence. An effective trick is to clean the equipment in both the forward-flow and the reverse-flow directions (Figure 5).

SANITARY DESIGN

One of the greatest impediments to achieving turbulence in cleaning is the presence of dead ends in process pipelines and other equipment (Peter, 1983). A dead end can be a length of pipe that is wetted by the cleaning solution but without sufficient velocity to clean the surfaces. A common example is the bypass line, shown in Figure 6. When the heat exchanger is cleaned, solutions cannot flow through the dirty bypass unless someone opens the bypass valve. This may or may not happen. It should also be noted that when the bypass valve is open, the total solution flow is split in two directions: through the equipment and through the bypass line. The flow rate through each is therefore reduced and the velocity of the cleaning solution is compromised.

Figure 7 shows some design tricks that can eliminate the creation of dead ends before they are built into the system. For example, branch lines from the main line should have the valve installed not more than one diameter from the wall of the main pipeline. This ensures turbulence in the branch – that it will not be a dead end for cleaning. Tees in the main line should be manufactured tees made with smooth rounded contours that are sanitary and cleanable.

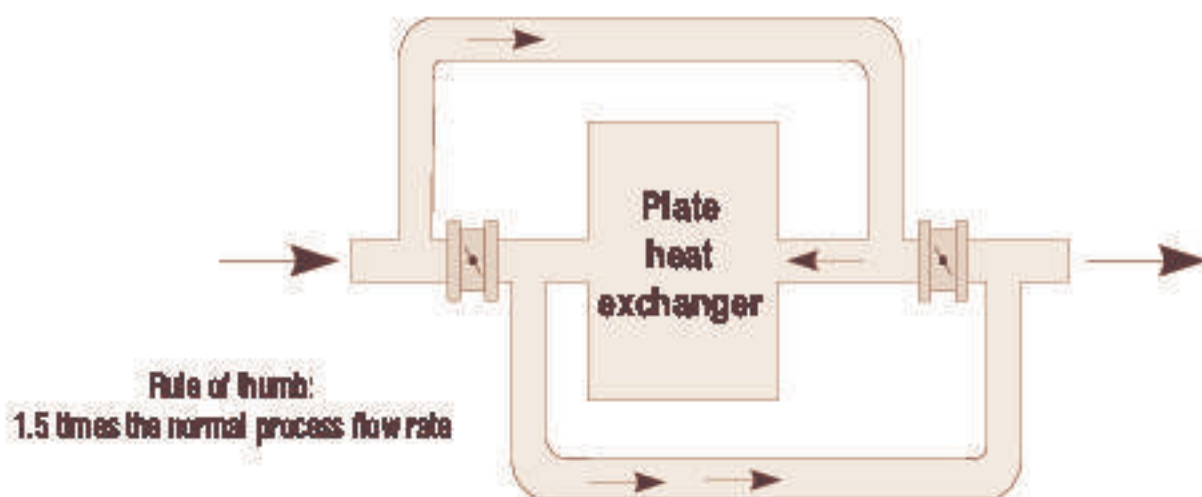


Figure 5. Turbulence in process equipment.

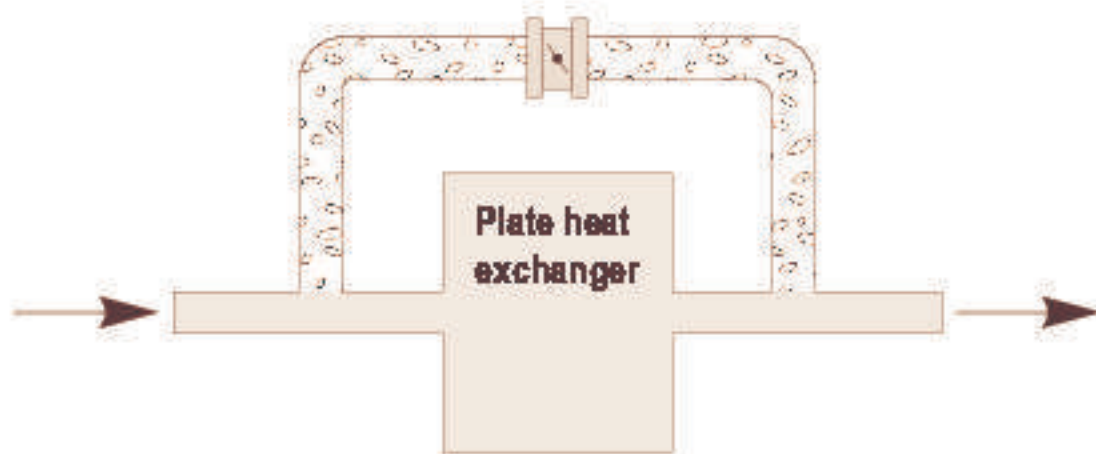


Figure 6. Dead ends and turbulence: did the bypass get cleaned?

Fitted joints, that is homemade or fabricated-in-the-field tees, are not sanitary and should not be accepted.

Figure 8 shows an innocent looking tee with a valve on the branch line. This section of pipe was opened for inspection and the branch pipe was packed with soil. The soil buildup was not removed during CIP because the cleaning velocity was insufficient or because the dead end was more than one pipe diameter.

During construction, piping should be welded using sanitary welding procedures including (for stainless steel) butt welding with an inert gas purge. Pipelines should be self-draining and without high spots or domes where air can

become trapped and prevent cleaning solutions from touching those parts of the pipe.

For processing equipment the American Meat Institute created a task force to improve equipment design with the goal of eliminating harborage areas where microorganisms can collect and grow. The result is a set of guidelines, the Ten Principles of Sanitary Design (Stout, 2003). These principles, for food processing equipment, are as follows:

1. *Cleanable to microbiological level.* A piece of equipment must be more than just visually cleanable – over the entire life of the equipment.

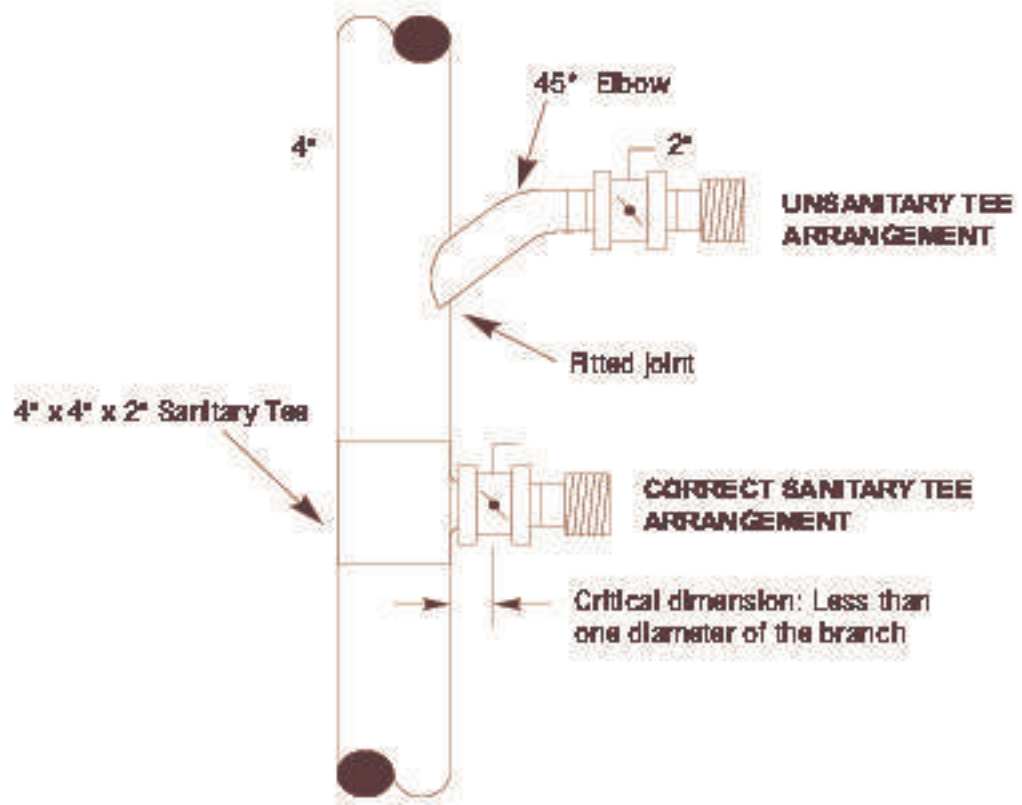


Figure 7. Eliminating dead ends with sanitary design.



Figure 8. Buildup of scale in the dead end branch of a tee.

2. *Made of compatible materials.* Construction materials must be compatible with the product, the environment and with the cleaning materials.
3. *Accessible for inspection, maintenance and cleaning.* A person without tools must be able to inspect and clean the equipment.
4. *No product or liquid collection.* The equipment must be self draining with no areas where water or product can accumulate.
5. *Hollow areas hermetically sealed.* Hollow areas must be eliminated or hermetically sealed by continuous seam welding to eliminate any area where soil could accumulate.
6. *No niches.* There may be no harborage points: cracks, crevices, pits, dead ends, or niches. This encompasses sanitary welding in process pipelines.
7. *Sanitary operational performance.* The equipment must perform so that it does not harbor bacteria or contribute to microbiological contamination.
8. *Hygienic design of maintenance enclosures.* Control panels, junction boxes, belt guards, gear enclosures etc. are designed to ensure that neither water nor product accumulate in or on the enclosure.
9. *Hygienic compatibility with other plant systems.* Any new piece of equipment must be compatible with steam, air, water and other utilities and systems in the plant.
10. *Validate cleaning and sanitizing protocols.* The equipment manufacturer and equipment purchaser must work together during the equipment design stage to design cleanability into the machine before it is built.

THE CLEANING LOOP

A cleaning loop is the path that the cleaning solution flows during a CIP cycle. It begins at the CIP system and ends at the CIP system (Figure 9). Designing and planning cleaning loops is essential to achieving effective cleaning along the entire path that product follows through the plant.

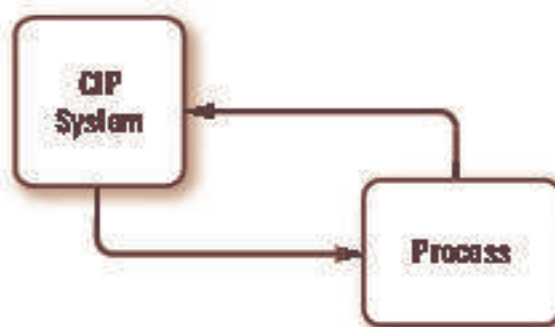


Figure 9. The cleaning loop.

Sanitary design is not just about individual tanks or pieces of equipment, it is about processing systems. Cleaning a fermentor, for example, encompasses much more than the tank itself. It includes the external heat exchanger, the product inlet and product outlet pipes, CO₂ collection lines, additive addition lines, pressure relief valves, and more. "How do we clean it?" and "what cleaning loops are necessary?" are key questions that must be asked early in the design stage.

Completely cleaning a fermentor system requires not one, but several cleaning loops (Figures 10a–10d). Some of these loops and their separate requirements include:

- Mash filling pipelines (minimum 3 m/s CIP velocity).
- Fermentor CIP sprayhead (pressure requirement).
- External heat exchanger loop (1.5 times normal process flow).
- Fermented product emptying pipeline (minimum 3 m/s CIP velocity).

The loops must be planned such that there are no lengths of pipe that lie between two loops and are therefore not included in either loop. Ideally, loops will overlap.

Validation of cleaning

When the cleaning process is complete we must know if the equipment got cleaned properly before it is committed to a new batch of product. If the final product is infected, we know that cleaning was not effective but it is then too late.

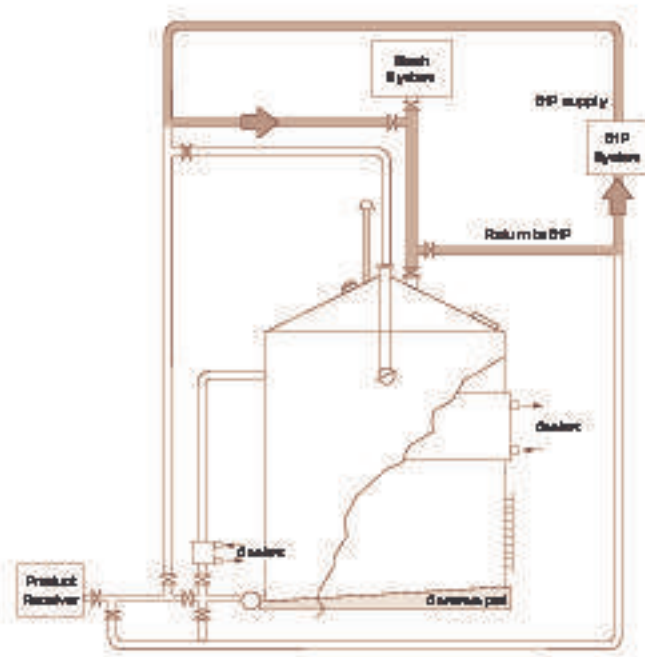


Figure 10a. The wash CIP piping loop.

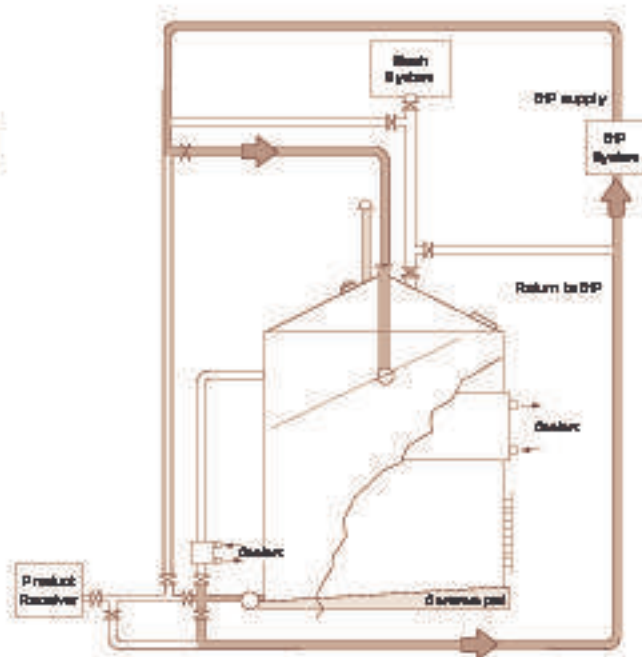


Figure 10b. The fermentation CIP sprayball loop.

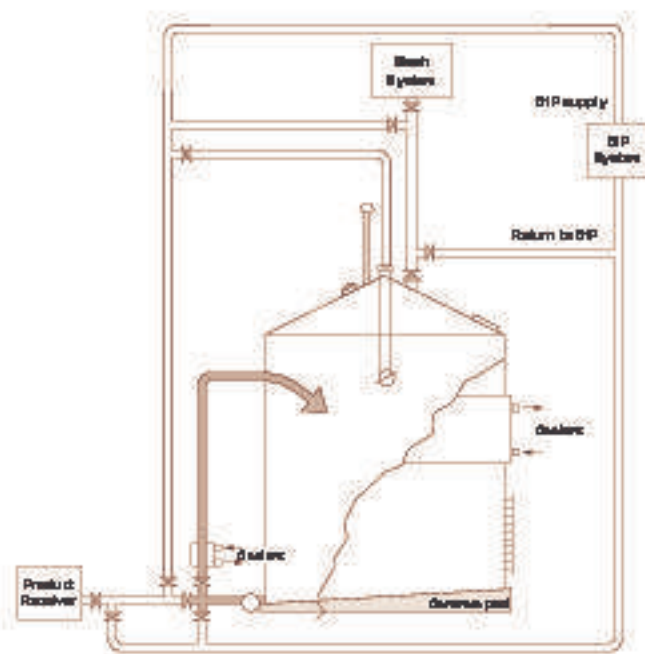


Figure 10c. The external heat exchanger loop.

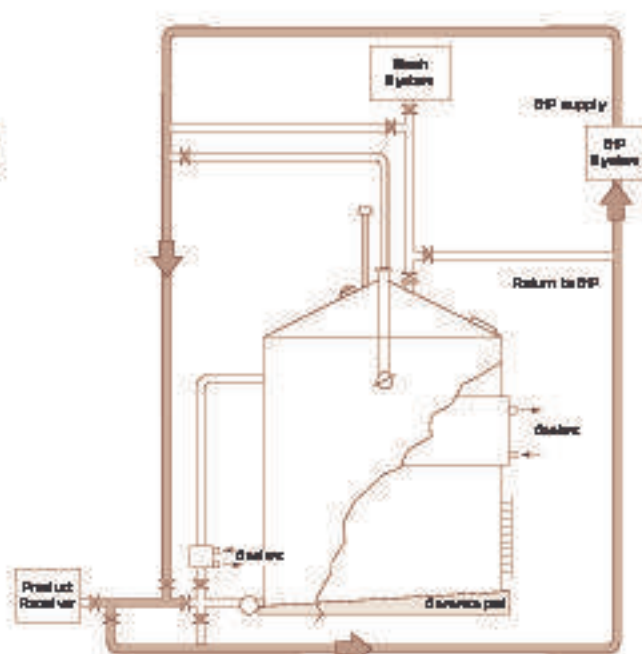


Figure 10d. The fermented product loop.

Temperature, pressure and flow records can be used to document that the CIP programme ran successfully. If automation does not provide these reports, the parameters can be checked and recorded by the operators. These records are often part of a formal HACCP program.

Visual inspection may be possible from manways, inspection ports or windows. This immediately provides an indication of gross deficiencies in the cleaning process and appropriate measures can be taken before the next batch is started.

Microbiological swabs and plating, along with ATP bioluminescence swabs, are more specific indicators of successful cleaning and sanitizing. An ATP bioluminescence swab indicates the amount of soil left on a surface that may look 'clean' (Ehrenfeld *et al.*, 1996). A big advantage is that the result is known in less than one minute. Again, appropriate action (repeat the CIP process) can be taken. Microbiological swabs and plating can tell us how much of what organisms are present, but results are not known for 2-5 days. Newer rapid methods are shortening this time.

Examples of CIP cycles

A TYPICAL CIP CYCLE FOR TANKS AND PIPELINES

- A. *Prerinse to the sewer.* Removes gross amounts of soil before the main wash. It is common to save the water rinse (item C) and reuse it for this step. This practice conserves water, and the rinse water usually has a small amount of detergent in it that enhances the effectiveness of the prerinse.
- B. *Alkaline (caustic) wash.* For organic and oily soils, caustic soda is most commonly used. It often has additives to improve wetting and rinsing properties. Strengths from 1 to 3 % by weight are common and it is used at temperatures from ambient up to 180°F. It is a more effective cleaner at the warmer temperatures.
- C. *Water rinse.* Rinses out the washing water. It is often saved for reuse as the prerinse. The source should be fresh, clean water so as not to recontaminate.

D. *Acid wash and water rinse (optional).* This additional cleaning is done to prevent scale formation, for example in beer kegs, or to remove scale deposits.

E. *Sanitizing rinse.* A sanitizing agent may be injected into the clean rinse water to reduce microorganisms on the clean surfaces to an acceptable level.

CLEANING PROCEDURE FOR CO₂ SCRUBBER

- A. Stop flow of CO₂ through the scrubber and remove CO₂ from inside the scrubber by venting or rinsing with fresh water. Residual CO₂ in the scrubber will neutralize the caustic solution.
- B. Make a caustic soda solution 2 to 3% by weight at ambient temperature or preferably warmed to 100 to 120°F. Make enough to maintain a level in the bottom of the scrubber when recirculating.
- C. Circulate the caustic solution through the scrubber sprayer for at least 1 hr. Several hours may be required depending on the soil load.
- D. After 15 to 30 minutes take a sample of the caustic and titrate to make sure it has not been neutralized by residual CO₂ in the scrubber. If less than 2% strength, add more caustic to get 2 to 3%.
- E. Drain caustic, then rinse using burst rinse (water for 30 sec, drain for 3 min.). Repeat burst rinse cycle until rinse water shows no caustic when tested with phenolphthalein or litmus paper.
- F. Prepare acid wash, 1 to 2%, using Scalebite™ at ambient temperature. Circulate for 1 hr.
- G. Drain acid solution and rinse using burst rinse, three cycles.
- H. Prepare Iotech™ solution, 25 ppm at ambient temperature, and recirculate for 30 mins.
- I. Drain Iotech™ solution and rinse using burst rinse, three cycles.
- J. Scrubber is ready to bring back on stream.

PROCEDURES FOR DE-SCALING FERMENTORS

The following is an approach to descaling tanks and equipment after beerstone or scale has accumulated over a period of time. Since scale amounts and compositions vary from time to time and place to place, some trial and error is usually required.

- A. *Prerinse the tank to remove heavy soil.* Use fresh water or water with a little caustic, like the saved final rinse water from washing another tank. Do not save this liquid in the CIP system.
- B. *Main caustic wash.* Caustic strength at 3 to 5%, temperature 120 to 190°F. This will be similar to the normal caustic wash and when finished, the tank should be clean except for the scale or beerstone. Addition of sodium hypochlorite (bleach) to caustic solutions may help to attack the scale. It is used at concentrations of 200 to 400 ppm as active chlorine. **CAUTION** – never mix hypochlorite (bleach) with acid cleaners.
- C. *Scale-removing caustic wash.* Use caustic as in step 2 but with addition of Scaleban™ as a supplement. For infrequent de-scaling, add 5 oz Scaleban™ for every gallon of the caustic solution. Same temperatures, 120 to 190°F. Warmer is usually better. Circulate several hours if possible. Use kit to titrate EDTA, the active ingredient in Scaleban™. Add more Scaleban™ if EDTA gets depleted. For routine scale control, 1 to 3 oz of Scaleban™ is added to each gallon of the normal caustic solution.
- D. *Rinse with clean water. Inspect visually.* Note: when tank is wet you may not see the scale. When it dries, the scale is more visible.
- E. *Scale-removing acid wash.* If scale remains after the Scaleban™ wash, an acid cleaner may be required. Scalebite™ is a formulated acid cleaner that is used between 1 and 3% in water. It is recirculated several hours. Note: Scalebite™ is safe with stainless steel but does attack mild steel, especially at warmer temperatures. Sulfamic acid is also effective against some scales. Like Scalebite™, it is used in concentrations between 1 and 3 %, temperatures up to 140°F.

Problem areas

When a contamination problem develops, one of the first questions asked is 'How did the infection develop?' One of the most difficult challenges in industrial sanitation is in keeping a continuous fermentation system free of infection. Doug Banks from New Zealand's Dominion Breweries, which has successfully operated breweries with continuous fermentation of beer and no infection for many years, classifies sources of contamination into two groups, point sources and dead ends, based on years of experience:

Point sources are sources that occur only from time to time. They may appear and then disappear pretty much at random. Some point sources include:

- Bad pump seals that allow contamination to be drawn in from the outside environment by a Venturi effect of the flowing liquid.
- A piece of equipment that was missed during regularly scheduled cleaning.
- An employee with dirty boots, etc. brings contamination into the system by climbing into a clean tank or some other area to make some final adjustment or repair.
- A cleaning sprayball has become plugged.
- Sample ports have been forgotten during cleaning and have become infected.
- A solution used for sanitizing small pieces of equipment out of place has stood for days, losing its effectiveness.
- The cleaning solution used was too dilute.
- The wind blows contaminated air or an aerosol into equipment when it is temporarily opened after cleaning and before use.
- Insects carry contamination into a piece of equipment temporarily left open.

Dead ends are sources of contamination that are always in contact with the process stream. Usually these are the most serious causes of contamination. Some examples are:

- Dead ends in piping that cannot be thoroughly cleaned.
- Scale built up inside fermenting tanks or coolers. Scale cannot be cleaned because the cleaning compounds cannot penetrate the scale once it is thick enough.
- Carbon dioxide vent lines on fermentors into which fermenting liquid has flowed or been sprayed as an aerosol.
- Faulty check valves
- Contaminated yeast
- Poor drainage of cleaning solution from a tank while it is being cleaned.
- Seats on valves that have worn and begun to develop cracks
- Non-sanitary pipe connections, especially pipe threads. These will trap liquid in the threads that cannot be removed by cleaning.

Some of the likely ultimate sources of contamination include:

- Grains being brought into a plant carry large numbers of a variety of microorganisms
- People and the food they bring into the plant
- Insects

The most likely sources of contamination, though, are within the plant itself. Infection sources are often found in scale, dead ends, even in coolers, spilled material left on the ground, material in sewers that can be splashed into the air as an aerosol, dirty and contaminated carbon dioxide lines and aerosols created when opening contaminated equipment such as perhaps the beer well.

Hidden issues related to chemistry occur when cleaning tanks that have a CO_2 atmosphere. The CO_2 will react with caustic to form sodium carbonate, a cleaner that is much weaker than caustic soda (Figure 11). However, if this reacted solution is analyzed by the normal single end-point titration, the effect is not detected. Carbonate titrates just like the hydroxide. This problem can be overcome by replenishing the reacted caustic or by venting the vessel completely before cleaning. The correct titration uses barium chloride first, then acid. The method

can be found in Alltech's Laboratory Manual (Alltech, 2001).



Figure 11. Dilution of caustic by carbon dioxide.

A CASE STUDY: CLEANING A FERMENTOR

Cleaning the inside of a fermentor with a sprayhead and cleaning the tank outlet (Figure 12)

The normal flow through a sprayhead is around 100 gallons/min (about 380 liters/min). For a 6-inch fermentor outlet pipe, the minimum velocity for cleaning is not reached until the flow rate is 410 gallons/min. This is a serious cleaning deficiency and it is common to see gross accumulations of soil on the top half of these outlet pipes because they do not even fill with cleaning solution when the sprayhead is being used.

The cleaning and sanitizing program

A routine and effective microbiological sampling program should be in operation. Sampling should be planned so as to provide a complete, overall picture of the state of sanitation in the plant at any time. Special attention should be paid to an evaluation of the cleaning procedures in place. Infections usually develop in areas where cleaning is not effective or is missed. Swabs should be taken from cleaned equipment. An ATP detecting luminometer can provide more immediate evaluation on the effectiveness of cleaning. Strengths of cleaning and sanitizing solutions should be measured routinely, as well as temperatures of cleaning solutions.

Sanitation Quality Control is like preventive maintenance for the product. It is troubleshooting designed to identify potential problems so that they can be corrected before damage is done to the product. There are four basic components in an effective sanitation quality control program:

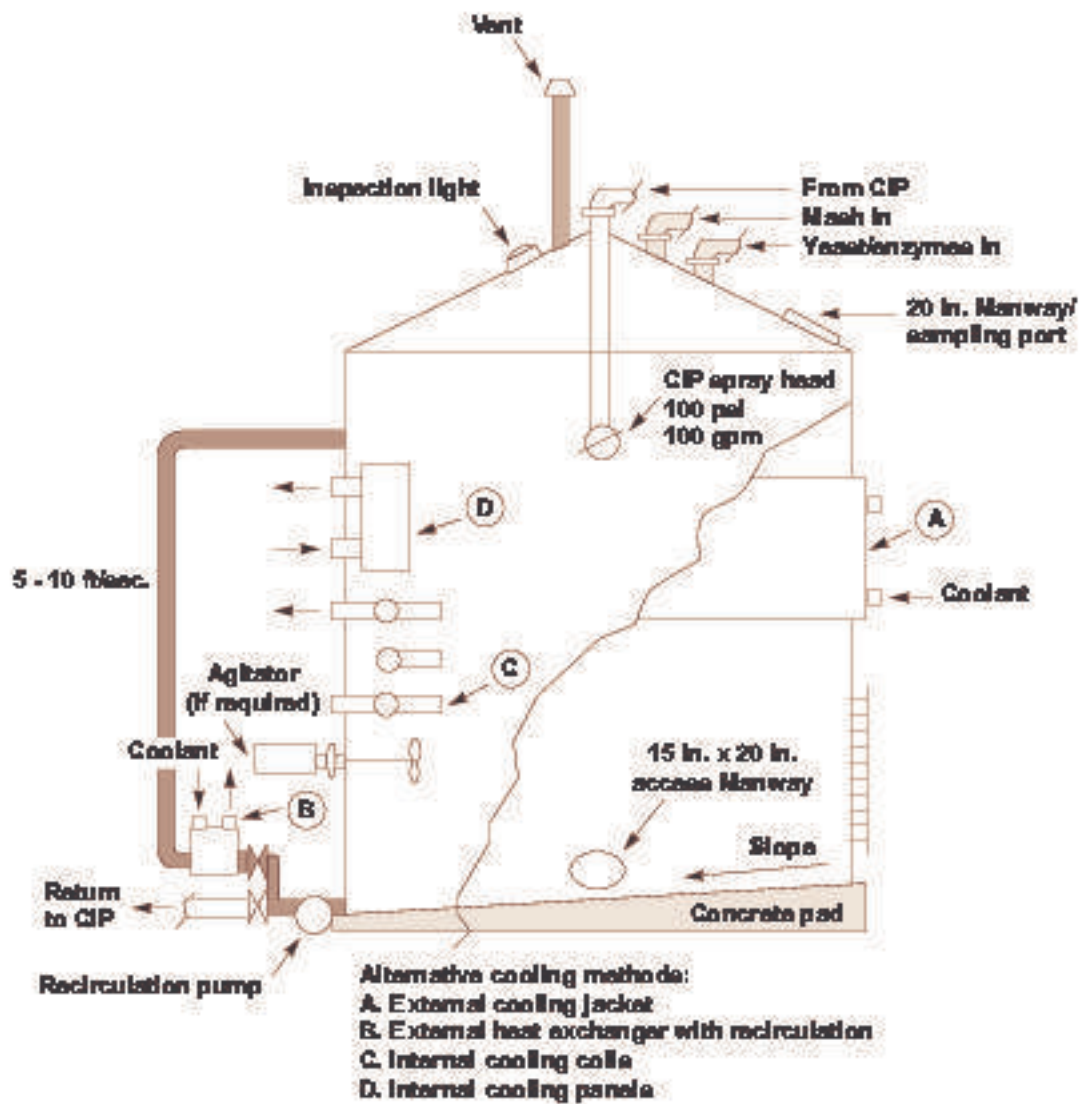


Figure 12. Cleaning a fermenter.

A. The Sanitation Plan

1. Master sanitation schedule
2. Times, temperatures, materials, strengths for every cleaning job
3. Detailed written instructions for every cleaning job

B. Measurements and Standards

Every cleaning and sanitizing process should have, as an objective, the achievement of an end result that can be measured and compared to a predetermined standard.

1. *Visual inspection* - gives a 'go/no go' result immediately. Wet surfaces can appear clean when they are actually dirty, so the visual inspection is best done when the surface is dry. This should also include 'white glove' checks.
2. *ATP-detecting luminometer* - immediate quantitative results for presence of ATP, which indicates cleaning was not complete.
3. *Microbiological* - a time of 24 hrs to 1 week is required before results are known. Tests include forcing tests, swabs, pour plates and millipore filtering. Different tests are

specified at different stages of the process and each test has standard results or control limit.

C. Records

These should include: when was the cleaning really done (vs schedule), automatic or manual recording of temperatures and strengths, when was maintenance done (UV lights renewed, eg), problems encountered when the job was done.

D. Results

Immediate reporting of microbiological results and charting trends for statistical quality control are of key importance.

Summary

For every cleaning and sanitizing problem there is a solution, in fact there can be many solutions. Unfortunately the solutions are not available as defined recipes in a cookbook. The Four Ts, our cleaning and sanitizing bag of tricks, experience and trial and error are the tools at our disposal. We know that the program is to first remove the dirt, and then sanitize. Sanitizing dirt may work for a short time but it is not a permanent solution. We must also determine the acceptable levels of cleanliness and sanitation and then avoid excesses that are hard on the equipment and costly in terms of time, money and utilities.

We must use our knowledge of the Four Ts of cleaning and sanitizing to find a combination of time, temperature, turbulence and titration that is both effective and economical. Finally, we must realize that while CIP is the ideal, COP combined with CIP is usually the reality.

"Regardless of technology, the most important food plant sanitation approach is getting back to basics, which means having motivated, passionate people who know both the importance of and how to clean effectively. It comes down to training and motivation; simply put, how to use mechanical action, with the right detergent, at the right concentration for the right time at the right temperature with the right attitude, and giving people credit for the good work they do."

(Stout, 2002).

Cleaning and sanitation is an area where the quality control principle of 'continuous improvement' can be effectively applied. No plant is perfectly clean. There is always room for improvement, and small improvements can accumulate into major improvements in the overall efficiency and profitability of the plant.

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Recovery



Chapter 22

Ethanol distillation: the fundamentals

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Fundamentals of a distilling system

Certain fundamental principles are common to all distilling systems. Modern distillation systems are multi-stage, continuous, countercurrent, vapor-liquid contacting systems that operate within the physical laws that state that different materials boil at different temperatures.

Represented in Figure 1 is a typical distillation tower that could be employed to separate an ideal mixture. Such a system would contain the following elements:

- a. a feed composed of the two components to be separated,
- b. a source of energy to drive the process (in most cases, this energy source is steam, either directly entering the base of the tower or transferring its energy to the tower contents through an indirect heat exchanger called a reboiler),
- c. an overhead, purified product consisting primarily of the feed component with the lower boiling point,
- d. a bottoms product containing the component of the feed possessing the higher boiling point,
- e. an overhead heat exchanger (condenser), normally water-cooled, to condense the vapor

resulting from the boiling created by the energy input. The overhead vapor, after condensation, is split into two streams. One stream is the overhead product; the other is the reflux which is returned to the top of the tower to supply the liquid downflow required in the upper portion of the tower.

The portion of the tower above the feed entry point is defined as the 'rectifying section' of the tower. The part of the tower below the feed entry point is referred to as the 'stripping section' of the tower.

The system shown in Figure 1 is typical for the separation of a two component feed consisting of ideal, or nearly ideal, components into a relatively pure overhead product containing the lower boiling component and a bottoms product containing primarily the higher boiling component of the original feed.

If energy was cheap and the ethanol-water system was ideal, then this rather simple distillation system would suffice for the separation of the beer feed into a relatively pure ethanol overhead product and a bottoms product of stillage, cleanly stripped of its ethanol content. Unfortunately, the ethanol-water (beer) mixture is not an ideal system. The balance of this chapter

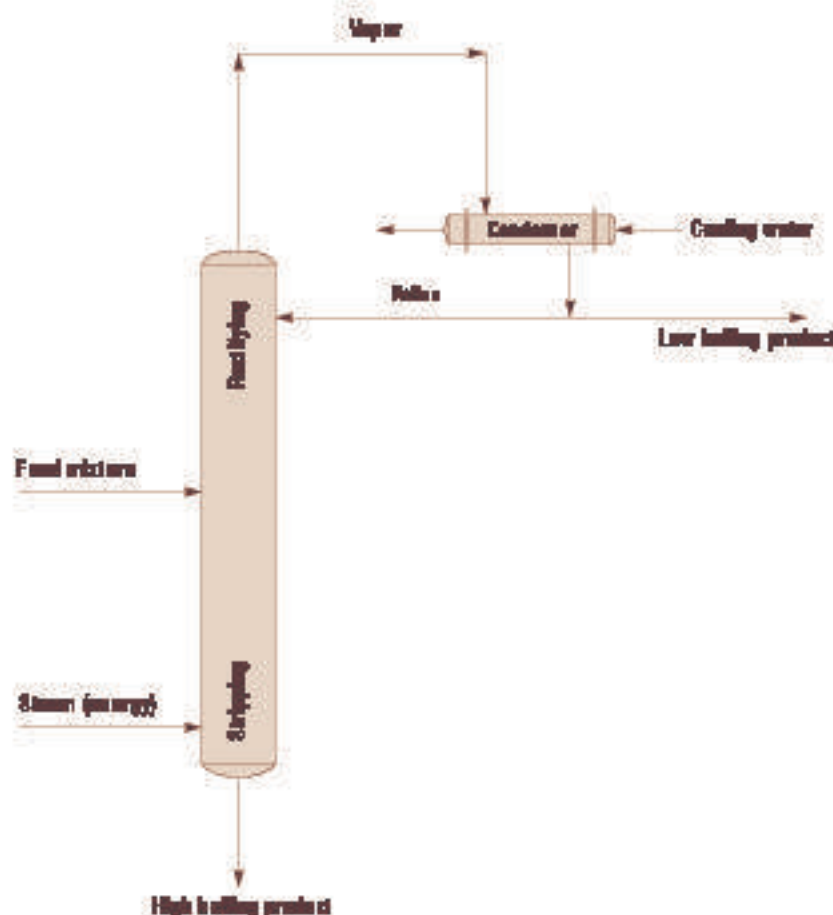


Figure 1. Ideal distillation system.

will be devoted to a description of the modifications required of the simple distillation system in order to make it effective for the separation of a very pure ethanol product, essentially free of its water content.

Figure 2 expands on Figure 1 by showing some additional features of a distillation tower. These are:

- The highest temperature in the tower will occur at the base.
- The temperature in the tower will regularly and progressively decrease from the bottom to the top of the tower.
- The tower will have a number of similar, individual, internal components referred to as 'trays' (these may also be described as stages or contactors).
- Vapor will rise up the tower and liquid will flow down the tower. The purpose of the tower internals (trays) is to allow intimate contact between rising vapors and descending liquids correlated with separation of vapor and liquid.

Figure 3 shows a vapor-liquid equilibrium diagram for the ethanol-water system at atmospheric pressure. The diagram shows mole percent ethanol in the liquid (X axis) vs mole percent ethanol in the vapor (Y axis). The plot could also be made for volume percent in the liquid vs volume percent in the vapor and the equilibrium curve would only be slightly displaced from that shown in Figure 3. Mole percent is generally used by engineers to analyze vapor/liquid separation systems because it

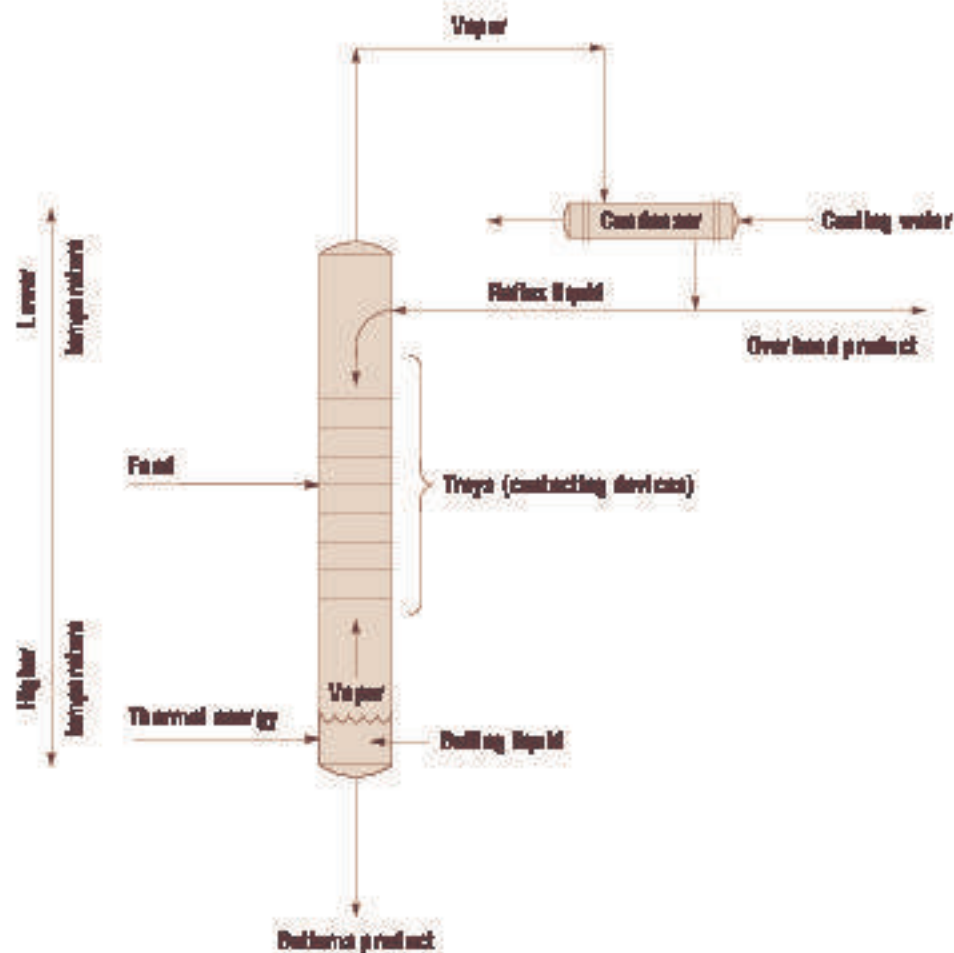


Figure 2. Typical distillation relationships.

relates directly to molecular interactions, which more closely describe the process occurring in a distillation system.

Analysis of the ethanol-water distillation system is mathematically straightforward when using molar quantities rather than the more common measurements of volume or weight. This is because of an energy balance principle called 'constant molar overflow'. Essentially, this principle states that the heat (energy) required to vaporize or condense a mole of ethanol is approximately equal to the heat (energy) required to vaporize or condense a mole of water; and is approximately equal to the heat (energy) required to vaporize or condense any mixture of the two. This relationship allows the tower to be analyzed by graphic techniques using straight lines. If constant molar overflow did not occur, then the tower analysis would

become quite complex and would not lend itself easily to graphic analysis.

Referring to Figure 3, a 45° line is drawn from the compositions of 0, 0 to 100% and 100%. This 45° line is useful for determining ranges of compositions that can be separated by distillation. Since the 45° line represents the potential points at which the concentration in the vapor equals the concentration in the liquid, it indicates those conditions under which distillation is impossible for performing the separation. If the equilibrium curve contacts the 45° line, an infinitely large distillation tower would be required to distill to that composition of vapor and liquid. Further, if the equilibrium curve crosses the 45° line, the mixture has formed an azeotrope. This means that even if the tower were infinitely large with an infinite amount of energy, it would be impossible to distill past that point by simple rectification.

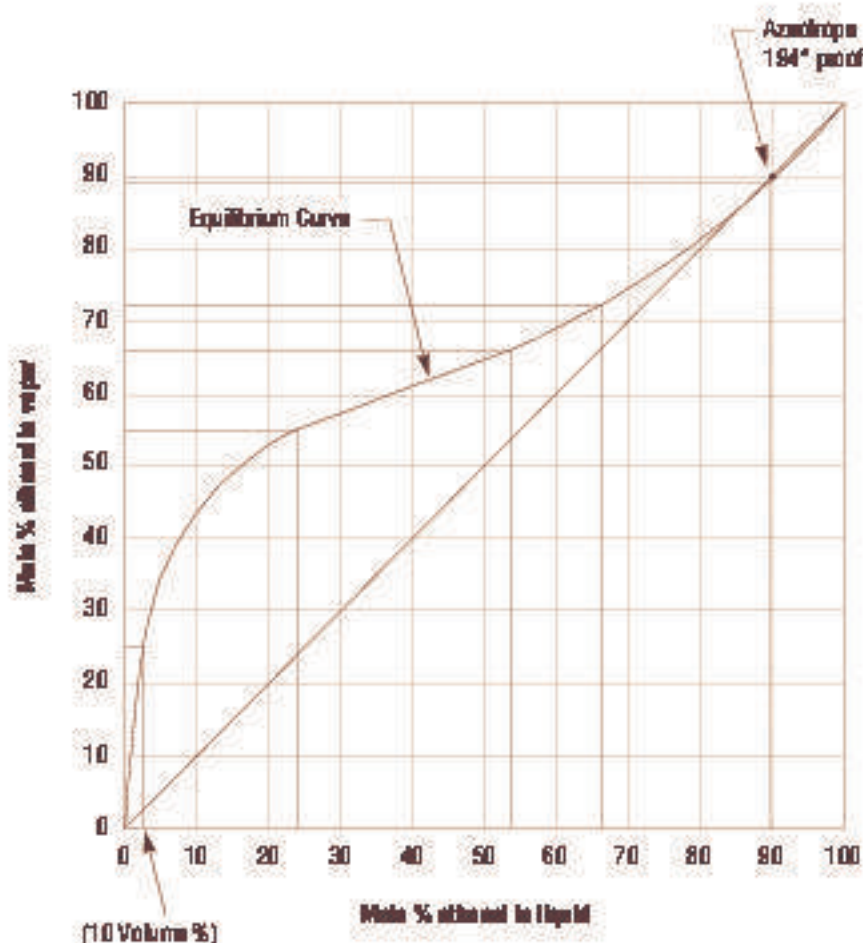


Figure 3. Vapor/liquid equilibrium for the ethanol/water system at atmospheric pressure.

Consider a very simple system consisting of a pot filled with a mixture of ethanol in water (a beer) containing 10% by volume ethanol (3.3 mole %). This composition is identified in the lower left portion of Figure 3. A fire could be kindled under the pot, which would add thermal energy to the system. The pot would begin to boil and generate some vapor. If we gathered a small portion of the vapor initially generated and measured its ethanol content, we would find about 24 mole % ethanol (53 volume %). If we condense this vapor (note: there will be only a small amount of this vapor), boil it in a second pot and again collect a small amount of the initial vapor generated, this second vapor would contain about 55 mole % (83 volume %) of ethanol (see Figure 3). If we should continue this simplified process to a third and fourth

collection of small amounts of vapor, analysis would reveal that each successive portion of vapor would become richer in ethanol.

Thus we have created a series of steps by which we keep increasing the ethanol content of the analyzed sample, both liquid and vapor. Unfortunately, this oversimplified process is idealized; and practically speaking, is impossible. However if we had supplied our original pot with a continuous supply of ethanol-water feed and vapor generated in the first pot was continuously condensed and supplied to the second pot, etc. then the process becomes similar to the industrial distillation tower operation shown in Figure 2.

How far can this process be extended? Could we produce pure ethanol by continuously extending our process of boiling and reboiling?

The answer is, no! We would finally reach a point in one of the downstream pots, where the vapor boiling from the liquid was of the same composition as the liquid from which it was being generated. This unfortunate consequence limits our ability to produce anhydrous ethanol from a dilute ethanol-water feed. What we finally encounter in our simplified process is the formation of an *azeotrope*. This is a concentrated solution of ethanol and water that when boiled produces a vapor with a composition identical to the composition of the liquid solution from which it originated.

In summary then, we are limited in ethanol-water purification in any single multistage distillation tower to the production of azeotropic ethanol-water mixtures. These azeotropic

solutions of ethanol and water are also known as constant boiling mixtures (CBM) since the azeotropic liquid will have the same temperature as the azeotropic equilibrium vapor being boiled from itself. Without some sort of drastic process intervention, further ethanol purification becomes impossible. The question then becomes: What can we do to make it possible to produce anhydrous ethanol? Methods of doing so will be covered later in this chapter.

Figure 4 depicts the structure of the distillation process by dividing the vapor/liquid equilibrium information into three distinct zones of process and equipment requirements: stripping, rectifying and dehydration. This division is the basis for the design of equipment and systems to perform the distillation tasks.

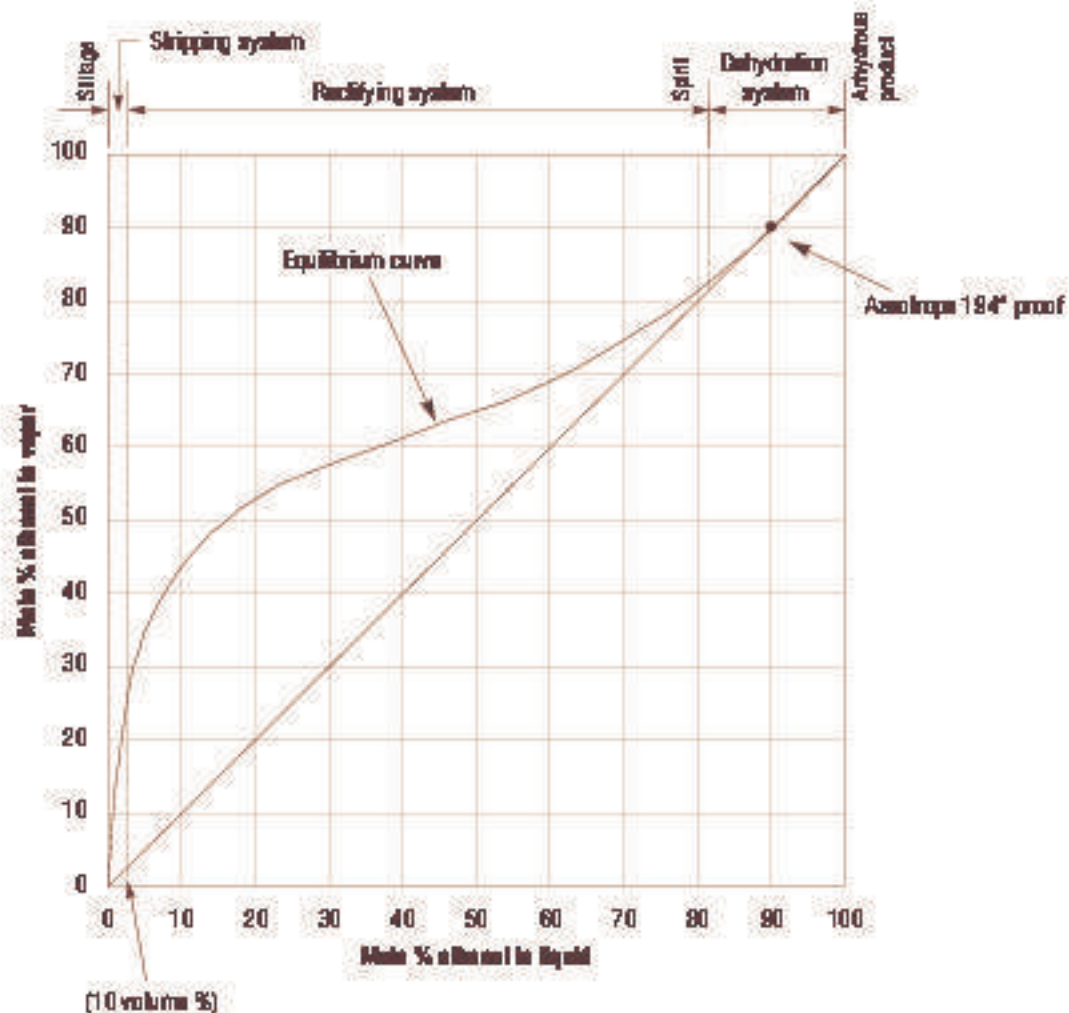


Figure 4. Structuring the distillation system strategy.

Considerations in preliminary design

The engineer, given the assignment of designing a distillation tower, is faced with a number of fundamental considerations. These include:

- What sort of contacting devices should be employed? (e.g. trays or packing). If trays are chosen, what type will give the most intimate contact of vapor and liquid?
- How much vapor is needed? How much liquid reflux is required? (What ratio of liquid:vapor is required?)
- How much steam (energy) will be required?
- What are the general dimensions of the distillation tower?

DISTILLATION CONTACTORS

Trays are the most common contactor in use. What are the functions expected of tray contactors in the tower? Figure 5 depicts a single tray contactor in a distillation tower and shows the primary functions desired:

- mixing rising vapor with a falling fluid
- allow for separation after mixing
- provide path for liquid to proceed down the tower
- provide path for vapor to proceed up the tower

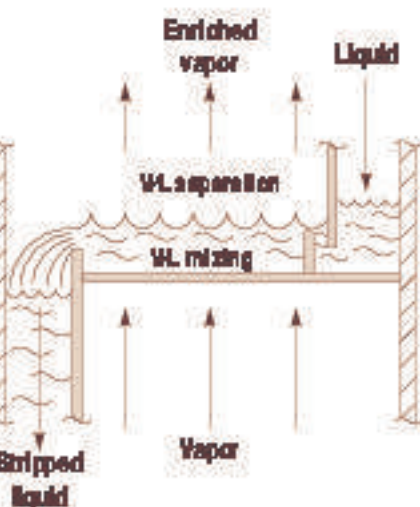
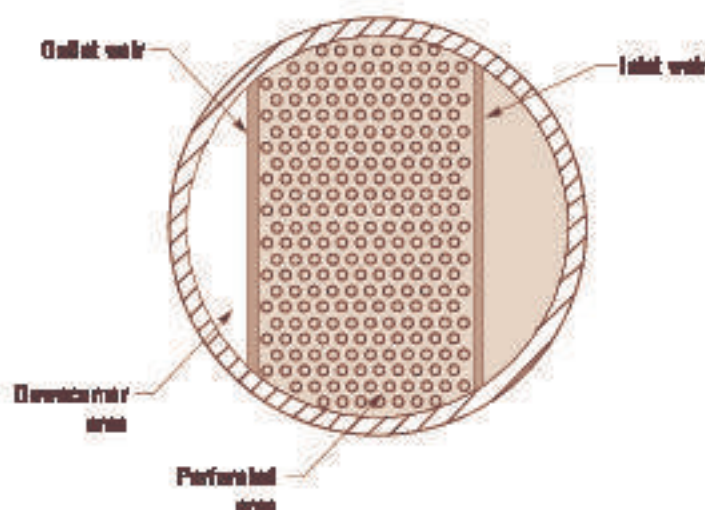


Figure 5. Distillation tray functions.

Figure 6 depicts a perforated tray contactor with certain accoutrements required to control the flow of liquid and vapor and to assure their intimate contact. Another type of tray contacting device, the disc-and-donut or baffle tray is shown in Figure 7. The characteristics of this type of contactor make it especially useful for distilling materials such as dry-milled grain beer, which would foul ordinary trays such as perforated, valve, etc.

ENERGY ANALYSIS

In addition to the selection of the basic contacting device, the energy requirement must be

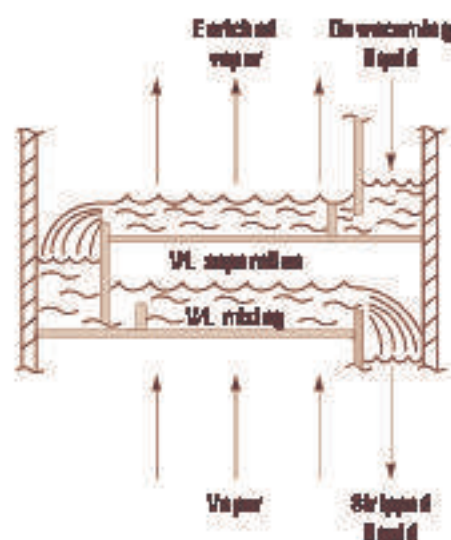


Figure 6. Perforated trays.

established. This is accomplished by analyzing the vapor/liquid equilibrium data from Figure 4, for the liquid:vapor flow ratio to perform a continuous series of steps within the limits of the equilibrium curve. Table 1 demonstrates a

simplified procedure to calculate the approximate energy requirement from the liquid:vapor flow ratio that will be employed in the tower design. Repetition of this type of calculation for different conditions produces a

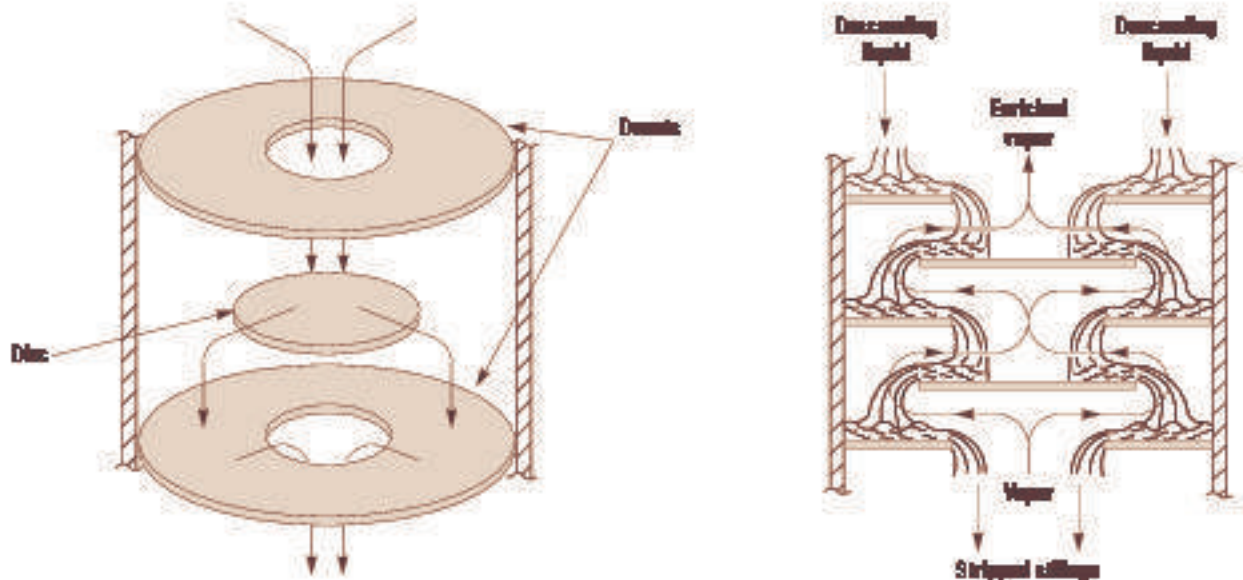


Figure 7. Disc-and-downcomer trays.

Table 1. Simplified calculations for steam requirements for ethanol distillation.

Example 1. Calculate the steam required (lb/gallon of product) to strip 100 gpm of a 10% volume beer (90 gpm water/10 gpm ethanol).

$$L/V^* = 5.0 \text{ (typical for a 10% volume beer) or } L = 5 \cdot V$$

$$L = 90 \text{ gpm} \cdot 500 \text{ lb/hr} = 45,000 \text{ lb/hr} = 5 \cdot V$$

$$\text{gpm}$$

$$\text{Therefore, } V = 9,000 \text{ lb/hr (steam)}$$

$$\text{And } 9,000 \text{ lb/hr (steam)} \cdot \frac{\text{hr}}{10 \text{ gpm (product)}} = 15 \text{ lb steam/gallon of product}$$

$$\text{60 min}$$

Example 2. Calculate the steam required to strip 100 gpm of a 5% volume beer (95 gpm water/5 gpm ethanol).

$$L/V = 6.33 \text{ (typical for a 5% volume beer) or } L = 6.33 \cdot V$$

$$L = 95 \text{ gpm} \cdot 500 \text{ lb/hr} = 47,500 \text{ lb/hr} = 6.33 \cdot V$$

$$\text{gpm}$$

$$\text{Therefore, } V = 7,500 \text{ lb/hr (steam)}$$

$$\text{And } 7,500 \text{ lb/hr (steam)} \cdot \frac{\text{hr}}{5 \text{ gpm (product)}} = 25 \text{ lb steam/gallon of product}$$

$$\text{60 min}$$

*L and V are liquid and vapor flow rates, respectively, expressed in lb-moles per hr.

Note: all bases of calculation are simplifying assumption of water (L) and steam (V). Therefore: $\frac{L(\text{lb-moles/hr})}{V(\text{lb-moles/hr})} = \frac{L(\text{lb/hr})}{V(\text{lb/hr})}$

design chart like that shown in Figure 8 for the ethanol-water system. Such a graph is useful when calculations are needed to ascertain technical and economic feasibility and preliminary conditions for the design.

Figure 9 demonstrates how the liquid:vapor flow ratio, in connection with the number of stages (theoretically ideal trays) required for a specified separation between ethanol and water, is graphically determined. Note that the stages are constructed by drawing straight lines vertically and horizontally between the equilibrium curve (previously determined experimentally) and the operating lines. For an ethanol stripper/rectifier, there are two operating lines: one for the rectification section and one for the stripping section. The operating lines represent the locus of concentrations within the distillation tower of the passing liquid and vapor streams. The operating lines for a given tower

are based on the energy input, as calculated and represented in Figure 8. Because of the principle of constant molal overflow, the operating lines can be represented as straight lines. If constant molal overflow was not valid for the ethanol/water distillation, then these lines would be curved to represent the changing ratio of liquid flow to vapor flow (in molar quantities) throughout the tower. The slope of the operating line (the ratio of liquid flow to vapor flow) is also called the *internal reflux ratio*. If the energy input to a tower is increased while the beer flow remains constant, the operating lines will move toward the 45° line, thus requiring fewer stages to conduct the distillation. Likewise if the energy input is reduced (lowering the internal reflux ratio), the operating lines will move toward the equilibrium curve, reducing the degree of separation achievable in each stage and therefore

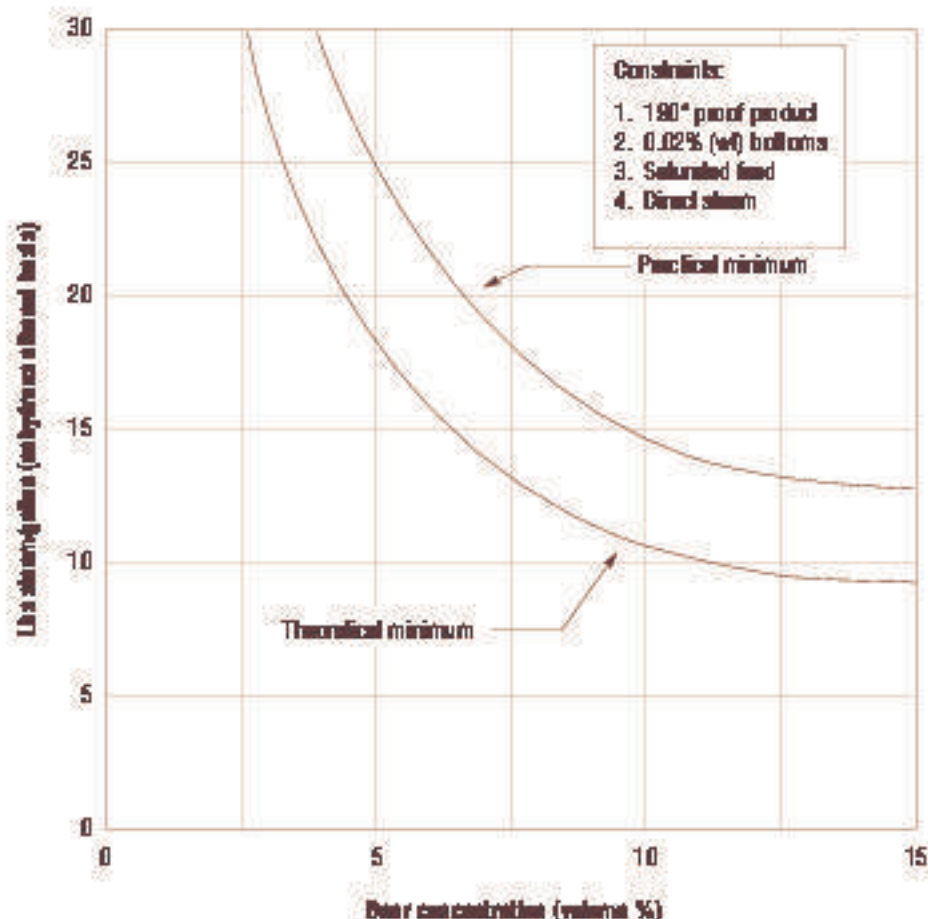


Figure 11. Stages required for the ethanol stripper/rectifier.

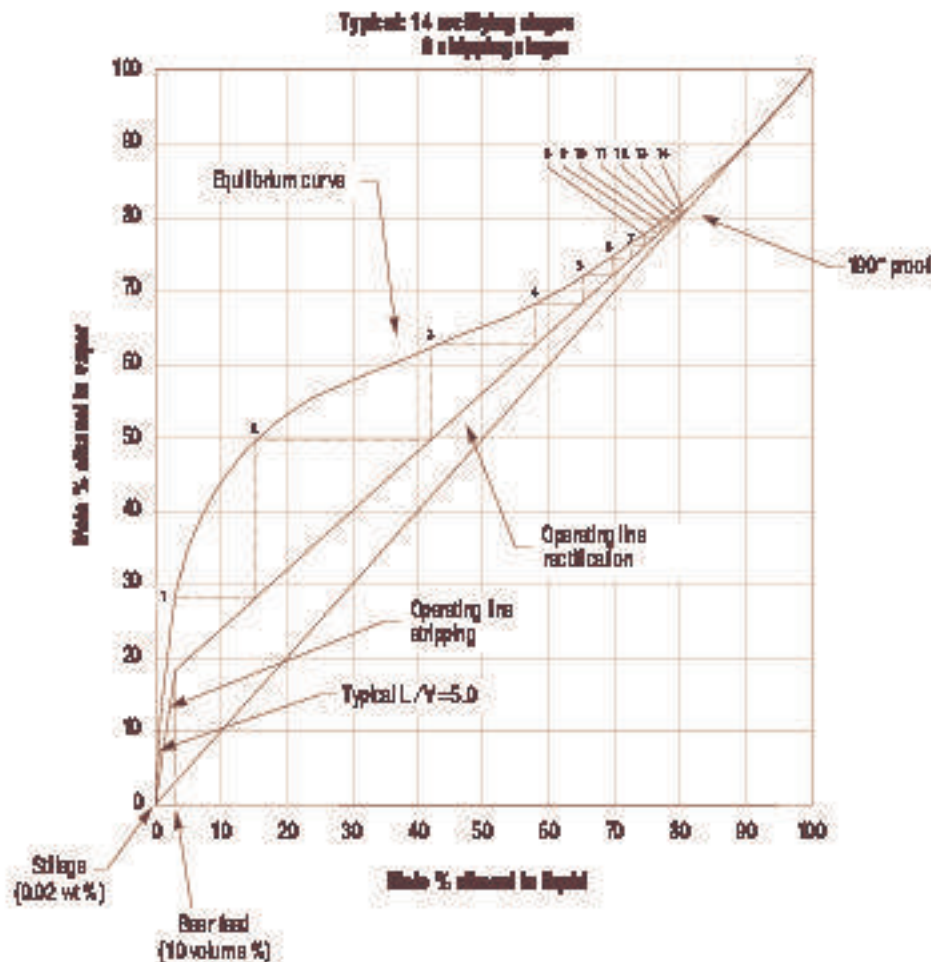


Figure 9. Vapor/liquid equilibrium stage analysis.

requiring more stages to conduct the distillation. The calculations underlying the preparation of Figure 9 go beyond the scope and intent of this text, but have been included for continuity. The dashed lines represent the graphical solution to the design calculations for the number of theoretical stages required to accomplish a desired degree of separation of the feed components. Figure 9 is referred to as a *McCabe-Thiele diagram*. For further pursuit of this subject, refer to the classical distillation textbook by Robinson and Gilliland (1950).

TOWER SIZING

The goal of the design effort is to establish the size of the distillation tower required. Table 2 shows the basic procedure to determine the

diameter required for the given distillation tower. Since all of the distillation 'work' is done by the trays, the tower is actually the 'container' to surround the vapor and liquid activity that is 'managed' by the trays. Tower diameter design is, therefore, actually the design of the necessary tray diameter for proper vapor/liquid interaction and movement.

The f factor (vapor loading) is an empirically determined factor that depends primarily upon tray type and spacing, fluid physical properties, froth stability and surface tension at the operating conditions of the system. The proper values for f are determined by field observations. In summary then, the f factor can be described as an adjusted velocity term (units are ft/sec) that when multiplied by the square root of the density ratio of liquid to vapor, will give the allowable vapor velocity in the empty tower shell, such

Table 2. Calculations for tower sizing (base of stripper).

Example: Calculate tower diameter required for a 10 % volume beer at 100 gpm (1.5 lbs steam/gallon of product)

W	Vapor flow rate	= 9,000 lb/hr (steam)
P	Operating pressure at base	= 1.34 ATM
M _{wa}	Average MW of vapor	= 18 lb/lb-mole
ρ _L	Liquid mixture density	= 59.5 lb/ft ³ (227 °F)
T	Absolute operating temperature	= 687 °R
D	Tower inside diameter in inches	
f	Vapor loading factor	= 0.05-0.3

Sizing equation:
$$D = 0.2085 \sqrt{\frac{W}{f \sqrt{\frac{P \cdot M_{wa} \cdot \rho_L}{T}}}} = 0.2085 \sqrt{\frac{9000}{f \sqrt{\frac{1.34 \cdot 18 \cdot 59.5}{687}}}} = \frac{16.45}{\sqrt{f}}$$

Assuming $f = 0.16$ (specific to tray design and spacing), the tower diameter is:

$$D = \frac{16.45}{\sqrt{0.16}} = 41.125 \text{ inches}$$

Tower diameter calculation utilizes the following equation. Values for the terms are indicated above.

$$D = 0.2085 \sqrt{\frac{W}{f \sqrt{\frac{P \cdot M_{wa} \cdot \rho_L}{T}}}}$$

The final design equation can be derived beginning with the fundamental equation:

$$u = f \sqrt{\frac{\rho_L - \rho_V}{\rho_V}}$$

Where	u	= average vapor velocity in empty tower shell (ft/sec)
	ρ _L	= liquid density (lb/ft ³)
	ρ _V	= vapor density (lb/ft ³)
	f	= tower vapor loading factor (ft/sec)

(Note: For most cases ρ_L is much greater than ρ_V, so that ρ_L - ρ_V ≈ ρ_L. For example, water (steam) at 212°F and atmospheric pressure: ρ_L = 59.8 lb/ft³ and ρ_V = 0.0373 lb/ft³. Then ρ_L - ρ_V = 59.7627 lb/ft³ ≈ 59.8 lb/ft³, which results in a negligible 0.06% error.)

Consequently
$$u \approx f \sqrt{\frac{\rho_L}{\rho_V}}$$

Imposing the equation of continuity: $W = A \cdot \rho_V \cdot u$ or $u = W/A \cdot \rho_V$

Where	A	= tower cross-section area (ft ²)
	ρ _V	= vapor density (lb/ft ³)
	u	= average vapor velocity in empty tower shell (ft/sec)
and	W	= vapor mass flow (lb/hr)

Substituting for u in the equation above:

$$\frac{W}{A \cdot \rho_V} \approx f \sqrt{\frac{\rho_L}{\rho_V}} \quad \text{then} \quad \frac{W}{A} \approx f \sqrt{\rho_L \cdot \rho_V} \quad \text{or} \quad A \approx \frac{W}{f \sqrt{\rho_L \cdot \rho_V}}$$

Use the Ideal Gas Law to express the vapor density:

$$\rho_v = \frac{P \cdot M_{\text{vso}}}{R \cdot T} \quad \text{Then by substitution one obtains} \quad A = \frac{W}{f \cdot \sqrt{\frac{P \cdot M_{\text{vso}} \cdot \rho_L}{R \cdot T}}}$$

Using the Universal Gas Constant $R = 0.73 \text{ (ft}^3\text{)(atm)/(lb-mole)(}^\circ\text{R)}$ the equation becomes:

$$A = \frac{W}{1.17 \cdot f \cdot \sqrt{\frac{P \cdot M_{\text{vso}} \cdot \rho_L}{T}}} \quad \text{Now} \quad A = \frac{\pi \cdot D^2}{4} = 0.7854 \cdot D^2$$

$$\text{and} \quad D^2 = \frac{W}{0.9192 \cdot f \cdot \sqrt{\frac{P \cdot M_{\text{vso}} \cdot \rho_L}{T}}} = \frac{1.0679 \cdot W}{f \cdot \sqrt{\frac{P \cdot M_{\text{vso}} \cdot \rho_L}{T}}}$$

$$\text{Adjusting units: } D = \frac{1.043 \cdot 12}{60} \cdot \sqrt{\frac{W}{f \cdot \sqrt{\frac{P \cdot M_{\text{vso}} \cdot \rho_L}{T}}}} \quad \text{Therefore, } D \text{ (inches)} = 0.2085 \cdot \sqrt{\frac{W}{f \cdot \sqrt{\frac{P \cdot M_{\text{vso}} \cdot \rho_L}{T}}}}$$

that liquid entrainment and/or vapor phase pressure drop in the tower will not be excessive.

Excessive vapor velocity will first manifest itself by causing excessive liquid entrainment rising up the tower, causing loss of separation efficiency. Ultimately the excessive entrainment and pressure drop will cause tower flooding.

To achieve a well-balanced tower design, the foregoing analysis must be performed at each stage of the tower, from bottom to top. Composition changes, feed points, draws, etc., each can cause a different requirement. The tower must be examined to locate the limiting point.

Similar analyses, with empirically-observed performance coefficients, are applied to vapor passing through the trays and through the liquid, and to the movement and control of liquid passing through downcomers and across the trays. These analytical procedures are beyond the scope of this text. Reference should be made to the aforementioned text by Robinson and Gilliland for further information.

Considerations in optimizing distillation system design

Optimizing the technical and economic design of distillation equipment and similar gas and

vapor/liquid mass transfer systems involves a number of interrelated parameters. The positive/negative balance of a variety of contacting devices with different capacities and efficiencies for promoting vapor/liquid mass transfer must be taken into consideration. Along with the technical issues considered in such designs, economical operation is essential not only in the reduction of energy and other direct costs, but also in relation to investment and return on investment from the operation being considered. In this respect, distillation towers are not independent process-wise, as consideration must also be given to other auxiliaries such as reboilers, condensers, pumps, controls and related equipment.

SIZING TOWERS

In determining optimum diameter and height of towers for distillation, absorption, stripping and similar mass transfer operations, design factors are affected by whether the installations will be indoors or outdoors. With indoor installations, building height limitations, as well as floor level accessibility, are an important factor in the design. Where there are height limitations, towers must be increased in diameter to provide for reduced tray spacing, which in turn will require

lower vapor velocities. With outdoor installations, literally the 'sky is the limit', and refinery and petrochemical towers of 200 feet in height are not uncommon.

In either case, indoors or outdoors, the interrelated tower diameter and tray spacing are limited by allowable entrainment factors (f factors) (Katzen, 1955). If outdoors, tower heights and diameters must be related to maximum wind loading factors in the specific plant location and may be complicated by allowance for earthquake factors.

TRAY AND PACKING SELECTION

Vapor/liquid contacting devices may be of two distinct types, namely packed or tray (staged) towers. In packed towers, the transfer of material between phases occurs continuously and differentially between vapor and liquid throughout the packed section height. By contrast, in tray towers, the vapor/liquid contact occurs on the individual trays by purposely interrupting down-flowing liquid using downcomers to conduct vapor-disengaged liquid from tray to tray and causing the vapor/liquid contact to occur between cross-flowing liquid on the tray with vapor flowing up through the tray. In other words, the vapor/liquid contact is intermittent from tray to tray, and is therefore referred to as being stagewise. Thus, for any given separation system, the degree of vapor/liquid contact will be greater with a greater height of the packed section, or in the case of tray towers, a greater number of trays used.

It is generally considered that packing-type internals may be used with relatively clean vapor and liquid systems where fouling is not a problem. Economics indicate that packing is applicable in small and modest sized towers. As the towers become larger, packing becomes complicated by the need for multiple liquid redistribution points to avoid potential vapor/liquid bypassing and reduction in efficiency. Structured packings (Fair *et al.*, 1990; Bravo *et al.*, 1985) are designed to minimize these problems by reducing the height requirement and controlling, to some extent, the distribution of liquid. However, high fabrication and specialized installation costs would indicate that these are applicable only for relatively low-volume, high-value product processing.

Trays of various types are predominant in vapor/liquid contacting operations, particularly on the very large scale encountered in the petroleum and petrochemical industries, in large scale operations of the chemical process industries and in the large scale plants of the motor fuel grade ethanol industry.

The venerable bubble cap tray, with a wide variety of cap sizes, designs and arrangements to maximize contact efficiency, has fallen out of favor during the past few decades because of the relatively high cost of manufacture and assembly. Valve trays of several types have taken over in operations requiring a relatively wide vapor handling capacity range (turndown). This has been extended by use of different weights of valves on the same tray. Specialty trays such as the Ripple, Tubogrid, tunnel cap and others designed to improve contact under certain specific circumstances have been used to a limited extent.

The long established perforated tray is a contacting tray into which a large number of regularly oriented and spaced small circular openings have been drilled or punched. These trays are commonly referred to as 'sieve trays' because of the original practice of putting the maximum number of holes in any given tray area. This original design produced a fairly inefficient operation at normal loading, and a very inefficient operation with decreased vapor loading. About 50 years ago, engineers began to suspect that the design approach had been in error, and that the hole area in the trays should be limited by the hole velocity loading factor to obtain maximum contact by frothing, as indicated in Figure 10.

The hole vapor loading factor (or perforation factor) is defined as the vapor velocity through the perforations adjusted by the square root of the vapor density at the specific tower location of a given perforated tray. With the parallel development of separation processes in the petroleum refining, chemical and ethanol industries, the modern approach has developed to what is now called 'perforated tray' design. The Fractionation Research Institute of the American Institute of Chemical Engineers diverted its efforts from bubble cap studies to perforated tray testing, and have established a basis for the design of perforated trays with high efficiency and wide capacity range (Raphael Katzen Associates, 1978).

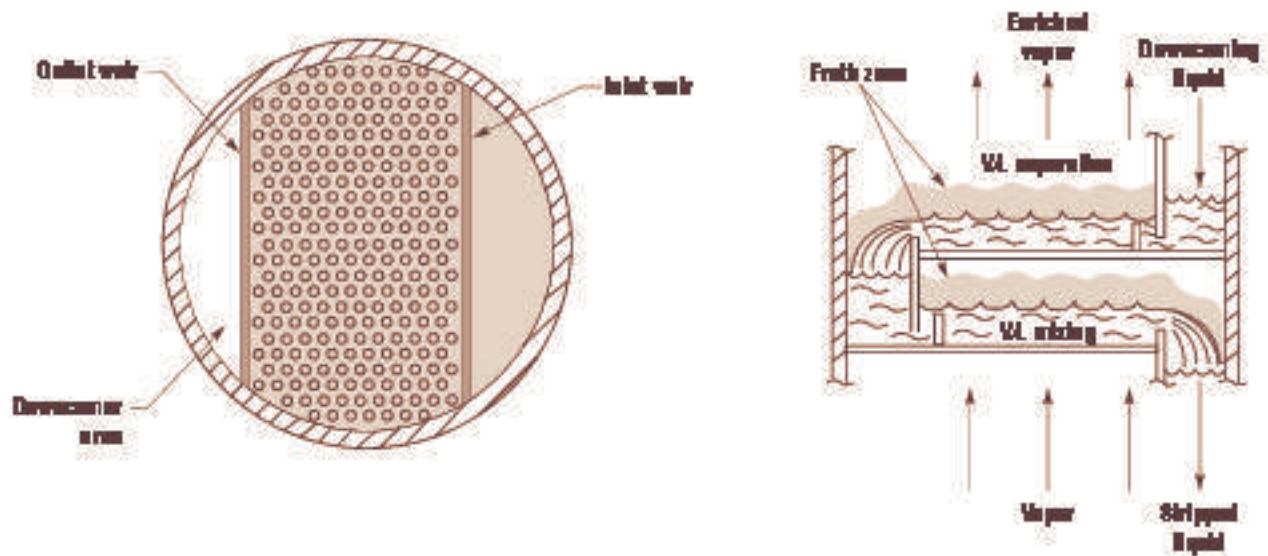


Figure 10. Perforated tray frothing.

Where foaming or tray fouling (caused by deposition of solid materials in the tower feed) can be an operational problem, novel designs such as the baffle tray may permit extended operating time between cleanings. Baffle trays may take a number of different forms. They can be as simple as appropriately spaced, unperforated, horizontal metal sheets covering as much as 50–70% of the tower cross sectional area; or they may take the form of a series of vertically spaced, alternating, solid disc-and-donut rings (see Figure 7). Towers up to 13 ft diameter are in operation using this simple disc-and-donut design concept.

Although system-specific data have been developed for each type of tray, it is difficult to correlate tray loading and efficiency data for a wide variety of trays on a quantitative basis. Each system must be evaluated based upon empirically-derived loading factors for vapor and liquid operations within the tower.

AUXILIARIES

Energy input is of prime importance in tower design, particularly in ethanol stripping and rectification units. In aqueous and azeotrope-forming systems, direct steam injection has been

common practice to maintain simplicity. However, the need to reduce the volume of waste going to pollution remediation facilities has minimized use of this simple steam injection technology to avoid the dilution effect of the steam being condensed and added to the stillage. Direct steam injection transfers both the energy and the water into the process. By imposing a heat exchanger (reboiler) between the steam and the process, only the energy is transferred into the tower. The condensate water is returned in a closed loop to the boiler, thus reducing the bottoms outflow from the process. Reboilers are thus growing in acceptance, and several types may be employed. Kettle and thermosyphon reboilers are preferred where fouling is not a problem. Where fouling can occur, high velocity, forced-circulation, flash heating reboilers are preferred. Figure 11 depicts the reboiler energy transfer by a forced-circulation reboiler as compared to Figure 1 which depicts direct steam injection.

Thermocompression injection of steam has also been utilized where low pressure vapors are produced from flash heat recovery installations and where higher pressure motive steam is also available.

Condenser design would appear to be simple. However, in many cases, water limitations require adapting condenser designs to the use

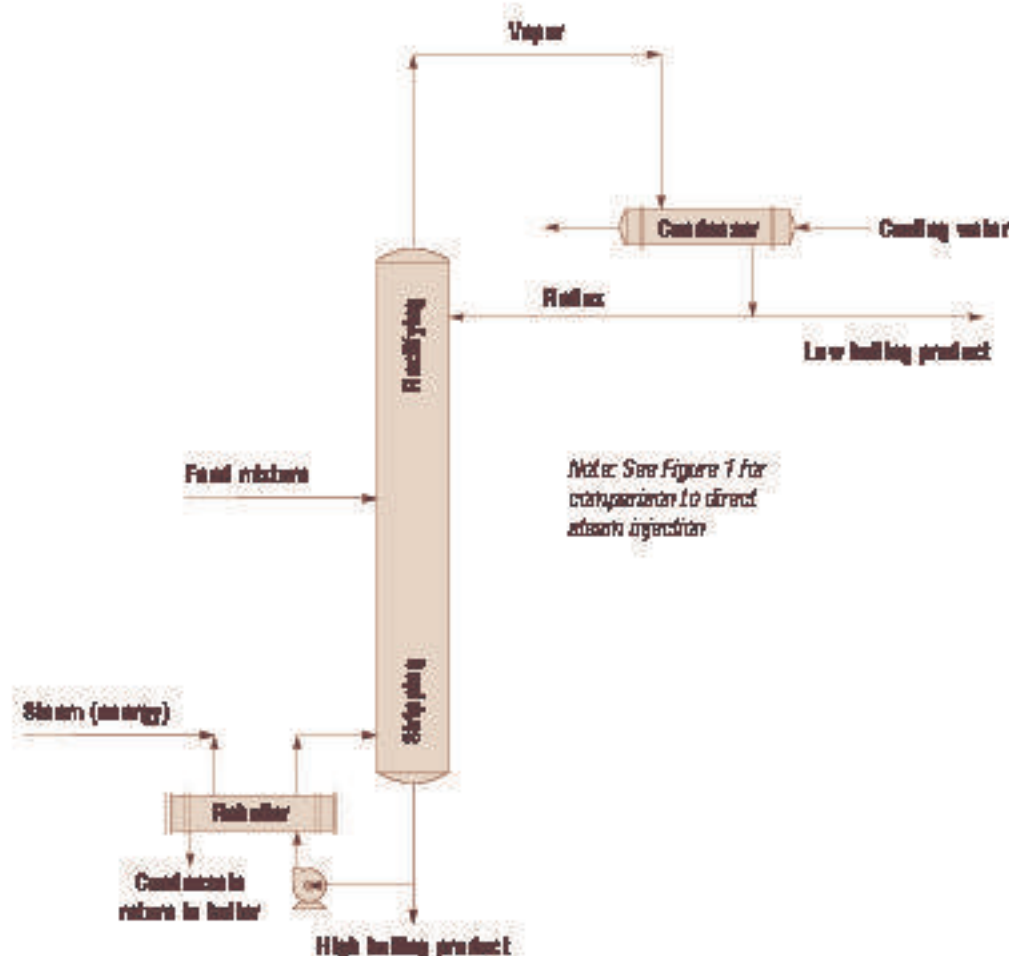


Figure 11. Energy transfer by a forced-circulation reboiler.

of cooling tower water with limited temperature rise and minimal scale-forming tendencies. On the other hand, where water is extremely scarce, air-cooled condensers are used.

Energy conservation

The increasing cost of thermal energy, whether provided by natural gas, fuel oil, coal or biomass, is fostering an increased emphasis on heat recovery and a reduction in primary thermal energy usage (Fair, 1977; Petterson *et al.*, 1977; Mix *et al.*, 1978). Conventional bottoms-to-feed heat exchangers are now being supplemented with recovery of overhead vapor latent heat by preheating feed streams and other intermediate process streams. Techniques of multistage

distillation (similar to multiple effect evaporation) are also practiced. Pressure-to-atmospheric, atmospheric-to-vacuum, or pressure-to-vacuum tower stages are utilized, with the thermal energy passing overhead from one tower to provide the reboiler heat for the next one. Two such stages are quite common and three stage systems have also been utilized (Katzen, 1980; Lynn *et al.*, 1986).

Furthermore, the modern technique of vapor recompression, commonly used in evaporation systems, is also being applied to distillation systems. Such a system can provide for compression of overhead vapors to a pressure and temperature suitable for use in reboiling a lower pressure stripping tower. However, the compression ratios required for such heat recovery may consume almost as much

electrical energy as would be saved in thermal input. Alternative systems, using vapor recompression as an intermediate stage device in the distillation system, have also been proposed.

Control systems

Control systems can vary from manual control, through simple pneumatic control loops to fully automated distributed control (Martin *et al.*, 1970). High level computer control has facilitated the application of sophisticated control algorithms, providing more flexibility, reduced labor and higher efficiency with lower capital investment. Such systems, when properly adapted to a good process design, have proven more user-friendly than the control techniques utilized in the past.

Economic design

In integrating the technology discussed, the final analysis must be economic. Alternative systems must be compared on the basis of investment requirements, recovery efficiency and relative costs of operation. Thus, any heat exchangers installed for heat recovery must show a satisfactory return on the investment involved in their purchase and installation. In comparing alternative separation systems, the overall equipment costs must be compared against energy and other operating costs to determine which system offers the best return. Modern computer-assisted designs incorporate economic evaluation factors so economic optimization can be determined rapidly.

Ethanol distillation/dehydration: specific systems technology

Proven industrial technologies are available for distillation of various grades of ethanol from grain, sugarcane, molasses and other feedstocks. Improvements have been made over the years, particularly during development of the motor fuel grade ethanol industry. In such installations, a key requirement is the minimization of total energy usage.

The operation that has been most subject to critical comment is the distillation process. Many relatively new 'authorities' in the field have based their criticism on technologies that go back 50-60 years, and have created an unwarranted condemnation of distillation as a viable process for low energy motor fuel grade ethanol production. Systems developed over the years will be described to show that much of such criticism is unwarranted and unjustified.

PRODUCTION OF INDUSTRIAL ETHANOL

Prior to the emphasis on motor fuel grade ethanol, the major ethanol product utilized worldwide was high purity, hydrous industrial ethanol, which is generally produced at a strength of 96° GL (192° US proof) (°GL = degrees Gay Lussac = % by volume ethanol; US proof = 2 x % by volume ethanol). Efficient systems have been in commercial operation for many years for the production of such high grade ethanol from ethylene, grain, molasses and sulfite waste liquor. The basic distillation system is shown in Figure 12.

In the case of synthetic ethanol (outside the scope of this publication), the beer stripping tower is not required and the refining system is a simple three tower unit, which achieves 98% recovery of the ethanol in the crude feed as a first grade product. The final product may contain less than 5 ppm total impurities and has a 'permanganate time' of more than 60 minutes.

For the production of industrial or beverage spirit products made by fermentation of grain, molasses or sulfite liquor, the system utilizes the full complement of equipment shown in Figure 12. The beer feed is preheated from the normal fermentation temperature in several stages, recovering low level and intermediate level heat from effluent streams and vapors in the process. This preheated beer is degassed and fed to the beer stripper, which has stripping trays below the beer feed point and several rectifying trays above it. The condensed high wines from the top of this tower are then fed to the extractive distillation tower, which may operate at a pressure of 6-7 bars (87-101.5 psi). In this tower, most of the impurities are removed and carried overhead to be condensed as a low grade ethanol

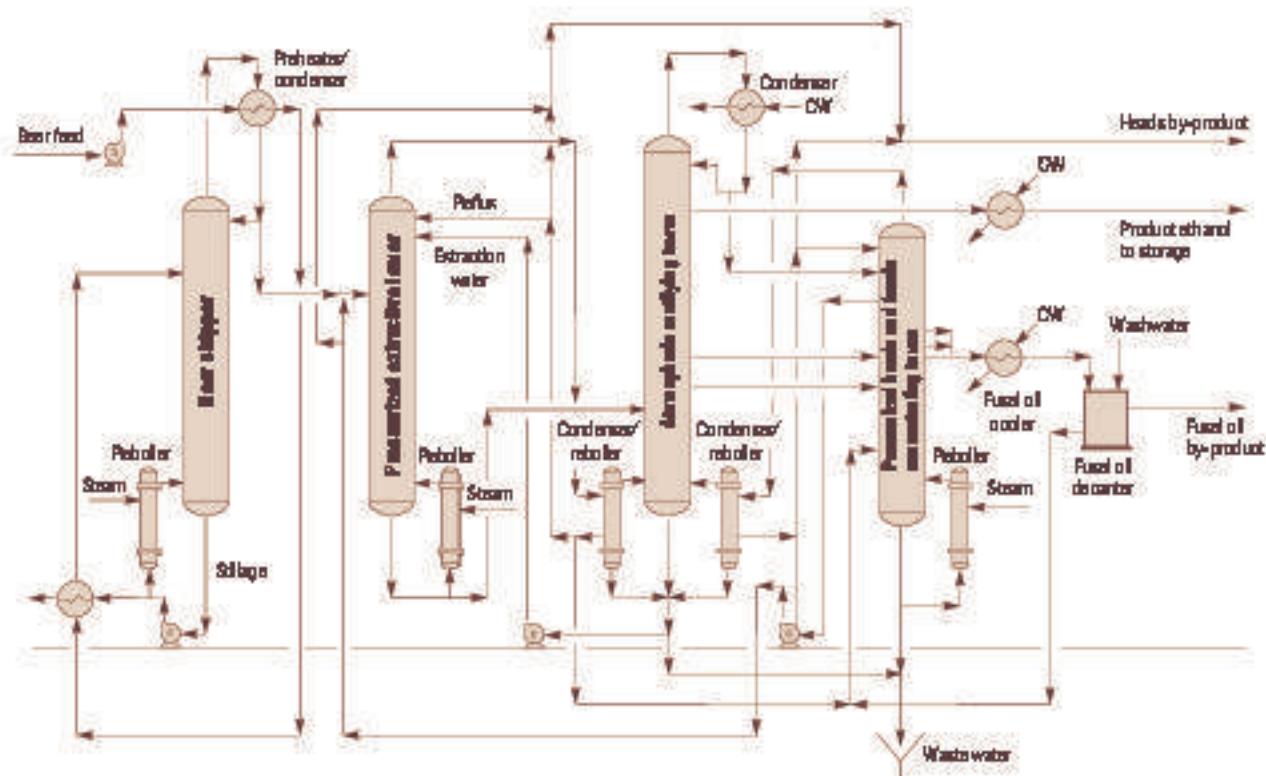


Figure 12. Low energy-consuming high grade hydrous ethanol distillation.

stream, from which a small purge of heads (acetaldehyde and other low boiling impurities) may be taken while the primary condensate flow is fed to the concentrating tower. The purified, diluted ethanol from the bottom of the extractive distillation tower is fed to the rectifying tower, which has an integral stripping section. In this tower, the high grade ethanol product, whether industrial or potable, is taken as a side draw from one of the upper trays. A small heads cut is removed from the overhead condensate. Fusel oils (mixtures of higher alcohols such as propyl, butyl, and amyl alcohols and their isomers, which are fermentation by-products or 'congeners') are drawn off at two points above the feed tray but below the product draw tray to avoid a buildup of fusel oil impurities in the rectifying tower. The overhead heads cut and the fusel oil draws are also sent to the concentrating tower.

It should be noted that the rectifying tower is heated by vapors from both the pressurized extractive distillation tower and the pressurized concentrating tower.

In the concentrating tower, the various streams of congener-containing draws are concentrated.

A small heads draw is taken from the overhead condensate, which contains the acetaldehyde fraction along with a small amount of the ethanol produced. This may be sold as a by-product or burned as fuel. A fusel oil side draw is taken at high fusel oil concentrations through a cooler to a washer. In the washer, water is utilized to separate the ethanol from the fusel oil, with the washings being recycled to the concentrating tower. The decanted fusel oil may be sold as a by-product. The ethanol recovered from the crude streams is taken as a side draw from the concentrating tower and fed back to the extractive distillation tower for re-purification and recovery of its ethanol content.

In an early version of this system, installed more than 60 years ago for the production of potable ethanol from grain and from molasses, all towers were operated at atmospheric pressure. However, installations made within the past 40 years utilize the multistage pressure system to reduce energy consumption to a level of about 50% of the all-atmospheric system.

The commercial installations utilizing the multistage pressure, or 'pressure cascading'

technique operate with a steam consumption of 3.0-4.2 kg of steam/liter (25-35 lb/gallon) of 96° GL ethanol. This may be compared to about 6 kg of steam/liter for earlier conventional distillation systems.

Production of anhydrous ethanol

Systems have been designed and installed for production of extremely dry and very pure anhydrous ethanol for food and pharmaceutical use, primarily in aerosol preparations. These systems, as shown in Figure 13, yield ethanol containing less than 200 ppm water (99.98° GL), less than 5 ppm total impurities and more than 60 minutes permanganate time.

The two tower dehydrating system has been operated in two super-anhydrous plants in Canada, and was used to produce motor fuel grade ethanol (99.5° GL) in four installations in Cuba (prior to the advent of the Castro regime). The dehydrating tower and the entrainer-recovery tower are operated at atmospheric pressure. Thus, they may utilize either low pressure steam, hot condensate or hot waste streams from other parts of the ethanol process to minimize steam usage. To simplify equipment

and minimize investment, a common condensing and decanting system is used for the two towers.

The entrainer used to remove water as a ternary (three component) azeotrope may be benzene, heptane (C_6-C_7 cut), cyclohexane, n-pentane, diethyl ether or other suitable azeotropic agents. The entrainer serves to create a three component azeotrope that boils at a temperature lower than any of the three individual components and lower than the ethanol/water binary (two component) azeotrope. Therefore the ternary mixture will pass overhead from the tower, carrying the water upward. Upon condensing, the mixture separates in a decanter into an entrainer-rich layer and a water-rich layer.

The hydrous ethanol feed enters the dehydrating tower near the top. The feed contacts the entrainer in the upper section of the tower. The three component mixture in this section of the tower seeks to form its azeotrope, but is deficient in water and contains more ethanol than the azeotrope composition. Therefore, the ethanol is rejected downward in the liquid and is withdrawn as an anhydrous product from the bottom of the tower. The water joins the entrainer, passing upward as vapor to form a mixture that is near the azeotrope

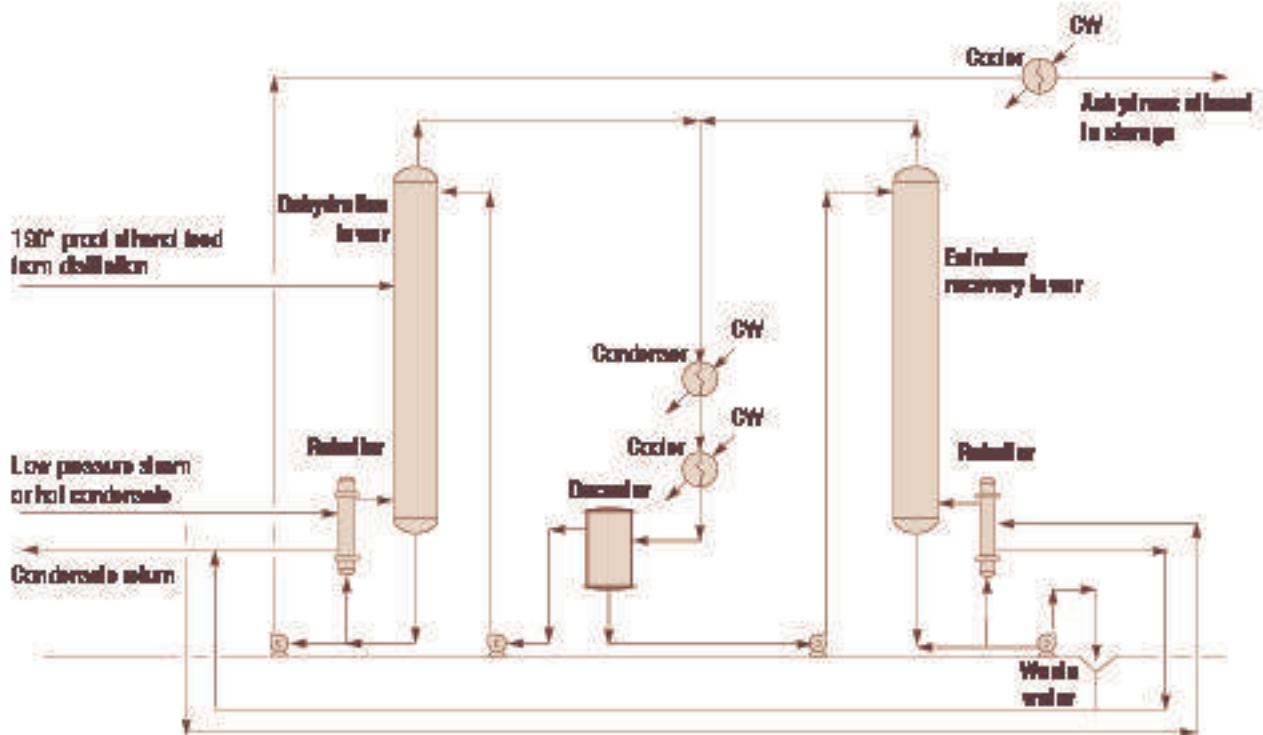


Figure 13. High grade anhydrous ethanol system.

composition for the three components. The condensed mixture separates into two layers in the decanter and the entrainer-rich layer is refluxed from the decanter back to the top of the tower. The aqueous layer is pumped from the decanter to the entrainer-recovery tower, in which the entrainer and ethanol are concentrated overhead in the condenser-decanter system. The stripped water, emerging from the base of the tower, may go to waste. If it has substantial ethanol content, it may be recycled to the spirit unit, but this introduces the risk of traces of the entrainer in the hydrous ethanol which may not all be sent to the dehydration system. This system operates with a steam consumption of 1-1.5 kg/liter (8.3-12.5 lb/gallon) of anhydrous ethanol depending on the quality of product required. As indicated above, a major part of the equivalent steam energy can be provided by hot condensate and hot waste streams from the spirit unit.

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