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The effect of dephlegmation on the relative volatility of fruit spirit components

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1. Summary

With the support of the National Research, Development and Innovation Fund, within the framework of the KMR-2 project, a research was carried out by WESSLING Hungary Kft. between 2013 and 2015, in connection with changing the distillation parameters of fruit spirits, among other things. Within the framework of the research, characteristic volatile components of different fruits (apples, pears, sour cherries, apricots and plums) were investigated. It was determined that, during distillation, the different components are transferred into the distillate according to typical distillation curves, so they can be grouped easily according to their propensity to be enriched in the vapor phase at the end of the vapor pipe in the heads, hearts or the tails phase. When analyzing sample fractions taken systematically during the distillation, a clear correlation could be demonstrated between the change in the partial condensation used in the distillation, the so-called dephlegmation degree, and the change in the relative volatility of the volatile components entering the distillate from the vapor phase during distillation. When the dephlegmation degree decreased, of the components analyzed, the relative volatility of methanol compared to ethanol decreased, while it increased for all other components analyzed, i.e., the concentration of the volatile components entering the distillate during the preparation of fruit spirits will be higher or, in other words, the fruity character will be more intense if the dephlegmation degree is lower. Given the results of the project, it becomes possible to influence the distillate composition consciously by changing the distillation parameters.

2. Selection of the components to be analyzed and the measurement method

When determining the range of volatile components to be analyzed, several factors were taken into consideration. On the one hand, components that are relevant from the point of view of meeting legal requirements of fruit spirits, such as methanol **[1]** and 9 other legally prescribed components **[2]** were analyzed. On the other hand, those components were selected which can be considered main aromas of the fruits investigated, i.e., which have a major effect on the development of the characteristic smell and taste specific of the fruit for the consumer, such as gamma-decalactone in the case of apricots **[3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15].** Furthermore, among the components to be analyzed were also included several compounds that can indicate distillation errors, such as 2-phenylethanol and allyl alcohol.

When selecting the components that can be considered main aromas, the scientific literature, as well as the results of our own previous research and of studies carried out by external experts were used.

In total, approximately 75 to 80 compounds – a different number for each fruit – were analyzed by a GC-MS method.

[1] WESSLING Hungary Kft.

Distillate fractions were analyzed, based on the Annex to Commission Regulation No 2870/2000 **[2]**, by a method developed by WESSLING Nonprofit Kft., suitable for the quantitative determination of the volatile components of fruit spirits to be analyzed:

Measurement technique: Gas chromatography-mass spectrometry (GC-MS)

Sample amount: 1 µl distillate, 1:100 split

Injector: split/splitless liner filled with glass wool, 240 °C

Carrier gas: Helium, 1 ml/min, constant flow rate

Gas chromatography column: ZB-Wax 30 m × 0.25 mm × 0.25 µm

Temperature program: 40 °C (2.5 min), 8 °C/min to 170 °C, 35 °C/min to 240 °C (3.25 min)

Transfer line temperature program: 170 °C (18.5 min), 35 °C/min to 240 °C (3.5 min)

Ion source temperature: 230 °C

Quadrupole analyzer temperature: 150 °C

Ionization energy: 70 eV

Detection: selective ion monitoring (SIM)

3. Basic principles for the preparation of test samples

There were two objectives for the preparation of the fraction samples tested. On the one hand, we wanted to determine the distillation curves related to the relative volatility of the individual components, and on the other hand, we focused on the dependence of the curves on the dephlegmation degree.

The method of preparation of the test samples was as follows: several (2 to 4) distillation procedures were carried out in a series, on the same distillation apparatus, starting with homogeneous, fermented mash prepared from a single fruit species. The only difference between distillation procedures of the same series was that different dephlegmation degrees were created by changing a single distillation parameter. This way, the concentration change of the components found in the fraction samples of the given distillation procedure can be related to the change in the dephlegmation degree.

Taking into consideration that, during distillation, volatile components enter the vapor phase from the fruit mash based on their relative volatility compared to ethanol, samples were taken during distillation from the distillate fraction in a way to ensure obtaining valuable information for the entire distillation procedure. At the beginning of the distillation, in the so-called heads phase, samples were taken more frequently, so that conclusions could be drawn from concentration data still changing in an exponential fashion for certain components.

During distillation, the composition of the fruit spirit changes in accordance with the actual dephlegmation degree – i.e., in close connection with the amount of material recondensing from the vapor phase into the liquid phase by way of partial condensation. There are several distillation parameters suitable for influencing the dephlegmation degree, such as changing the heating intensity, or the temperature or the mass flow of the cooling water entering the dephlegmator. The change in the ethanol concentration of the resulting distillate is closely related to the dephlegmation degree, and the same relationship can be demonstrated in the case of the change of the dephlegmation degree and the vapor pipe temperature as well.

4. Classification of the distillation curves

In the series of experiments, roughly 2000 distillate fractions were prepared in 40 distillation procedures on three different pieces of distillation apparatus, providing a statistically significant database after the measurements and the evaluation. Although the dephlegmation degree was changed in different ways on the different pieces of distillation apparatus, the same conclusions could be drawn in each case, regarding the characteristic distillation properties of the individual components.

Plotting the average concentrations of the volatile components that could be detected in the individual distillate fractions in a coordinate system where the concentration of the given component (mg/l) and the concentration of ethanol (%) were shown on the vertical axis and the resulting distillate volume (ml) on the horizontal axis, a distillation curve is obtained. Distillation curves of the same component obtained from different distillation series are similar in nature, although their shape can vary significantly, as a function of the dephlegmation degree connected to the given apparatus and the given distillation procedure.

If similar conditions are ensured during different distillation processes, in terms of the dephlegmation degree, the shapes of the curves connected to the individual components will be similar, regardless of the distillation apparatus. This characteristic curve, showing concentration changes in the distillate fractions from the heads to the tails, can be classified according to its shape.

Below are shown typical curves, based on which general statements can be made about the distillate components that can be classified into a given type. The curves presented will form in the case of a deliberately chosen dephlegmation target function, where the temperature of the vapor pipe increases during the distillation procedure with a constant slope.

Below are shown diagrams, similar in shape to theoretical curve types, that were plotted based on actual distillation results, obtained on a column-type distillation apparatus (**Figures 1-7**). Sharp breaks in the case of the curves in the examples – mainly in the first third of the distillation – are related to the regulation of the distillation apparatus.

Type „A" components are so-called heads-type components, i.e., their concentration drops sharply after the appearance of the heads, such as in the case of ethyl acetate (**Figure 1**).

It is characteristic of components with a type „B1" distillation curve that their concentration in the vapor phase increases around the end-cut , therefore, it depends on the correct determination of the end-cut , to what extent they can influence the composition of the hearts (**Figure 2**).

The concentration of components condensing according to the type "B2" distillation curve is highest in the middle third of the hearts. Their quantities in the hearts are not influenced significantly by changing either the begin-cut or the end-cut (**Figure 3**).

Type „B3" and „B4" curves are similar in nature. The main difference between them is that, in the case of the „B3" type, the concentration of the given components in the distillate drops after a short, sharply rising stage, while in the case of the „B4" type, there is no rising stage at the beginning of the distillation (**Figures 4 and 5**).

The concentration of methanol remains approximately constant during the distillation. The methanol concentration of the hearts cannot be influenced significantly by changing the begin-cut and the end-cut. (**Figure 6**).

Fusel alcohols, such as 1-propanol, 1-butanol, etc., behave similarly during the distillation (**Figure 7**).

5. The effect of the dephlegmation degree on changes in the curves

Curves that are different from those corresponding to the linearly rising vapor pipe temperature target function can be created during the distillation, by changing the dephlegmation degree. The goal of changing the curve is usually to achieve higher concentrations of certain aroma components in the hearts, thereby providing a more intense odor and taste, characteristic of the given fruit species. In other cases, it could also be an objective to reduce the concentration of unwanted components in the hearts.

Based on conclusions that can be drawn from analyses dealing with changes in the dephlegmation degree, the following general rules can be formulated, regarding distillation parameters and distillate composition:

- The system's reaction to an increase in the dephlegmation degree during the distillation will be a decrease in the vapor pipe temperature and, at the same time, the alcohol content of the distillate fraction corresponding to the given period of time, i.e., the alcohol yield increases.
- The system's reaction to a decrease in the dephlegmation degree during the distillation will be an increase in the vapor pipe temperature and, at the same time, the alcohol content of the distillate fraction corresponding to the given period of time, i.e., the alcohol yield decreases.
- The concentration of methanol increases, if the dephlegmation degree increases.
- The behavior of all other volatile components tested is the opposite of that of methanol, i.e., the concentration of the components in the distillate fraction corresponding to the given period of time will be higher, if the dephlegmation degree decreases, than it would have been if the dephlegmation degree had remained the same.
- Excessive reduction of the dephlegmation degree could be accompanied by such a decrease in the alcohol yield in the hearts, which could make the entire process uneconomical.
- The average concentration of fusel alcohols in the hearts increases if the dephlegmation degree decreases.
- To regulate the dephlegmation degree, a system should be used which causes only a slight hysteresis of only a few tenths of a degree Celsius relative to the planned temperature of the vapor pipe. Otherwise, the concentrations of the components to be influenced will react with large fluctuations, and so not only the effect of the change in the vapor pipe temperature planned for the entire distillation process, but also the effect of large amplitude fluctuations due to the inertia of the regulation will prevail.

To confirm the above rules, a few typical diagrams are shown:

Figure 8 shows that a higher concentration in the case of a type B1 component was caused by the lower dephlegmation value set in series 3, while the average alcohol yield for the hearts was lower than in series 2. Fluctuations in the component concentrations depicted coincide with those of the alcohol curve, but they occur in the opposite direction. Changes corresponding to changes in the vapor pipe temperature, which, in turn, are related to changes in the dephlegmation degree, can be traced all the way through in changes in the concentration of the given component.

In **Figure 9**, the effect of the large fluctuations, which can be traced in the temperature of the vapor pipe, is shown by connecting the corresponding extreme values. It is clear that changes in the dephlegmation degree within a short period of time – for example, a sudden change in the heating intensity in the case of a wood-burning distillation apparatus, where wood is placed intermittently in the furnace, or when, during regulated distillation, the cooling water to achieve the cooling of the dephlegmator starts intermittently – the actual concentrations of the distillate components also show significant fluctuations, which causes the actual distillation curve to deviate from the theoretical distillation curve corresponding to steady dephlegmation.

Figure 10 shows a typical example of how the concentration of a main aroma, important to us, can be adversely affected by a sudden increase in the dephlegmation degree during distillation. In the top part of the figure, the vapor pipe temperature, changing proportionally to the dephlegmation degree, is shown. In the bottom part of the figure, changes in the alcohol content of the distillate and the concentration of a type B1 component are shown. Important corresponding points are connected by arrows. A steep drop in the vapor pipe temperature indicates that there was a sudden increase in the dephlegmation, as a result of which – unlike the theoretical distillation curve characteristic of the type B1 component – what happened was not that the concentration of the type B1 component rose sharply towards the end-cut separation point, but, because of the strong increase in the dephlegmation degree, the concentration of the given components started to drop sharply. Therefore, a lot less aroma component could enter the hearts, than would have been there, had the dephlegmation degree remained steady.

6. Conclusions

The role of the dephlegmation degree in the development of the quality of fruit spirits can be summarized as follows: a tastier, better smelling product with a higher main aroma concentration can be prepared from a fruit mash raw material of given composition, if the distillation is carried out with a not too strong dephlegmation. Another advantage of the lower dephlegmation degree is that the methanol concentration of the product will also be lower. Besides these advantages, a disadvantage is that, for the hearts, the alcohol yield will be slightly lower than it would be if a stronger dephlegmation had been applied.

7. References

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