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Distillation Techniques in the Fruit Spirits Production

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Abstract

During the distillation of the fermented fruit mash or juice, ethanol and water are the carriers of a huge number of the other volatile aroma compounds. Unique and distinctive flavour of the final spirits depends on their quantity and quality. Fruit spirits have higher concentration of almost all types of volatile compounds with comparing to other types of distilled spirits. The art of distillation run is to obtain the best balance between congeners present. Two different types of distillation equipment are used for the production of fruit spirits: copper Charentais alembic and batch distillation columns. Although both distillation methods are based on the same theoretical principles, a different quantity of the flavour compounds of the final spirits is produced by using different distillation equipment. The main difference was shown in different distributions of the methanol, n-propanol, higher alcohols and fatty acid esters. Distillation methods need to be adjusted for each fruit spirits regardless to distillation equipment employed because fermented mash of different fruit varieties has a different requirement for distilling. Alembic stills yield better aroma and more characteristic fruit distillates but are slow and require more labour. Column still cleans the distillate giving a decent aroma and higher concentration of alcohol.

Keywords: alembic, distillation column, fruit spirits, distillation cut, aroma compounds

1. Introduction

Fruit spirits are popular alcohol beverages due to their unique flavour. They are consumed in various countries all over the world. Very often fruit spirits represent the national drink of the country, so the Hungarians are proud on their apricot spirits; French on Calvados; Italians on apple spirits [1]; Greeks on mulberry spirits [2]; Balkan countries [3, 4] and Eastern European countries on plum spirits [5]; and Germans and Swiss on their 'kirschwasser' [6]. Although fruit spirits could be made from each type of fruit that contains at least a few amounts of sugar,

either cultured or wild fruit, the most popular fruit spirits are made from plums, cherries, apples, pears, apricots and quinces. The nice, unique and pleasant aroma is common for all of them. The main ingredients of these beverages are water and ethanol, and they account around 99% of the total content of the spirits. Nevertheless, the fruit spirits are not a pure diluted ethanol; in that case one could not make differences between plum spirits from quince or pear spirits. Fruit spirits must be recognised on the raw material from which it obtained. Hundreds of different compounds, so-called congeners, have been identified in fruit spirits, present in very low concentration but crucial for the quality of beverages. The composition and concentrations of these congeners vary depending on the cultivar used for the production, fermentation procedure, yeast strain used, time of storage of fermented mash before distillations, distillation technique, use of post distillation processes and maturation of spirits. Thus, it seems that the quality of spirit and its identity and character are influenced by a huge number of factors. Some authors favoured raw material as a factor of great influence on character and authenticity of fruit spirits [7–9]; others said that fermentation is the most important activities in aroma compound production; another, however, wrote that distillation is a technique that manages the composition of aroma compounds present in the spirits [10–12], whilst some other authors highlighted the ageing of spirits in creating their unique quality [13, 14]. However, the truth is somewhere between of all these views. Nevertheless all researchers are agreed that all phases have to be adequate carried out in order to achieve the fruit spirits premium quality.

The production of fruit spirits has a long tradition in Croatia and the other West Balkan countries (Bosnia and Herzegovina, Serbia, Montenegro, Macedonia, Kosovo and Albania). The most popular is plum brandy or *Sljivovica* although recently; all kinds of fruit are used in spirits production. Traditional production of the fruit spirits involves the use of simple distillation pot still (Charentais alembic or French style). In the last decade, the batch distillation columns (German style) are introduced in the production of spirits in small distilleries. The distinctive identity of spirits can be affected by various distillation devices used. Very often the distillation run is left to the skills of distiller, and sometimes they have no experience to govern the distillation, resulting unpleasant and pungent flavour of the fruit spirits obtained, without distinctive identity.

For this reason, this chapter has an aim to give an overview of the basis of distillation process and main characteristics of commonly used distillation techniques in fruit spirits production.

2. Theory of distillation

Simply, distillation is the process in which a liquid is vaporised (turned to steam), recondensed (turned back into a liquid) and collected in a container. Distillation is a very old separation technology for separating liquid mixtures into their individual components by the application of heat. The basis for the component separation is differences in their boiling points. Mixture of two or more compounds is separated by heating it to a certain temperature and condensing the resulting vapours. The vapour above a boiling mixture becomes richer in more volatile components. Consequently, a boiling mixture becomes richer in less volatile components. That means that the original mixture will contain more of the less volatile material.

2.1. Distillation of binary mixture (ethanol-water)

Spirits mainly consist of the ethanol and water in quite equal portions. Alcohol has a lower boiling point than water (78.5°C compared to 100°C for water). Depending on the ratio of alcohol to water, mixture will boil at all temperatures between 78.5 and 100°C. Due to differences in boiling points, the vapour above the liquid will be richer in alcohol than water at the any moment of evaporation. Alcohol-water relationship between gaseous and liquid alcohol-water mixtures is shown in **Figure 1**. As it can be seen in **Figure 1**, vapour phases are richer in the ethanol than the liquid, at any given mixture. Assuming, a mixture (A) of 6/94% of ethanol and water is supposed to be separated by distillation. The vapour above the liquid in the moment of equilibrium achieved will be about 42% of ethanol (A₁). Distilling the mixture of 42/58% of ethanol and water (A₁) produces a distillate that is about 78% ethanol and 22% water (A₂), and further distillation of the liquid mixture (A₂) will give a vapour with about 86% of ethanol (A₃). This means that initial alcohol strength of liquid was 6% (w/w), and after three distillations, the strength of liquid was 86% (w/w). Further, distillations will produce mixtures that are closer to the azeotropic ratio of 95.6/4.4% of ethanol and water. At this concentration, the alcohol in the vapour phase is no longer more concentrated than in the liquid phase, and fractional distillation no longer works. A mixture of this composition is called an 'azeotropic mixture'. An azeotropic mixture itself cannot be separated by ordinary distillation, and, usually, special methods are required. Generally, a third substance must be introduced into the mixture to permit separation by distillation, or some other separation schemes must be used, e.g. distillation under lower pressure not at the atmospheric pressure.

Referring to **Figure 1**, some main remarks could be given. If we put in ratio concentration of ethanol in the vapour to concentration of ethanol in the liquid (that is in this case A₁/A), we will get 42/6 = 7. It means sevenfold increase concentration of alcohol. The next step of distillation gives ratio A₂/A₁, that is 78/42 = 1.9 and finally A₃/A₂ or 86/78 = 1.1. It is obvious that the highest strength of ethanol happened when the concentration of ethanol was the lowest in the initial liquid. Here is about equilibrium ratio (*K* value) or distribution coefficient. It represents the ratio of the mole fraction some particular component in the vapour, *y*-axis to the mole fraction in the liquid *x*-axis. *K* value is defined by

$$K = \frac{y_A}{x_A} \quad (1)$$

where *y_A* and *x_A* are the mole fractions of component *A* in the vapour (*y*) and liquid phases (*x*). For the more volatile components, the *K* values are greater than 1, whereas for the less volatile components are less than 1. The *K* value is sometimes called the equilibrium 'constant', but this is misleading as it depends strongly on temperature and pressure or composition [15].

It is important to know how ease or difficult; the two components will be separated from the binary mixture (e.g. mixture of component *A*, more volatile component, and *B* less volatile component). Comparing the *K* values for these two components, relative volatility (denoted by α) obtained:

$$\alpha = \frac{\frac{y_A}{x_A}}{\frac{y_B}{x_B}} = \frac{K_A}{K_B} \quad (2)$$

Relative volatility is a measure of the differences in volatility between two components and hence their boiling points. It indicates how easy or difficult a particular separation will be. Thus, if the relative volatility between two components is equal to 1, separation is not possible by distillation. The larger the value of α , above 1, the greater the degree of separability, i.e. the easier the separation.

The values of α will be less dependent on temperature than the values of K since the K all increases with temperature in a similar manner. In general, relative volatility of a mixture changes with the mixture composition.

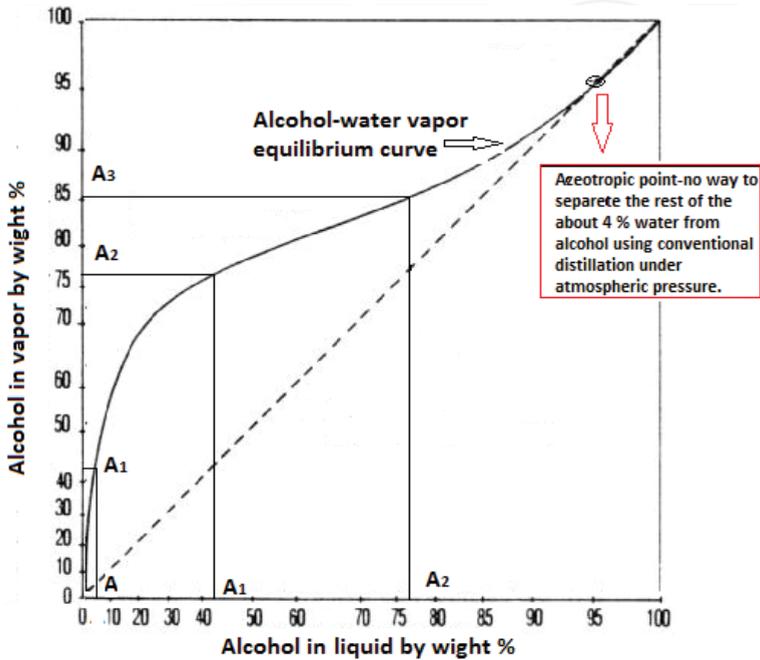


Figure 1. Vapour-liquid equilibrium of ethanol-water showing distillation steps of the mixture.

2.2. Distillation of multicomponent mixture (fermented mash)

In the production of fruit spirits, the initial material for distillation is fermented mash (or juice) that contains the ethanol and water as main compounds and a huge number of other volatile compounds that have a very large boiling point difference (e.g. acetaldehyde 20.8°C and benzaldehyde 179°C). These are collectively known as congeners, and they give the spirits authenticity and flavour. Some congeners are desirable in small quantity; others should be removed as more as possible during distillation. It is complicated to measure the relative volatility for each individual component in a multicomponent mixture. There are many reasons for that, and some of them are the following: compositions and concentrations of compounds are changing continuously with time, the aroma compounds are highly dependent on ethanol content in the liquid phase from which they are vaporising and compounds interact with themselves and between each other.

Distillation is performed with the aim to concentrate ethanol and desirable aroma compounds, so the relative volatility for the each individual component (i) is defined with respect to ethanol (E) and denoted by

$$\alpha_i = K_i/K_E \quad (3)$$

In that sense, all congeners could be separated with respect their α value on the:

- compounds with $\alpha > 1$ (these compounds are more volatile than ethanol)
- compounds with $\alpha < 1$ (these compounds are less volatile than ethanol)
- compounds with $\alpha = 1$ (separation of these compounds from ethanol is not possible)

Congeners rarely have a permanent α value greater than 1 or less than 1, due to the congeners that will distill differently depending on compositions of initial mash, their solubility in the ethanol and water, content of ethanol, variation of ethanol content in the vapour during distillation, distillation technique employed and regime of distillations. Some of the important congeners that almost ever have $\alpha > 1$ are acetaldehyde, typical representative of the first distillation fraction, or opposite, acetic acid that almost ever has $\alpha < 1$ and distills in the third fraction. Thanks to the differences in boiling points of congeners, their different solubility in the ethanol or water and the variation of ethanol content in the vapour during the distillation of all congeners will distill separately [16]. It is the basis for the separation of unwanted compounds, or concentration wanted volatile compounds during distillation of fermented fruit mash. The possibility of the separation volatile compounds enables the distiller to have a control over the process of the separation a large group of volatile compounds and ensure the production, health and pleasant quality of fruit spirits.

3. The distillation cut

During distillation ran the ethanol and water are the two main components which are actually carriers of all other volatile compounds (**Figure 2**). It could be considered that the ethanol vapour will carry over the compounds favouring spirits aroma and flavour and therefore the quality.

At the very beginning, the high volume of ethanol comes out of the still together with high volatile compounds. Through the time volume of alcohol is decreased followed by water, and low volatile compounds increased. According to this, the distillate is cut to three cuts or fractions: the head, the heart and the tail. The heads contain higher concentration of low boiling point components and mainly contain undesirable compounds. These compounds would give the distillates an unpleasant, strong and sharp flavour. In the first cut, there is a higher concentration of some toxic compounds, and therefore it must be eliminated. The best part of the run is the middle part of the distillation, the final spirits. It is a distillate rich in ethanol that is carrying a pleasant and fruity aroma compounds. The heart cut is a very clean taste lacking the sharp bite of the heads. The last cut is the tail fraction, which has to be eliminated from the heart, since it contains unpleasant fatty and oil compounds. In this fraction, the main carrier is the water. The water is carrying longer molecules, which are usually unpleasant and

can be identified by the distinctive smell of 'wet dog'. The tail fractions (with or without head adding) are collected and redistilled, because it contains a relatively high concentration of alcohol and a valuable congeners.

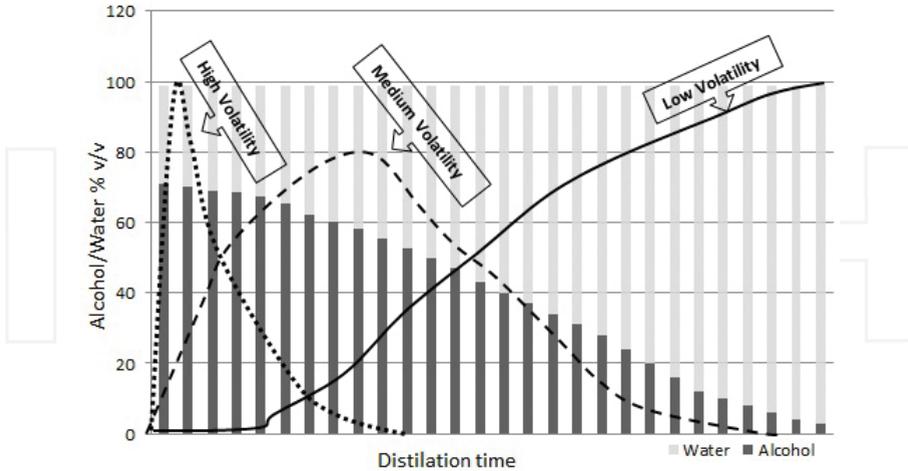


Figure 2. Distillation run of ethanol and congeners that distinguish by volatility. Adapted from © 2001 The International Centre for Brewing and Distilling [17].

3.1. How to make cuts during distillation run

In order to produce an aromatic, harmonised and pleasant fruit distillate, it is necessary to know the right time for distillation cut. During the distillation of ethanol and congeners, it is possible to manipulate the separation of volatile compounds, to clean undesirable and to concentrate desirable aroma compounds. Aroma profile of distillates very often depends on the skill of distiller to cut adequately distillation fractions. The head and tail fractions could be cut on the basis of sensory evaluation of distiller. The presence and absence of volatile congeners that give a sharp, strong and unpleasant smell to the head fraction can be cut points for the switching to the heart fraction. Also, the tail fraction starts with flavour that gives a faded, dull character to the distillates, and it should not be difficult for the sensory evaluation and separation. Experienced distillers do this very well by smell. Taste and smell still remain the most reliable method of determining when to make a cut.

The second indicator of cut points that can be used is the percent alcohol of the spirits that's flowing out of the still, especially for the separation of the heart from the tail cut. The ethanol strength could be the limiting values for the switching from the heart to the tail. This limiting value varies depending on distillation equipment involved, the fruit variety used, the quality of fermented mash, etc. Finally, the third indicator of the cut points that can be used is the temperature of the vapour before its entering to the condenser. Distiller can make the first cut in the run, when the temperature of vapour in the copper pipe reaches approximately 74–76°C. The heart cut from the tail can be made when the temperature of vapour in

the copper pipe reaches around 87–88°C, and tail distills until temperature reaches 92–93°C, when distillation could be over.

Each of above-mentioned manners of distillation cut has a shortcoming, and the best way is to use all of them as guideline for the separation of congeners during distillation.

4. The two main distillation techniques

Distillation may be carried out batchwise or continuously. Nevertheless, for the production of fruit spirits, batch distillation is used. Two different types of distillation equipment are commonly used for the production of fruit spirits: copper Charentais alembic (French style) and batch distillation columns (German style). It is important to carry distillations out slowly regardless the type distillation equipment employed. Fast distillation could lead the development of hot spots and consequent accelerated thermal degradation of the final spirit.

4.1. Distillation in the Charentais alembic

In the Balkan countries, a copper alembic pot still has been utilised in artisanal distilleries, small commercial and medium-sized distilleries, in the production of fruit and wine brandy. It consists of a copper boiler, a hat, a copper pipe (pipe is not like swan neck) and a condenser (**Figure 3**). The pot still is usually heated by direct fire (fuelled by firewood or, in recent times, by natural gas). Distillation in alembic pot stills requires multiple distillations (usually double) to achieve high degree of alcohol. The aim of the first distillation is to exhaust, as much as possible, alcohol from the fermented mash. Collected distillate is called raw distillate (or low spirits) with alcohol content around 15–25% (v/v), that depends on how rich in alcohol-fermented mash was. The second stage of distillation is carried out which aimed at intensification and purification of the alcohol and has to be carried out much more carefully than the first one. In the second distillation, raw distillate is distilled with separation of three fractions. The head fraction (or cut) is collected in the amount from 1 to 2% per 100 L of raw spirits. The amount of head depends on how damaged fermented mash was. If fermented mash waits for long time until distillation is carried out, then higher head needs to be separated. The heads are thrown out because many unwanted and toxic compounds are present. Therefore, it is most important adequately to separate the heads from the hearts than the tails from the hearts. The heart fraction starts coming out at 60 to 70% (v/v) of ethanol (depends on how rich in alcohol raw spirits was) and collects until the alcohol decrease to 40–50% (v/v). The exception is Williams pear spirit. In the production of this spirit, the heart fraction needs to be cut at the lower alcohol degree (below 40%, v/v) due to the ethyl decanoate ester which distills at the beginning of the tail fraction. This ester is very important for the Williams pear spirits aroma. Research from Spaho et al. [18] showed that distillation cut of the heart fraction from the tail fraction, at 50% (v/v) of ethanol, proved to be better for the sensory impression of plum spirits made from more aromatic plum like Pozegaca and Bilska rana. The opposite rule was observed for the Stanley variety (less aromatic plum), where a better quality of brandy was achieved with a distillation cut at a lower alcohol content (40% v/v ethanol). After the heart

is separated, the tail fraction distills until the end, actually, until alcohol degree achieved 3 or 5% (v/v). Measuring the alcohol content during distillation is carried out by alcoholmeter. The tail is collected and could be redistilled later or could be saved and added to the next run. During distillation, all variables are needed to keep constant and flow rate to adjust to 15–25 mL/min.



Figure 3. Traditional copper alembic pot still. The hat plays a role in the reflux because the vapour came in and will partially condense and run back down to the original liquid in the boiler and be redistilled. The flavour of final spirits was influenced by the shape and size of the hat [19].

Obtained heart fraction usually has an alcohol strength of 45–70% (v/v) that is strongly depends on kind and variety of fruit used for the spirits production [20].

Sometimes, in the Balkan countries, plum spirits, so-called Sljivovica, was produced by single-stage distillation in the alembic pot still. This type of spirits is very aromatic with so many congeners, and some of them are not desirable (Table 1). Sljivovica, produced by single-stage distillation, has had a double higher content of acetic acid and esters, a higher content of higher alcohols and acetaldehyde than Sljivovica produced by double distillations.

Stage of distill.	Alcohol (% v/v)	Total acids (g/L)	Aldehyde (mg/L a.a.)	Esters (mg/L a.a.)	Higher alc. (mg/L a.a.)	Methanol (% v/v a.a.)
Single	43.8	1.39	448.19	6611.4	4779.39	0.84
Double	60.6	0.36	209.68	3243.0	3264.11	1.03

Table 1. Average content ($n = 5$) of the main congeners in Sljivovica produced by single- and double-stage distillation [3].

Apart from ethanol, a content of methanol was higher in the Sljivovica obtained by double-stage distillation (**Table 1**). This is because the methanol follows the ethanol during distillation, and it concentrates more, together with ethanol.

4.2. Distillation in the batch distillation column

Batch distillation column style requires just one distillation to achieve high alcohol degree [21, 22]. In single-stage distillation, also these fractions are separated: the head, heart and tail. Distillation column consists of a copper pot still fitted with column with trays and a dephlegmator (**Figure 4**). In the fruit spirits production, column usually consists of three ball trays.



Figure 4. Steam-fired batch distillation column still with three trays and dephlegmator above them. Reflux rate is varied by changing the cooling rate in dephlegmator.

At the very beginning of distillation, the vapour mixture of volatile compounds goes from the boiler to the dephlegmator. Incoming vapour is partially condensed in the dephlegmator, returning a portion of it in trays. This process is called reflux, and liquid from a dephlegmator is called phlegm or reflux condensate. The reflux condensate feeds the trays in column. During distillation, the vapour coming up through the column vaporises alcohol from reflux condensate, leaving more water to keep dripping down to the next lower tray. During this countercurrent contact of vapour and liquid, which happened on each tray, the vapour stream becomes richer in light components, and the liquid stream becomes richer in heavy

components. At every interface between the liquid layer and the condensed layer, contact is occurring causing greater separation of the compounds present. This process is called rectification. Consequently, as more trays are used in distillation, a greater concentration of alcohol and lower concentration of congeners are obtained. Some of these congeners are very pleasant aroma compounds, and it is not desirable to clean the alcohol too much. So, the rectification must be run very carefully, getting in mind what aroma compounds we want to have in the distillate [20, 23–25]. That means that sometimes all three trays should be active, and sometimes not, depending on how clean or how flavourful distillate needs to be.

Since the alcohol was cleaning and concentrating at the trays in the column, it starts coming out of the condenser at 70–87% (v/v). The fewer amounts of heads are collected than in alembic pot (~0.5 to 1% per 100 L of fermented mash). The head fraction is collected until content of alcohol decreased at 75–55% (v/v). The heart is obtained with approximately 65–78% (v/v) in volume around 5–10 L per 100 kg mash. After the heart is separated, the tail fraction distills until distillate obtained has an alcohol content of approximately 20–30% (v/v). All the above-mentioned alcohol contents varied from run to run and strongly depend on how much alcohol in the fermented mash has.

The main characteristic of a batch distillation column is that concentrations and temperatures are changing with time at any part of the column, so two methods can be carried out [26]: constant reflux ratio (with variable product composition at distillate) or variable reflux (with constant product composition, for one component, at distillate product). It is usually to carry out distillation with constant reflux ratio.

5. Distribution of volatile compounds during distillation by using different distillation equipment

Although both distillation techniques are performed on the same theoretical basis and in both cases three fractions have been obtained, there are several important differences in the content of ethanol and congeners that are crucial for the flavour of spirits. The first difference is content of alcohol that entails a lot of other differences. For alembic distillation, the alcoholic strength in the heart fraction is significantly lower than alcoholic strength in the heart fraction obtained by using distillation column although both distillation techniques recovered the same amount of ethanol in the heart fraction [27]. Congeners are present in very small amounts in fruit spirits but with a large influence on the bouquet and flavour. Distribution of the main congeners during distillation by using different distillation equipment, simple alembic pot and distillation column, was shown in **Figure 5**.

As it can be seen in **Figure 5**, the main differences occurred in distribution of methanol, fatty acid esters, n-propanol and isoalcohols. The main reason, for those differences, lies in the fact that those compounds show different behaviours depending on content alcohol in liquid and vapour during distillation. They will distill following their relationship with alcohol rather than their boiling point.

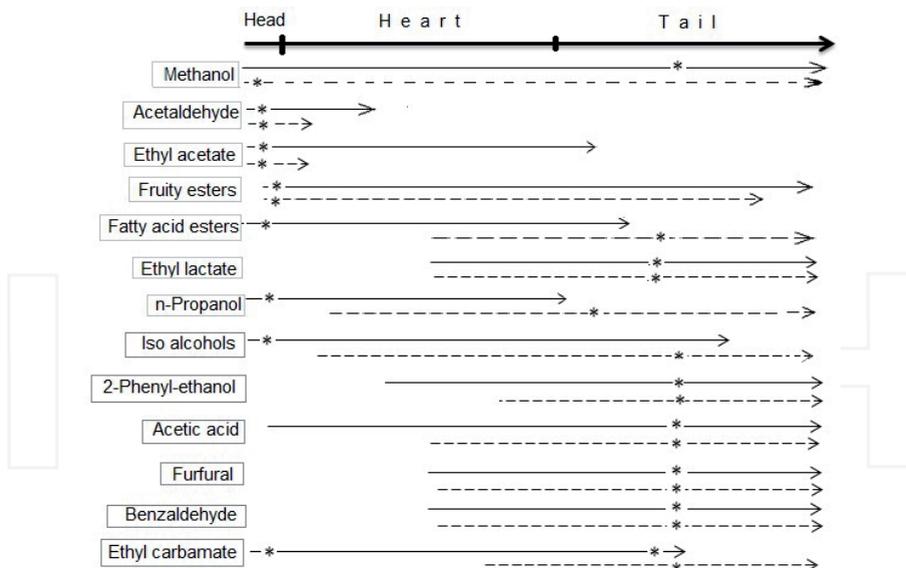


Figure 5. Distribution of main volatile compounds by using different distillation equipment: *full line*, alembic distillation; *dashed line*, column distillation and *, shows the cut where higher component is accumulated (this figure is created thanks to results of the authors) [10, 12, 18, 20, 21, 27–33].

Methanol is often the most concentrated compounds in fruit spirits [2, 8, 12, 18, 34]. Methanol is not a by-product of alcohol fermentation but is released very intensively during this process. The methanol was produced during the processing and storage of fermented mash via the effects of enzymes on pectin in the cell wall. Actually, methanol is formed from the demethoxylation of the esterified methoxyl groups in pectin.

It is characteristic to fruit brandies, significantly higher than in cereal distillates [34]. Its presence in the spirits is proof of natural origin of fruit spirits because the pectin is a natural constituent of fruits. Concentration of methanol is dependent mainly on the applied technique of the fruit treatment and the distillation and second from the fruit kind and variety.

There are different views on methanol impact to flavour of distillates. Such, Ribéreau-Gayon [35], considered the methanol imparts a cooked cabbage odour in spirits, with a threshold of 1200 mg/l. Claus and Berglund [21] wrote that methanol is considered to be a positive flavour constituent in distilled spirits. Nevertheless, most researchers say methanol is colourless volatile compounds with a mild or bland odour and does not affect the flavour of distillates [10, 32, 36, 37]. However, it is one of the most important compounds to control in the spirits due its dangerous effect to human health. In some quantities, the methanol can be dangerous because it is metabolised to formaldehyde and formic acid, which is primarily responsible for most of the toxic effects of methanol [38]. Since it is toxic to humans, the maximum level of methanol is fixed by EU Regulations No. 110/2008. According to these regulations, the concentration of methanol in fruit spirits should not exceed to 12 g/L alcohol 100% (v/v).

The boiling point of methanol is 64.7°C , and it is completely soluble in water. Considering methanol contents in the distillates obtained by different distillation techniques the results reported by several authors are vary. Methanol appears in almost equal concentration in all fractions of distillation due to the formation of azeotropic mixtures [39, 40]. It is really difficult to separate the methanol from the ethanol-water mixture. When low alcohol mixture (like fruit-fermented mash) is distilled in simple pot still, methanol will go out following his solubility in water rather than his boiling point. Methanol is highly soluble in water, therefore, methanol will distill more at the end of distillations, when vapours are richer in water. That means that methanol will accumulate more in the tail fraction [7, 32], during distillation in alembic pot still as it showed in **Figure 6**.

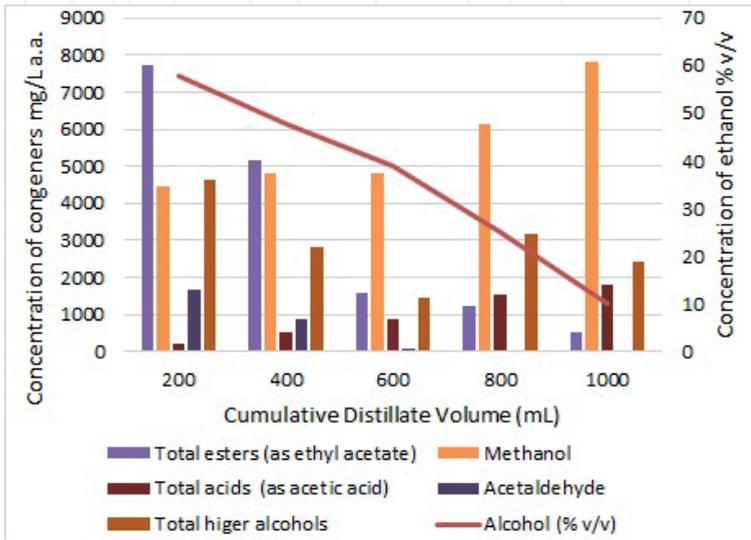


Figure 6. Concentration of the main congeners separated during distillation in alembic pot still: volume 10 L [30].

When high alcohol mixture distills, methanol will evaporate following his boiling point and will be present in the first fraction of the distillation in higher concentration. It appears mainly in the head fractions when distillation column was used [21]. Results of Cortes et al. [32] showed the concentration of the methanol was seven times higher in the case of industrial distillation (means higher concentrates and cleanses of ethanol) than the concentration of methanol in the distillates obtained by simple pot still. The opposite results are given by Arrieta-Garay [20]; there is no difference in methanol content depending on distillation system employed (alembic pot still or packed column distillations), whilst Leaute [16] and Garcia-Llobodanin et al. [27] reported that methanol content was higher in alembic distillates than in the column distillates.

The higher alcohols are quantitatively the largest group of the aroma volatile compounds in the distilled alcoholic drinks [32, 41]. They are also called fusel oil although they are not

oils. It is due to form oil blotches in low alcoholic liquids because they are partially soluble in water. Higher alcohols are formed during the fermentation process and are considered as by-product of alcohol fermentation. They are produced by yeast during alcoholic fermentation, through the conversion of the branched chain amino acids present in the medium.

The chemical classes of higher alcohols include numerous alcohols. The largest share in the higher alcohol group was amylic alcohols, 2-methyl-1-butanol (active amyl alcohol), 3-methyl-1-butanol (isoamyl alcohol), 2-methyl-1-propanol (isobutyl) and 1-propanol, which are in the highest concentration present in plum brandy [18]. Very high content of 1-propanol may be an indicator for the spoilage of fruit mash.

The quantities of the other higher alcohols were very low. The shares of 1-hexanol, 1-butanol, 1-pentanol and 2-butanol were less than 5% of the total amount of the higher alcohols [18]. The compounds 1-butanol and 1-hexanol are formed during alcoholic fermentation by the hydrolysis of the corresponding acetates.

The content of 2-butanol is usually associated with a low quality of raw materials and is related to bacterial action during fermentation. Its presence negatively influences to flavour.

1-Hexanol is an alcohol originating only from raw material [2]. The level of 1-hexanol is considered the sensory relevance especially in the apple ciders and associated with a grassy scent in distillates. But, when it is present above 100 mg/L a.a. then 1-Hexanol is responsible for the very intensive grassy flavour and distillates is unpleasant both in aroma and taste. It is estimated that the presence of 1-hexanol in the above-mentioned concentrations imparts to wines and distillates fruity, liquorice and even a toothpaste-flavour profile [42].

2-Phenyl-ethanol is an aromatic alcohol and has a rose-like odour. It contributes to pleasant flavour of fruit distillates due its very low odour threshold. Bacteria, fungi and yeasts may synthesise 2-phenyl-ethanol using L-phenylalanine as a substrate, which allows this metabolite to be deemed as a potent genotypic marker for grape marc spirits [43].

2-Methyl-butanol and 3-methyl-butanol are the most abundant minor components of spirits synthesised by yeast. In trace amounts in fruit spirits, there are also trans-3-hexenol, cis-3-hexenol and trans-2-hexenol, 1-octanol, 3-ethoxy-1-propanol allyl and benzyl, alcohol which are more characteristic for stone fruit spirits.

Higher alcohols make an important contribution to the aroma profile of distillates. They are responsible for the pleasant flavour and give an essential character of fruit distillates just when they are present in smaller quantities. However, high amounts can affect the distillate flavour, giving a strong, pungent smell and taste [2, 32]. Total higher alcohol concentrations, higher than 3500 mg/L (a.a.), are accepted as being an indicator of poor quality [43].

The level of higher alcohol in fruit spirits is influenced by fruit variety, fermentation conditions, employed distillation and distillation equipment.

Higher alcohols have boiling points lower than 200°C and are alcohol soluble and partially water soluble. During distillation of low alcohol mixture, they will distill when the vapour is rich in alcohol (they want to escape from the water in the mash, due to their low water solubility). It means they will appear mainly in the head fraction although they have high

boiling point. When distilling mixture has higher concentration of alcohol (higher than 40% (v/v) [44]), higher alcohol will distill following the boiling points, and their concentration will increase as the distillation process progresses. This explains why distillates in the column showed higher concentration of higher alcohol in the tail [21] and distillates in pot still (**Figure 6**) showed higher concentration of higher alcohol in the head [18, 40].

Higher concentration of this important flavour compounds is observed in the distillates obtained in the distillation column still than in the distillates obtained in the alembic pot still [27, 40, 43].

Esters are formed during alcoholic fermentation via yeast metabolism and qualitatively present the major class of flavour compounds in distillates because they have low sensory threshold value. Esters, generally, are associated with a pleasant, fruity and flowery aroma. Their contribution to flavour is strongly influenced by their concentration.

Ethyl acetate is the major ester present in distilled alcoholic beverages. In small quantities, ethyl acetate contributes to the pleasant smell of distillates giving them a fruit character. In large amounts, it contributes to a sharp smell and gives a UHO tone (glue smell) of flavour. Ethyl acetate perception threshold of 180 g/hl a.a. gives to the spirits an acidic character [2]. High concentrations of ethyl acetate are indicative of prolonged storage of the raw material and probable acetic bacteria spoilage but could be also influenced by the distillation process. Ethyl acetate in fruit spirits constitutes even more than 80% of all the esters [18]. The importance of ethyl acetate is such that the ratio of total esters and ethyl acetate is used as indicator of quality of spirits. The higher this ratio, the higher the quality of the final product. Boiling point of ethyl acetate is 77.1°C, and it distills mainly in head fraction in both distillation techniques used. Distillates obtained in the alembic pot still showed a higher amount of ethyl acetate in comparing with distillates obtained with distillation in distillation column [16, 33], whilst some results [27] showed the higher concentration of ethyl acetate in distillate obtained by using packed distillation column.

Esters of acetic acid and higher alcohols such as isoamyl acetate, isobutyl acetate and 2-phenylethyl acetate are presence in relatively significantly amount in all fruit distillates. They are mostly responsible for the flowery and fruity aroma of the distillates. Isoamyl acetate is associated with odour and flavour of bananas, whilst isobutyl acetate is more common to raspberry flavour. Esters C₆-C₁₂ are slightly higher in packed column distillates than alembic distillates [45].

Ethyl lactate is considered to give the distillates a buttery flavour and smell of rancid butter, with a perception threshold of 250 mg/l. Its presence can be linked to a malolactic fermentation, which is considered spoiled. In low concentration, lower than 154 mg/L [19], being favourable, stabilise the odour and smoothens the firm character of certain substances [2]. Ethyl lactate is associated with tail fraction of the distillate [18]. The concentration of ethyl lactate was higher in the distillates obtained by using alembic pot still than column. It comes from both the double distillation technique and the malolactic fermentation [16].

2-Phenylethyl acetate is acetate with rose odour. Although it has a high boiling point, it distills in all distilled fractions due to its partial solubility in water. Rodríguez Madrera and Mangas Alonso [10] report that 2-phenylethyl acetate distills mainly in head fractions.

Diethyl succinate gives a fusel-like [42] and camphor-like character. This ester derives mainly from bacterial spoilage [46] and distills in tail fraction in the bout distillation techniques.

Ethyl esters from middle-chain fatty acids (hexanoic, octanoic, decanoic and dodecanoic) are compounds of particular interest in fermented beverages and spirits on account of contributing fruity and flowery smells and their relatively high levels [47]. They are produced during the raw material fermentation. Beyond these, ethyl hexanoate is the most abundant of all middle-chain fatty acid esters. Hexanoate (ethyl caproate) supplies an aroma of fruit (banana, green apple, melon, etc.), and, so, its presence is beneficial for the spirit. Ethyl octanoate (ethyl caprylate) is more pungent and less fragrant, decanoate (caprate) is less intensive and gives fatty tones and dodecanoate (laurate) is less aromatic and has a waxy candle-like odour [19]. Despite high boiling point of fatty acid esters, they are distilled in the first fractions during pot still distillation due to their better solubility in ethanol than water [16]. During column distillation fatty acid esters are accumulated in tail fractions. There are higher amounts of these fatty acid esters in alembic distillate than in column distillate.

Ethyl esters of long-chain fatty acids are important just when they are present in higher concentration. Then, they may contribute to odours giving to spirits a candle wax and stearin tone. Esters from this group are also poorly soluble in water, so their elevated concentrations may cause turbidity and flocculation and therefore be important factors of distillate instability [48].

The major **carbonyl compound** in distillates is acetaldehyde, a direct alcoholic fermentation by-product. Moreover, significant acetaldehyde concentration may be formed by oxidation of ethanol by acetic acid bacteria in the presence of oxygen. That is one of the reasons why distillation should be carried out as soon as possible after fermentation is finished. The content of acetaldehyde is not influenced by a variety of raw material [48]; it is influenced by the strains of yeasts [49], by fermentation process and manner of distillation cut.

It has a distinctive aroma characteristic, and when it presents in higher concentration, it has a sensorial negative impact. Its importance derives not just from the pungent smell it brings along, as well as its chemical reactivity. This makes it a harmful component for the consumers. It is usually associated with intoxication and 'hangover' symptoms such as nausea, vomiting, restlessness, sweating, confusion, decrease in blood pressure, higher heart rate and headache [50]. Some authors [33, 51] established 120 g/hl a.a. of total aldehydes (mainly acetaldehyde) as limiting values before they significantly affect the aroma of the spirit.

In low concentration odour of acetaldehydes, resemble hazelnuts, cherry and overripe apples. It has a relatively low odour perception threshold. As acetaldehyde has a low boiling point, its largest concentration is distilled into the head portion of the distillate (**Figure 6**). It is completely soluble in both water and ethanol. The lower concentration of acetaldehyde is reported in distillates obtained in alembic pot still than in column distillation [16].

Acetaldehyde accounts for c. 90% (v/v) of the total aldehyde content in spirits. Other aldehydes, important for the quality of spirits, are isobutyraldehyde, 2-propenal (acrolein), and 3-hydroxy-2-butanone (acetoin) 2,3-butanedione (diacetyl). The presence of aromatic defects

in spirits is related to metabolites such as acrolein (highly toxic substance) and diacetyl. Acetoin is related to carbohydrate metabolism and can be formed by enzymatic condensation of two acetaldehyde molecules or from diacetyl reduction. Acetals are products of condensation of aliphatic aldehydes and alcohols. Acetals contribute to aroma of numerous alcoholic beverages obtained from fruits. They impart a delicate pleasant taste and bouquet to alcoholic beverages. The sum of acetaldehyde + acetal, defined as total acetaldehyde, shows rather low values that confirms a mostly correct technological process, with a regular fermentation without oxidative events.

Acetaldehyde and other short-chain aliphatic aldehydes (propanal, butanal, pentanal, (E)-2-pentenal, 2-methyl-1-butanal and 3-methyl-1-butanal) have pungent, rancid and fatty odour, which may increase the tang of distilled beverages. In general, aldehydes with up to eight carbon atoms, such as acetaldehyde, formaldehyde, acrolein, benzaldehyde and furfural, have penetrating odours, generally sickening, which are considered undesirable in spirits [52]. Long-chain aldehydes are characterised by pleasant aroma. Most of them are present at levels below their individual perception thresholds [53].

Benzaldehyde is one specific aldehyde especially important for the spirits made from stone fruits like plum, cherry and apricot. Benzaldehyde is formed by hydrolysis of amygdaline present in fruit seeds and stones. It contributes to bitter almond, marzipan, cherry flavour in spirits. Benzaldehyde and benzyl alcohol are present in spirits in much higher concentrations if the mash is fermented with stones. It is not desirable in higher amount but in small amount contributes to complexity of flavour. Benzaldehyde is a high boiling point compound and distills mainly in tail regardless of distillation technique employed.

Furfural is aldehyde formed during distillation due to dehydration of residual sugars (pentoses) caused by heating in acid conditions and/or Maillard reaction. Furfural may be formed as a result of oxidation of ascorbic acid [54]. Thus, furfural is a normal constituent of fruit distillates and can be used as an indicator of distillate naturalness. Its sensor effect to the distillate can be seen through its influence to the distillate aroma that is increased by the smell of bitter almond, whilst the increased furfural concentrations may contribute to the 'hotness' of spirits.

The furfural quantity in the dried fruit distillate is naturally higher because the raw material itself has already experienced one heating process where pentose and pentosane dehydration and furfural formation occurred [55].

Furfural is a compound that is soluble in water and for this reason distills mainly in the tail fraction regardless of distillation technique employed. The higher concentration of furfural is ascribed to longer duration of distillation [56]. Its content is higher in spirits obtained by using alembic pot in comparison with the column distillation [48]. The probable reason for this is heating the alembic during double stage of distillation by direct flame.

Acetic acid accounts for more than 90% (v/v) of the total acidity in spirits. Acetic acid is a by-product of alcohol fermentation. It can be formed during the catabolism of sugar in the presence of oxygen and the yeast *Saccharomyces cerevisiae*. Acetic acid is produced by oxidation of acetaldehyde, and its content in alcoholic beverages mainly depends on the yeast strain applied. High level of acetic acid in the fermented mash is associated with contamination with

acetic bacteria. In that case, the content of acetic acid is increased, and ethanol is decreased. This is owing to the conversion of the alcohol in acetic acid. A high level of acetaldehyde directly determined the acetic acid concentration in the analysed plum brandies [5].

Acetic acid is an important compound for the quality of spirits. Acetic acid has a distinctive sour taste and pungent smell, but the low concentration of acetic acid is desirable since low beverage acidity is an indicator of better quality and consumer acceptance [52]. In **Figure 6**, it can be seen that acetic acid is present in tail. It was mainly found in the last fractions [10, 16], owing to its high boiling point (117°C) although Rodríguez-Bencomo et al. [33] observed that it could be more concentrated in the head when using variable internal column reflux.

Other volatile acids important for the distillates are present in much lower quantities than acetic acid. Those are carboxylic acids and fatty acids like formic, propionic, butyric, isobutyric, caproic, undecanoic, myristic, valeric, isovaleric, 2-methylbutyric and pelargonic acids [51]. Fatty acids are known to play an important role in the sensory quality of beverages. They contribute to flavour as precursors of volatile compounds. They built esters with higher alcohols.

Caprylic, capric and lauric acids are, second to acetic acid, the most abundant free fatty acids; they are produced by yeast-mediated metabolism of carbohydrates. Short-chain free fatty acids have unpleasant odours similar to rancid butter and putrid cheese, and their presence at high levels is an indicator of poor quality fruit mash.

Hydrocyanic acid (HCN) initially occurs in bound form in the stones of the fruits and is released through enzymes during the maturation process and after the harvest. Hydrocyanic acid is formed by enzymatic hydrolysis of cyanogenic glycosides (such as amygdaline) during alcoholic fermentation. Spontaneous fermentation of fruit pulp resulted in much higher amounts of HCN in the spirits obtained in relation to the contents observed in the distillates from the mashes fermented with the addition of *S. bayanus* wine yeast. In the majority of fermented mashes, the maximum dynamics of HCN liberation was recorded on the first day of the process [57].

During hydrolysis of cyanogenic glycosides, benzaldehyde also occurred. It means that one product of hydrolysis is desirable (consumers often desire the typical 'bitter almond'), and the other be accompanied by detrimental influences and health risks [58]. It is particularly important not to largely crush the stone during preparation of stone fruits mashes for the fermentation. Another important item is that distiller should not be carried out distillation of fermented mash with stone in the pot. Investigation of Schehl et al. [58] showed that the presence or absence of stones in the mashes cannot be used as a general quality criterion. Their data provide strong evidence that the preference bitter almond flavour of spirits or the spirit, without this flavour, will remain a matter of personal taste. The boiling point of HCN is 25.7°C so it seems to be distilled in the first fraction.

Regulation (EC) No. 110 (2008) stipulates that the maximum hydrocyanic acid content in stone fruit spirits and stone fruit mark spirits shall amount to 7 g/hl of 100% (v/v) alcohol (70 mg/l).

Ethyl carbamate (EC) or urethane occurs naturally in many fermented foods and beverages. Possible routes of EC formation in alcoholic beverages are associated with the reaction

between ethanol and nitrogen precursors, such as urea, carbamyl phosphate (e.g. fermented beverages) and cyanide (e.g. spirits) [59]. Cyanate is probably the ultimate precursor in most cases, reacting with ethanol to form the carbamate ester. Ethyl carbamate forms in stone fruit distillation, when exposed to light, from the natural precursors of fruit mash and ethyl alcohol. It is a potentially carcinogenic substance found in significant amounts in distilled fermented beverages, particularly in stone fruit spirits. The EC levels increase with product overheating during the distillation of spirits, especially in the distillation of some beverages rich in cyanogenic glycosides, such as amygdalin in some stone fruit brandies. Current EU legislation determines a maximum EC amount of 150 µg/l in distilled beverages.

There is high variability in ethyl carbamate content. Ethyl carbamate distills more in head and tail fractions than in the heart [59], while Alcarde et al. [60] reported that content of ethyl carbamate is increased during distillation process.

6. Alembic pot still versus column still

One of the most relevant steps in elaboration of spirits is distillation process. Distillation process can be used to correct possible mistakes that have occurred during the previous processing of the raw material. In addition, inadequate distillation can cause many defects that are difficult to eliminate by the following technological processes. During the distillation, heat facilitates the fitting of volatile compounds into resulting spirits. For the production of fruit spirits, alembic pot still and batch distillation column are the most suitable because spirits will retain the decent fruit aroma and flavour. Volatile compounds will distill differently depending on the distillation equipment used although, in accordance with results of Cortes et al. [32], for most of the compounds, there were no difference in concentration regarding the distillation equipment used. However, the concentrations of volatile compounds were influenced by processing and storage of raw material more than distillation equipment used.

Alembic stills yield better aroma that comes from fruit, the so-called primary flavour [12]. The alembic pot still produces distillates that retain the character and personality of their source ingredients. This method is slow and requires more labour, but the usage of simple copper still was preferred by several authors [16, 40]. Also, results of García-Llobodanin et al. [61] showed the distillation of pear wine with less in copper alembic leads to a better quality product.

Higher concentration of alcohol and higher separation of other volatile compounds were achieved during distillation in batch column still, giving a decent aroma of distillates. The greater yield is obtained in recovered ethanol, allowing an increased productivity by means of column distillation. This type of distillation is more effective. Nevertheless, the column-distilled spirits contained four times more esters, 20% more higher alcohols, 40% less acetaldehyde and 10% less methanol than alembic spirits [27]. Some results referred that distillates made by using a distillation column had higher sensory acceptance than distillates made in alembic pot [4, 12]. Opposite results were showed by Alcarde et al. [52]. According to these

authors a sensory acceptance of cleaner fruit spirits (spirits with lower content of esters, aldehydes, higher alcohols, and methanol) was higher. The art of distillation run is to obtain the best balance between congeners present.

Also, less aromatic fruit varieties can be used to produce distillates with aromatic characteristics similar to more aromatic variety if a suitable distillation process in distillation column is used.

According to Matias-Guiu et al. [11], the traditional distillation with an alembic pot still allows limited intervention during the distillation process (only the heating power in the boiler can be manipulated) to modify the composition of the distillate. A more flexible system is the batch distillation column (in which the reflux rate can be varied in a wide range). In the same time, the other investigation [27] showed that the process with batch distillation column is much less reproducible than alembic distillation.

Claus and Berglund [21] are observed that distillates produced in the alembic pot still are usually stored in wood for many years (e.g. Cognac and Whisky), whereas the distillates produced in the distillation column are stored in the glass and consumed as clear spirits. I consider that raw material rather determinates whether distillates will be stored in wood or not. The author of this chapter considers the way of ageing that is determinates by raw material used rather than the distillation apparatus. In fruit spirits long ageing would mark the primary flavour of fruit. If distiller produced a distinctive flavour of some fruit, regardless of distillation apparatus used, it should protect the pure fruity note, not to give the distillates a strong and too much complex flavour gained during maturation in wood (quaternary flavour). If aromatic fruit spirits need to be stored in wood, then it should be just for a whilst how they would retain a fruity touch.

7. Conclusion

The choice of distillation technique using either pot still or distillation column is dependent mainly of the consumers' desire for the typical and individual flavour and style of the particular fruit spirits. In that sense, distillation method should be adjusted for each fruit type and variety. Production of various kinds of fruit spirits requires an individual approach based on the application of knowledge and understanding the processing of desirable qualities of the spirits. Adequate managing of distillation technique enables production of the unique product.

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