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Study By Simulation Of The Behavior Of Aroma Compounds during Malt Whisky Distillation With A Stupfler Type Filling Column.

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Abstract. Batch distillation column is frequently used in Eastern countries to produce fruit spirits. This kind of distillation offers good possibilities of separation thanks to its flexibility in terms of operating modes. However, the separation of the volatile compounds is not well understood and controlled. This project, by the use of the commercial simulator ProSim's BatchColumn®, investigated the behavior of numerous volatile compounds during batch distillation of a barley fermented mash in a whisky distillery. The study clearly illustrated the distribution of the volatile compounds between the different distillate fractions: discarded head, recycled head, heart, and recycled tail.

Keywords Batch distillation, Simulation of distillation, Alcohol spirits, Volatile compounds, Aroma compounds.

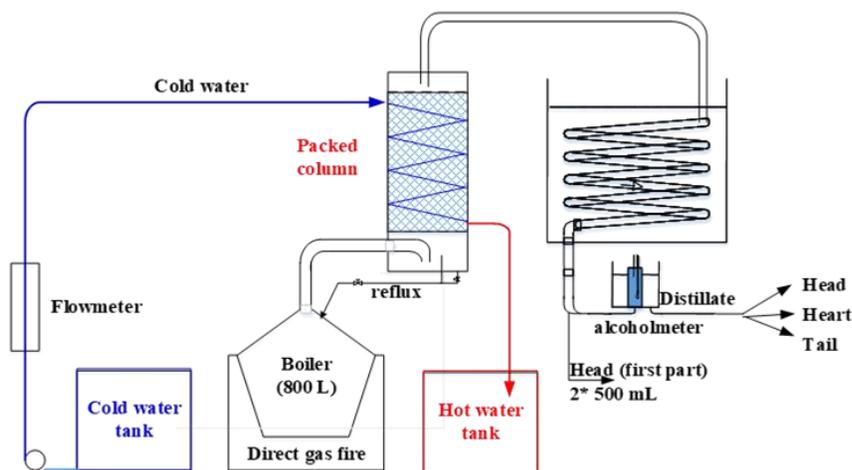
Introduction

Spirits are alcoholic beverages produced from agricultural raw materials. Water and ethanol represent 97 to 99 % of the total volume but the wide variety of volatile compounds usually named “congeners” at very low concentrations define the quality, flavor, and aroma of the spirit ^[1]. During batch distillation the distillate is separated into different fractions (head, heart and tail) but it is important to note that the fractions of head and tail are in many cases wholly or partially recycled in the initial load of the following run. In general, cuts are carried out by measuring the ethanol content of the distillate or by olfaction and tasting. However, this strategy, which is highly empirical, is not sufficiently effective on its own without a good understanding of the different behaviors of the volatile compounds during distillation ^[1,2].

In literature, researchers validated the use of simulation for this process by using self-made software or using commercial ones such as Aspen or ProSim's Batch Column® ^[3]. In a previous study we simulated the behavior of fifty-seven volatile compounds with two modes of discontinuous distillation (a distillation with a Stupfler® type filling column and a laboratory column with 10 perforated trays) ^[4]. The same concentration of 10⁻⁶ w/w was considered in order to visualize the behavior of each compound. The ProSim® BatchColumn software was used, and a heterogeneous approach was selected for the thermodynamic model (the NRTL activity coefficient model was chosen to represent the non-ideality of the liquid phase while the ideal gas model was used for the gas phase). The study clearly showed that the behaviors of the compounds are directly dictated by the ethanol concentrations of the boiling liquids in the columns, especially the upper part, and the variation in their volatility coefficient as a function of the ethanol content. However, the results of this study were limited to a qualitative aspect of the congeners' behaviors since it did not consider the actual composition of the barley fermented mash. The objective of this work was therefore to consider the actual concentrations of the mash compounds.

Material and Methods

The experimental study was conducted in Ergaster distillery which produces Whisky from a barley fermented mash. The equipment was a Stupfler®-type column still made entirely of copper. Three main parts can be distinguished (**Fig. 1**): a direct-fired boiler; a packed column (height 1.3 m and diameter 0.3 m) in which reflux is obtained by a coiled cold-water flow present in the packing; and a total condenser. Leaving the condenser, the distillate flows through an alcoholometer for temperature and alcoholic strength by volume measurements before being collected in different tanks.



Packed column

Fig. 1 Ergaster distillation plant

The distillation consisted of several steps: heating and filling of the column then distillation of the head, heart and tail fractions. Durations and operating parameters (gas pressure and cold-water flow) are shown in **Fig. 2**. At the beginning of the head distillation, the first liter was definitely discarded, subsequently, 6 L were collected in the head tank before starting the heart distillation step. The end of the heart distillation was decided when the coiled cold-water flowrate was at its maximum value and the ethanol content began to drop. Then the tail fraction was collected until an ethanol fraction around 0.13 w/w. The second part of head and tail fractions were put aside to be recycled into the boiler of the next distillation. The large variation of the operating parameters was applied to maintain a constant heart ethanol concentration. The parameters monitored over time were the volume of the heating gas used, the inlet and outlet temperatures of the coiled cold-water and its flowrate, and the mass and ethanol content of the distillate respectively with a weighing scale and the Anton Paar density meter® DMA 35.

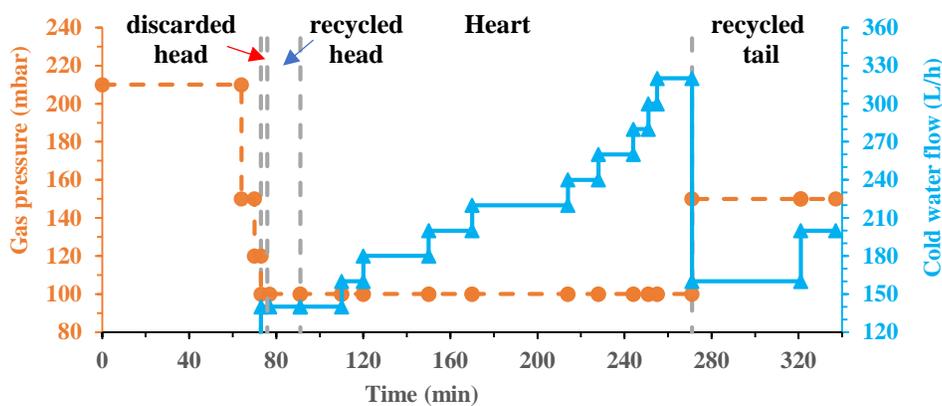


Fig. 2 Operating parameters

The initial solution was a 739 L mixture of the fermented mash and the recycled head and tail fractions of the previous distillation. Its analysis was carried out by the Labeo laboratory. The solution was first distilled according to the commission regulation (EC) No 2870/2000 (Official Journal of the European Communities, 2000). This laboratory distillation was conducted on a 100 mL test sample according to the OIV-MA-BS-02 method for spirit beverages^[5]. Then, two analysis methods were used on the distillate: a GC-FID chromatography and a GC-MS analysis after liquid/liquid extraction using a dichloromethane/pentane (1/2 v/v) mix. Details of the analyses are described in a previous study^[6].

The construction of the simulation modules with ProSim® BatchColumn software aimed first at representing as faithfully as possible the mass of distillate collected and its ethanol mass fraction. The thermodynamic approach was the heterogeneous one using the NRTL coefficient validated by the research team^[7,8]. The simulation module consisted of a boiler, a trayed column and a total condenser. The boiler and condenser had an efficiency of one. The filling of

the column was represented by 12 trays of 0.8 efficiency with a retention of 0.25 L, and a tray of 0.35 efficiency with a retention of 2.4 L to represent the area under the column where the steam from the boiler comes to bubble. The dead volume represented by the condenser and the alcoholmeter holder was fixed at 3 L. Pressure was set at one atm and pressure drop was neglected. Heat losses along the column were defined to represent cold water circulation and wall losses. Many steps were considered to take into account the operating parameters and fit as tight as possible the ethanol content and distillate mass profiles.

Results and Discussion

The initial solution had an ethanol content of 9.08 %vol (a mass fraction of 0.0728 g/g). Its analysis allowed to quantify 30 volatile compounds (**Table 1**). A very wide concentration range can be observed with a variation of a factor of more than 10^4 . Esters are in greater number and with the highest concentrations. The compounds written in *italics* could not be simulated because their equilibrium data are unknown to the research unit. For the simulation, the mass concentrations were calculated by considering the density of the analyzed solution.

Table. 1 Composition of the initial solution

| Alcohols | | | Esters | | |
|---------------------|-----------------|------------------|--------------------------------|-----------|------------|
| 3-methylbutan-1-ol | 123-51-3 | 93.5 mg/L | ethyl acetate | 141-78-6 | 169.0 mg/L |
| 2-methylpropan-1-ol | 78-83-1 | 62.9 mg/L | ethyl 2-hydroxypropanoate | 97-64-3 | 118.7 mg/L |
| propan-1-ol | 71-23-8 | 52.1 mg/L | diethyl butanedioate | 123-25-1 | 2.2 mg/L |
| 2-methylbutan-1-ol | 137-32-6 | 47.0 mg/L | 3-methylbutyl acetate | 123-92-2 | 0.9 mg/L |
| 2-phenylethanol | 60-12-8 | 38.5 mg/L | ethyl octanoate | 106-32-1 | 678.6 µg/L |
| methanol | 67-56-1 | 5.0 mg/L | ethyl decanoate | 110-38-3 | 506.7 µg/L |
| butan-1-ol | 71-36-3 | 0.8 mg/L | <i>ethyl formate</i> | 194-94-4 | 540.0 µg/L |
| hexan-1-ol | 11-27-3 | 0.3 mg/L | <i>Ethyl propionate</i> | 105-27-3 | 327.3 µg/L |
| <i>1-Octanol</i> | <i>111-87-5</i> | <i>77.2 µg/L</i> | <i>Ethyl palmitate</i> | 628-97-7 | 296.2 µg/L |
| prop-2-en-1-ol | 107-18-6 | 10.0 µg/L | <i>Ethyl laurate</i> | 106-33-2 | 263.4 µg/L |
| | | | 2-phenylethyl acetate | 103-45-7 | 255.1 µg/L |
| | | | ethyl hexanoate | 123-66-0 | 231.5 µg/L |
| | | | ethyl butanoate | 105-54-4 | 219.1 µg/L |
| | | | <i>isobutyl acetate</i> | 110-19-0 | 178.9 µg/L |
| | | | <i>ethyl stearate</i> | 111-61-5 | 52.1 µg/L |
| | | | ethyl 2-methylpropanoate | 97-62-1 | 33.4 µg/L |
| | | | <i>ethyl benzoate</i> | 93-89-0 | 14.2 µg/L |
| | | | <i>3-methylbutyl decanoate</i> | 2306-91-4 | 10.7 µg/L |

In italic the compounds without NRTL coefficients

Fig. 3 shows that with these parameters, the simulation accurately represents the evolution of the cumulative distillate mass collected and its ethanol content over time.

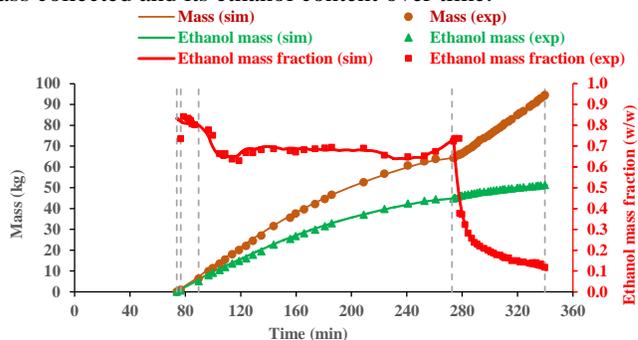


Fig. 3 Experimental and simulated data during the distillation

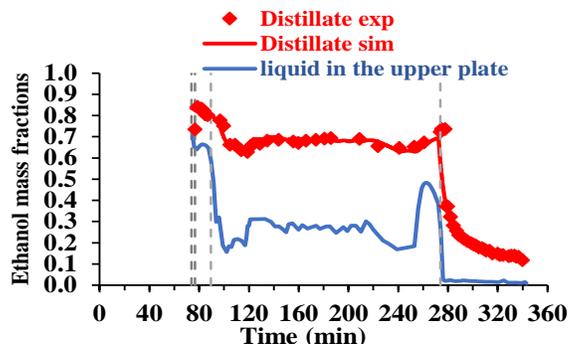


Fig. 4 Ethanol concentration of the distillate and upper tray

Knowing that the behavior of volatile compounds depends essentially on the ethanol concentration of the boiling liquid, we have shown in **Fig.4**, the simulation of the ethanol content of the upper part of the column. It may be observed that ethanol mass fraction of the liquid in the upper tray drops very rapidly between 0.2 and 0.3 w/w.

Fig. 5 and **Fig.7** show the concentration profiles of the simulated compounds and **Table. 2** their distribution in the fractions of distillate (discarded head, recycled head, heart, recycled tail, residue).

Table. 2 distribution of the simulated compounds between the discarded and recycled head, heart, tail and residue cuts

| Values in % w/w | Discarded head | Recycled head | Heart | Recycled tail | Residue | Heart + recycled fractions |
|---------------------------|----------------|---------------|-------|---------------|---------|----------------------------|
| ethanol | 1.2 | 8.2 | 74.2 | 12.2 | 4.2 | 94.6 |
| water | 0.02 | 0.15 | 2.7 | 3.6 | 93.6 | 6.4 |
| Alcohols | | | | | | |
| 3-methylbutan-1-ol | 0.5 | 17.7 | 81.3 | 0.6 | 0.0 | 99.5 |
| 2-methylpropan-1-ol | 2.0 | 19.2 | 77.9 | 0.8 | 0.0 | 97.9 |
| propan-1-ol | 1.3 | 11.3 | 80.5 | 6.0 | 0.9 | 97.8 |
| 2-methylbutan-1-ol | 0.8 | 12.2 | 83.1 | 3.6 | 0.3 | 99.0 |
| 2-phenylethanol | 0.0 | 0.0 | 9.9 | 20.5 | 69.7 | 30.3 |
| methanol | 0.7 | 4.8 | 57.8 | 19.3 | 17.4 | 81.9 |
| butan-1-ol | 0.8 | 14.2 | 82.7 | 2.3 | 0.1 | 99.1 |
| hexan-1-ol | 0.1 | 5.7 | 83.7 | 8.9 | 1.6 | 98.3 |
| prop-2-en-1-ol | 0.6 | 6.7 | 72.6 | 14.4 | 5.7 | 93.6 |
| Aldehydes | | | | | | |
| acetaldehyde | 14.8 | 56.2 | 29.0 | 0.0 | 0.0 | 85.2 |
| 2-methylpropanal | 14.8 | 59.5 | 25.7 | 0.0 | 0.0 | 85.2 |
| Esters | | | | | | |
| ethyl acetate | 9.9 | 46.6 | 43.4 | 0.0 | 0.0 | 90.1 |
| ethyl 2-hydroxypropanoate | 0.0 | 0.1 | 30.1 | 22.3 | 47.5 | 52.5 |
| diethyl butanedioate | 0.0 | 0.0 | 7.6 | 11.3 | 81.1 | 18.9 |
| 3-methylbutyl acetate | 13.5 | 59.8 | 26.6 | 0.0 | 0.0 | 86.4 |
| ethyl octanoate | 1.6 | 71.6 | 26.8 | 0.0 | 0.0 | 98.5 |
| ethyl decanoate | 0.4 | 29.9 | 69.7 | 0.0 | 0.0 | 99.6 |
| 2-phenylethyl acetate | 0.0 | 2.0 | 97.7 | 0.3 | 0.0 | 100.0 |
| ethyl hexanoate | 8.0 | 41.6 | 50.3 | 0.0 | 0.0 | 91.9 |
| ethyl butanoate | 17.9 | 64.3 | 17.5 | 0.0 | 0.0 | 81.8 |
| ethyl 2-methylpropanoate | 20.9 | 66.5 | 12.2 | 0.0 | 0.0 | 78.8 |

For most of the cases, alcohols have their concentration which is high at the beginning of distillation and then decreases because of their exhaustion except 2-phenylethanol (**Fig.6**). The alcohols with the highest concentration peaks are in descending order 3-methylbutan-1-ol, 2-methylpropan-1-ol, 2-methylbutan-1-ol and propan-1-ol. This is consistent with their high concentrations in the initial mash and their high volatility.

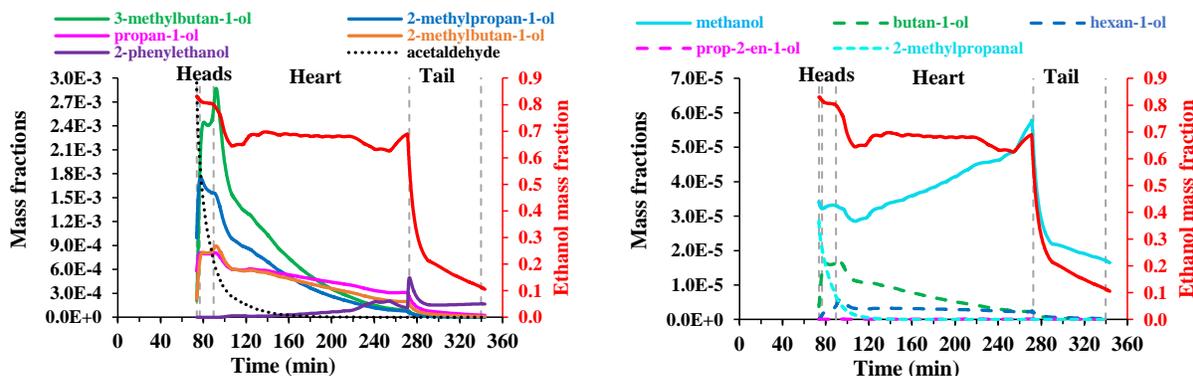


Fig.5 concentration profiles of alcohols and acetaldehydes

Methanol, having quite a low concentration in the initial solution and a low volatility coefficient, has its concentration that increases with time. 17.4 % of its initial quantity remains in the residue (Table.2). 2-phenylethanol which has the lowest volatility among the alcohols (**Fig.6**) concentrates only when the ethanol mass fraction decreases at the beginning of the tail fraction extraction and 69.9 % remain in the residue (Table 2).

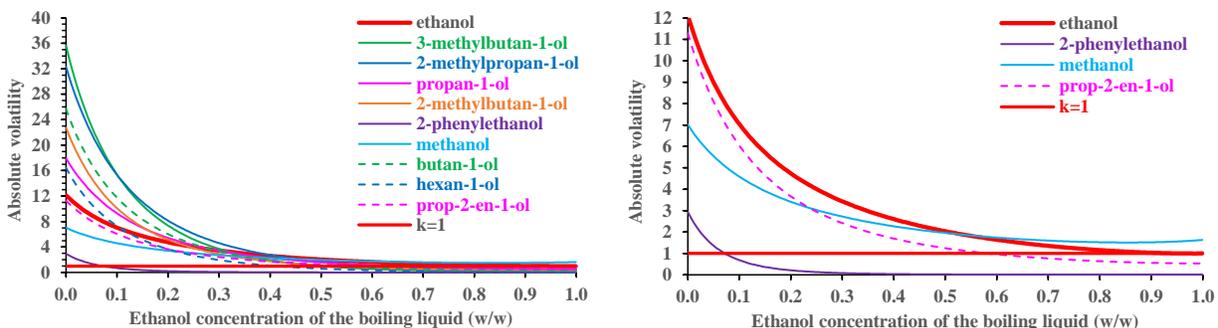


Fig.6 Absolute volatility of alcohols according to the ethanol mass fraction of the boiling liquid

Acetaldehyde and 2-methylpropanal, which have high volatilities, concentrate in the first fractions and 14.8% are eliminated with the discarded head fraction.

Among the esters (**Fig. 7**), ethyl acetate concentrates very strongly at the beginning of distillation and 9.9 % are eliminated by the discarded head fraction. However, other esters, initially in much lower concentrations, are also removed with this fraction (Table 2), including ethyl 2-methylpropanoate (20.9 %), ethyl butanoate (17.9 %) and 3-methylbutyl acetate (13.5 %). Again, these behaviors can be explained by their high volatility factors (**Fig. 8**).

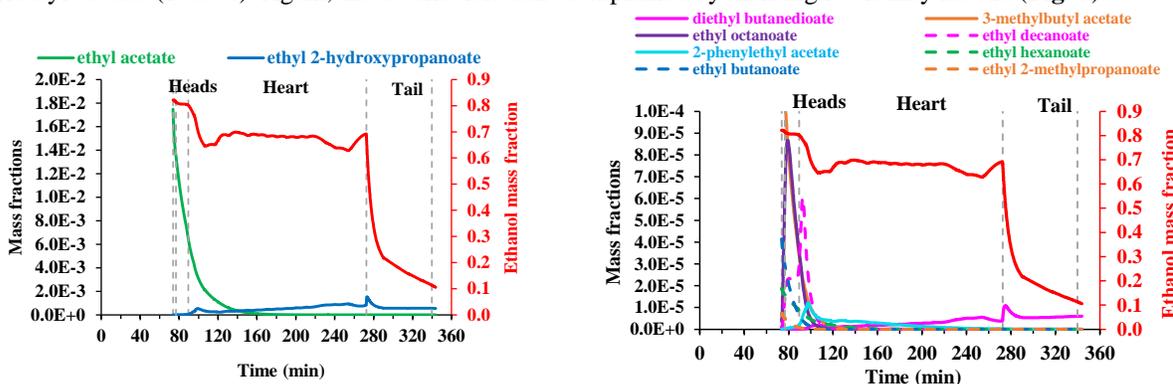


Fig.7 concentration profiles of esters

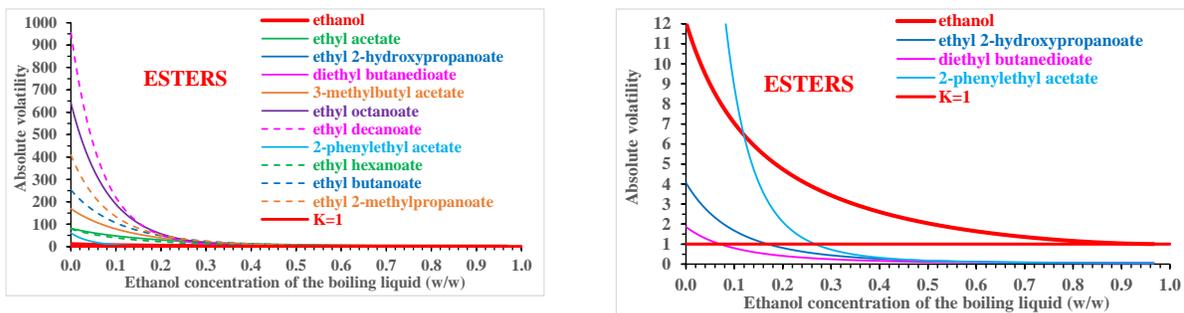


Fig.8 Absolute volatility of alcohols according to the ethanol mass fraction of the boiling liquid

On the contrary, ethyl 2-hydroxypropanoate and diethyl butanedioate whose volatilities are very low, just like 2-phenylethanol shown previously, concentrate at the end of distillation when the ethanol content of the distillate decreases sharply. A significant portion of these compounds remain in the residue, 52.4% and 18.6% respectively.

Considering the natural gas consumption (PCI of 11.47 kWh/Nm³), the energy needed is estimated at 1800 MJ/hLa.a. (anhydrous alcohol) considering an ethanol extraction efficiency of 94.6%. According to our personal data (**Table. 3**), this consumption is lower than the simple batch distillation (without column) practiced for the production of AOC cognac and calvados Pays d'Auge, but much higher than those corresponding to spirits produced in multi-stage continuous columns such as Armagnac and Rum from Martinique.

Table. 3 energy consumption to produce 1 hL of anhydrous alcohol

| Batch simple distillation | MJ/hLa.a. | Continuous multi-stage distillation | MJ/hLa.a. |
|----------------------------------|------------------|--|------------------|
| AOC Cognac | 2100 à 2300 | AOC Armagnac | 600-930 |
| AOC Calvados Pays d'Auge | 2800 | AOC Calvados | 900-1850 |
| | | AOC Rhum de la Martinique | 860 |

Conclusion

This study has made it possible to understand the behaviors of volatile flavoring compounds during multi-stage discontinuous distillation and to confirm some theories of the research unit. This process, mostly used in fruit spirit production, allows small units to produce the new spirit in a single distillation step and thus with reduced energy consumption and a lower distillation time compared to double batch distillation. The batch process makes it possible to partially separate the head compounds by the definitive elimination of the first part of the distillate. This removal also makes it possible to extract the dead volume remaining in the condenser coil from the end of the previous distillation. Most of the water remain in the residue as well as very low volatility compounds such as acids^[4]. In the future, our aim is to compare in more details the separation of volatile compounds with the other two modes of distillation: double batch distillation and continuous multi-stage distillation.

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References

1. N. Spaho, 2017. Distillation techniques in the fruit spirits production. In: Mendes M., F., Ed. Distillation - Innovative Applications and Modeling. IntechOpen, 129-152. DOI: 10.5772/66774.
2. X.F. Xiang, Y.B. Lan, X.T. Gao, H. Xie, Z.Y. An, Z.H. Lv, S. Yin, C.Q. Duan and G.F. Wu. 2020. Characterization of odor-active compounds in the head, heart, and tail fractions of freshly distilled spirit from Spine grape (*Vitis davidii* Foex) wine by gas chromatography-olfactometry and gas chromatography-mass spectrometry. Food Res. Int. 137, 109388. DOI: 10.1016/j.foodres.2020.109388.
3. A. Douady, C. Puentes, P. Awad and M. Esteban-Decloux, 2019. Batch distillation of spirits: Experimental study and simulation of the behaviour of volatile aroma compounds. J. Inst. Brew. 125, 268–283. DOI: 10.1002/jib.560.
4. M. Esteban-Decloux, N.G.R. Tano and H. Grangeon. Study by simulation of the behaviors of volatile aroma compounds during batch multi-stage distillation of spirits. Food Bioprod. Process. Submitted.
5. OIV 2014. Recueil des méthodes internationales d'analyse des boissons spiritueuses d'origine vitivinicole. <http://www.oiv.int/fr/normes-et-documents-techniques/methodes-danalyse/recueil-des-methodes-internationales-danalyse-des-boissons-spiritueuses-dorigine-vitivinicole>.
6. M. Esteban-Decloux, J.C. Dechatre, P. Legendre and H. Guichard. 2021. Cider distillation with double batch mode: influence of the recycling of the different fractions. LWT, 146, 111420, doi: 10.1016/j.lwt.2021.111420
7. C. Puentes, X. Joulia, V. Athès and M. Esteban-Decloux, M. 2018. Review and thermodynamic modeling with NRTL model of vapor-liquid equilibria (VLE) of aroma compounds highly diluted in ethanol-water mixtures at 101.3 kPa. Ind. Eng. Chem. Res. 57, 3443–3470. DOI: 10.1021/acs.iecr.7b03857.
8. C. Puentes, X. Joulia, J.P. Vidal and M. Esteban-Decloux., 2018. Simulation of spirits distillation for a better understanding of volatile aroma compounds behavior: Application to Armagnac production. Food Bioprod. Process., 112, 31-62. DOI: 10.1016/j.fbp.2018.08.010.