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Simulation of the behaviour of volatile compounds during batch multi-stage distillation of whisky

Martine Esteban-Decloux,^{1*}  N'Guessan Charles Romaric Tano¹ and Hervé Grangeon²

In the spirits industry, understanding the behaviour of volatile flavouring compounds (congeners) during distillation is important. This simulation study with the ProSim software[®], BatchColumn, investigates the influence of different parameters of a multi-stage batch distillation on 57 congeners from five chemical families (alcohols, aldehydes, esters, acids, and terpenes). Industrial and laboratory scale whisky distillations were conducted with a fermented malted barley mash. The simulations illustrated the behaviour of volatile compounds based on how their volatility varied with ethanol concentration. The distribution of compounds between the different fractions (head, heart, tail and residue) was calculated. Further, optimisation strategies for the industrial distillation were tested by simulation. These included (1) cutting distillation later (ethanol mass fraction of 0.061 instead of 0.105) as the recovery of pleasant compounds is small compared to that of acids; (2) choosing an ethanol mass fraction during the heart extraction around 0.60 (67% v/v), rather than 0.67 (75% v/v) as it increases the recovery of compounds of interest and decreases the duration of distillation and energy costs and (3) enabling a higher concentration of ethanol at the beginning of the distillation to obtain better separation of aldehydes and esters. © 2022 The Authors. *Journal of the Institute of Brewing* published by John Wiley & Sons Ltd on behalf of The Institute of Brewing & Distilling.

Keywords: batch distillation; simulation; whisky; volatiles; aroma compounds

Introduction

Spirits are alcoholic beverages produced from agricultural raw materials. Chemically, spirits consist of water and ethanol (representing 97 to 99% of the volume), and a wide variety of volatile compounds at low concentrations which define the quality, flavour, and aroma of the spirit. These flavouring compounds termed 'congeners' belong to different chemical families including alcohols, esters, aldehydes, acids and terpenes. They derive from raw materials and/or are generated during the production process whose conditions vary according to the desired spirit. Accordingly, the composition is different with different flavours and aromas from one spirit to another (Luna et al, 2019).

The production of spirits comprises five main steps; the extraction of the raw material, fermentation, distillation of the fermented must (wash), aging of the distillate in wooden barrels, blending of different casks and dilution of the aged distillate to the desired level of ethanol (Puentes et al, 2018b). Distillation is the key process in the production of spirits and consists of separating the constituents of a mixture based on differences in volatility. Three different types of distillation equipment are commonly used to produce spirits. **Simple discontinuous distillation** is carried out in a copper Charentais-type alembic to produce Cognac and Calvados pays d'Auge, and in a pot still for whisky and other spirits. A minimum of two consecutive distillations is required, first the distillation of the fermented must and then, the distillation of the raw distillate ('low wine') with recycling (Decloux and Joulia, 2009; Esteban-Decloux et al, 2021). **Batch distillation** is performed in a column requiring one run to achieve a high alcohol content in the distillate. This approach is commonly used to produce fruit

spirits (Spaho, 2017) and gin. **Multi-stage continuous distillation** is used for larger production capacity spirits such as rum, Calvados, Armagnac, whisky, vodka, and neutral alcohol (Decloux and Joulia, 2009). In all cases, separation of components is achieved with the fractionation of the distillate over time (in the case of batch distillations) or with extraction from several plates for continuous multi-stage distillation.

In France, during the last two decades, the multi-stage batch distillation column has been used in the production of spirits particularly in smaller distilleries producing whisky, as it offers operational flexibility and energy efficiency. In this method, trays or packing are installed in the column to allow contact between a rising vapour from the boiler and a descending liquid reflux from the partial or total condenser. These contacts at each stage allow mass and energy exchange between the two streams which creates a concentration gradient in the column, with the most volatile compounds being concentrated at the top. During the distillation of a simple water-ethanol mixture (at a given reflux rate and heating

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power), ethanol being more volatile than water is always concentrated at the top of the column until it is exhausted from the boiler. As distillation is carried out, the concentration of ethanol in the distillate decreases over time as it is gradually depleted from the column unless the reflux rate is increased. Depending on the operational parameters, the resulting ethanol concentration can have different profiles. In the case of a distillation of fermented must to produce spirits, aroma compounds adopt different behaviours depending on their volatility which changes with ethanol concentration.

As noted above, one of the strategies to separate compounds from the final product during batch distillation is to split the distillate over time into different fractions. These are - in order of production - the head, the heart, and the tail. The 'head' is more concentrated in highly volatile compounds and contains both undesirable compounds and compounds of interest. As undesirable compounds give the distillate an unpleasant, strong, and pungent flavour, this fraction must be separated. The 'heart' corresponds to the distillate that is rich in ethanol and carries a pleasant aroma. This cut represents the distillate of interest and, after aging and dilution, constitutes the spirit. The last cut or 'tail' contains a high concentration of unpleasant fatty and oily compounds. The head and tail fractions are usually wholly or partially recycled in the following run to optimise ethanol recovery. In general, the distillation cuts are determined by measuring the ethanol content of the distillate or by olfaction and tasting - an approach which depends on the distiller's experience. However, this strategy, which is empirical in nature, would not be sufficiently effective without an understanding of the different behaviours of the volatile compounds during distillation and the influence of process parameters (Spaho, 2017; Xiang et al, 2020).

Most studies with discontinuous multi-stage distillation of spirits are at a laboratory scale (packed column of less than 240 mL) and involve comparisons of operating conditions on the composition of the heart (and the quality of the spirits) and on process properties such as reproducibility (Carvalho et al, 2011; Garcia-Llobodanin et al, 2011; Arrieta-Garay et al, 2013; de Lucca et al, 2013; Arrieta-Garay et al, 2014a,b; Matias-Guiu et al, 2016; Rodríguez-Bencomo et al, 2016; Matias-Guiu et al, 2018; Spaho et al, 2019). Rodríguez-Bencomo et al. (2016), using the same wine, reported the effect of different distillation operating modes by varying the reflux in a packed column. The results showed that a high reflux rate at the beginning of distillation reduced the impact of unpleasant compounds in the heart with a high content of acetaldehyde and ethyl acetate. Using this strategy, 40% fewer head compounds (including 50% less acetic acid) were recovered in the heart, reducing their sensory impact by 70%. The application of high reflux rates impacted on the composition of the distillate, increasing its alcoholic strength and reducing the concentration of 1-hexanol and other higher alcohols.

Other researchers validated the use of simulation in this field by using bespoke software (Osorio et al, 2004; Scanavini et al, 2010), or commercial packages such as Aspen (Gaiser et al, 2002), ChemCad (Claus and Berglund, 2009), and Prosim software including ProSimPlus (Puentes et al, 2018b) or BatchColumn (Esteban-Decloux et al, 2014; Deterre et al, 2014; Douady et al, 2019; Hodel et al, 2021). Comparison of simulated and experimental data allowed the verification of the simulation modules. Several reports used simulation to develop new recipes or to reduce the concentration of certain compounds (De Lucca et al, 2013; Osorio et al, 2005; Batista and Meirelles, 2011; Baudouin et al, 2014). In addition, simulation tools make it possible to study the influence of

different operating parameters on the composition of the distillate without having to perform numerous experiments together with the analysis of compounds. However, to be able to simulate the behaviour of volatile compounds diluted in the ethanol-water matrix, it is necessary to understand the variation of the absolute volatility coefficients as a function of the ethanol content of the boiling liquid. Puentes et al. (2018a) evaluated the experimental equilibrium of congeners diluted in ethanol-water matrix and determined the NRTL (New Random Two Liquid) model coefficients allowing the representation of volatility data as a function of ethanol concentration.

This study has two aims: first, to determine the influence of different parameters and operating modes in multi-stage discontinuous distillation on the behaviour of volatile flavour compounds and secondly to propose a strategy for the optimisation of the production of new make whisky. This involves a comparative study by simulation with ProSim® BatchColumn of 57 volatile compounds from five chemical families (alcohols, esters, aldehydes, acids, and terpenes) diluted in an ethanol-water matrix. Two case studies are reported: distillation in a whisky distillery (Distillerie Ergaster) and distillation using a laboratory column, both with a fermented malted barley mash. From this, potential strategies for optimising the distillation operations are proposed.

Materials and methods

For each case study, initial experiments were performed to obtain data for the configuration of the simulation modules before using them to study the behaviours of the aroma compounds.

Materials

For the Ergaster distillation, 700 L of a fermented barley mash (697.5 kg at ethanol mass fraction of 0.06106) and 39 L of the head and tail fractions of the previous distillation (37.25 kg at ethanol mass fraction of 0.29206). For laboratory distillation, 1503 g of the barley fermented must was used from Ergaster distillery.

Distillation equipment. The distillation equipment of the Ergaster distillery is shown in Figure 1A with a Stupfler®-type column still made from copper. Three main parts can be identified: (1) a direct fired boiler; (2) a packed column (height 1.3 m and diameter 0.3 m) in which reflux is obtained using a coiled cold water flow present in the packing. Below the column, a level control system limits the amount of liquid by sending the excess back into the boiler; (3) total condenser consisting of a coil immersed in a tank containing 1000 L of water. Leaving the condenser, the distillate flows through a beaker with an alcoholometer for temperature and alcoholic strength by volume measurements before being collected in different tanks.

The laboratory distillation system (Figure 1B) consists of a series of two isolated Vasse® Oldershaw column sections, each containing five perforated trays. These two sections are connected by a double glass tube. The boiler is heated by a Labmaster® electrical heater. At the top of the column, a heat exchanger is used to condense the rising vapour into a liquid which is then separated into reflux and distillate. The distillate is further cooled down in a refrigerant. The cooling water used in the heat exchangers is at 4°C and circulates in series from the refrigerant to the condenser. The reflux valve magnetically operates to obstruct or allow the distillate to flow towards the collection vials. Reflux is regulated by setting a total cycle time and a distillate extraction time.

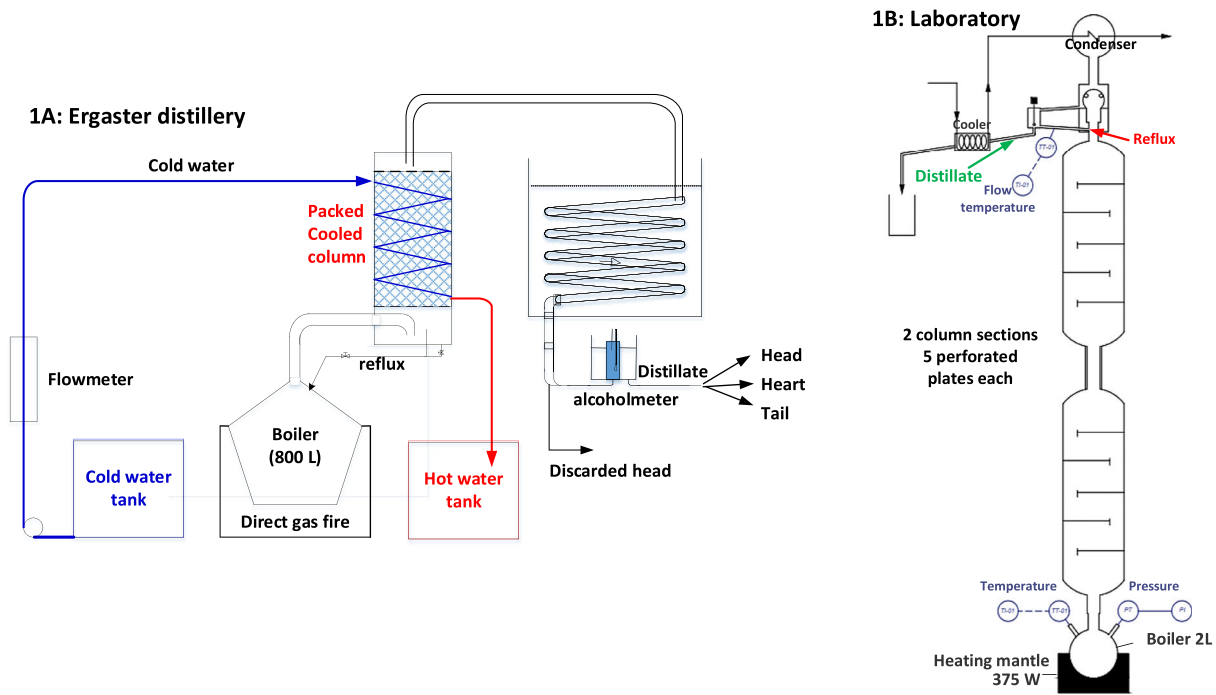


Figure 1. Distillation systems of Ergaster distillery (A) and the laboratory (B). [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/jib.704)]

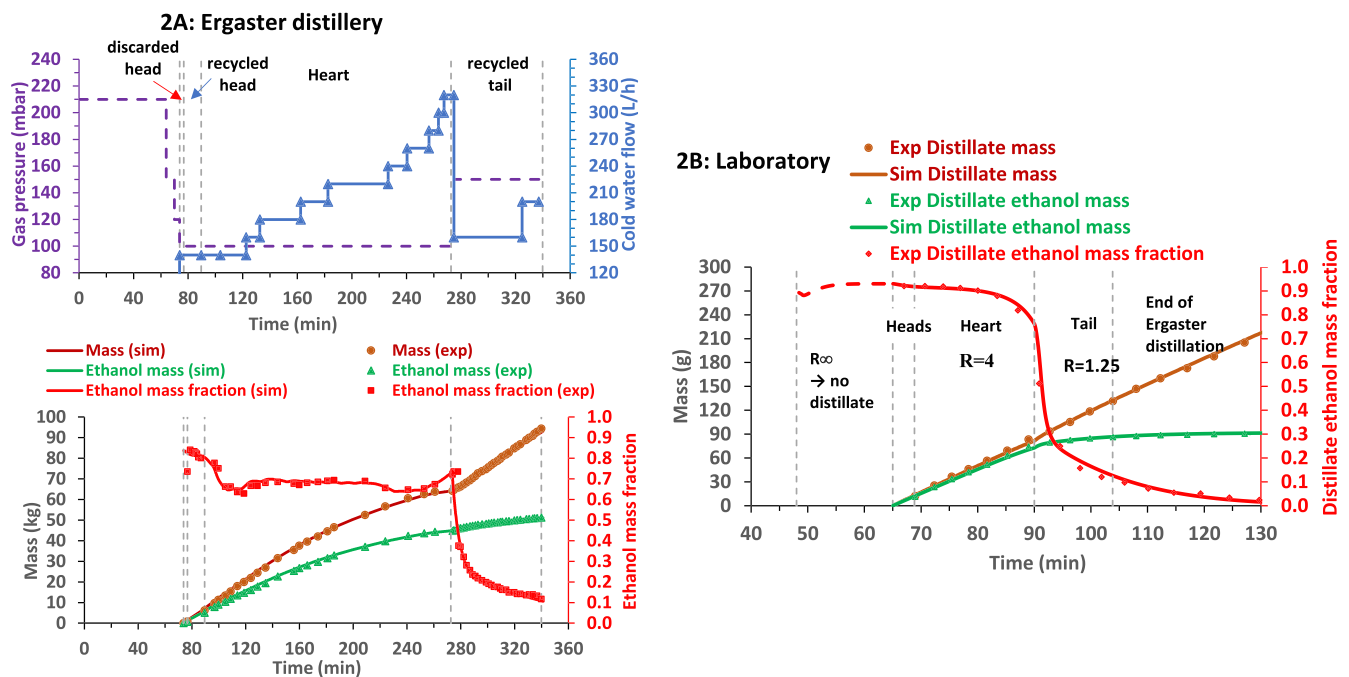


Figure 2. Operating parameters, experimental and simulated results of the distillation in the Ergaster distillery (A) and the laboratory (B). [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/jib.704)]

Industrial scale distillation of whisky. The distillation consisted of several steps: heating and filling of the column then distillation of the head, heart and tail fractions. Duration and operating parameters (gas pressure and cold water flow) are shown in Figure 2A. At the beginning of the head distillation, the first litre was discarded, with 6 L collected in the head tank before starting the heart distillation step. The choice of the cut was made by the head distiller based on olfactory criteria. The second part of head

and tail fractions were put aside to be recycled in the next distillation. The end of the heart distillation was determined when the cold water flowrate was at its maximum and the ethanol concentration dropped. There can be some variation in operating parameters, reflecting the objectives of the distiller. For example, during the heart distillation, constant heating power was maintained (through a constant heating gas pressure) while the cold water flowrate was gradually increased. This was to maintain a constant

ethanol concentration in the heart, since increasing the cold water flowrate increases the condensation in the column and the reflux rate, ensuring a better compound separation of the mixture, which is depleted over time.

The parameters monitored over time were the volume of the heating gas, the inlet and outlet temperatures of the cold water and flowrate, the temperature at different locations of the distillation set-up (dome of the boiler, bottom and top of the column), the mass and ethanol content of the distillate using a weighing bottle and Anton Paar density meter® DMA 35. The relationship between gas pressure and effective heat transfer was determined separately with water.

The construction of the simulation modules aimed to represent the mass of distillate collected and the ethanol mass fraction of the distillate. For this, 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. The ideal gas model was used for the gas phase (with the exception of the acids whose gas phase was represented by an association model), as suggested in previous work (Esteban-Decloux et al, 2014; Puentes et al, 2018a,b). The binary interaction coefficients needed for this model were obtained from a database. Numerous studies comparing experimental data and simulated values have shown the consistency of selected coefficients (Deterre et al, 2014; Esteban-Decloux et al, 2014; Puentes et al, 2018b, Douady et al, 2019). The simulation module consisted of a boiler, a tray column and a total condenser. The boiler and condenser had an efficiency of one. The filling of the column was represented by 12 trays with an efficiency of 0.8 and a retention of 0.25 L each, and a tray with an efficiency of 0.35 and a retention of 2.4 L to represent the area under the column where the steam from the boiler comes to boil. The volume of the condenser was set at 3 L to account for the retention in the coil and the alcoholmeter holder. The pressure was set to one atmosphere and the pressure drop was neglected. Heat losses were programmed along the column to represent the cold water circulation and the losses through the wall. Many steps were added to consider the numerous parameter changes to fit the ethanol content and distillate mass profiles. Figure 2A shows that with these parameters, the simulation accurately represents the evolution of the cumulative distillate mass and its ethanol content over time.

Laboratory scale distillation. Distillation was performed at a constant heating power of 375 W during several phases: heating and filling of the column, then 15 minutes without extraction of the distillate (infinite reflux rate step) followed by two consecutive distillation steps, with a reflux rate of 4 and 1.25. The infinite reflux phase was applied to establish a high concentration of ethanol in the column and to obtain concentrated distillate fractions at the beginning of the extraction. The increase over time of the boiler liquid temperature and the pressure drop in the column were monitored. In addition, the fractionation of the distillate into 22 vials made it possible to determine the cumulative mass of distillate over time and the ethanol content using an Anton Paar® DMA 35 density meter.

The simulation module was less complex as most of the necessary data was available. The thermal losses used for the simulation were from experiments to determine the thermal characterisation of the column with neutral alcohol (for minimum heat loss) and water (for the maximum). Figure 2B shows the variation in the ethanol mass fraction of the distillate, the cumulative distillate mass

and the cumulative ethanol mass for both the experiment and simulation. The effect of the infinite reflux rate phase can be observed, which it made it possible to concentrate ethanol the first distillate samples and obtain a constant plateau of the mass fraction around 0.9 (93.3% v/v). Due to the high ethanol concentration of these first samples, about 80% of the initial ethanol mass was recovered from an extraction of about 5% of the initial amount.

To compare with the Ergaster distillation, an arbitrary fractionation of the distillate from the laboratory scale distillation was used based on that at the Ergaster distillery: discarded head, recycled head, heart and recycled tail fractions representing (respectively) 1.2%, 8.3%, 74.3% and 12% of the total ethanol mass. Figure 2B shows the respective duration of these separations.

Results and discussion

Comparison of the behavior of volatile flavour compounds

In addition to the water-ethanol binary system, 57 volatile compounds were considered for the simulation (Table 1). A mass fraction of 10^{-6} was selected for all compounds in order to make a comparative study of their behaviours. This low concentration was chosen to avoid the influence of these compounds in the ethanol concentration profiles.

To interpret the behaviour of volatile compounds during distillation, it is essential to know their absolute volatility as a function of the ethanol content of the boiling liquid. The absolute volatility coefficient (k_i) of a compound (i) is the ratio of its mole fraction in the vapor phase (y_i) in equilibrium with the mole fraction in the liquid phase (x_i). The absolute volatility of a compound is highly dependent on the ethanol content of the boiling liquid in which they are located (Decloux et Coustel, 2005; Puentes et al, 2018a). Accordingly, before focusing on the behaviour of volatile compounds during the two distillation modes, the results of the simulation were used to represent the ethanol mass fraction profiles of the liquid in the upper tray of the installations. By knowing these values, it is possible to interpret the behaviour of the volatile compounds. Figure 3A indicates that, in the case of the Ergaster distillation, the ethanol mass fraction of the liquid in the reflux drops rapidly between 0.2 and 0.3. Before the tail cut, the increase in the ethanol content beyond that of the distillate, is related to the large flow of cold water to maintain the ethanol concentration of the distillate, causing an increase in the ethanol content in the reflux at the top of the column. In the laboratory distillation (Figure 3B), the ethanol mass fraction of the upper tray remains at a value greater than 0.8 during the recovery of the heart.

Alcohols. The mass fraction profile of alcohols during Ergaster and laboratory distillations are presented in Figure 4A and 4B respectively. In the case of the Ergaster distillation where the ethanol mass fraction of the liquid at the top of the column never exceeds 0.8 and drops to around 0.3, most alcohols have a maximum concentration at the beginning of distillation that decreases slowly over time. The maximum mass fraction does not exceed 4×10^{-5} - a concentration factor of 40 compared to the initial concentration of 10^{-6} . The compounds with different behaviours are methanol, prop-2-en-1-ol and 2-phenylethanol. Methanol and prop-2-en-1-ol have mass fractions that remain low ($< 1.5 \times 10^{-5}$) and increase slightly over time. With 2-phenylethanol, the concentration is significant in the distillate when the ethanol mass fraction in the distillate becomes less than 0.4.

Table 1. Volatile aroma compounds (common name in *italics*)

13 ALCOHOLS	CAS	10 ALDEHYDES	CAS	14 ESTERS	CAS	10 ACIDS	CAS	10 TERPENES	CAS
methanol	67-56-1	acetaldehyde (<i>ethanal</i>)	75-07-0	ethyl acetate	141-78-6	formic acid (<i>methanoic acid</i>)	64-18-6	α -limonene (<i>d-limonene</i>)	5989-27-5
prop-2-en-1-ol (<i>allyl alcohol</i>)	107-18-6	prop-2-enal (<i>acrolein</i>)	107-02-8	2-methylpropyl methanoate (<i>isobutyl formate</i>)	542-55-2	acetic acid (<i>ethanoic acid</i>)	64-19-7	α -pinene (<i>alpha-pinene</i>)	80-56-8
propan-1-ol	71-23-8	1-propanal	123-38-6	1-methylethyl acetate (<i>isopropyl acetate</i>)	108-21-4	propanoic acid (<i>propionic acid</i>)	79-09-4	β -pinene (<i>beta-pinene</i>)	127-91-3
propan-2-ol (<i>isopropanol</i>)	67-63-0	butanal	123-72-8	ethyl 2-hydroxypropanoate (<i>ethyl lactate</i>)	97-64-3	butanoic acid (<i>butyric acid</i>)	107-92-6	myrcene (<i>myrcene</i>)	123-35-3
butan-1-ol	71-36-3	2-methylpropanal (<i>isobutanal</i>)	78-84-2	ethyl butanoate (<i>ethyl butyrate</i>)	105-54-4	2-methylpropanoic acid (<i>isobutyric acid</i>)	79-31-2	α -phellandrene (<i>alpha-phelladrene</i>)	99-83-2
2-methylpropan-1-ol (<i>isobutanol</i>)	78-83-1	Pentanal (<i>n-valeraldehyde</i>)	110-62-3	ethyl 2-methylpropanoate (<i>ethyl isobutyrate</i>)	97-62-1	2-methylbutanoic acid (<i>2-methylbutyric acid</i>)	116-53-0	terpinolene	586-62-9
2-methylpropan-2-ol (<i>tert-butanol</i>)	75-65-0	3-methylbutanal (<i>isovaleraldehyde</i>)	590-86-3	ethyl 3-methylbutanoate (<i>ethyl isovalerate</i>)	108-64-5	n-pentanoic acid (<i>valeric acid</i>)	109-52-4	citral (<i>geranial</i>)	141-27-5
pentan-1-ol (<i>n-amyly alcohol</i>)	71-41-0	nonanal	124-19-6	3-methylbutyl acetate (<i>isopentyl acetate</i>)	123-92-2	3-methylbutanoic acid (<i>isovaleric acid</i>)	503-74-2	Linalool (<i>linalyl alcohol</i>)	78-70-6
2-methylbutan-1-ol (<i>active amyly alcohol</i>)	137-32-6	1,1-diethoxyethane (<i>acetal</i>)	105-57-7	diethyl butanedioate (<i>diethyl succinate</i>)	123-25-1	hexanoic acid (<i>caproic acid</i>)	142-62-1	α -terpineol	98-55-5
3-methylbutan-1-ol (<i>isoamyly alcohol</i>)	123-51-3	furan-2-carbaldehyde (<i>furfural</i>)	98-01-1	ethyl hexanoate (<i>ethyl caproate</i>)	123-66-0	octanoic acid (<i>caprylic acid</i>)	124-07-2	linalool oxide (<i>E-linalool oxide</i>)	34995-77-2
(Z)-hex-3-en-1-ol	928-96-1			hexyl acetate	142-92-7				
hexan-1-ol (<i>hexanol</i>)	111-27-3			2-phenylethyl acetate	103-45-7				
2-phenylethanol	60-12-8			ethyl octanoate (<i>ethyl caprylate</i>)	106-32-1				
				ethyl decanoate (<i>ethyl caprate</i>)	110-38-3				

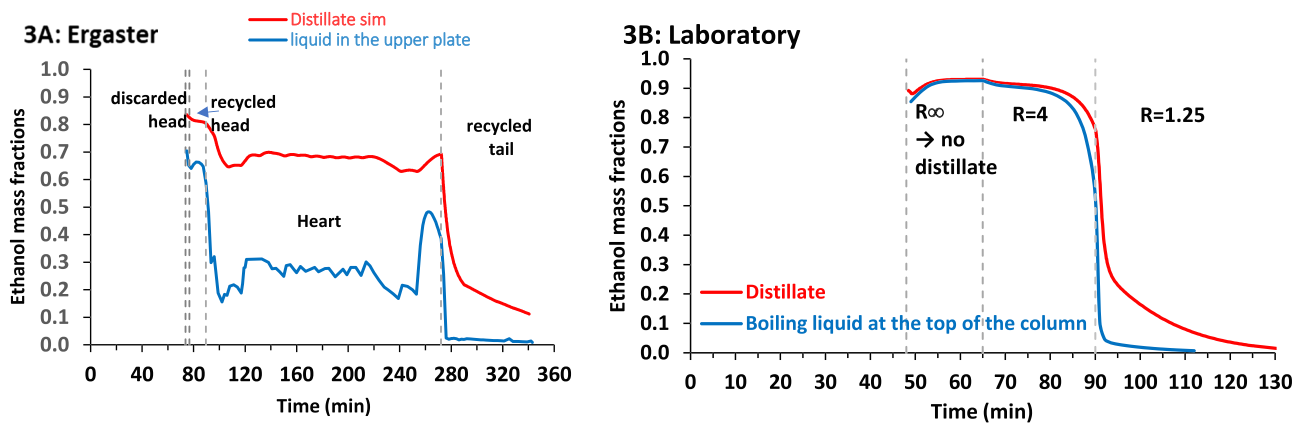


Figure 3. Ethanol mass fractions of the distillate and the liquid at the top of the column during the distillation in the Ergaster distillery (A) and the laboratory (B). [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

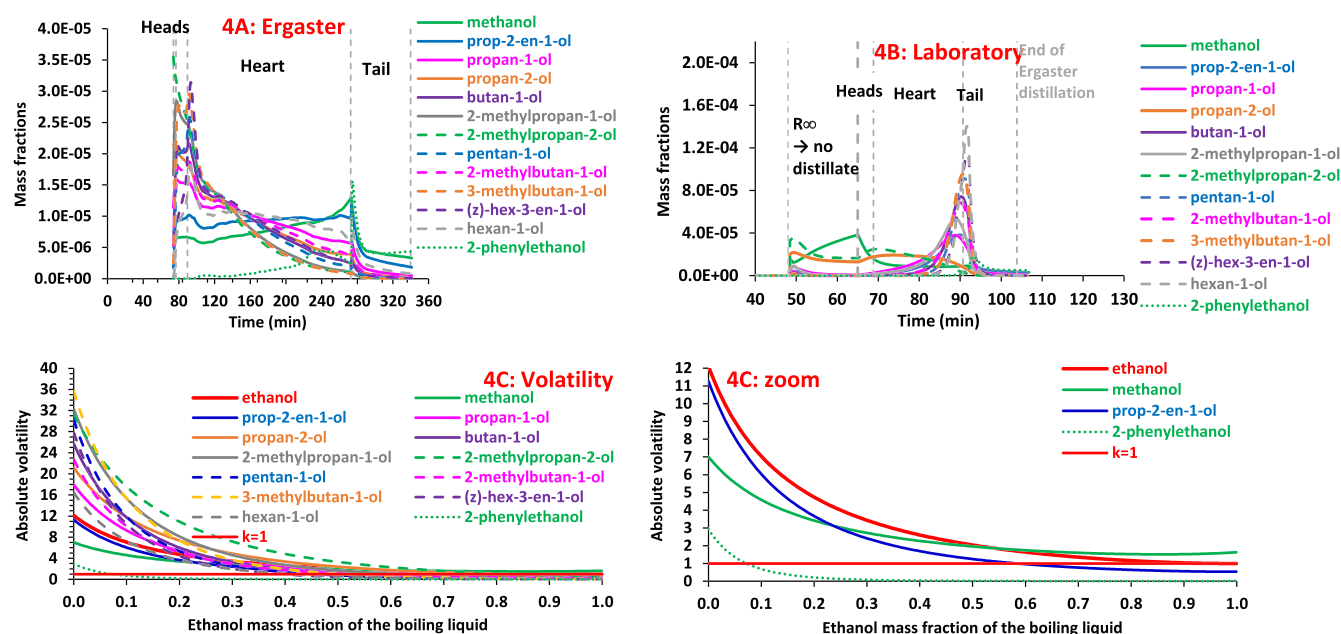


Figure 4. Mass fraction profiles of alcohols during Ergaster (A) and laboratory (B) distillations and their absolute volatility with ethanol mass fraction of the boiling liquid (C). [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

With the laboratory experiment (Figure 4B), the ethanol mass fraction of the liquid at the top of the column is above 0.8 until the end of the heart extraction phase. Most alcohols concentrate in the distillate when the ethanol content starts to drop at the end of the heart recovery. With the hypothesis of an initial mass fraction in the boiler of 10^{-6} , the highest peaks reach a maximum concentration of 1.6×10^{-4} . Only methanol, propan-2-ol and 2-phenylethanol have different behaviours. Methanol concentrates at the top of the column during the infinite reflux rate phase and is recovered in relatively higher amounts as soon as the head fraction extraction starts. Propan-2-ol has a similar behaviour, except that its concentration at the top of the column drops slightly during the phase at infinite reflux rate. For 2-phenylethanol, this alcohol accumulates only when the tail fraction is distilled. The mass fraction of these compounds does not exceed 4×10^{-5} .

To explain the different behaviours in the two case studies and between the alcohols, it is necessary to consider the variation in absolute volatility as a function of the ethanol content in the boiling liquid (Figure 4C). All alcohols have absolute volatilities that

decrease with the increase in the ethanol content of the boiling liquid. Some of them have volatilities that become lower than one, indicating that at the boiling temperature of the liquid, the concentration in the liquid phase remains greater than that in the vapour. Only methanol has a volatility that becomes higher than the volatility of ethanol beyond an ethanol mass fraction of 0.55. The volatility of 2-phenylethanol is particularly low ($k_{2\text{-phenylethanol}} < 4$) and is always less volatile than ethanol.

It is possible to explain the different behaviours observed during the two distillation runs. During the laboratory distillation, where the ethanol content in the upper tray is high due to the infinite reflux rate phase, most alcohols are less volatile than ethanol and have an absolute volatility lower than one. Therefore, they tend to be sent back to the bottom of the column. Only when the ethanol concentration of the trays decreases, do they concentrate in the upper trays with absolute volatilities higher than one and that of ethanol. During the Ergaster distillation, the ethanol content of the upper tray being much lower, these alcohols have higher

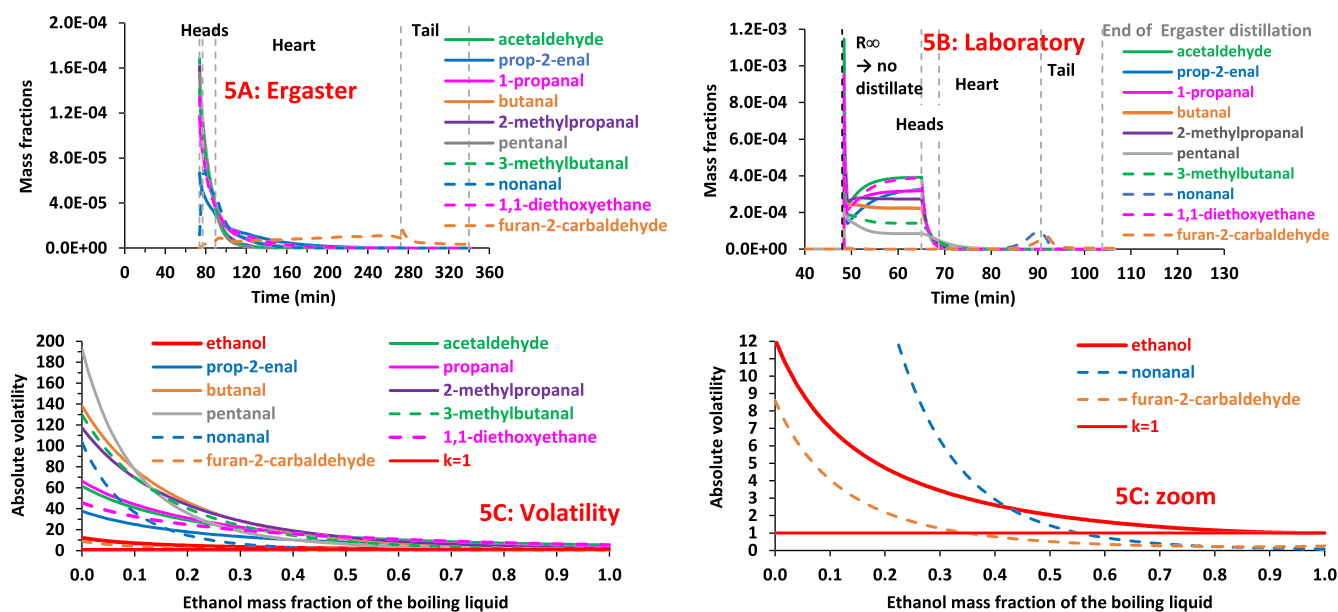
Table 2. Partition of compounds between the discarded head, recycled head, heart, recycled tail and residue as a mass percentage for the Ergaster and laboratory distillations

Values as %	Discarded head		Recycled head		Heart		Recycled tail		Residue	
	Ergaster	Lab.	Ergaster	Lab.	Ergaster	Lab.	Ergaster	Lab.	Ergaster	Lab.
ethanol	1.2	1.2	8.3	8.3	74.3	74.3	12.0	12.0	4.2	4.2
Alcohols										
methanol	0.7	2.9	4.9	14.7	58.1	51.3	18.9	16.1	17.4	15.0
prop-2-en-1-ol	0.7	0.0	6.9	0.3	72.6	67.0	14.2	25.0	5.7	7.7
propan-1-ol	1.3	0.1	11.5	0.7	80.4	84.9	5.9	13.0	0.9	1.3
propan-2-ol	2.2	1.0	14.7	8.1	79.5	86.7	3.3	3.9	0.3	0.3
butan-1-ol	0.8	0.0	14.7	0.0	82.1	80.8	2.2	19.0	0.1	0.2
2-methylpropan-1-ol	2.1	0.0	19.6	0.3	77.5	91.3	0.8	8.3	0.0	0.0
2-methylpropan-2-ol	3.5	1.3	21.6	11.1	74.2	86.8	0.6	0.8	0.0	0.0
pentan-1-ol	0.4	0.0	13.7	0.0	84.4	73.1	1.5	26.8	0.0	0.1
2-methylbutan-1-ol	0.8	0.0	12.6	0.0	82.7	79.5	3.6	20.0	0.3	0.5
3-methylbutan-1-ol	0.6	0.0	18.7	0.0	80.2	78.4	0.6	21.5	0.0	0.0
(z)-hex-3-en-1-ol	0.1	0.0	7.7	0.0	89.9	60.5	2.3	39.3	0.1	0.2
hexan-1-ol	0.1	0.0	6.4	0.0	83.0	62.0	8.8	38.0	1.6	0.0
2-phenylethanol	0.0	0.0	0.0	0.0	9.9	1.4	20.3	27.8	69.8	70.9
Aldehydes										
acetaldehyde	15.5	27.0	57.7	65.1	26.9	7.9	0.0	0.0	0.0	0.0
prop-2-enal	6.3	23.1	30.9	64.1	62.8	12.8	0.0	0.0	0.0	0.0
1-propanal	11.0	22.7	48.1	65.3	40.9	12.0	0.0	0.0	0.0	0.0
butanal	15.1	16.6	60.4	62.1	24.5	21.3	0.0	0.0	0.0	0.0
2-methylpropanal	15.0	19.9	60.2	64.6	24.7	15.5	0.0	0.0	0.0	0.0
pentanal	14.6	6.5	59.8	39.7	25.6	53.8	0.0	0.0	0.0	0.0
3-methylbutanal	13.3	10.7	56.5	52.8	30.2	36.5	0.0	0.0	0.0	0.0
nonanal	2.2	0.0	42.7	0.0	55.1	100.0	0.0	0.0	0.0	0.0
1,1-diethoxyethane	12.3	26.8	47.6	64.8	40.1	8.4	0.0	0.0	0.0	0.0
furan-2-carbaldehyde	0.1	0.0	2.8	0.0	63.4	35.2	20.3	47.2	13.3	17.6
Esters										
ethyl acetate	10.0	15.7	47.0	61.1	43.0	23.2	0.0	0.0	0.0	0.0
2-methylpropyl methanoate	8.8	16.8	42.9	62.1	48.4	21.1	0.0	0.0	0.0	0.0
1-methylethyl acetate	15.0	13.6	60.4	57.5	24.6	28.9	0.0	0.0	0.0	0.0
ethyl 2-hydroxypropanoate	0.0	0.0	0.1	0.0	29.9	7.1	22.3	39.6	47.6	53.3
ethyl butanoate	17.9	5.4	64.6	35.3	17.6	59.3	0.0	0.0	0.0	0.0
ethyl 2-methylpropanoate	20.9	8.7	66.9	46.8	12.2	44.5	0.0	0.0	0.0	0.0
ethyl 3-methylbutanoate	16.2	1.5	62.9	13.8	20.7	84.7	0.0	0.0	0.1	0.0
3-methylbutyl acetate	13.5	0.2	59.8	2.1	26.7	96.5	0.0	1.2	0.0	0.0
diethyl butanedioate	0.0	0.0	0.0	0.0	7.6	0.8	11.1	15.0	81.3	84.2
ethyl hexanoate	8.0	1.2	41.6	11.7	50.3	86.9	0.0	0.2	0.1	0.0
hexyl acetate	7.5	0.0	61.8	0.2	30.7	92.3	0.0	7.5	0.0	0.0
2-phenylethyl acetate	0.0	0.0	2.2	0.0	97.4	45.3	0.4	54.7	0.0	0.0
ethyl octanoate	1.8	0.0	75.2	0.0	22.9	84.1	0.0	15.9	0.0	0.0
ethyl decanoate	0.5	0.0	37.5	0.0	62.0	74.7	0.0	25.3	0.0	0.0
Acids										
formic acid	0.0	0.0	0.0	0.0	0.2	0.0	0.7	0.3	99.1	99.6
acetic acid	0.0	0.0	0.0	0.0	0.2	0.0	1.1	0.6	98.7	99.4
propanoic acid	0.0	0.0	0.0	0.0	0.8	0.0	2.2	1.8	97.0	98.2
butanoic acid	0.0	0.0	0.0	0.0	9.3	1.1	11.6	16.4	79.1	82.5
2-methylpropanoic acid	0.0	0.0	0.0	0.0	9.7	1.3	10.3	14.7	79.9	84.1
2-methylbutanoic acid	0.0	0.0	0.0	0.0	8.9	1.0	11.9	16.7	79.2	82.3
n-pentanoic acid	0.0	0.0	0.0	0.0	9.3	1.1	12.5	17.7	78.2	81.2
3-methylbutanoic acid	0.0	0.0	0.1	0.0	28.6	6.5	22.6	39.8	48.8	53.7
hexanoic acid	0.0	0.0	0.4	0.0	64.1	24.3	22.3	58.8	13.1	16.9
octanoic acid	0.0	0.0	0.0	0.0	11.5	1.7	13.7	20.2	74.8	78.1

(Continues)

Table 2. (Continued)

Values as %	Discarded head		Recycled head		Heart		Recycled tail		Residue	
	Ergaster	Lab.	Ergaster	Lab.	Ergaster	Lab.	Ergaster	Lab.	Ergaster	Lab.
Terpenes										
d-limonene	28.1	2.6	66.3	22.1	5.7	75.3	0.0	0.0	0.0	0.0
α -pinene	29.8	12.8	70.2	57.7	0.0	29.5	0.0	0.0	0.0	0.0
β -pinene	17.7	10.0	64.5	51.9	17.8	38.1	0.0	0.0	0.0	0.0
myrcene	26.0	6.9	67.9	42.5	6.1	50.6	0.0	0.0	0.0	0.0
α -phellandrene	12.2	7.9	53.7	45.8	34.1	46.3	0.0	0.0	0.0	0.0
terpinolene	26.0	2.8	66.3	20.9	7.3	76.2	0.0	0.2	0.4	0.0
citral	0.1	0.0	8.0	0.0	91.9	56.6	0.0	43.4	0.0	0.0
linalool	4.8	0.0	72.7	0.1	22.4	80.3	0.0	19.6	0.0	0.0
α -terpineol	0.0	0.0	3.4	0.0	93.5	49.8	3.0	50.1	0.1	0.1
linalool oxide	0.0	0.0	3.3	0.0	95.7	49.3	0.9	50.7	0.0	0.0


Figure 5. Mass fraction profiles of aldehydes during Ergaster (A) and laboratory (B) distillations and their absolute volatility with ethanol mass fraction of the boiling liquid (C). [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

volatilities, and the concentration is significant from the beginning of the distillation run. The concentration subsequently decreases due to their exhaustion.

The differences in the behaviour of methanol between the two distillations can also be explained by the variation in absolute volatility with the ethanol content of the liquid. During laboratory distillation, the ethanol content on each tray increases at infinite reflux rate. Because of its positive volatility at high ethanol concentration, methanol concentrates in the upper plates. The concentration of methanol is therefore at its highest at the beginning of the run, and then decreases. However, the absolute volatility of methanol is never high: the initial mass fraction does not exceed 4×10^{-5} and methanol remains in all the distillate fractions. In contrast, during the Ergaster distillation where there is no infinite reflux rate phase and where the ethanol mass fraction of the liquid on the upper plate rapidly decreases to around 0.3, the absolute volatility of methanol remains low and below that of ethanol. The amount of methanol extracted in the first fractions

is therefore small and the increase in concentration over time is explained by the increase in volatility with the decrease of the ethanol content.

2-Phenylethanol, whose absolute volatility is particularly low, is extracted towards the end of both distillations, when the ethanol concentration of the liquid in the trays drops significantly.

From these results, the distribution of each alcohol in the different fractions was calculated (Table 2). Except for 2-phenylethanol, most alcohols, under both distillation conditions, are mainly recovered in the heart. However, the second fraction with the highest concentration of alcohols differs between the two distillation methods with the recycled head fraction in the Ergaster distillation and the recycled tail fraction in the laboratory distillation. Unlike the other alcohols, methanol does not concentrate in the head fraction with a significant proportion remaining in the residue ($\sim 15\%$). Similarly, a significant amount of prop-2-en-1-ol ($> 7.5\%$) is lost in the residue, together with 2-phenylethanol ($> 70\%$). However, unlike the laboratory distillation, a small amount

of 2-phenylethanol is recovered in the heart fraction during the commercial distillation. In the literature, Spaho (2017) presented a review of the behaviour of some compounds in industrial distillations with 2-phenylethanol a tail compound, and propan-1-ol and methanol as head compounds. However, these results cannot be used for comparison as there is no information on the ethanol concentration of the liquid from which the distillate is generated. Conversely, Luna et al. (2019) in their study at a laboratory scale indicated that methanol is distributed over the entire distillation and, particularly, the tail fraction.

Aldehydes. In both small and large scale distillations and with the exception of furan-2-carbaldehyde, aldehydes are at a maximum concentration at the beginning of distillation (Figures 5A and 5B). The proportion in the head fractions (discarded and recycled) is important (Table 2). Furan-2-carbaldehyde behaves differently with a much lower concentration than the other aldehydes and an important presence in the tail fraction when the ethanol concentration in the distillate starts to drop. These behaviours can easily be explained by considering the absolute volatility curves. All aldehydes of the main category have higher absolute volatilities than ethanol at the high ethanol concentration in the liquid (Figure 5C). However, as the absolute volatility decreases with the increase in ethanol content, the concentration decreases at the top of the column during the phase at infinite reflux rate, resulting in a lower concentration in the first fraction of distillate for the laboratory distillation (Figure 5B). On the other hand, furan-2-carbaldehyde has a very low absolute volatility at a high ethanol content, becoming more volatile than ethanol below 0.42 and being extracted in the distillate only at the end of the heart extraction.

Esters. As with the main aldehydes, most esters are concentrated in the early distillate fractions (Figures 6A and 6B). Similarly, the period with infinite reflux during laboratory distillation results

in a decrease in the concentration of esters in the first fractions of distillate. The compounds with different behaviours are ethyl 2-hydroxypropanoate, diethyl butanedioate, 2-phenylethyl acetate and ethyl decanoate. Ethyl 2-hydroxypropanoate and diethyl butanedioate are mainly extracted in the tail fraction and a proportion remains in the residue. While 2-phenylethyl acetate and ethyl decanoate are extracted in the tail fraction during the laboratory distillation, they are distributed in the recycled head and heart fractions during the Ergaster distillation. Again, it is possible to explain these behaviours by considering the differences in the volatility coefficient with the ethanol content of the liquid (Figure 6C). Most esters have volatilities that are higher than one and that of ethanol. However, compounds with atypical behaviours have lower volatilities, less than one over a wide range of ethanol concentration. The least volatile esters are ethyl 2-hydroxypropanoate and diethyl butanedioate. Overall, most esters are recovered in the head fraction, and are present in a greater proportion during the Ergaster distillation, where the compounds have higher volatilities due to the lower ethanol concentration at the top of the column (Table 2).

Acids. Most acids are concentrated in the tail and residue fractions (Figures 7A and 7B). This is explained by their low volatility which is not greater than one below an ethanol mass fraction of 0.25 (Figure 7C). However, in the case of the Ergaster distillation (Figure 7A), where the liquid ethanol concentration in the column are lower (Figure 3A) than in the laboratory experiment (Figure 3B), these acids start to be extracted during the heart distillation. Formic, acetic, and propionic acids essentially remain in the boiler and are removed with the residue (Table 2). This is explained by their absolute volatilities which are always lower than one.

Terpenes. Most terpenes are concentrated in the first distillate fractions (Figures 8A and 8B), with a greater proportion when distilled at Ergaster. Terpenes exhibiting different behaviours include

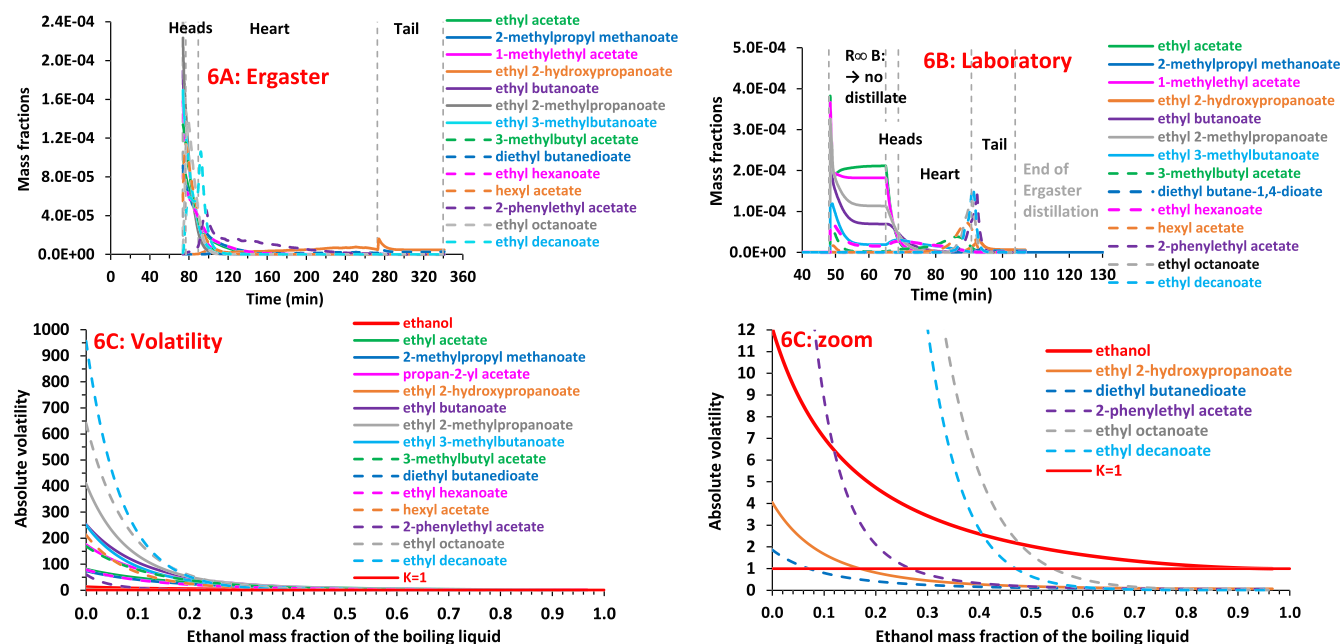


Figure 6. Mass fraction profiles of esters during Ergaster (A) and laboratory (B) distillations and their absolute volatility with ethanol mass fraction of the boiling liquid (C). [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

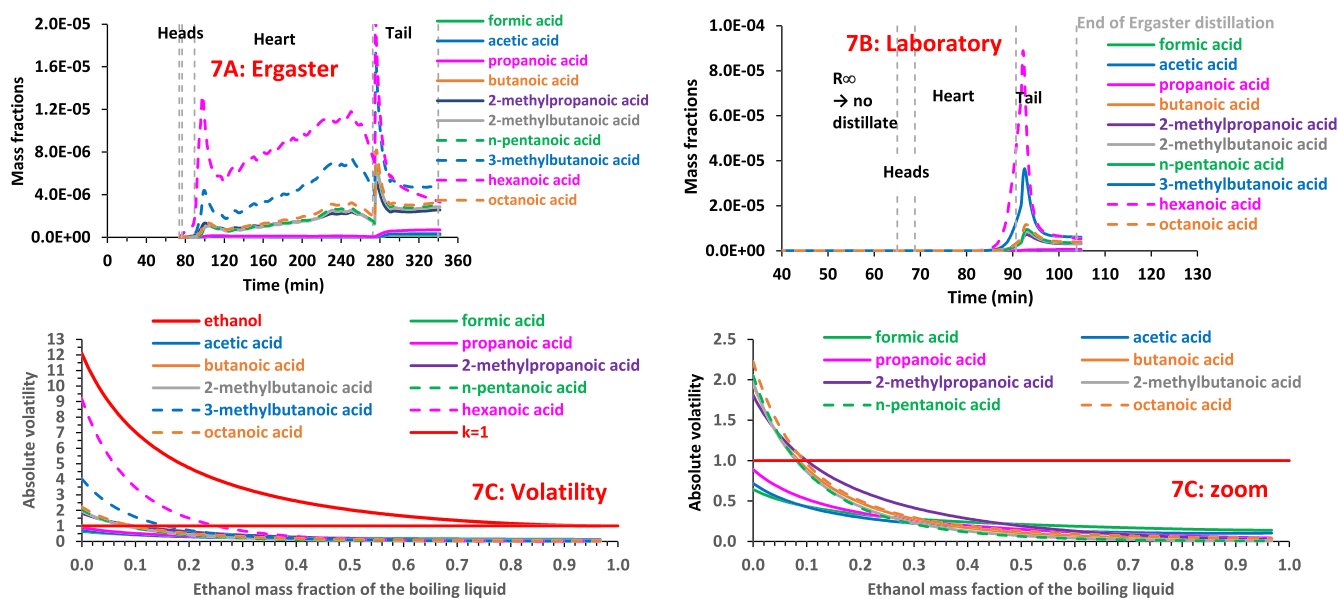


Figure 7. Mass fraction profiles of acids during Ergaster (A) and laboratory (B) distillations and their absolute volatility with ethanol mass fraction of the boiling liquid (C). [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.com)]

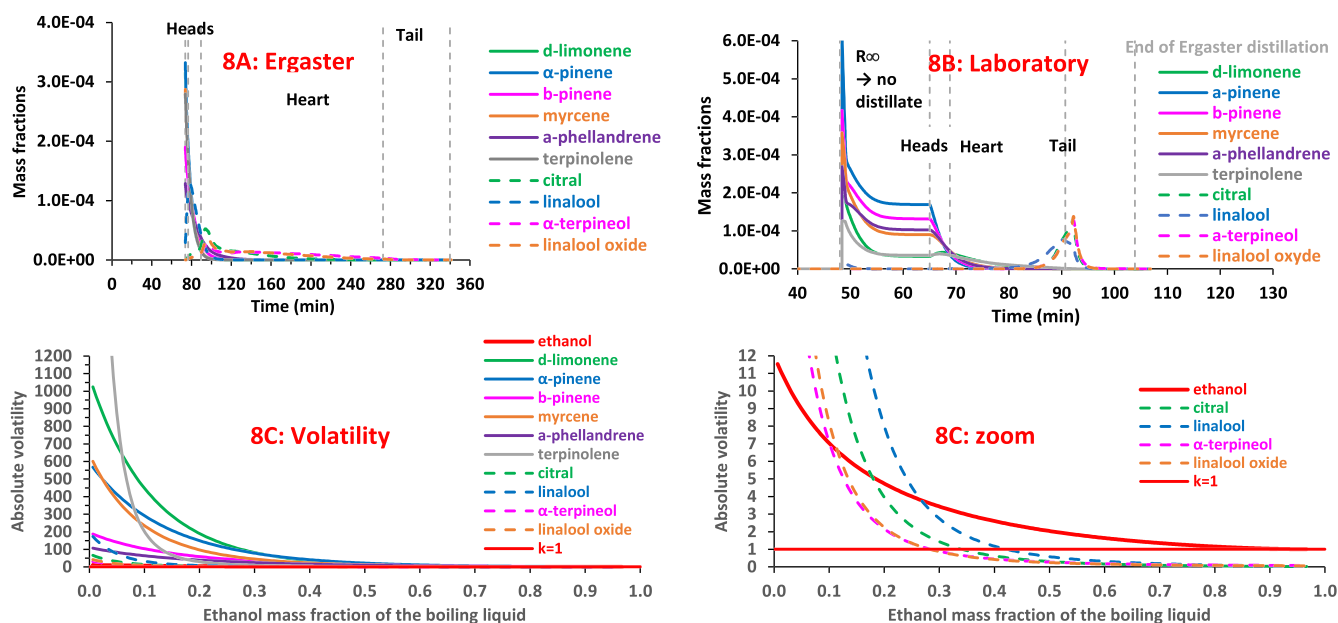


Figure 8. Mass fraction profiles of terpenes during Ergaster (A) and laboratory (B) distillations and their absolute volatility with ethanol mass fraction of the boiling liquid (C). [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.com)]

citral, linalool, α -terpineol and linalool oxide. During the laboratory distillation (Figure 8B), they concentrate in the tail fraction, whereas in the Ergaster distillation (Figure 8A), linalool and citral exhibit maximum concentration at the beginning of the distillation while α -terpineol and linalool oxide are distributed throughout all fractions. Again, these behaviours can be explained by considering their respective volatilities according to the ethanol content (Figure 8C).

Summary. Overall, conducting two distillation runs under different operating conditions, combined with the simulation of a large number of volatile compounds at the same initial concentration, made it possible to show the influence of the ethanol

content in the column on the behaviour of the volatile aroma compounds.

While most alcohols are distributed in all fractions during the Ergaster distillation, where the heart is extracted at an ethanol mass fraction around 0.67. In the laboratory distillation they only start to appear when the ethanol mass fraction of the distillate starts to decrease. Since these compounds contribute to the quality of the spirit, it is important to limit the ethanol concentration of the distillate during distillation so that they concentrate in the heart fraction. Conversely, for 2-phenylethanol which contributes a fruity and floral note (Spaho, 2017; Esteban-Decloux et al, 2021) but with low volatility, it could be interesting to collect the heart until a lower ethanol content. With regard to methanol, often

noted for its toxicity (Spaho, 2017), a simple multi-stage distillation does not separate it effectively, reflecting its volatility being similar to that of ethanol. With whisky this is not a concern due to the very low content of methanol in the wash. Most of the aldehydes studied are concentrated at the beginning of the distillation regardless of the operating distillation mode. The behaviour of most esters depends on the ethanol content in the column: the higher the ethanol content, the more the esters are returned to the boiler. This

could be used to better separate aldehydes and esters, including ethyl acetate, which is classified as an unwanted aroma compound by Luna et al. (2019). Indeed, by imposing a very high reflux rate at the beginning of the distillation, it may be possible to increase the aldehyde concentration at the top of the column and reduce that of some esters. With acids, most are concentrated in the tail fraction and the residue. The appearance of acids at the end of the distillation may be one of the reasons to evaluate cutting the tail.

Table 3. Comparison of the recovery of compounds (% initial mass) in the distillate for a different final ethanol mass fraction in the distillate

Final ethanol mass fraction	0.105	0.061		0.020		total
Recovery	%	%	increase	%	increase	increase
ethanol	95.8	97.7	2.0%	99.3	1.7%	3.7%
water	6.15	7.83	27.4%	11.12	42.0%	80.8%
Alcohols						
methanol	82.6	87.5	5.9%	93.4	6.9%	13.2%
prop-2-en-1-ol	94.3	96.7	2.6%	98.9	2.3%	4.9%
hexan-1-ol	98.4	99.3	0.9%	99.9	0.6%	1.5%
2-phenylethanol	30.2	37.5	24.0%	50.0	33.4%	65.4%
Esters						
ethyl 2-hydroxypropanoate	52.4	59.8	14.2%	71.4	19.4%	36.3%
diethyl butanedioate	18.7	23.3	24.8%	31.8	36.6%	70.5%
Acids						
formic acid	0.9	1.3	41.8%	2.1	59.9%	126.8%
acetic acid	1.3	1.9	48.3%	3.1	65.8%	145.8%
propanoic acid	3.0	4.3	42.6%	6.8	58.5%	126.1%
butanoic acid	20.9	25.8	23.6%	34.6	34.1%	65.7%
2-methylpropanoic acid	20.1	24.6	22.3%	32.6	32.8%	62.5%
2-methylbutanoic acid	20.8	25.8	24.1%	34.8	34.7%	67.2%
n-pentanoic acid	21.8	27.0	24.0%	36.3	34.4%	66.7%
3-methylbutanoic acid	51.2	59.0	15.1%	70.8	20.0%	38.1%
hexanoic acid	86.9	91.6	5.5%	96.6	5.4%	11.2%
octanoic acid	25.2	30.9	22.3%	40.7	31.9%	61.4%

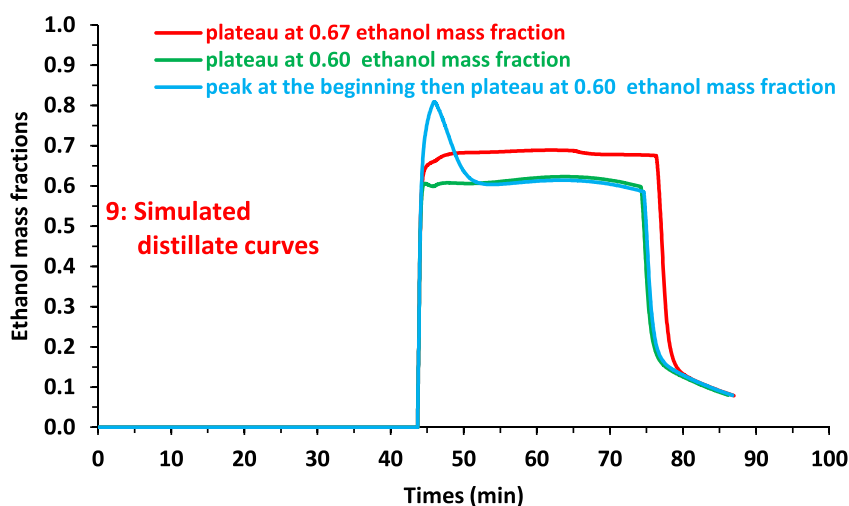


Figure 9. Profiles of the simulated distillate with a plateau of ethanol mass fraction of 0.60 and 0.67 and with a peak at the beginning. [Colour figure can be viewed at wileyonlinelibrary.com]

Table 4. Partition of compounds as a mass percentage across the five fractions of the simulated distillations with a plateau of the ethanol mass fraction of the heart of 0.60 and 0.67

Values in %	Discarded head		Recycled head		Heart		Recycled tail		Residue		Heart + recycled fractions		Difference 0.67-0.60
	0.60	0.67	0.60	0.67	0.60	0.67	0.60	0.67	0.60	0.67	0.60	0.67	
ethanol	1.2	1.2	8.3	8.3	74.3	74.3	12.0	12.0	4.2	4.2	94.6	94.6	0.0
Alcohols													
methanol	0.5	0.6	4.7	4.7	57.6	57.3	18.0	17.8	19.2	19.6	80.3	79.8	-0.4
prop-2-en-1-ol	0.8	0.8	7.0	6.7	71.2	70.5	14.1	15.0	6.9	7.0	92.3	92.2	-0.1
propan-1-ol	1.7	1.7	11.4	11.1	79.3	79.2	6.3	6.6	1.3	1.3	97.0	97.0	0.0
propan-2-ol	2.7	2.6	14.0	14.2	79.3	79.1	3.6	3.5	0.5	0.5	96.8	96.9	0.1
butan-1-ol	2.4	2.4	15.0	14.3	79.8	79.9	2.6	3.2	0.2	0.2	97.4	97.4	0.0
2-methylpropan-1-ol	3.7	3.6	18.9	18.8	76.4	76.5	0.9	1.1	0.0	0.0	96.3	96.3	0.1
2-methylpropan-2-ol	4.7	4.6	19.9	20.7	74.6	74.0	0.8	0.7	0.0	0.0	95.3	95.4	0.1
pentan-1-ol	2.3	2.3	16.0	14.7	79.8	80.2	1.9	2.7	0.1	0.1	97.6	97.6	0.0
2-methylbutan-1-ol	1.9	1.9	13.1	12.4	80.6	80.5	4.0	4.7	0.5	0.4	97.7	97.7	0.0
3-methylbutan-1-ol	3.5	3.5	19.7	18.7	76.1	76.7	0.7	1.1	0.0	0.0	96.5	96.5	0.1
(z)-hex-3-en-1-ol	1.8	1.8	14.2	12.4	81.0	81.0	2.9	4.6	0.2	0.2	98.1	98.1	0.0
hexan-1-ol	1.0	1.0	9.2	8.2	78.1	76.7	9.5	11.9	2.1	2.1	96.9	96.8	0.0
2-phenylethanol	0.0	0.0	0.2	0.2	8.0	4.1	18.9	17.2	72.8	78.5	27.2	21.5	-5.7
Aldehydes													
acetaldehyde	11.9	11.7	35.5	38.1	52.6	50.3	0.0	0.0	0.0	0.0	88.1	88.3	0.3
prop-2-enal	7.1	7.0	24.9	26.7	67.7	66.1	0.2	0.2	0.0	0.0	92.9	93.0	0.2
1-propanal	12.8	12.5	37.3	39.9	49.9	47.6	0.0	0.0	0.0	0.0	87.2	87.5	0.3
butanal	22.1	21.5	50.8	53.3	27.1	25.1	0.0	0.0	0.0	0.0	77.9	78.5	0.6
2-methylpropanal	20.0	19.5	48.4	51.0	31.7	29.5	0.0	0.0	0.0	0.0	80.0	80.5	0.5
pentanal	23.8	22.9	53.3	55.3	22.9	21.7	0.0	0.0	0.0	0.0	76.2	77.1	0.8
3-methylbutanal	20.5	19.9	49.3	51.8	30.2	28.3	0.0	0.0	0.0	0.0	79.5	80.1	0.6
nonanal	11.1	10.7	40.2	39.5	48.7	49.8	0.0	0.0	0.0	0.0	88.9	89.3	0.4
1,1-diethoxyethane	9.3	9.1	29.7	32.0	60.9	58.8	0.0	0.0	0.0	0.0	90.7	90.9	0.2
furan-2-carbaldehyde	0.3	0.4	4.3	3.7	60.0	56.2	20.8	24.1	14.6	15.6	85.1	84.0	-1.0
Esters													
ethyl acetate	14.3	14.0	40.6	43.0	45.1	43.0	0.0	0.0	0.0	0.0	85.7	86.0	0.4
2-methylpropyl methanoate	12.4	12.1	37.6	39.8	50.0	48.1	0.0	0.0	0.0	0.0	87.6	87.9	0.3
1-methylethyl acetate	24.1	23.3	53.1	55.2	22.8	21.4	0.0	0.0	0.0	0.0	75.9	76.6	0.8
ethyl 2-hydroxypropanoate	0.1	0.1	1.1	0.8	25.4	17.9	23.6	24.4	49.9	56.8	50.1	43.1	-7.0
ethyl butanoate	30.1	29.0	56.0	57.9	13.9	13.1	0.0	0.0	0.0	0.0	69.9	71.0	1.1
ethyl 2-methylpropanoate	36.5	34.9	56.3	57.9	7.2	7.2	0.0	0.0	0.0	0.0	63.5	65.0	1.6
ethyl 3-methylbutanoate	27.6	26.5	55.7	57.4	16.7	16.1	0.0	0.0	0.0	0.0	72.4	73.5	1.1
3-methylbutyl acetate	23.3	22.5	52.7	54.5	24.0	23.0	0.0	0.0	0.0	0.0	76.7	77.5	0.8
diethyl butanedioate	0.0	0.0	0.2	0.2	5.8	3.2	10.8	9.6	83.2	87.0	16.8	13.0	-3.7
ethyl hexanoate	12.2	11.8	37.9	39.7	50.0	48.5	0.0	0.0	0.0	0.0	87.8	88.2	0.4
hexyl acetate	21.7	20.8	53.9	54.2	24.4	25.1	0.0	0.0	0.0	0.0	78.3	79.2	0.9
2-phenylethyl acetate	1.2	1.2	14.7	11.9	83.0	83.0	1.1	3.8	0.0	0.0	98.8	98.8	0.0
ethyl octanoate	43.8	41.3	53.4	54.1	2.8	4.6	0.0	0.0	0.0	0.0	56.2	58.7	2.6
ethyl decanoate	46.1	42.9	52.1	51.6	1.8	5.5	0.0	0.0	0.0	0.0	53.9	57.1	3.2
Acids													
formic acid	0.0	0.0	0.1	0.0	0.8	0.5	1.4	1.3	97.7	98.2	2.3	1.8	-0.5
acetic acid	0.0	0.0	0.1	0.0	0.9	0.5	1.8	1.6	97.3	97.8	2.7	2.2	-0.6
propanoic acid	0.0	0.0	0.1	0.1	1.4	0.9	2.9	2.6	95.5	96.5	4.5	3.5	-1.0
butanoic acid	0.0	0.0	0.3	0.2	6.9	3.9	11.5	10.3	81.3	85.5	18.7	14.5	-4.2
2-methylpropanoic acid	0.0	0.0	0.3	0.3	7.4	4.5	10.4	9.4	81.8	85.8	18.1	14.2	-3.9
2-methylbutanoic acid	0.0	0.0	0.3	0.2	6.6	3.6	11.7	10.5	81.5	85.7	18.5	14.3	-4.2
n-pentanoic acid	0.0	0.0	0.3	0.2	6.9	3.8	12.3	11.1	80.5	84.9	19.4	15.0	-4.4
3-methylbutanoic acid	0.0	0.0	1.0	0.7	24.1	16.3	24.0	24.7	50.9	58.2	49.1	41.7	-7.3
hexanoic acid	0.2	0.2	3.6	2.8	58.2	51.0	24.0	30.3	13.9	15.7	85.8	84.1	-1.7
octanoic acid	0.0	0.0	0.4	0.3	8.8	5.1	13.7	12.5	77.1	82.1	22.9	17.9	-4.9

(Continues)

Table 4. (Continued)

Values in %	Discarded head		Recycled head		Heart		Recycled tail		Residue		Heart + recycled fractions		Difference 0.67-0.60
	0.60	0.67	0.60	0.67	0.60	0.67	0.60	0.67	0.60	0.67	0.60	0.67	
Terpenes													
d-limonene	55.1	52.0	44.1	46.7	0.8	1.2	0.0	0.0	0.1	0.1	44.9	48.0	3.1
α -pinene	49.6	47.3	48.9	50.9	1.5	1.8	0.0	0.0	0.0	0.0	50.4	52.7	2.3
β -pinene	28.2	27.4	54.9	57.2	16.9	15.4	0.0	0.0	0.0	0.0	71.8	72.6	0.8
myrcene	47.6	45.3	50.5	52.4	1.9	2.3	0.0	0.0	0.0	0.0	52.4	54.7	2.3
a-phellandrene	18.7	18.2	47.1	49.6	34.2	32.1	0.0	0.0	0.0	0.0	81.3	81.8	0.5
terpinolene	48.7	45.0	49.9	51.7	1.4	3.4	0.0	0.0	0.0	0.0	51.3	55.0	3.8
citral	2.7	2.7	22.9	19.3	74.3	77.1	0.2	0.9	0.0	0.0	97.3	97.3	0.0
linalool	23.9	23.1	69.1	62.5	7.0	14.4	0.0	0.0	0.0	0.0	76.1	76.9	0.8
α -terpineol	0.9	0.9	10.7	8.9	84.0	82.3	4.3	7.8	0.1	0.1	99.0	99.0	0.0
linalool oxide	1.1	1.1	13.2	10.9	83.9	83.3	1.8	4.6	0.0	0.0	98.9	98.9	0.0

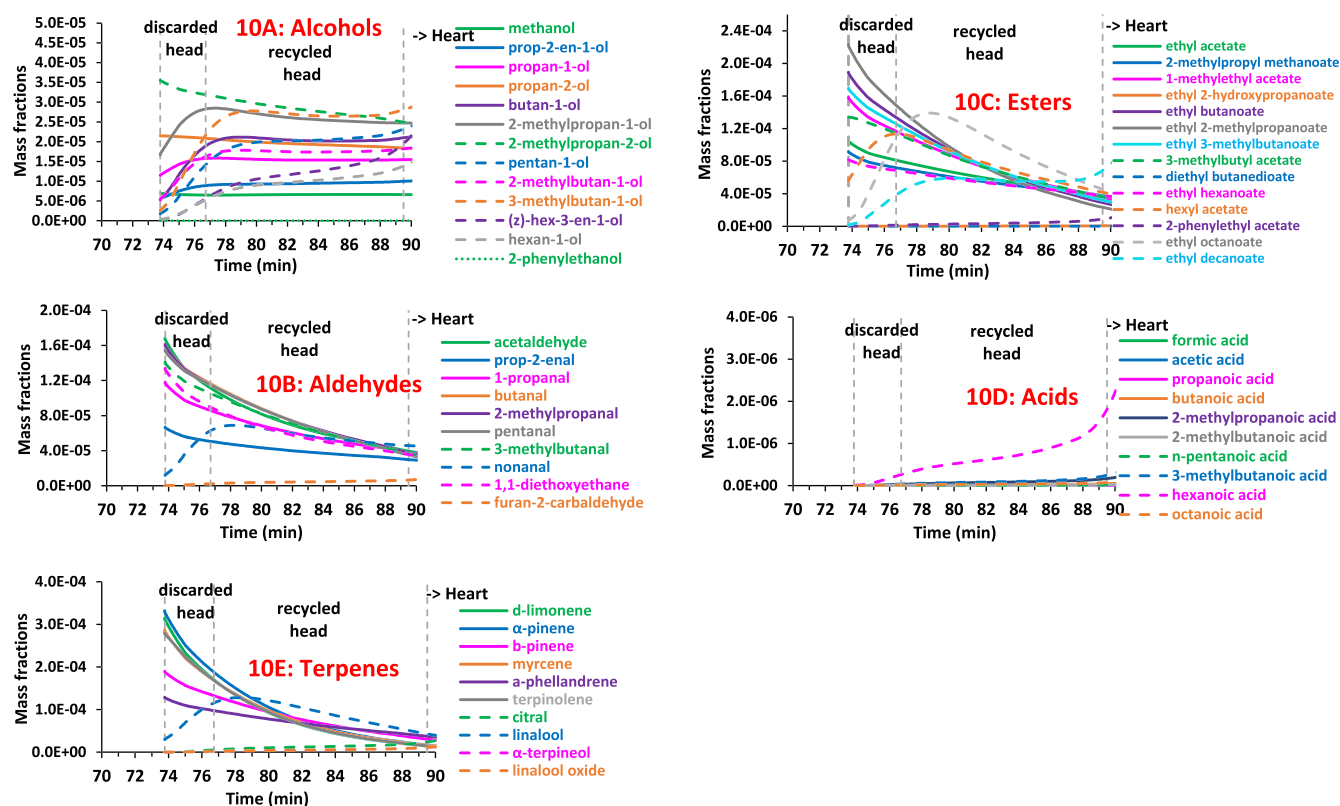


Figure 10. Behaviour of the volatile alcohols (A), aldehydes (B), esters (C), acids (D) and terpenes (E) during the head fraction extraction of Ergaster distillery distillation. [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

Optimisation of the distillation process at Ergaster distillery

The above study observed the different behaviours of volatile compounds based on the different ethanol concentration profiles. Accordingly, several strategies could be explored to optimise the distillation process in order to recover more of the compounds of interest.

Influence of ethanol concentration at the end of the tail fraction. Here, the focus was on stopping the distillation later to potentially increase the recovery of pleasant compounds (2-

phenylethanol and ethyl 2-hydroxypropanoate) that are partially lost in the residue without increasing the content of unpleasant compounds (diethyl butanedioate and acids).

The distillation end condition for the new simulations was an ethanol mass fraction in the distillate of 0.061 (7.6% v/v) (for the wash one) and 0.020 (2.5% v/v), instead of 0.105 (13% v/v). The same simulation parameters were considered, and no additional steps were introduced other than stopping the distillation at a lower ethanol mass fraction (see Table 3). The overall distillation time increased from 341 to 369 minutes (+ 8.2%) for the wash

Table 5. Partition of compounds as a mass percentage across the five fractions of the simulated distillations with a plateau of the ethanol mass fraction of the heart at 0.60 and a peak of ethanol at the beginning

Values in %	Discarded head		Recycled head		Heart		Recycled tail		Residue		Heart + recycled fractions		Difference with peak- without peak
	Peak	Peak	Peak	Peak	Peak	Peak	Peak	Peak	Peak	Peak	Peak		
ethanol	1.2	1.2	8.3	8.3	74.3	74.3	12.0	12.0	4.2	4.2	94.6	94.6	0.0
Alcohols													
methanol	0.5	0.7	4.7	4.8	57.6	57.1	18.0	18.1	19.2	19.3	80.3	80.0	-0.3
prop-2-en-1-ol	0.8	0.6	7.0	4.9	71.2	73.5	14.1	14.1	6.9	6.9	92.3	92.5	0.2
propan-1-ol	1.7	1.2	11.4	9.2	79.3	82.1	6.3	6.2	1.3	1.3	97.0	97.6	0.6
propan-2-ol	2.7	2.2	14.0	14.8	79.3	79.0	3.6	3.5	0.5	0.5	96.8	97.3	0.5
butan-1-ol	2.4	1.0	15.0	9.0	79.8	87.2	2.6	2.6	0.2	0.2	97.4	98.8	1.4
2-methylpropan-1-ol	3.7	1.9	18.9	15.2	76.4	82.0	0.9	0.9	0.0	0.0	96.3	98.1	1.8
2-methylpropan-2-ol	4.7	3.9	19.9	23.3	74.6	72.0	0.8	0.7	0.0	0.0	95.3	96.1	0.8
pentan-1-ol	2.3	0.7	16.0	7.2	79.8	90.1	1.9	1.8	0.1	0.1	97.6	99.2	1.6
2-methylbutan-1-ol	1.9	0.9	13.1	8.0	80.6	86.7	4.0	4.0	0.5	0.5	97.7	98.7	1.0
3-methylbutan-1-ol	3.5	1.1	19.7	10.1	76.1	88.1	0.7	0.7	0.0	0.0	96.5	98.9	2.5
(z)-hex-3-en-1-ol	1.8	0.4	14.2	4.4	81.0	92.2	2.9	2.9	0.2	0.2	98.1	99.4	1.4
hexan-1-ol	1.0	0.3	9.2	3.2	78.1	84.8	9.5	9.5	2.1	2.2	96.9	97.5	0.7
2-phenylethanol	0.0	0.0	0.2	0.0	8.0	8.0	18.9	19.2	72.8	72.7	27.2	27.2	0.0
Aldehydes													
acetaldehyde	11.9	16.6	35.5	45.8	52.6	37.6	0.0	0.0	0.0	0.0	88.1	83.4	-4.7
prop-2-enal	7.1	10.0	24.9	33.8	67.7	56.0	0.2	0.2	0.0	0.0	92.9	90.0	-2.9
1-propanal	12.8	16.3	37.3	48.1	49.9	35.5	0.0	0.0	0.0	0.0	87.2	83.7	-3.5
butanal	22.1	20.3	50.8	61.8	27.1	17.9	0.0	0.0	0.0	0.0	77.9	79.7	1.9
2-methylpropanal	20.0	20.9	48.4	59.2	31.7	19.9	0.0	0.0	0.0	0.0	80.0	79.1	-0.9
pentanal	23.8	16.0	53.3	62.7	22.9	21.3	0.0	0.0	0.0	0.0	76.2	84.0	7.8
3-methylbutanal	20.5	17.2	49.3	60.5	30.2	22.3	0.0	0.0	0.0	0.0	79.5	82.8	3.3
nonanal	11.1	3.0	40.2	24.3	48.7	72.7	0.0	0.0	0.0	0.0	88.9	97.0	8.1
1,1-diethoxyethane	9.3	14.0	29.7	39.4	60.9	46.7	0.0	0.0	0.0	0.0	90.7	86.0	-4.6
furan-2-carbaldehyde	0.3	0.1	4.3	1.4	60.0	62.7	20.8	20.9	14.6	14.9	85.1	85.0	-0.1
Esters													
ethyl acetate	14.3	14.8	40.6	51.8	45.1	33.4	0.0	0.0	0.0	0.0	85.7	85.2	-0.5
2-methylpropyl methanoate	12.4	13.2	37.6	48.3	50.0	38.5	0.0	0.0	0.0	0.0	87.6	86.8	-0.7
1-methylethyl acetate	24.1	17.1	53.1	63.1	22.8	19.8	0.0	0.0	0.0	0.0	75.9	82.9	7.1
ethyl 2-hydroxypropanoate	0.1	0.0	1.1	0.2	25.4	25.7	23.6	23.8	49.9	50.3	50.1	49.7	-0.4
ethyl butanoate	30.1	17.6	56.0	65.8	13.9	16.7	0.0	0.0	0.0	0.0	69.9	82.4	12.5
ethyl 2-methylpropanoate	36.5	19.0	56.3	67.0	7.2	14.0	0.0	0.0	0.0	0.0	63.5	81.0	17.5
ethyl 3-methylbutanoate	27.6	14.2	55.7	62.6	16.7	23.1	0.0	0.0	0.0	0.0	72.4	85.8	13.3
3-methylbutyl acetate	23.3	10.7	52.7	56.4	24.0	32.9	0.0	0.0	0.0	0.0	76.7	89.3	12.6
diethyl butanedioate	0.0	0.0	0.2	0.0	5.8	5.6	10.8	10.9	83.2	83.4	16.8	16.6	-0.2
ethyl hexanoate	12.2	8.7	37.9	45.2	50.0	46.1	0.0	0.0	0.0	0.0	87.8	91.3	3.5
hexyl acetate	21.7	6.1	53.9	40.8	24.4	53.1	0.0	0.0	0.0	0.0	78.3	93.9	15.6
2-phenylethyl acetate	1.2	0.3	14.7	3.1	83.0	95.7	1.1	1.0	0.0	0.0	98.8	99.7	0.9
ethyl octanoate	43.8	4.5	53.4	28.6	2.8	66.9	0.0	0.0	0.0	0.0	56.2	95.5	39.3
ethyl decanoate	46.1	3.2	52.1	19.9	1.8	77.0	0.0	0.0	0.0	0.0	53.9	96.8	42.9
Terpenes													
d-limonene	55.1	21.6	44.1	68.1	0.8	10.3	0.0	0.0	0.1	0.1	44.9	78.4	33.5
α -pinene	49.6	27.4	48.9	66.6	1.5	6.0	0.0	0.0	0.0	0.0	50.4	72.6	22.2
β -pinene	28.2	22.0	54.9	65.7	16.9	12.3	0.0	0.0	0.0	0.0	71.8	77.9	6.2
myrcene	47.6	23.2	50.5	67.8	1.9	8.9	0.0	0.0	0.0	0.0	52.4	76.8	24.4
α -phellandrene	18.7	16.9	47.1	58.6	34.2	24.5	0.0	0.0	0.0	0.0	81.3	83.1	1.9
terpinolene	48.7	12.5	49.9	57.9	1.4	29.6	0.0	0.0	0.0	0.0	51.3	87.5	36.3
citral	2.7	0.6	22.9	5.9	74.3	93.4	0.2	0.1	0.0	0.0	97.3	99.4	2.1
linalool	23.9	4.4	69.1	30.0	7.0	65.6	0.0	0.0	0.0	0.0	76.1	95.6	19.5
α -terpineol	0.9	0.2	10.7	2.6	84.0	92.8	4.3	4.3	0.1	0.1	99.0	99.6	0.6
linalool oxide	1.1	0.3	13.2	3.1	83.9	94.9	1.8	1.7	0.0	0.0	98.9	99.7	0.8

and to 422 minutes (+ 14.3%) for the second simulation to reach an ethanol mass fraction of 0.061 and 0.020, while the ethanol recovery only increased by 2.0% and 1.7% and the water collected increased by 27.4% and 42.0%. With regard to the aroma compounds, the recovery of 2-phenylethanol and 2-hydroxypropanoate increased by 24% and 14% from the 0.105-distillation to the 0.061-distillation and 33% and 19% for the 0.02-distillation. Unfortunately, these increases are small compared to the increase in the recovery of unpleasant compounds as diethyl butanedioate and acids, suggesting it is not advantageous to push distillation too far.

However, before any definitive conclusion can be made, it would be wise to use the initial concentrations of the different compounds. This would enable the actual quantities that can be recovered and the relevance of the compromises between the recovery of the compounds of interest and those which are unwanted. This analysis would also need to consider the cost of energy since the distillation would be longer to obtain a low ethanol concentration, together with a greater recycling of water when recycling the tail fraction.

Determination of the best ethanol concentration during the heart extraction. A key question was running a distillation during the heart distillation step with an ethanol mass fraction of 0.67 (75% v/v) and another at around 0.60 (67% v/v). The advantages and disadvantages of each of these factors was evaluated in terms of distillation time, recovery of aroma compounds in the heart and energy consumption.

The idea was to simulate distillation at the Ergaster distillery with a lower ethanol concentration and observe the differences. However, as the simulation module was too complex and inflexible, it did not have the predictive quality required. Therefore, it was decided to construct a much simpler and more flexible simulation based on the study conducted with the laboratory column.

For both cases (high and low ethanol concentration), the same process was considered (a column with seven theoretical stages in total with an efficiency of 0.5 for the intermediate trays). The initial solution was with the laboratory column, with 1503 g with an ethanol mass fraction of 0.06106 and the same volatile compounds with the same mass fraction of 10^{-6} . After the filling phase, four major steps were considered for each simulation: discarded head, recycled head, heart and tail with ethanol extraction yield of 1.2, 8.3, 74.3 and 12.0%. For these steps and for both simulations, the same heating power of 375 W was used. To obtain different ethanol mass fraction plateaux (0.60 or 0.67), only the reflux rate was modified from one case to another. The ethanol content profiles of the distillate are shown in Figure 9.

Changes over time of the mass fractions of the different compounds (not shown) remain almost the same for both distillations as the same process was used and only the reflux rate was different. The small differences in values are due to the difference in the profile of ethanol concentration and the volatility of the compounds. These profiles are like those from the Ergaster distillation, other than the profile from the distillation of the head fraction. This difference is due to the ethanol peak at the beginning of the Ergaster distillation, where it was preferred to keep a constant ethanol concentration from the beginning of the run.

The percentage recovery of the volatile compounds in the fractions during the two distillations is detailed in Table 4. To highlight the differences, the recovery amounts of the compounds in the heart and in the recycled fractions for each distillation were calculated and the differences between high and low ethanol plateau

were estimated. There is almost no change in the alcohols, except for 2-phenylethanol where less is recovered during the distillation with a high ethanol plateau (-5.7%). For the aldehydes, there are also no significant differences. For the esters, ethyl 2-hydroxypropanoate and diethyl butanedioate, less is recovered during the distillation with a high ethanol plateau (-7.0% and -3.7%), while marginally more ethyl octanoate and ethyl decanoate are recovered (2.6% and 3.2%), together with some terpenes. Less acids are recovered, which is linked to their volatility profile and that distillation at higher ethanol concentration induces a lower extraction yields of acids.

Conducting the heart distillation step with different ethanol contents has an impact on the behaviour of volatile flavour compounds and their extraction in the heart and recycled fractions. The recovery of compounds such as 2-phenylethanol and ethyl 2-hydroxypropanoate are greater in the heart distillate at an ethanol mass fraction of 0.60 compared to 0.67. Most esters follow the same trend, but with small variations. Based on these results, distillation at lower ethanol concentrations is of more interest, as in addition to the higher recovery of desired compounds, this process has the advantage of being shorter and less energy intensive.

Peak in ethanol concentration at the beginning of distillation. In the case of the Ergaster distillery, the compounds in the head fractions have either an unpleasant or positive impact on quality. To identify the behaviour of the compounds during the distillation of the two head fractions (discarded and recycled), this was explored in more detail. Figure 10 shows the compounds that concentrate strongly in the first fraction including esters (except 3-methylbutyl acetate, diethyl butanedioate, ethyl hexanoate, hexyl acetate, 2-phenylethyl acetate, ethyl octanoate and ethyl decanoate), aldehydes (except nonanal and furan-2-carbaldehyde) and terpenes (except linalool, linalool oxide).

It would be of interest to increase the concentration of these highly volatile compounds so as to reduce the volume of the first discarded fraction and reduce the loss of interesting compounds. The laboratory column distillation, with the sharp increase in ethanol concentration at the beginning, shows that it is possible to reduce in the discarded head fraction, alcohols, esters (except ethyl acetate, 2-methylpropyl acetate and terpenes), while increasing the extraction of aldehydes (Figures 4B, 5B, 6B and 8B). Consequently, we tested by simulation the creation of an ethanol concentration peak at the beginning of the distillation (Figure 9) and calculated the distribution of the compounds in the different fractions by imposing the same ethanol proportion in each one (1.2, 8.3, 74.3 and 12.0%). Table 5 shows that the creation of the peak, under the conditions tested, reduces the recovery of some aldehydes but increases the recovery of pleasant esters such as ethyl octanoate and decanoate (~+40%) and terpenes such as d-limonene, terpinolene, myrcene and α -pinene (>+30%). This suggests that it would be advantageous for ethanol to concentrate at the beginning of the distillation with circulation of a moderate flow of cold water (which increases the reflux rate) until the end of the filling phase. This would create a greater gap in concentrations between aldehydes and esters.

Conclusions

Simulation of 57 volatile flavouring compounds belonging to five chemical families (alcohols, aldehydes, esters, acids, and terpenes) may have different behaviours and consequently partition in the head, heart and tail fractions, according to the batch distillation

process. These differences were explained by the variations in volatility of the compounds with the ethanol concentration of the boiling liquid.

This work showed that there is no advantage to push the distillation process too far as the recovery of unpleasant compounds (acids) increases together with increased energy consumption, distillation time and the amount of water recovered in the distillate. Further a distillate with an ethanol mass fraction of the heart of 0.60 (67% v/v) is more advantageous than at 0.67 (75% v/v) in the recovery of the flavour compounds of interest and energy cost. Finally, there is an interest in creating a peak of ethanol concentration at the beginning of the distillate extraction to promote a greater difference in the volatility between the required compounds and those whose concentration should be limited.

The work reported here provides a better understanding of the behaviour of volatile flavour compounds during multi-stage discontinuous distillation. This process, mostly developed in fruit spirit production and by small distilleries, offers possibilities for the separation and recovery of compounds due to the flexibility of operating modes. It also clearly illustrates the value of simulation processes in distilling research and industry.

Author contributions

Martine Esteban-Decloux - conceptualisation, methodology, investigation, data curation, writing (review and editing), supervision, project administration, funding acquisition. N'Guessan Romaric Tano - methodology, investigation, writing (original draft). Hervé Grangeon - methodology, investigation.x

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