Received: 15/12/2022 Revised: 17/04/2023 Accepted: 06/06/2023 Published: 06/10/2023

ORIGINAL ARTICLE
DOI 10.58430/jib.v129i3.28

INSTITUTE OF BREWING & DISTILLING

Behaviour of volatile compounds during batch multi-stage distillation of whisky: experimental and simulation data

• Martine Esteban-Decloux[1] • Hervé Grangeon[2]
• N'Guessan Charles Romaric Tano[1]

[1] Université Paris-Saclay, INRAE, AgroParisTech, UMR SayFood, 91120 Palaiseau, France
[2] Ergaster distillery, 1, Avenue du Parc F-60400 PASSEL, France

martine.decloux@agroparistech.fr

This is an open access article distributed under the terms of the creative commons attribution-non-commercial-no-derivatives license (http: // creativecommons.org/licenses/by-nc-nd/4.0/), which permits non-commercial re-use, distribution, and reproduction in any medium, provided the original work is properly cited, and is not altered, transformed or built upon in any way.

Abstract

This study characterised the behaviour of congeners during the multi-stage discontinuous distillation of whisky using a Stupfler-type still. It investigated the influence of recycling the head and tail fractions on the composition of the unaged spirit and, for the compounds with known equilibrium data, to validate the capability of software tools to simulate their behaviour during distillation. To this end, profile curves of ethanol (% ABV) and 45 aroma compounds (mg/L) during distillation are reported, with 27 compounds compared to simulated data using ProSim® BatchColumn software. Further, the mass distribution of each compound in the fractions of discarded head, recycled head, heart, tail and residue are estimated. Assuming that this distribution was maintained during each distillation, it was shown that for the wash, a pseudo-steady state was achieved in less than five distillations with the true recovery rate of each compound in the heart assessed. This study demonstrates that during distillation, the congeners behave according to the ethanol content of the boiling liquid in the column. It provides information on the separation of volatile compounds in a batch still with a distillation column above the heater. Additionally, the data highlights the importance to the unaged spirit of recycling the head and tail fractions. These results provide useful information for distillers to choose the appropriate way of collecting the heart fraction.

Keywords:

Batch distillation, simulation, whisky, volatile compounds, aroma compounds

© 2023 Institute of Brewing & Distilling

Introduction

In the spirits industry, understanding the behaviours of volatile flavouring compounds (congeners) during distillation is important (Luna et al. 2019). Batch distillation performed in a column is commonly used to produce fruit spirits (Spaho 2017), which allows, the production of unaged spirit in a single run from the fermented mash ('wash'). The distillate is split into three fractions: head, heart and tail. The head and tail fractions are fully or partially recycled in the following distillation.

Most studies in the literature relate to laboratory scale multi-stage batch distillation of spirits and compare the effect of different operating conditions on the composition of the heart fraction. Recently, Esteban-Decloux et al (2022) reported a laboratory- and industrial-scale study (750 L boiler) to analyse, by simulation, the behaviour of 57 congeners from five chemical families (alcohols, aldehydes, esters, acids, and terpenes) at the same initial mass fraction of 10^{-6}. The results of this study were qualitative as it did not consider the composition of the solution loaded into the boiler.

Further, most studies do not consider the total or partial recycling of the head and tail fractions from the previous distillation. Da Porto et al (2010) considered the single recycling of the head and tail fractions during the steam distillation of grappa and Esteban-Decloux et al (2021) conducted pilot plant experiments to study the influence of recycling heads and tails in the double batch distillation of cider. With the limited number of experimental distillations in both studies, a steady state was unlikely to be reached.

This study was devised to compensate for the limits of the previous reports. Here, the composition of the solution loaded into the boiler (wash + recycled fractions) is considered. The objectives are (i) to compare the experimental concentration of the distillate over time with those from the simulation and (ii) to quantify the evolution of heart fraction compounds with the number of successive distillations with recycling.

Materials and Methods

Initial boiler load

The wash was obtained from an all-malt barley wort fermented with a distilling yeast. The fermentation (100 h cycle time) was performed by the Uberach brewery in Alsace, France. 656.3 L (at 20°C) of wash was loaded into the boiler. The density, measured with an Anton Paar density meter® DMA 35, was 997.3 g/L at 20°C with an alcoholic strength by volume at 20°C or ABV (Alcohol by Volume) of 7.54% v/v after a laboratory distillation with an Anton Paar density meter® DMA 4500. Ignoring dissolved solids, this is equivalent to an ethanol mass fraction of 0.06016, a density of 987.8 g/L at 20°C and a mass of 648.2 kg (Table 1). To this were added water (31.42 L at 40°C (31.16 kg)) previously used to flush the system and 33.23 kg mixture of the head and tail fractions from the previous distillation (35.07% ABV). Overall, considering only the volatile molecules, the initial solution weighed 712.62 kg with an ethanol mass fraction of 0.06833. This data was used for the simulation and the material balance calculations.

Distillation equipment

The distillation used a Stupfler® type column still made of copper (Figure 1). In this set-up, the three main parts include: (1) direct fired boiler; (2) packed column (height 1.3 m and diameter 0.3 m) with reflux by a coiled cold-water flow in the packing. Below the column, a level control system limits the amount of liquid by sending any excess back into the boiler and (3) a total condenser consisting of a coil immersed in about 1000 L of water. Leaving the condenser, the distillate flows through a beaker with temperature sensor and alcoholometer before being collected in tanks.

Distillation of whisky

Different parameters were monitored over time including pressure and volume of the heating gas, the flowrate, inlet and outlet temperatures of the water, the temperature at different locations of the distillation (dome of the boiler, bottom and top of the column), and the mass and ethanol content of the distillate, using a scale and Anton Paar density

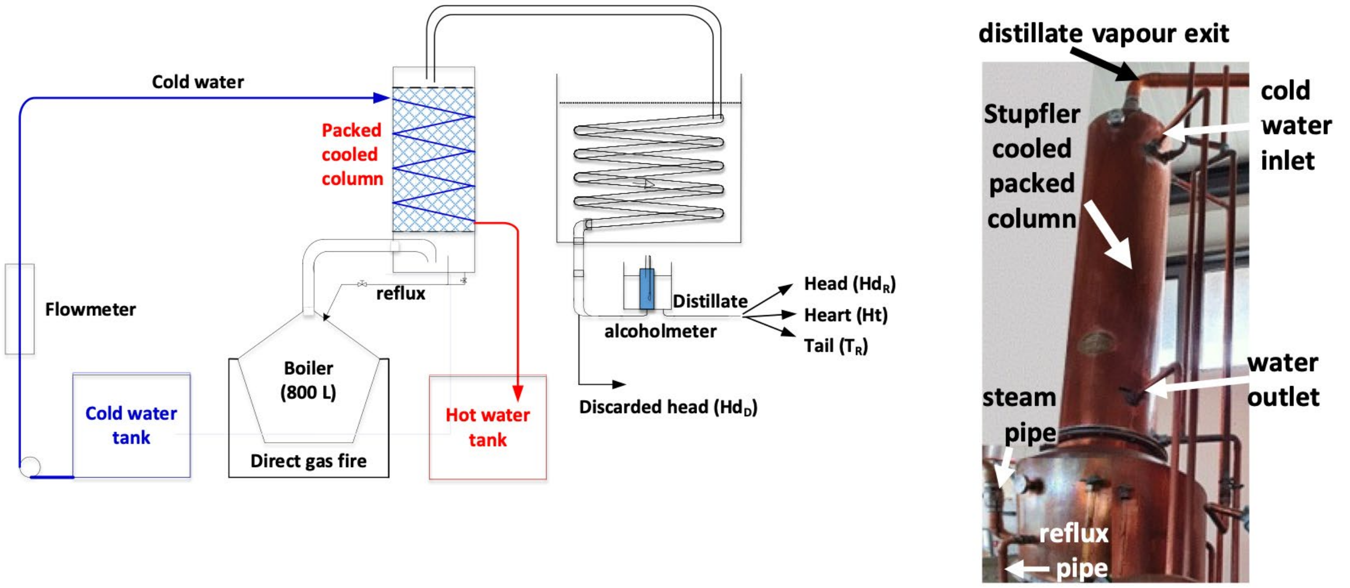
Table 1.

Mass balance of the initial boiler load.

	raw wash	wash with only volatile molecules	rinse water	Recycled head + tail	Boiler considering only volatile compounds
mass (kg)		648.23	31.16	33.23	712.62
ρ at 20 °C (kg/L)	0.99730	0.98776	0.99820	0.95548	0.98649
V (L at 20 °C)	656.26	656.26	31.22	34.78	722.38
ABV (% v/v)	7.54	7.54	0.0	35.07	8.53
Ethanol volume (L at 20°C)	49.50	49.50	0.0	12.20	61.70
Ethanol mass fraction		0.06016	0.00000	0.28975	0.06833
Ethanol mass (kg)	39.06	39.06	0.0	9.63	48.69

Figure 1.

Ergaster distillation column.



meter® DMA 45. Due to the pipeline connection, the final mass of the residue could not be determined. Duration and operating parameters (gas pressure and cold-water flow) are shown in Figure 2.

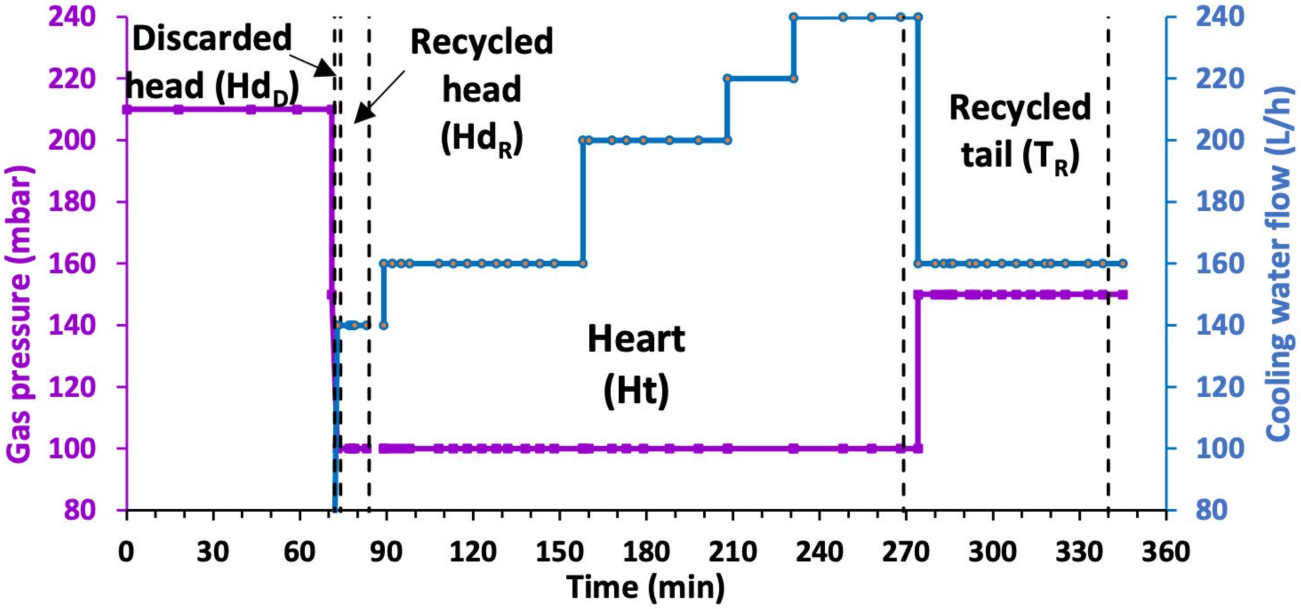
After heating and filling the column, the distillate was separated into several fractions. At the beginning of the head distillation, the first litre (Hd_D) was discarded, then about 6 L of the head collected before the heart distillation step. The choice of the cut was made by the distiller according to sensory criteria. The second part of the head fraction (Hd_R) and the tail fraction (T_R) were recovered and recycled to the boiler for the next distillation. During the heart distillation (Ht), constant heating power was maintained (through 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 increased the condensation in the column and the reflux rate, ensuring a better separation of compounds, which declined over time. The choice between the heart and the tail fractions was made from two parameters (i) high flow rate of the cooled water resulting in a low distillate flow rate and (ii) notes of overripe fruit mixed with leather in the distillate.

Measurement of ethanol content

The ethanol content of distillates was measured using an Anton Paar density meter® DMA 4500 at 20°C, with an accuracy of ± 0.00005 g/mL. Outputs were the density of the solution, temperature and

Figure 2.

Distillation parameters.



% ABV. To obtain the mass balance and calculate concentrations for the simulation, ethanol mass fractions were determined from density measurements using the mathematical model reported by the International Organization of Legal Metrology (1975).

Analysis of volatile compounds

The samples were sent to the BNIC (Bureau National Interprofessionnel du Cognac) laboratory for analysis by GC-FID (Gas Chromatography – Flame Ionisation Detector).

For the main compounds (higher alcohols, aldehydes, esters), the samples were adjusted to 40 or 70% v/v depending on ABV and related calibrations. 4-methylpentan-2-ol (CAS 108-11-2) at 28 g/L in absolute alcohol was used as an internal standard. The analysis was performed using gas chromatography (Agilent 7890A) equipped with a flame ionisation detector and a polar chromatographic column (CPWax 57 CB, 50 m x 0.25 mm, 0.25 µm). Hydrogen was the carrier gas with a flowrate of 1.4 mL/min. The detector flame was maintained with a constant flow of hydrogen and compressed air at 30 mL/min and 320 mL/min, respectively. The injector and detector were set to 220°C. Sample (0.4 µL) was injected in split mode (25:1 ratio). The oven temperature was maintained at 35°C for the first 5 minutes and increased by 4°C per minute until 220°C. This temperature was maintained for 10 minutes. Compounds were identified by comparing their retention times to those of standards. Calibration was established from standard solutions in hydroalcoholic mixtures at 40 and 70% (v/v).

After adjustment of samples to 40% ABV, volatile fatty acids were extracted from 25 mL with 4 mL of 50/50 dichloromethane/hexane. Three internal standards (4-methylpentanoic acid, undecanoic acid, heptadecanoic acid) at 600 mg/L in the extraction solvent were added (200 µL). A reference solution prepared with analytical standards in a hydroalcoholic mixture at 40% v/v, as well as an internal control (brandy at 70% v/v) were included from the extraction phase to validate the procedure. After extraction, the GC analysis was performed using an Agilent 6890N equipped with a flame ionisation detector. The device had a polar capillary column type STABILWAX (30 m x 0.25 mm, 0.25 µm) coupled with a column type RTX1 (15 m x 0.25 mm, 0.25 µm) on the detector side. The latter was added to allow better separation of acids. Hydrogen, the carrier gas was used at a flow rate of 1.4 mL/min. The flame of the detector was maintained by a constant flow of hydrogen and compressed air.

The injector and detector were at 250°C, with sample (0.5 µL) injected in splitless mode. The oven temperature was maintained at 45°C for 1 min, then increased by 15°C per minute until 80°C and 4°C per minute until 250°C, which was maintained for 15 min. The compounds were identified by comparing their retention times to those of reference solutions.

Pre-treatment of wash for analysis

Since the wash contains particles and insoluble solutes, a pre-treatment was necessary. First a known mass of wash (m_{wash}) was taken. Its density was measured at 20°C (ρ_{wash}) in order to determine its volume at 20°C (V_{wash}). This mass of wash was determined by ensuring that all ethanol had been collected in distillate (D1) with a quantified mass (m_{D1}). Its density at 20°C (ρ_{D1}), ethanol content (ABV_{D1}) and the concentration of all volatile compounds ($x_{i\text{-}D1}$) were measured. Thus, it was possible to determine the volume of ethanol in D1 ($V_{Eth\text{-}D1}$) equivalent to that of the wash used ($V_{Eth\text{-}wash}$), and therefore the ethanol content of the wash (ABV_{wash}) as % v/v. Knowing that in simulation, it is not possible to take into account dissolved dry matter and it is necessary to have mass or molar fractions of the compounds, from the ABV_{wash}, its density at 20°C ($\rho_{wash\text{-}only\text{-}volatiles}$) and its mass ($m_{wash\text{-}only\text{-}volatiles}$) without dissolved matter other than volatile compounds were deduced.

Then, distillate (D2) with a known composition was taken. This distillate D2 was diluted to the same ABV as the wash and distilled (D3). Knowing the masses of D2 used (m_{D2}) and D3 (m_{D3}), as well as the analysis of the compounds in both solutions ($x_{i\text{-}D2}$) and ($x_{i\text{-}D3}$), a recovery factor (F_i) of the laboratory distillation (equation 1) was calculated for each compound *i*, as well as the initial mass present in the wash ($m_{i\text{-}wash}$) (equation 2), and therefore the mass fraction of each compound without taking into account non-volatile compounds ($x_{i\text{-}wash}$) (equation 3):

$$F_i = \frac{m_{D3} * x_{i-D3}}{m_{D2} * x_{i-D2}} \qquad \text{(Eqn.1)}$$

$$m_{i-wash} = \frac{m_{D1} * x_{i-D1}}{F_i} \qquad \text{(Eqn.2)}$$

$$x_{i-wash} = \frac{m_{i-wash}}{m_{wash-only-volatiles}} \qquad \text{(Eqn.3)}$$

Simulation of the distillation

ProSim® BatchColumn software was used for simulation 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 with the exception of the acids whose gas phase was represented by an association model, as suggested previously (Esteban-Decloux et al. 2014; Puentes et al. 2018a, b). The NRTL coefficients were obtained from the database with checking of consistency of the selected coefficients (Esteban-Decloux et al. 2014; Puentes et al. 2018b; Douady et al. 2019).

The construction of the simulation modules aimed to represent the evolution over time of the mass and the ethanol mass fraction of the distillate. The simulation module consisted of a boiler, a column and a total condenser. The boiler and condenser had an efficiency of 1. The column was represented by 13 plates: 12 plates having an efficiency of 0.8 and a retention of 0.25 L to represent the packed column, and 1 plate having 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 bubbles into the volume of liquid coming down from the packed column. The flow in the condenser (coil immersed in water) is piston-like, but, in the simulation, the condenser is defined as a theoretical stage with perfect mixing. Accordingly, the volume of condenser (0.1 L) was chosen and the time between the exit of the vapour from the top of the column and the arrival of the distillate liquid into the alcoholmeter was determined according to the distillate flow. The pressure was set to 1 atm and any pressure drop was neglected. Heat losses were considered along the column to represent the cold water circulation and the losses through the wall.

Results and discussion

Volatile compounds in the wash and boiler

As compounds can have different names, each molecule is reported with its CAS number (Chemical Abstracts Service) and IUPAC name (International Union of Pure and Applied Chemistry) followed by the common name in italics. The concentrations of the main volatile compounds quantified in the wash and the recycled solution from the previous distillation (Hd_R+T_R) are shown in Table 2. Considering the respective masses of the wash and the recycled solution, the composition of the solution loaded into the boiler was calculated. Table 2 also reports the molecules that could be simulated as well as their mass fraction in the boiler.

For the wash, the main compounds are the higher alcohols (3-methylbutan-1-ol, 2-methylpropan-1-ol, propan-1-ol and 2-methylbutan-1-ol). 2-phenylethanol is also concentrated while methanol was at a very low concentration. The two main esters were ethyl acetate and ethyl 2-hydroxypropanoate (ethyl lactate). With ethyl acetate, return of the recycled solution leads to a sharp increase in the concentration in the boiler. The concentration of acetic acid is suggested by the BNIC laboratory to be a concern. The recycled fraction, although highly concentrated in some compounds, does not necessarily result in an increase in concentration in the boiler. This reflects the dilution by the addition of rinse water (31.2 L) and recycled fractions (34.8 L).

Distillation balance

The distillate mass and ethanol content were monitored over time. From these data, the ethanol balance during the distillation was established (Table 3). The total distillate mass was 88.83 kg with partition as ollows: discarded head (HdD), 0.9%- recycled head (HdR), 5.7%- heart (Ht), 60.5%- and recycled tail (TR), 32.9%. In the distillate 95.0% of the initial ethanol content was recovered.

Table 4 presents the balance calculated for each volatile compound, based on the sum of fifteen samples whose mass and composition were measured. For some compounds (meso-2,3-butanediol, ethyl formiate and some acids), the figures are not reliable due to laboratory difficulties. On the other hand, it is normal that 2-phenylethanol, 2-hydroxypropanoate, diethyl butanedioate, furan-2-carbaldehyde and acetic and propanoic acids are not 100% recovered in distillate fractions as these compounds are of low volatility and remain in the residue or waste (W) (Douady et al. 2019; Esteban-Decloux et al. 2022).

Table 2.

Composition of the wash, recycled head and tail mixture ($Hd_R + T_R$) and the solution loaded in the boiler with an indication if the compound is considered for simulation and its mass fraction.

CAS	Compound	wash	Hd_R+T_R	Boiler	Sim	X_{boiler}
64-17-5	Ethanol (% v/v)	7.54	37.33	8.53	yes	0.0683
			Alcohols (mg/L)			**mass fraction**
67-56-1	methanol	4.49	22.01	5.10	yes	5.17E-6
71-23-8	propan-1-ol *(propanol)*	50.99	183.22	54.70	yes	5.55E-5
71-36-3	butan-1-ol *(butanol)*	0.98	3.05	1.03	yes	1.04E-6
78-83-1	2-methylpropan-1-ol *(isobutanol)*	59.09	266.61	66.01	yes	6.69E-5
137-32-6	2-methylbutan-1-ol *(active amyl alcohol)*	44.81	190.97	49.51	yes	5.02E-5
123-51-3	3-methylbutan-1-ol *(isoamyl alcohol)*	112.76	386.28	120.06	yes	1.22E-4
111-27-3	hexan-1-ol *(hexanol)*	0.30	0.56	0.29	yes	2.99E-7
60-12-8	2-phenylethanol	75.77	141.84	75.01	yes	7.60E-5
513-85-9	levo-2,3-butanediol	1.80	2.63	1.75		1.77E-6
5341-95-7	meso-2,3-butanediol	0.27	0.91	0.28		2.88E-7
107-18-6	prop-2-en-ol *(allyl alcohol)*	0.00	0.00	0.00	yes	0.0E+0
100-51-6	2-phenylmethanol	0.00	0.00	0.00		
78-92-2	butan-2-ol	0.00	0.00	0.00		
928-96-1	(z)-hex-3-en-1-ol	0.00	0.00	0.00	yes	0.0E+0
			Esters (mg/L)			
141-78-6	ethyl acetate	567.21	7543.44	873.66	yes	8.86E-4
97-64-3	ethyl 2-hydroxypropanoate *(ethyl lactate)*	121.88	438.13	130.76	yes	1.33E-4
105-54-4	ethyl butanoate *(ethyl butyrate)*	0.19	7.87	0.55	yes	5.57E-7
123-92-2	3-methylbutyl acetate *(isoamyl acetate)*	0.94	43.53	2.95	yes	2.99E-6
123-25-1	diethyl butanedioate *(diethyl succinate)*	1.96	9.95	2.24	yes	2.27E-6
123-66-0	ethyl hexanoate *(ethyl caproate)*	0.25	19.25	1.15	yes	1.17E-6
106-32-1	ethyl octanoate *(ethyl caprylate)*	0.63	39.27	2.45	yes	2.49E-6
110-38-3	ethyl decanoate *(ethyl caprate)*	0.41	12.98	0.99	yes	1.01E-6
110-19-0	2-methylpropyl acetate *(isobutyl acetate)*	0.41	11.15	0.90		
106-33-2	ethyl dodecanoate *(ethyl laurate)*	0.19	2.49	0.29		
109-94-4	ethyl formiate *(ethyl formate)*	0.60	6.23	0.84		

CAS	Compound	wash	Hd_R+T_R	Boiler	Sim	X_{boiler}
			Aldehydes (mg/L)			**mass fraction**
75-07-0	acetaldehyde *(ethanal)*	17.66	162.54	23.72	yes	2.4E-5
78-84-2	2-methylpropanal *(isobutanal)*	0.49	5.81	0.72	yes	7.3E-7
105-57-7	1,1-diethoxyethane *(acetal)*	12.14	63.10	13.96	yes	1.4E-5
98-01-1	furan-2-carbaldehyde *(furfural)*	1.72	17.50	2.39	yes	2.4E-6
30364-38-6	1,1,6-trimethyl-2H-naphtalene *(TDN)*	0.00	0.00	0.00		
			Acids (mg/L)			
64-19-7	acetic acid	873.00	1 150.00	841.00	yes	8.5E-4
79-09-4	propanoic acid	2.35	2.67	2.24	yes	2.3E-6
107-92-6	butanoic acid *(butyric acid)*	1.17	2.42	1.17	yes	1.2E-6
79-31-2	2-methylpropanoic acid *(isobutyric acid)*	4.81	13.27	4.96	yes	5.0E-6
503-74-2	3-methylbutanoic acid *(isovaleric acid)*	2.83	10.01	3.03	yes	3.1E-6
142-62-1	hexanoic acid *(caproic acid)*	1.90	8.50	2.12	yes	2.1E-6
124-07-2	octanoic acid *(caprylic acid)*	3.25	24.71	4.12	yes	4.2E-6
334-48-5	decanoic acid *(capric acid)*	1.22	8.82	1.52		
143-07-7	dodecanoic acid *(lauric acid)*	0.59	2.98	0.68		
544-63-8	tetradecanoic acid *(myristic acid)*	0.02	0.23	0.03		
57-10-3	hexadecanoic acid *(palmitic acid)*	0.22	2.62	0.33		
373-49-9	(Z)-hexadec-9-enoic acid *(palmitoleic acid)*	0.01	0.31	0.02		
57-11-4	octadecanoic acid *(stearic acid)*	0.02	0.09	0.02		
60-33-3	(9Z,12Z)-octadeca-9,12-dienoic acid *(linoleic acid)*	0.03	0.45	0.05		
109-52-4	pentanoic acid	0.00	0.00	0.00		
112-80-1	(Z)-octadec-9-enoic acid *(oleic acid)*	0.00	0.02	0.00		
463-40-1	(9Z,12Z,15Z)-octadeca-9,12,15-trienoic acid *(linolenic acid)*	0.00	0.01	0.00		

Table 3.

Global and ethanol mass balance.

	m (kg)	Distillate mass repartition	Ethanol mass fraction	ABV_{cal} (% v/v)	m_{Eth} (kg)	Ethanol yield	Ethanol repartition in distillate
Boiler	712.62		0.06833	8.53	48.69		
Discarded head (Hd_D)	0.80	0.9%	0.51344	59.26	0.41	0.8%	0.9%
Recycled head (Hd_R)	5.02	5.7%	0.78427	84.19	3.94	8.1%	8.5%
Heart (Ht)	53.79	60.5%	0.68139	75.28	36.65	75.3%	79.2%
Recycled tail (T_R)	29.22	32.9%	0.18016	22.18	5.26	10.8%	11.4%
Total Distillate	88.83				46.26	95.0%	

Table 4.

Experimental mass balance of the volatile compounds.

	m_{Boiler} (kg)	$\Sigma m_{Distillates}$ (kg)	$\frac{100*\Sigma m_{Distillates}}{m_{Boiler}}$		m_{Boiler} (kg)	$\Sigma m_{distillates}$ (kg)	$\frac{100*\Sigma m_{Distillates}}{m_{Boiler}}$
Alcohols				**Aldehydes**			
methanol	3.7E-3	3.4E-3	92.5%	acetaldehyde	1.7E-2	1.2E-2	69.9%
propan-1-ol	4.0E-2	4.1E-2	104.3%	2-methylpropanal	5.2E-4	5.7E-4	109.2%
butan-1-ol	7.4E-4	7.6E-4	102.5%	1,1-diethoxyethane	1.0E-2	9.0E-3	88.9%
2-methylpropan-1-ol	3.6E-2	3.5E-2	98.9%	furan-2-carbaldehyde	1.7E-3	1.5E-3	88.8%
2-methylbutan-1-ol	8.7E-2	8.6E-2	99.4%				
3-methylbutan-1-ol	4.8E-2	4.7E-2	98.6%				
hexan-1-ol	2.1E-4	1.4E-4	66.7%				
2-phenylethanol	5.4E-2	8.0E-3	14.7%	**Acids**			
Levo-2,3-butanediol	1.3E-3	8.5E-5	6.7%	acetic acid	6.1E-1	4.2E-2	7.0%
meso-2,3-butanediol	2.1E-4	9.2E-4	447.3%	propanoic acid	1.6E-3	1.8E-4	11.0%
Esters				butanoic acid	8.5E-4	1.7E-4	20.0%
ethyl acetate	6.3E-1	6.1E-1	97.4%	2-methylpropanoic acid	3.6E-3	1.2E-3	34.8%
ethyl 2-hydroxypropanoate	9.4E-2	4.0E-2	42.4%	3-methylbutanoic acid	2.2E-3	9.3E-4	42.4%
ethyl butanoate	4.0E-4	3.5E-4	88.3%	hexanoic acid	1.5E-3	6.9E-4	45.3%
3-methylbutyl acetate	2.1E-3	2.2E-3	103.4%	octanoic acid	3.0E-3	2.5E-3	84.1%
diethyl butanedioate	1.6E-3	1.0E-3	62.5%	decanoic acid	1.1E-3	1.3E-3	120.2%
ethyl hexanoate	8.3E-4	7.8E-4	92.9%	dodecanoic acid	4.9E-4	6.5E-4	132.8%
ethyl octanoate	1.8E-3	1.6E-3	92.4%	tetradecanoic acid	2.0E-5	2.6E-5	130.1%
ethyl decanoate	7.2E-4	7.3E-4	101.6%	hexadecanoic acid	2.4E-4	4.2E-4	180.0%
2-methylpropyl acetate	6.5E-4	5.7E-4	86.8%	(Z)-hexadec-9-enoic acic	1.8E-5	2.0E-5	108.8%
ethyl dodecanoate	2.1E-4	2.4E-4	112.0%	octadecanoic acid	1.6E-5	1.4E-5	89.0%
ethyl formiate	6.1E-4	8.8E-4	144.2%				

© 2023 Institute of Brewing & Distilling

Nevertheless, both high volatility acetaldehyde and ethyl butanoate should be fully recovered, suggesting some may have been lost through evaporation at the beginning of the distillation.

Ethanol concentration and distillate mass simulation

The simulation was based on experimental data. Two modules with the same scenario were constructed: (i) the simulation of 29 compounds (other than acids) that have known NRTL coefficients to represent their equilibrium data (see Table 2), and (ii) seven acids for which the model must consider the dimerisation phenomenon. The initial composition of the boiler was determined as mass fractions (see Table 2). In total, 27 steps (Table 5) were established for the distillation scenario to consider the changes in parameters and fit the profiles of ethanol concentration and cumulative distillate mass. Figure 3 presents a screenshot taken during the simulation of the heart distillation step.

The experimental and simulation results of distillate characteristics (ethanol and total mass, ethanol concentration) are presented in Figure 4. Overall, there is a good fit of the experimental data to the simulation curves. From this, the heart fraction is extracted at 75.3% ABV. However, there are some variations due to sudden changes in the cold-water flow.

Subsequently, using the experimental and simulation data, it was possible to plot the changes over time in the volatile compounds.

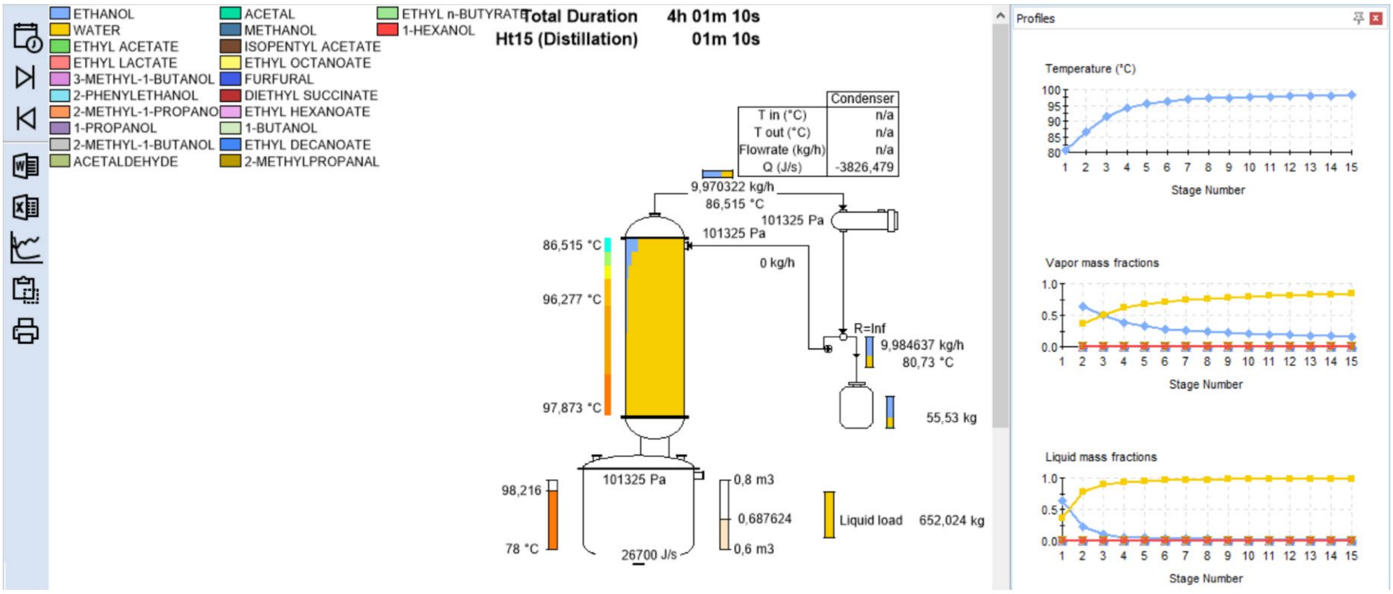
Changes in volatile compounds during distillation and comparison between experimental and simulation values

Absolute volatility

The behaviour of each volatile compound during distillation is directly related to its volatility coefficient (k_i) as a function of the concentration of ethanol in the boiling liquid (Esteban-Decloux et al. 2022). The volatility coefficient named in the figures 'absolute volatility' (k_i) is defined by the ratio of the molar concentration of the compound in the saturated vapour phase (y_i) to that in the boiling liquid phase (x_i) in equilibrium: $k_i = y_i/x_i$. The variation in volatility as a function of ethanol content is known for all compounds where their equilibrium data has been measured. These volatilities decrease with increasing ethanol concentration of the boiling liquid. Puentes et al (2018a) suggested the classification of volatile compounds in spirits with known data into three categories: light compounds more volatile than ethanol, heavy compounds less volatile than water and intermediate compounds. Therefore, the behaviour of the compounds depends on the ethanol concentration of the boiling liquids in the distillation unit.

Figure 3.

Simulation screenshot.



Total Duration 4h 01m 10s
Ht15 (Distillation) 01m 10s

	Condenser
T in (°C)	n/a
T out (°C)	n/a
Flowrate (kg/h)	n/a
Q (J/s)	-3826,479

Table 5.

Simulation steps.

Steps	filling	Hd0	Hd1	Hd2	Hd3	Hd4	Hd5	Ht0	Ht1	Ht2	Ht3	Ht4	Ht5	Ht6	Ht7	Ht8	Ht9	Ht 10	Ht11	Ht12	Ht13	Ht14	Ht15	Ht16	T0	T1	T2
Qb (W)	30.5	11.0	23.7	23.7	23.7	23.7	23.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7	35.0	35.0
														Heat losses (kW)													
pL2		0.30	1.70	1.47	1.50	1.55	1.50	2.70	2.70	2.90	2.90	2.90	2.90	3.20	2.90	2.70	2.50	2.90	2.80	3.10	3.20	3.00	3.10	3.90	3.90	6.00	6.00
pL3		0.30	1.80	1.77	1.60	1.65	1.60	2.60	2.32	2.37	2.47	2.45	2.50	2.20	2.25	2.30	2.35	2.40	2.40	2.40	2.40	2.40	2.70	2.90	2.90	1.60	1.60
pL4		0.30	1.70	1.47	1.30	1.65	1.40	1.40	1.42	1.42	1.47	1.55	1.80	1.90	1.90	1.90	2.10	1.80	2.00	2.00	2.00	2.00	2.00	2.00	2.00	1.50	1.50
pL5		0.30	1.15	1.37	1.20	1.25	1.30	1.30	1.32	1.37	1.37	1.45	1.50	1.60	1.65	1.70	1.75	1.70	1.73	1.73	1.80	1.80	1.80	1.80	1.80	1.40	1.40
pL6		0.30	1.05	1.27	1.10	1.15	1.20	1.20	1.22	1.22	1.27	1.35	1.40	1.50	1.50	1.50	1.50	1.60	1.63	1.63	1.63	1.70	1.60	1.70	1.70	1.30	1.30
pL7		0.30	0.95	1.17	1.00	1.05	1.10	1.10	1.12	1.17	1.17	1.25	1.30	1.40	1.45	1.50	1.55	1.50	1.53	1.53	1.60	1.60	1.60	1.60	1.60	1.20	1.20
pL8		0.30	0.85	1.07	0.90	0.95	1.00	1.00	1.02	1.02	1.07	1.15	1.20	1.30	1.30	1.30	1.30	1.40	1.43	1.43	1.43	1.50	1.50	1.50	1.50	1.10	1.10
pL9		0.30	0.75	0.97	0.80	0.85	0.90	0.90	0.92	0.97	0.97	1.05	1.10	1.20	1.25	1.30	1.35	1.30	1.33	1.33	1.40	1.40	1.45	1.40	1.40	0.90	0.90
pL10		0.30	0.65	0.87	0.70	0.75	0.80	0.80	0.82	0.82	0.87	0.95	1.00	1.10	1.10	1.10	1.10	1.20	1.23	1.23	1.23	1.30	1.30	1.30	1.30	0.80	0.80
pL11		0.50	0.55	0.77	0.60	0.65	0.70	0.70	0.72	0.77	0.77	0.85	0.90	1.00	1.05	1.10	1.15	1.10	1.13	1.13	1.20	1.20	1.25	1.20	1.20	0.70	0.70
pL12		0.40	0.45	0.67	0.50	0.55	0.60	0.60	0.62	0.62	0.67	0.75	0.80	0.90	0.90	0.90	0.90	1.00	1.03	1.03	1.03	1.10	1.10	1.10	1.10	0.60	0.60
pL13		0.30	0.30	0.57	0.40	0.45	0.50	0.50	0.52	0.57	0.57	0.65	0.70	0.80	0.85	0.90	0.95	0.90	0.93	0.93	1.00	1.00	1.05	1.00	1.00	0.50	0.50
pL14		1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
Criteria to		kg Eth	min	min	min	min	kg Eth	min	min	min	min	min	min	min	min	min	min	min	min	min	min	min	min	kg Eth	min	min	kg Eth
change step		0.410	78	80	80.5	81.0	4.350	110	120	130	155	160	165	185	200	205	210	215	220	230	235	240	250	41.000	274	300	46.264

Figure 4.

Changes over time in distillation parameters: experimental data (points) and simulation values (lines) of ethanol concentration (red), cumulative distillate (brown) and ethanol mass (green).

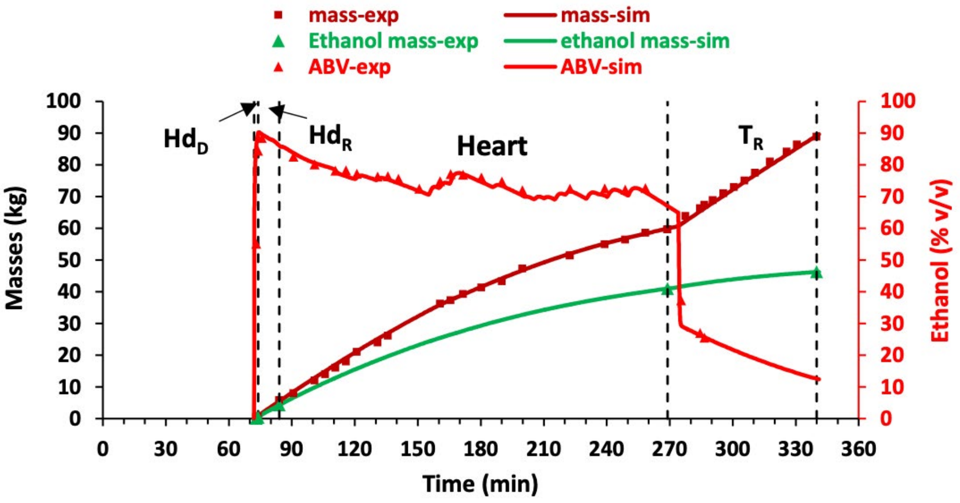
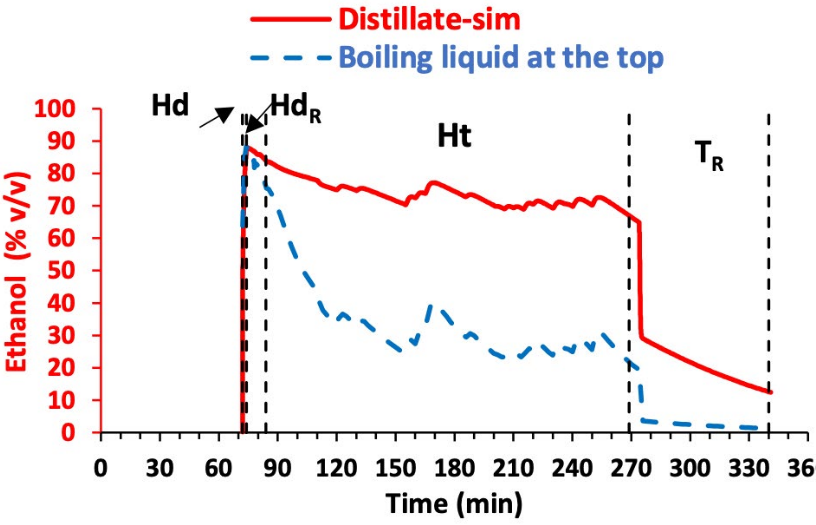


Figure 5.

Changes over time in the ethanol concentration of the distillate (red line) and the boiling liquid at the top of the column (blue dotted line).



Ethanol concentration in the boiling liquid at the top of the column

From the simulation, changes in the ethanol concentration of boiling liquid at the top of column was determined (Figure 5). This goes from a maximum of around 85% ABV during the extraction of the discarded head fraction (Hd_D), falls progressively for 40 minutes to reach 30% ABV where it stabilises throughout the recovery of the heart fraction. At 274 minutes, with the increase of heat and the decrease of cold-water flow in the column, the ABV decreases sharply. Therefore, it was chosen to interpret the behaviour of the quantified and simulated congeners by considering three categories according to their volatilities in three bands of ethanol concentration in the boiling liquid (> 85, 85-30 and < 30% v/v).

Profile of congeners with high volatility

Among the congeners, the compounds with a volatility greater than one (> 1) at 85% ABV in the boiling liquid are an alcohol (methanol), three esters (ethyl acetate, ethyl butanoate, ethyl hexanoate) and three aldehydes (acetaldehyde, 2-methylpropanal and 1,1-diethoxyethane). Figure 6 shows the variation in volatility with the ethanol concentration of the boiling liquid (A), and their concentration profile in the distillate over time (B). Ethyl acetate and the three aldehydes are concentrated in the first distillate fractions (Hd_D and Hd_R). Given the high concentration of ethyl acetate and acetaldehyde, interest in removing a small fraction of the head is understandable. The other two esters follow the same profile but with much lower concentration factors because their volatility in the liquid between 85 and 75% ABV is low.

Methanol has a volatility > 1 whatever the ethanol concentration but, with a very low value in comparison with the other compounds in this category. Therefore, methanol never concentrates strongly in the vapour phase and is present in all distillate fractions and as well as the residue (see Table 4). This confirms that the separation of the head fraction does not remove methanol but rather, aldehydes and ethyl acetate. For all compounds in this category, the simulation represents the experimental data well.

Profile of congeners with intermediary volatility

It is then possible to distinguish compounds that have volatilities > 1 in the boiling liquid above 30% ABV but have a volatility < 1 above 85% ABV (Figure 7). These compounds are delayed because their volatility becomes > 1 only at lower ethanol concentrations. But, with the sharp decrease in the ethanol concentration in the boiling liquid at the top the column, the volatility increases sharply as does the concentration in the distillate. Most compounds have a peak due to their partial exhaustion from the boiler. Most alcohols are present in this category (except methanol and 2-phenylethanol), three esters (3-methylbutyl acetate, ethyl octanoate, ethyl decanoate and 2-methylpropyl acetate which were not simulated), an aldehyde (furane-2-carbaldehyde) and an acid (hexanoic acid). Alcohols peak during the recycled head fraction or at the beginning of the heart extraction. This is due to their volatility being > 1. For these alcohols, there is a good match between the experimental and simulation data with a small overestimation for hexan-1-ol.

Esters, with higher volatilities than the alcohols, are quickly exhausted from the boiler, and concentrate in the first distillate fractions. Nevertheless, for ethyl octanoate and ethyl decanoate, the simulation predicted a later exit than found with the experimental data. Accordingly, their volatility may be underestimated in the range of 75-85% ABV. The experimental concentration of furan-2-carbaldehyde and hexanoic acid increases with time contrary to what is predicted by the simulation. This suggests that the volatility of furan-2-carbaldehyde and hexanoic acid is lower than that obtained from the equilibrium data. Accordingly, their behavior is closer to that of congeners with low volatilities.

Profiles of congeners with low volatility

Compounds that have low volatilities of < 1 at 30% ABV are considered (Figure 8). These are acids (acetic, propanoic etc), 2-phenylethanol, ethyl 2-hydroxypropanoate and diethyl butanedioate. Both 2-phenylethanol and ethyl 2-hydroxypropanoate exhibit high concentrations in the boiler, where their concentrations slightly increase during extraction of the heart and then decrease during the tail fraction. This is due to the increase in heating and reduced flow of cold water in the column. Here, the simulation generally represents the experimental data well. However, the simulation of acetic acid is poor reflecting analytical difficulties. Indeed, in previous studies (Puentes et al. 2018b; Douady et al. 2019) simulations of acetic acid are good. All other acids in this category and diethyl butanedioate follow a similar trend to 2-phenylethanol and ethyl 2-hydroxypropanoate, but at a much lower concentration. For these compounds, the simulation predicts the correct profiles but at the wrong concentration.

Figure 6.

Volatility curves of compounds with (A) volatilities > 1 at an ethanol concentration over 85% ABV and (B) concentration profiles of compounds in the distillate over time.

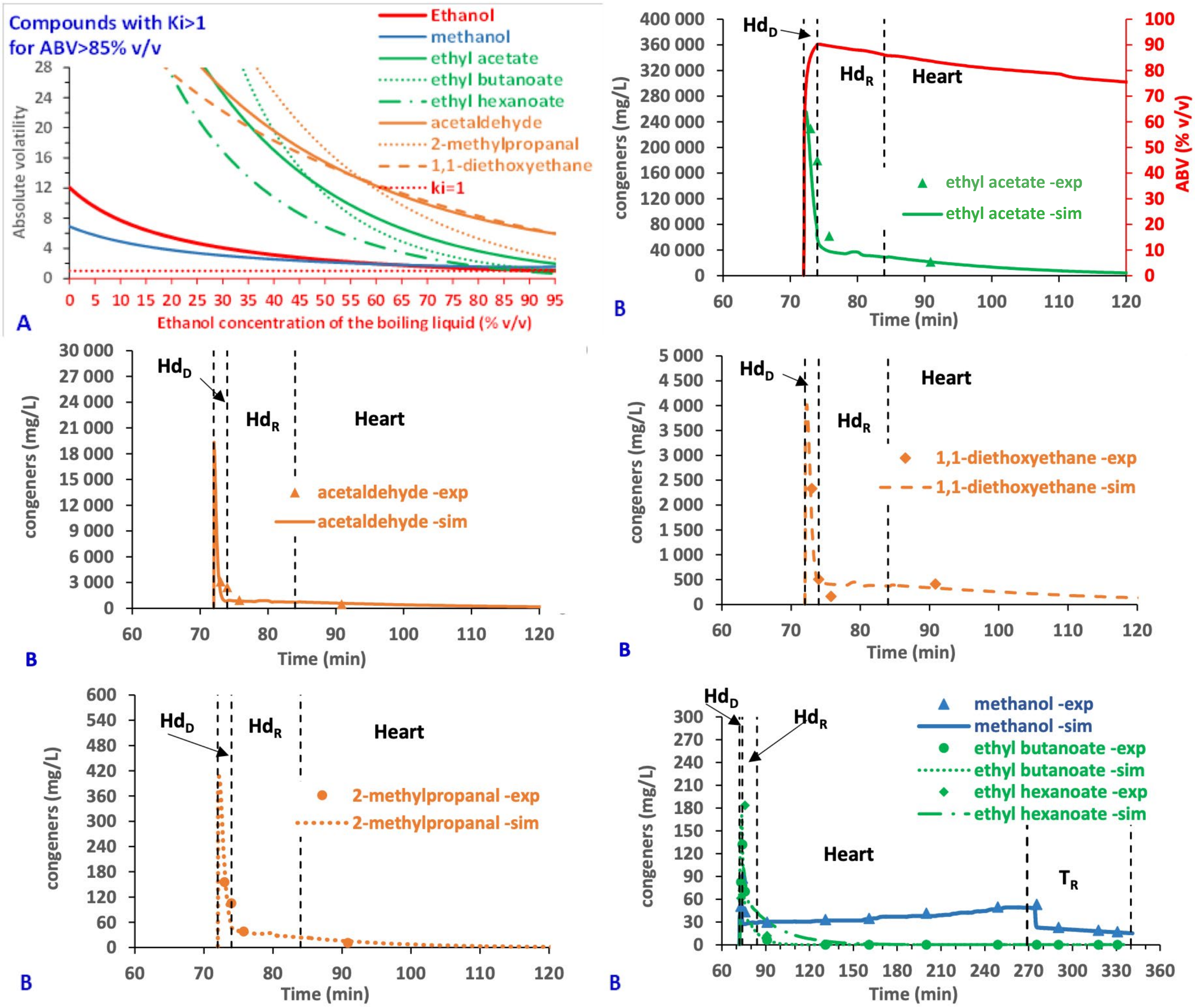
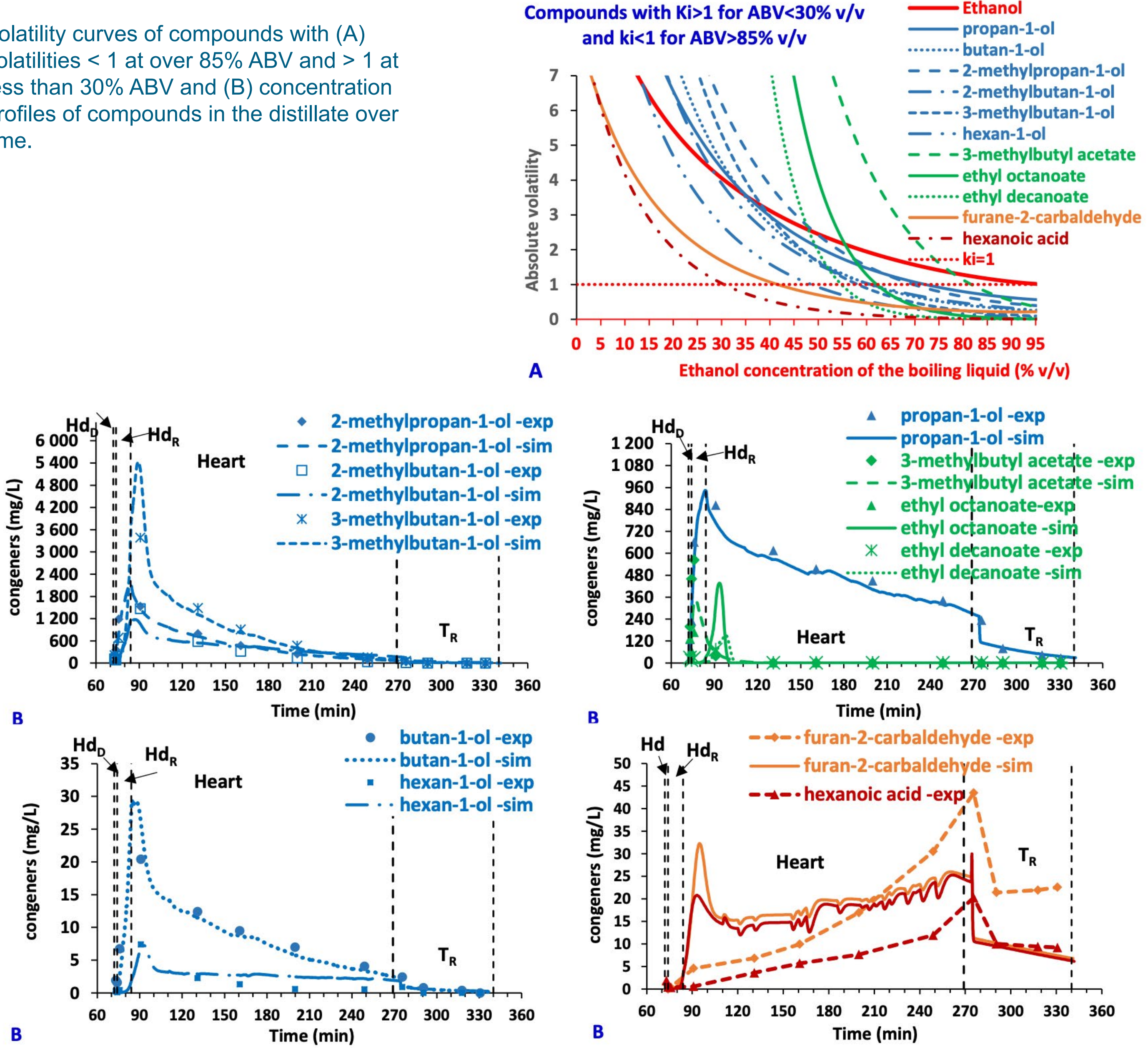


Figure 7.

Volatility curves of compounds with (A) volatilities < 1 at over 85% ABV and > 1 at less than 30% ABV and (B) concentration profiles of compounds in the distillate over time.



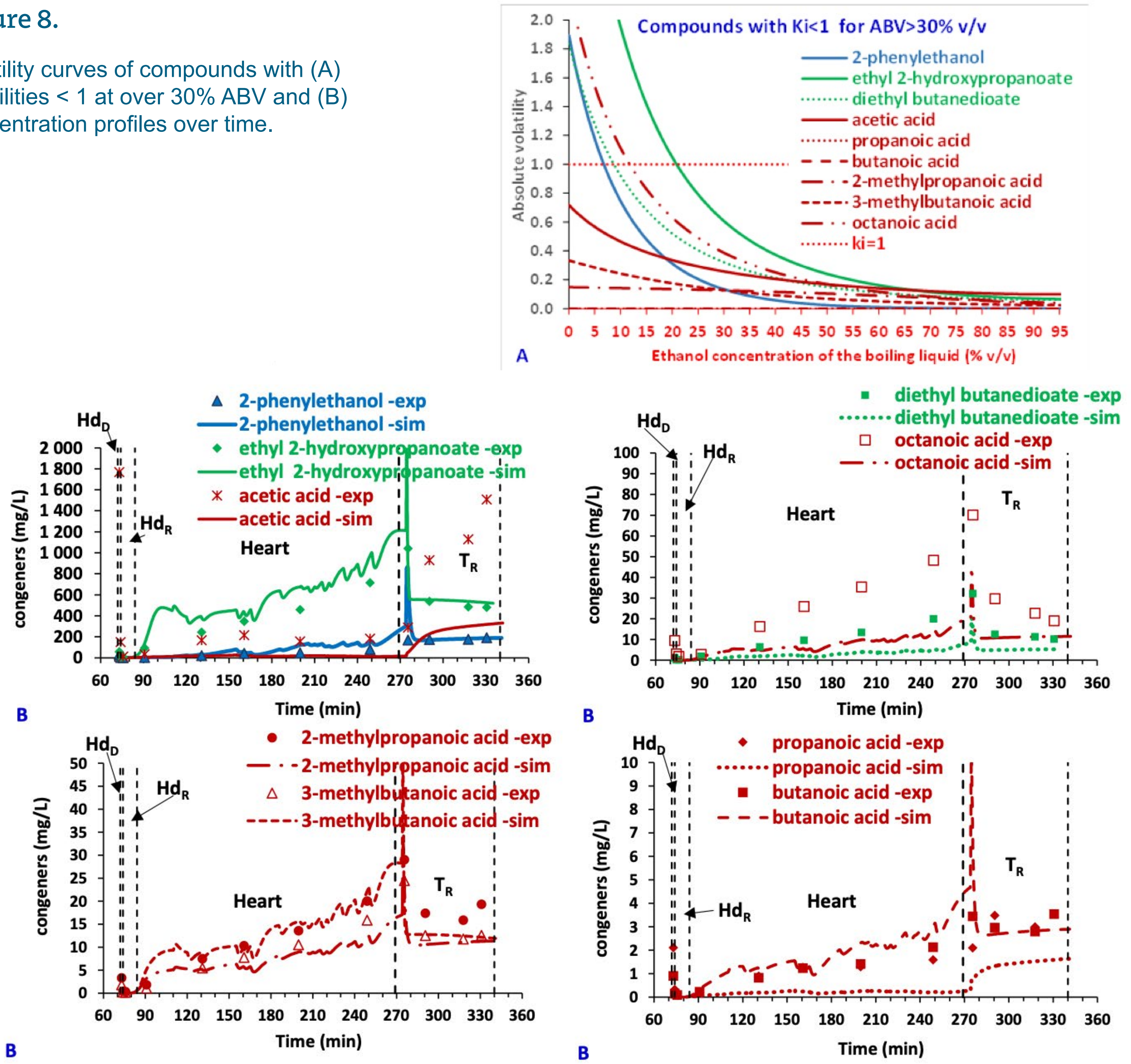
Distribution of volatile compounds in different fractions

Table 6 shows the distribution of the volatile compounds in the different fractions. The discarded head fraction (Hd$_D$), which represents 0.8 wt.% of the ethanol distribution, removes a significant amount of 2-methylpropanal (35.6%), ethyl acetate (30.2%), ethyl butanoate (25.2%), acetaldehyde (21.1%) and 1,1-diethoxyethane (17.1%). In addition, this fraction eliminates the dead volume from the end of the previous distillation and products coming from reactions between volatile fatty acids and the copper of the coil in the condenser-cooler solubilised at high ethanol concentration.

The residue (W), which represents 5.0 wt.% of the ethanol distribution, removes compounds having a negative impact on spirit quality (acids, diethyl butanedioate and 2-hydroxypropanoate) but, unfortunately, also more than 80% of 2-phenylethanol which has a positive organoleptic impact. The recycled fractions (Hd$_R$ and T$_R$) represent respectively 8.1% and 10.8% of the ethanol distribution. This supports the recycling of 2-phenylethanol (11.9%) and a high proportion of esters of interest such as 3-methylbutyl acetate (71.1%), ethyl hexanoate (86.9%), ethyl octanoate (74.3%) and ethyl decanoate (70.9%). Unfortunately, compounds contributing negative notes are also recovered including ethyl butanoate (60.8%),

Figure 8.

Volatility curves of compounds with (A) volatilities < 1 at over 30% ABV and (B) concentration profiles over time.



ethyl acetate (45.5%), acetaldehyde (40.0%), 2-methylpropanal (36.8%) and 1,1-diethoxyethane (23.3%). However, this recycling is mandatory as the ethanol yield of the distillation must comply with regulations that specify the maximum loss of alcohol allowed (Official Journal, 2012).

Influence of recycled fractions on the composition of the heart fraction

There are few studies that consider the influence of recycling of the head and tail fractions. Accordingly, data was used to characterise the concentration of the compounds in the heart with recycling of the head and tail. To achieve this, a mathematical model was developed with- at each run- a constant distribution of the compounds in the head, heart, tail and residue fractions (see Table 6) with a constant total mass in the boiler (712 kg). The first distillation started only with wash, with subsequent distillations considering recycled fractions and less wash to maintain the mass in the boiler. At each distillation run, the mass of compounds was calculated in each fraction according to distribution and recovery rate into the heart, based on the amount in the wash and the heart. Table 7 shows the recovery rate of each compound in the heart compared to the initial input of the wash as a function of 15 successive distillations in the mass balance streams reported in Figure 9.

For all compounds, including ethanol, the recycling of fractions allows an increase in their extraction rate compared to their initial input from the wash. For most compounds, a pseudo-steady state is achieved in less than five distillations. However, this

Table 6.

Distribution of compounds in different fractions.

mass distribution (wt.%)	Hd_D	Hd_R	Ht	T_R	W
ethanol	0.8	8.1	75.3	10.8	5.0
water	0.021	0.102	2.593	3.686	93.597
Alcohols					
methanol	0.8	4.5	59.3	16.7	18.8
propan-1-ol	*0.2*	*10.7*	*82.4*	*5.4*	*1.2*
butan-1-ol	0.0	8.1	89.6	2.0	0.2
2-methylpropan-1-ol	0.1	17.0	82.1	0.7	0.0
2-methylbutan-1-ol	0.0	7.7	88.6	3.3	0.4
3-methylbutan-1-ol	0.0	5.6	93.9	0.5	0.0
hexan-1-ol	0.0	1.0	89.3	7.6	2.1
2-phenylethanol	0.0	0.0	6.7	11.7	81.6
Esters					
ethyl acetate	22.3	33.7	44.0	0.0	0.0
ethyl 2-hydroxypropanoate	0.0	0.0	33.8	18.9	47.3
ethyl butanoate	25.2	60.8	14.0	0.0	0.0
3-methylbutyl acetate	1.3	71.0	27.7	0.0	0.1
diethyl butanedioate	0.0	0.0	9.3	10.7	80.1
ethyl hexanoate	3.0	44.4	52.6	0.0	0.1
ethyl octanoate	0.0	1.6	98.3	0.0	0.1
ethyl decanoate	0.0	0.5	99.5	0.0	0.0
Aldehydes					
acetaldehyde	31.6	27.4	40.9	0.0	0.0
2-methylpropanal	35.6	36.8	27.6	0.0	0.0
1,1-diethoxyethane	17.1	23.3	59.5	0.0	0.0
furan-2-carbaldehyde	0.0	0.3	68.0	17.1	14.6
Acids					
acetic acid	0.0	0.0	0.2	1.3	98.6
propanoic acid	0.0	0.0	0.7	2.6	96.7
butanoic acid	0.0	0.0	11.3	11.0	77.7
2-methylpropanoic acid	0.0	0.0	11.4	10.0	78.6
3-methylbutanoic acid	0.0	0.0	32.7	19.0	48.4
hexanoic acid	0.0	0.1	67.6	18.0	14.2
octanoic acid	0.0	0.0	13.8	12.6	73.6

Table 7.

Recovery rate of compounds based on the composition of the wash loaded in the boiler as distillation progresses.

Number of distillations	1	2	3	4	10	15
	m_{Heart}/m_{wash} (%)					
ethanol	75.3	90.2	92.3	92.7	92.8	92.8
water	2.59	2.70	2.70	2.70	2.70	2.70
Alcohols						
methanol	59.3	72.4	74.6	75.1	75.2	75.2
propan-1-ol	82.4	96.4	98.0	98.3	98.3	98.3
butan-1-ol	89.6	99.2	99.7	99.8	99.8	99.8
2-methylpropan-1-ol	82.1	97.4	99.4	99.7	99.8	99.8
2-methylbutan-1-ol	93.9	99.9	100.0	100.0	100.0	100.0
3-methylbutan-1-ol	88.6	98.8	99.4	99.5	99.5	99.5
hexan-1-ol	89.3	97.4	97.7	97.7	97.7	97.7
2-phenylethanol	6.7	7.5	7.6	7.6	7.6	7.6
Esters						
ethyl acetate	44.0	59.5	64.0	65.6	66.3	66.3
ethyl 2-hydroxypropanoate	33.8	40.5	41.5	41.7	41.7	41.7
ethyl butanoate	14.0	23.0	28.0	31.1	35.5	35.8
3-methylbutyl acetate	27.7	48.3	62.0	71.8	92.4	94.9
diethyl butanedioate	9.3	10.3	10.4	10.4	10.4	10.4
ethyl hexanoate	52.6	77.0	86.8	91.1	94.5	94.5
ethyl octanoate	98.3	100.0	99.9	99.9	99.9	99.9
ethyl decanoate	99.5	100.0	100.0	100.0	100.0	100.0
Aldehydes						
acetaldehyde	40.9	52.7	55.4	56.1	56.4	56.4
2-methylpropanal	27.6	38.3	41.7	43.0	43.7	43.7
1,1-diethoxyethane	59.5	74.1	76.8	77.5	77.7	77.7
furan-2-carbaldehyde	68.0	80.4	82.0	82.3	82.4	82.4
Acids						
acetic acid	0.16	0.16	0.16	0.16	0.16	0.16
propanoic acid	0.72	0.74	0.74	0.74	0.74	0.74
butanoic acid	11.3	12.6	12.7	12.7	12.7	12.7
2-methylpropanoic acid	11.4	12.6	12.7	12.7	12.7	12.7
3-methylbutanoic acid	32.7	39.2	40.1	40.3	40.3	40.3
hexanoic acid	67.6	80.5	82.2	82.6	82.6	82.6
octanoic acid	13.8	15.7	15.8	15.8	15.8	15.8

is not the case for ethyl butanoate, 3-methylbutyl acetate, ethyl hexanoate, ethyl octanoate and ethyl decanoate whose recovery rates increase across 15 successive distillations. This is explained by the proportion in the recycled head fraction (Hd_R), at respectively 60.8, 71.1, 86.9, 73.3 and 69.2%.

Additionally, the composition of the first calculated heart produced only with wash ($Ht_{1\text{-cal}}$), the calculated 15th heart ($Ht_{15\text{-cal}}$) and experimentally (Ht_{exp}) were compared (Table 8). Unlike the first calculated heart from the wash ($Ht_{1\text{-cal}}$), the composition of the calculated heart in pseudo-steady state ($Ht_{15\text{-cal}}$) is similar to experimental data from the distillation of the raw wash and recycled fractions mixed in the boiler. This is why, in studies to characterise the heart obtained from a given wash, it is recommended to perform several distillations with the addition of the recycled fractions.

Finally, sensory analysis of the heart fraction was performed using the odour active value (OAV) which is the ratio of the concentration of the molecule to its cut-off threshold, taken from Poisson and Schieberle (2008), Gao et al (2014) and Wang et al (2014). The concentration of the volatile compounds in pseudo-steady state ($Ht_{15\text{-cal}}$) and the experimental heart (Ht_{exp}) were assessed after dilution to 46% ABV. Due to its very low threshold, ethyl octanoate presents the highest OAV, confirming the importance of the recycling of Hd_R fraction. However, several sensory negative compounds have important OAVs (ethyl acetate, acetaldehyde and 1,1-diethoxyethane) despite their partial elimination in the discarded head fraction (Hd_D). Perhaps, depending on the composition of the wash, it may be necessary to increase the amount of the discarded head. Alternatively, the flow of cold water could be increased during the extraction of the discarded head fraction (Hd_D) to retain a higher concentration of compounds with a volatility always > 1 at 85% ABV, while delaying the loss of the compounds of interest.

Figure 9.

Mass balance after 15 distillations.

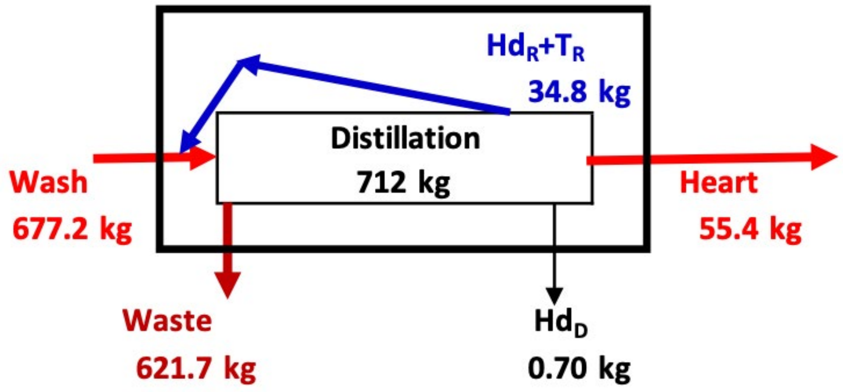


Table 8.

Composition and Odour Active Values of the simulation and experimental hearts.

	$Ht_{1\text{-cal}}$	$Ht_{15\text{-cal}}$	Ht_{exp}	Odor threshold (mg/L) at 46 %v/v			$Ht_{15\text{-cal}}$	Ht_{exp}	$Ht_{15\text{-cal}}$	Ht_{exp}
ethanol (% v/v)	72.4	75.8	75.3	a	b	c	46.0	46.0	OAV	OAV
Alcohols (mg/L)										
methanol	33.5	36.2	38.5			17.4	22.0	23.5	1.3	1.4
propan-1-ol	528.7	534.9	541.0	54			324.8	330.6	6.0	6.1
butan-1-ol	11.0	10.4	10.1		2.73		6.3	6.2	2.3	2.3
2-methylpropan-1-ol	609.3	629.0	582.6		28.30		381.9	356.0	**13.5**	**12.6**
2-methylbutan-1-ol	528.2	477.8	443.6				290.1	271.1		
3-methylbutan-1-ol	1 256.2	1196.9	1127.0		179.00		726.8	688.6	4.1	3.8
hexan-1-ol	3.3	3.1	1.9		5.37		1.9	1.2	0.4	0.2
2-phenylethanol	64.4	62.0	37.1		28.90		37.7	22.7	1.3	0.8
Esters (mg/L)										
ethyl acetate	1 726.6	2691.3	2372.4		32.60		1634.1	1449.6	**50.1**	**44.5**
ethyl 2-hydroxypropanoate	520	546.1	367.2		128.00		331.6	224.4	2.6	1.8
ethyl butanoate	0.3	0.7	0.4		0.08		0.4	0.3	5.4	3.2
3-methylbutyl acetate	1.4	4.1	2.1		0.09		2.5	1.3	**26.6**	**13.4**
diethyl butanedioate	2.3	2.2	10.1		35.00		1.3	6.2	0.0	0.2
ethyl hexanoate	0.2	1.0	0.7		0.06		0.6	0.4	**10.8**	**7.4**
ethyl octanoate	0.8	2.7	2.8		0.0129		1.7	1.7	**129.1**	**132.3**
ethyl decanoate	1.3	3.9	3.1		1.12		2.4	1.9	2.1	1.7
Aldehydes (mg/L)										
acetaldehyde	86	122.3	74.4	1.2			74.3	45.4	**61.9**	**37.9**
2-methylpropanal	1.7	2.3	3.3	1.3			1.4	2.0	1.1	1.5
1,1-diethoxyethane	90.8	100.5	106.9		2.09		61.0	65.3	**29.2**	**31.3**
furan-2-carbaldehyde	14.7	15.1	13.2		44.00		9.2	8.1	0.2	0.2
Acids (mg/L)										
acetic acid	17.1	14.7	158.0		160		8.9	96.5	0.1	0.6
propanoic acid	3.3	3.2	1.2	18.2			1.9	0.7	0.1	0.04
butanoic acid	1.7	1.6	1.2		0.964		1.0	0.7	1.0	0.8
2-methylpropanoic acid	6.9	6.5	11.2		1.58		3.9	6.8	2.5	4.3
3-methylbutanoic acid	11.6	12.2	8.4		1.05		7.4	5.1	7.0	4.9
hexanoic acid	16.1	16.7	5.9		2.52		10.2	3.6	4.0	1.4
octanoic acid	5.7	5.5	25.9	2.7			3.3	15.8	1.23	5.9

a: Wang et al (2014) b: Gao et al (2014) c: Poisson et Schieberle (2008) determined at 40% v/v and calculation for 46% v/v

Conclusions

This study reports experimental data on the evolution of volatile compounds during the discontinuous distillation of wash (from fermented malted barley) with a Stupfler-type column. Data is compared with simulation with most compounds well represented. The main outlier is acetic acid which reflects analytical issues. Although the simulation of other acids was consistent, the concentration can be overestimated or underestimated depending on the compound.

The percentage distribution of the compounds between the different distillate fractions (discarded head, recycled head, heart, tail) and waste were assessed using simulation and experimental data. Assuming that these distributions are maintained during each distillation and the mass in the boiler remained constant, 15 distillation runs were calculated, initially with only the wash and then with recycling of head and tail fractions. A pseudo-steady state was achieved in less than five distillations, and it was possible to estimate the true recovery rates of compounds in the heart. The difference between the first and fifth heart drives the recommendation to perform several distillations with the recycled fractions to better characterise the heart.

Using previously reported perception thresholds, the odour active values of the compounds in heart were determined. This confirmed the necessity to recycle the head fraction (Hd_R) to improve the recovery of esters of interest. Further, it is necessary to modify the parameters at the beginning of distillation to increase the difference between the high volatile compounds at high ethanol concentration (ethyl acetate, acetaldehyde 2-methylpropanal and 1,1-diethoxyethane) and compounds with volatility > 1 when the ethanol concentration of the boiling liquid is < 75% ABV.

Author contributions

Martine Esteban-Decloux: project administration, funding acquisition, methodology, investigation, writing (original draft).

N'Guessan Romaric Charles Tano: writing (review and editing).

Hervé Grangeon: owner of the Ergaster distillery, investigation, writing (review and editing).

Acknowledgements

This project was supported by ACTIA (Association de Coordination Technique pour l'Industrie Agro-alimentaire) as part of the "QUADIFERM" mixed technological network on the quality of distilled fermented products.

Conflict of interest

There is no conflict of interest.

References

da Porto C, Natolino A, de Corti D. 2010. Batch distillation of grappa: Effect of the recycling operation. *Int J Food Sci Technol* 45:271-277. https://doi.org/10.1111/j.1365-2621.2009.02131.x

Douady A, Puentes C, Awad P, Esteban-Decloux M. 2019. Batch distillation of spirits: experimental study and simulation of the behaviour of volatile aroma compounds. *J Inst Brew* 125:268–283. https://doi.org/10.1002/jib.560

Esteban-Decloux M, Deterre S, Kadir S, Giampaoli P, Albet J, Joulia X, Baudouin O. 2014. Two industrial examples of coupling experiments and simulations for increasing quality and yield of distilled beverages. *Food Bioprod Process* 92:343-354. https://doi.org/10.1016/j.fbp.2013.10.001

Esteban-Decloux M, Dechatre J-C, Legendre P, Guichard H. 2021. Double batch cider distillation: Influence of the recycling of the separated fractions. *LWT,* 146:111420. https://doi.org/10.1016/j.lwt.2021.111420

Esteban-Decloux M, Tano NGCR, Grangeon H. 2022. Simulation of the behaviour of volatile compounds during batch multi-stage distillations of whisky. *J Inst Brew* 128:171-187. https://doi.org/10.1002/jib.704

Gao W, Fan W, Xu Y. 2014. Characterization of the key odorants in light aroma type Chinese liquor by gas chromatography-olfactometry, quantitative measurements, aroma recombination, and omission studies. *J Agric Food Chem* 25:5796-5804. https://doi.org/10.1021/jf501214c

International Organization of Legal Metrology, 1975. International alcoholometric tables, OIML R22,. https://www.oiml.org/en/files/pdf_r/r022-e75.pdf

Luna R, Matias-Guiu P, López F, Pérez-Correa JR. 2019. Quality aroma improvement of Muscat wash spirits: A new approach using first-principles model-based design and multi-objective dynamic optimisation through multi-variable analysis techniques. *Food Bioprod Process* 115:208-222. https://doi.org/10.1016/j.fbp.2019.04.004

Official Journal of 9 November 2012. Decree No. 2012-1245 of 07/11/12 on waste and losses during the manufacture, processing and storage of alcohol and alcoholic beverages. 210-214. https://www.legifrance.gouv.fr/download/pdf?id=kr7bfGPcXYe55RYnLT-46BwZjgCJ5g7nDrxqDEoMGrY=

Poisson L, Schieberle P. 2008. Characterization of the key aroma compounds in an American Bourbon whisky by quantitative measurements, aroma recombination, and omission studies. *J Agric Food Chem* 14:5820–5826. https://doi.org/10.1021/jf800383v

Puentes C, Joulia X, Athès V, Esteban-Decloux M. 2018a. Review and thermodynamic modeling with NRTL model of vapour-liquid equilibria (VLE) of aroma compounds highly diluted in ethanol-water mixtures at 101.3 kPa. *Ind Eng Chem Res* 57:3443−3470. https://doi.org/10.1021/acs.iecr.7b03857

Puentes C, Joulia X, Vidal JP, Esteban-Decloux M. 2018b. Simulation of spirits distillation for a better understanding of volatile aroma compounds behavior: Application to Armagnac production. *Food Bioprod Process* 112:31-62. https://doi.org/10.1016/j.fbp.2018.08.010

Spaho N. 2017. Distillation techniques in the fruit spirits production. In: Mendes MF, Ed. Distillation-*Innovative Applications and Modeling.* IntechOpen, 129-152. https://doi.org/10.5772/66774

Wang X, Fan W, Xu Y. 2014. Comparison of aroma compounds in Chinese soy sauce and strong aroma type liquors by gas chromatography-olfactometry, chemical quantitative and odor activity values analysis. *Eur Food Res Technol* 5:813-825 https://doi.org/10.1007/s00217-014-2275-z