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Aroma profile design of wine spirits: Multi-objective optimization using response surface methodology

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ABSTRACT

Developing new distillation strategies can help the spirits industry to improve quality, safety and process efficiency. Batch stills equipped with a packed column and an internal partial condenser are an innovative experimental system, allowing a fast and flexible management of the rectification. In this study, the impact of four factors (heart-cut volume, head-cut volume, pH and cooling flow rate of the internal partial condenser during the head-cut fraction) on 18 major volatile compounds of Muscat spirits was optimized using response surface methodology and desirability function approaches. Results have shown that high rectification at the beginning of the heart-cut enhances the overall positive aroma compounds of the product, reducing off-flavor compounds. In contrast, optimum levels of heart-cut volume, head-cut volume and pH factors varied depending on the process goal. Finally, three optimal operational conditions (head off-flavors reduction, flowery terpenic enhancement and fruity ester enhancement) were evaluated by chemical and sensory analysis.

1. Introduction

One of the main challenges of the food and beverage industry is to obtain unique products in an increasingly competitive market. In the case of spirits, new operating strategies can improve quality, food safety and efficiency of the distillation process. Batch distillation is the most used technique to produce spirits, where the distillate is collected in three consecutive fractions: head-cut (waste), heart-cut (product) and tail-cut (waste), to obtain a product with minimum off-flavors and toxic compounds. Traditional systems, like copper *Charentais* alembics (French style), produce drinks with high levels of volatile compounds that enhance their genuineness, an important feature of distinctive alcoholic beverages. However, alembics allow limited control of the distillation process to improve the product. On the other hand, modern continuous columns are generally used to obtain spirits with a neutral aroma, intended for flavoring or ageing. In the spirits industry, batch columns (German style) represent an intermediate technique, which provide enhanced control of the rectification by varying the reflux rate; however, these systems are slow to respond, severely limiting the process flexibility. Many studies have reported the differences of the available spirits distillation systems (Alcarde, Souza, & Bortoletto, 2012; Christoph & Bauer-Christoph, 2007; Da Porto & Decorti, 2008; Madrera, Gomis, & Alonso, 2003; Porto, 2008).

An innovative experimental system is the batch packed column equipped with an internal partial condenser that allows fast and flexible control of the internal reflux rate (García-Llobodanin, Roca, López, Pérez-Correa, & López, 2011). This system has been compared with a traditional alembic by distilling wine and other fermented agricultural raw materials (kiwi, pear and grape pomace) showing significant differences (Arrieta-Garay et al., 2013, Arrieta-Garay, Blanco, et al., 2014; Arrieta-Garay, López-Vázquez, et al., 2014). In particular, high refluxes of early fractions removed acetaldehyde, ethyl acetate and acetal from the heart-cut, which resulted in a cleaner wine spirit (Matias-Guiu, Rodríguez-Bencomo, Orriols, Pérez-Correa, & López, 2016; Rodríguez-Bencomo, Pérez-Correa, Orriols, & López, 2016). Although packed columns increase distillation times and are difficult to control (García-Llobodanin et al., 2011), the variable internal cooling flow rate can quickly adapt the rectification level; hence, the producer can modify the volatile composition of the spirit throughout the process by specific operational strategies (Matias-Guiu et al., 2016).

The distillation of fermented beverages causes the reaction of several aroma compounds, such as terpenes (Baxter, Laurie, & Mchale, 1978; Bedoukian, 1986; Ohta, Morimitsu, Sameshima, Samuta, & Ohba, 1991; Osorio, Pérez-Correa, Belancic, & Agosin, 2004), esters (Fischer & Speier, 1895), furfural (Mottram, 2007; Nakama, Kim, Shinohara, & Omura, 2014; Yemiş & Mazza, 2012) and aldehydes (Kłosowski &

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Czupryński, 2006), which undergo transformations in a hot acid medium. It has been reported that the juice pH alters the microbiological behavior during the fermentation, affecting the aroma composition of pear and melon spirits (García-Llobodanin, Senn, Ferrando, Güell, & López, 2010; Gómez, Úbeda, & Briones, 2008). However, there is no information regarding the influence of pH during the distillation. Furthermore, the distillation behavior of each compound changes throughout the process (Jouret, Cantagrel, & Galy, 1998).

The aim of this study was to determine operational conditions for a batch distillation column with an internal partial condenser, to obtain different specific organoleptic characteristics for a Muscat wine spirit. Heart-cut volume (HTV), head-cut volume (HDV), pH (adjusted with sulfuric acid, a common technique used in marc storage (Lukić, Miličević, Tomas, Radeka, & Peršurić, 2012)) and cooling flow rate of the internal partial condenser during the head-cut fraction (CFR) were considered to be the main operational factors. To carry out the head-cut multi-objective optimization (18 compounds), response surface methodology (RSM) was applied by performing a central composite design with face centered axial points (Derringer & Suich, 1980). For the multi-objective optimization, the desirability function approach (Derringer & Suich, 1980) was used for the most relevant volatile compounds of Muscat spirits. In addition, optimal strategies were evaluated by sensory analysis.

2. Material and methods

2.1. Central composite design (CCD)

Design of experiments is widely used to unveil the impact of defined input process variables (factors) on output process variables (responses). The CCD is a type of design of experiments consisting of a 2-level full factorial design (FFD) with a center point and axial points (Montgomery, 2013). The FFD is a design that studies the effect of all possible combinations of 2 or more factors at 2 levels. Center point is an experimental run whose factor values are the average of the two levels of the FFD factors; they are usually replicated to estimate and improve the variance of the system. Axial points are experimental runs with the same factor values as the center point, except for one factor whose value is at a given distance (α) from the center point. Factor values are usually rescaled (coded): FFD points = ± 1, center point = 0, and axial points = ± α (one factor) and 0 (the other factors). Thereby, CCD results allow a statistical estimation of linear and quadratic effects on a given response with a reduced number of experiments.

For this study, a 3-level-3-factor CCD with face centered axial points (α = 1) and six replicates of the center point was designed (20 runs). Factors were head-cut volume (HDV), pH and cooling flow rate (CFR) of the internal partial condenser of the column. To minimize the number of runs, the factor HTV (heart-cut volume) was not considered; however, HTV was considered with the RSM, since 2 heart cuts were obtained from each experiment. Runs were ordered with a randomized 2-block design, to enhance the reliability and validity of the statistical analysis of the factor effects. Center point runs were randomized with a 2-block distribution (10 random runs with 3 center point replicates for each block). A blocking variable was included, to reduce the impact of possible nuisance variables throughout the experimentation period (2 month) (Montgomery, 2013). Table 1 shows all the experiments in the standard and real order of runs with coded and experimental values of the factors.

2.2. Wines

All experimental distillations were carried out at the Departament d'Enginyeria Química of the Universitat Rovira i Virgili. The CCD distillations used a *Vitis vinifera* "Muscat" wine (2015 vintage year), with an alcoholic strength by volume of 12.6% (*v/v*) and a pH of 3.20, which was donated by Dalmau Hermanos y Cía. Suc. S.A. (Tarragona, Spain).

Table 1
Central composite design 3-level-3-factor with face centered axial points (AP) and 6 center points (CP). Uncoded values are shown in brackets.

Run number	Run order	Head-cut volume (mL)	Cooling flow rate[a] (mL/min)	pH
1	2	−1 (5.00)	−1 (30.0)	−1 (1.70)
2	1	+1 (20.0)	+1 (100)	−1 (1.70)
3	5	+1 (20.0)	−1 (30.0)	+1 (3.20)
4	3	−1 (5.00)	+1 (100)	+1 (3.20)
5	12	+1 (20.0)	−1 (30.0)	−1 (1.70)
6	9	−1 (5.00)	+1 (100)	−1 (1.70)
7	10	−1 (5.00)	−1 (30.0)	+1 (3.20)
8	8	+1 (20.0)	+1 (100)	+1 (3.20)
9 (AP)	13	0 (12.5)	0 (65.0)	−1 (1.70)
10 (AP)	17	0 (12.5)	0 (65.0)	+1 (3.20)
11 (AP)	16	0 (12.5)	−1 (30.0)	0 (2.45)
12 (AP)	15	0 (12.5)	+1 (100)	0 (2.45)
13 (AP)	18	−1 (5.00)	0 (65.0)	0 (2.45)
14 (AP)	19	+1 (20.0)	0 (65.0)	0 (2.45)
15 (CP)	6	0 (12.5)	0 (65.0)	0 (2.45)
16 (CP)	4	0 (12.5)	0 (65.0)	0 (2.45)
17 (CP)	11	0 (12.5)	0 (65.0)	0 (2.45)
18 (CP)	7	0 (12.5)	0 (65.0)	0 (2.45)
19 (CP)	20	0 (12.5)	0 (65.0)	0 (2.45)
20 (CP)	14	0 (12.5)	0 (65.0)	0 (2.45)

[a] Partial condenser cooling was applied during the head-cut distillation only.

The pH of the wine was adjusted before each assay with sulfuric acid solution 2.5 M (GAB system, Barcelona, Spain) at three levels (3.20, 2.45 and 1.70) according to the CCD method (Table 1). The pH levels were chosen with the intention of observing marked differences.

Optimal distillations used *Vitis vinifera* "Muscat" (2016 vintage year) with an alcoholic strength by volume of 11.5% (*v/v*) and a pH of 3.20, as well as *Vitis vinifera* "Macabeo" (2016 vintage year) with an alcoholic strength by volume of 10.6% (*v/v*) and a pH of 2.95. Both wines were donated by Cooperativa de Vila-rodona (Vila-rodona, Tarragona, Spain). Their alcoholic strengths by volume were adjusted to 12.6% (*v/v*) with food-grade ethanol of 95% (*v/v*) (Droguería Boter SL, Badalona, Spain). According to the optimal conditions obtained with the study of Muscat wine (2015 vintage year), the wines' pH levels were adjusted before each assay with a sulfuric acid solution 2.5 M (GAB system, Barcelona, Spain) or sodium hydroxide solution 2.5 M (Sigma-Aldrich, St Louis, MO).

2.3. Distillation system

The distillation system (Fig. 1) was scaled down from a 50-L pilot-scale batch packed column (García-Llobodanin et al., 2011) to a 1.5-L glass laboratory scale. A Florence flask (2 L) was coupled to a packed glass column (filled with a 1.1 g copper mesh) and a glass tubular heat exchanger (partial condenser). Both inner heat tubes were 8 mm in internal diameter and 80 mm in length. The system was isolated and introduced in a fume hood with constantly recirculating air. The internal reflux was modified by changing the cooling water flow rate (at 20 °C) of the partial condenser with a peristaltic pump (313S; Watson-Marlow Ltd., Falmouth, UK). The boiler was heated with a heating mantle (Fibroman-C 1000 mL; JP Selecta S.A., Abrera, Spain). Distillate samples were collected in 20-mL test tubes. Test tubes were covered with perforated caps to minimize evaporation loss of the most volatile compounds. In addition, the system was equipped with four temperature sensors: two in the partial condenser system (shell outlet, T3; and shell inlet, T4), one after the partial condenser (outlet stream of the inner tube, T2) and half a meter away from the device (fume hood's room temperature, T1). Before the experiments, the peristaltic pump of the partial condenser was calibrated between 0 and 300 mL/min.

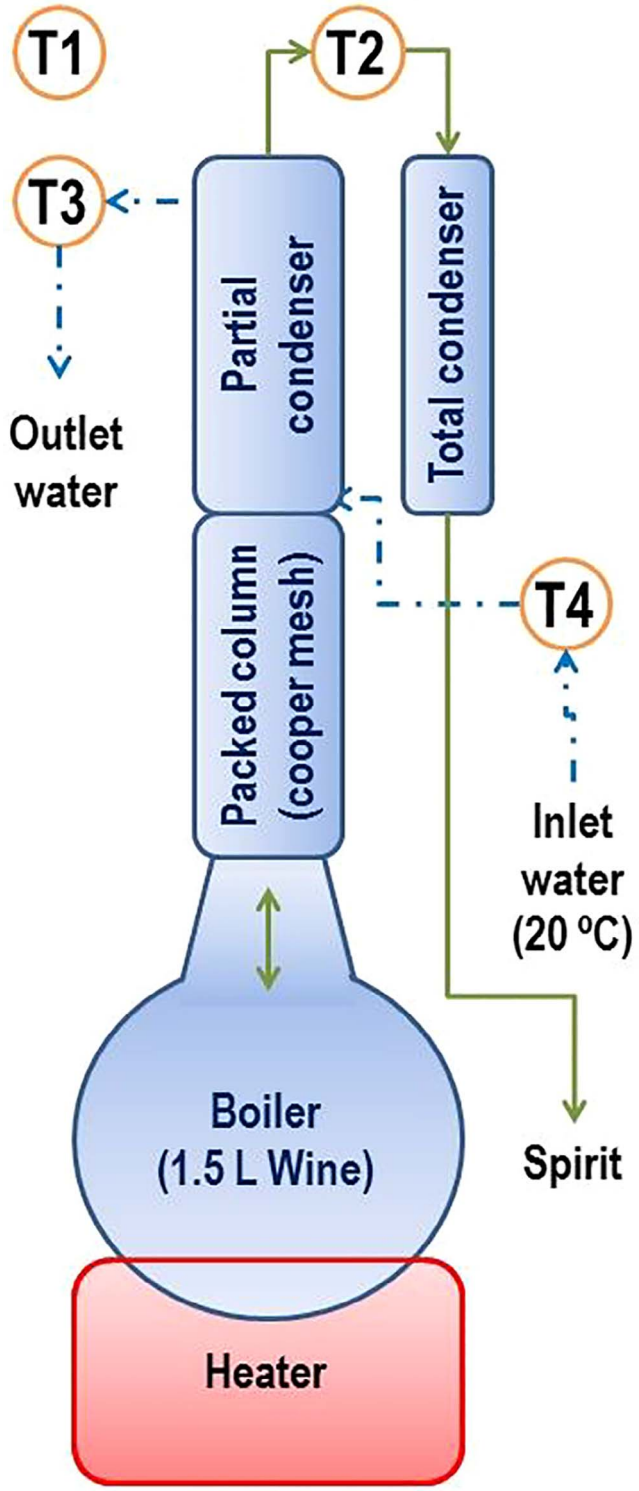

Fig. 1. Sketch of the distillation device. T1 to 4 are temperature sensors. Expect for T1, distances and dimensions between device parts were maintained using an original drawing.

2.4. Distillation process

Wine (1.5 L) was placed in the Florence flask with 3 g of pumice stone. The electrical heating mantle operated at a constant power of 410 W for the first 33 min. Then power was reduced and kept constant at 205 W until the end of each assay. Power values were calculated without considering heat loss. Afterwards, to ensure reproducibility of the first fraction, 300 mL/min of CFR was kept constant for 7 min to achieve total reflux. Power and time values were defined after preliminary experiments (data not shown). Then, 40 min (33 + 7 min) after the onset of the process, CFR was decreased to 100, 65 or 30 mL/min during an HDV of 20, 12.5 or 5 mL, according to the experimental design (Table 1). After the first sample (S1), the partial condenser was stopped and emptied (CFR = 0 mL/min). The next 13 samples (S2–S14) of 20 mL each were distilled without CFR. The last sample (S14) had an alcoholic strength by volume around 39% (*v/v*). Optimal distillations were performed with CFR and HDV values according to the optimal conditions obtained with the Muscat wine (2015 vintage).

2.5. Chemical analysis of wine and distilled fractions

Wine ethanol content was determined by ebulliometry (electronic ebulliometer; GAB instruments, Moja-Olèrdola, Spain), wine pH by a pH-meter (Crison Basic 20, L'Hospitalet de Llobregat, Spain) and ethanol content of all distillation samples (S1–S14) by an electronic density meter (DSA 5000 M; Anton Paar, Graz, Austria). Distilled samples were grouped in four fractions: head-cut (S1), heart-1 (S2–S7), heart-2 (S8–S13) and tail-cut (S14). An aliquot of 50 µL of the internal standard solution (400 mg/L of 2-octanol; Sigma-Aldrich, St Louis, MO) were added to 1 mL of each fraction (previously adjusted to an alcoholic strength by volume of 40% v/v). All analyses were performed 21 days after each distillation.

2.6. Chromatographic analysis

Chromatographic analyses were performed by using a gas chromatograph equipped with a flame ionization detector (GC-FID) (Agilent 6890, Agilent Technologies, Waldbronn, Germany), an autosampler (Agilent 7683, Agilent Technologies, Waldbronn, Germany) and a capillary polar column (MetaWAX, 60 m length, 0.25 mm ID and 0.5 µm phase thickness) from Teknokroma (Barcelona, Spain). Injection (2 µL) was done in split mode (1:5). Injector and detector temperatures were at 250 °C and 260 °C, respectively. Oven temperature program was: 40 °C (5 min), 7 °C/min up to 100 °C (15 min), 3 °C/min up to 140 °C and 2 °C/min up to 200 °C (5 min). Column-head flow was initially set at 0.5 mL/min (28 min) and increased with a rate of 5 mL/min^2 up to 1.1 mL/min (67 min) using helium as carrier gas. Quantifications were carried out by interpolation of calibration curves built with a synthetic hydro-alcoholic solution (40% *v/v* of ethanol) doped with all compounds at different levels. Reagents' CAS, supplier companies and Kovats retention indices are shown in Table S1. Detection and quantification limits were determined by signal-to-noise ratios (S/N) of 3 and 10, respectively.

2.7. Response surface methodology (RSM)

RSM aims to screen, model and optimize an experimental design by studying the relationships between two or more independent variables (factors) and a response (compound concentration). In addition to factors of CCD (HDV, pH and CFR of Table 1), the volume of the heart-cut fraction was added to the model as a fourth factor. For that, the composition of heart-1 (120 mL) plus a percentage of heart-2 (0–100% of 120 mL) was considered as a model response. The 0, 50 and 100% of heart-2 (HTV) were the three levels chosen for the RSM. It should be noted that the response variation produced by HTV is not necessarily linear, since the concentration of the compounds (g/hL a.a.) depends on the alcoholic content of both fractions (% *v/v*). In this way, the relative impact of distillation sub-fractions could be evaluated. Therefore, after the CCD was performed, a 3-level-4-factor RSM could estimate a second-degree polynomial model with all the compiled data.

2.7.1. Response surface models

In this study, sum-of-squares type III was used to calculate the error

Table 2
Compound groups, names, odor description, odor desirability, odor threshold and heart-cut maximum levels throughout CCD, and concentrations, standard deviation and significant differences ($p < .05$) between distillation fractions of the 6 RSM center point replicates).[a]

Compound		Odor description	Odor desirability	Odor threshold	Heart-cut maximum levels of CCD	Fraction concentration		
Group	Name					Head-cut	Heart-1 cut	Heart-2 cut
alcohol content	ethanol (% *v/v*)	alcoholic	–	–	71.0	87.7 ± 0.4c	70.5 ± 0.5b	55.2 ± 1.4a
head compounds	acetaldehyde	pungent	STB	25.0[b]	171	839 ± 102c	121 ± 10b	9.68 ± 0.64a
	acetal	fruity/sherry	–	0.250[b]	38.0	153 ± 25c	25.5 ± 1.7b	2.67 ± 0.29a
	ethyl acetate	solvent	STB	12.5[c]	35.4	227 ± 34b	18.5 ± 1.9a	3.72 ± 0.43a
fruity esters	ethyl butyrate	fruity	LTB	0.005[b]	0.263	1.95 ± 0.78	d. – n.q.	n.d.
	ethyl hexanoate	fruity	LTB	0.0013[b]	0.956	2.20 ± 0.98b	0.699 ± 0.065a	d. – n.q.
	ethyl octanoate	fruity	LTB	0.0005[b]	1.21	1.13 ± 0.43b	0.980 ± 0.113b	0.090 ± 0.031a
	ethyl decanoate	floral/brandy	LTB	0.105[d]	0.14	0.520 ± 0.092b	0.117 ± 0.007a	0.087 ± 0.024a
tail compounds	ethyl lactate	lactic	–	25.0[b]	28.7	0.396 ± 0.112a	10.3 ± 1.2b	35.6 ± 3.6c
	furfural	burned	–	5.10[c]	0.480	n.d.	d. – n.q.	0.600 ± 0.056
	β-phenylethanol	rose	–	2.50[b]	2.00	0.149 ± 0.024a	0.763 ± 0.077b	2.62 ± 0.26c
terpenic compounds	linalool	floral/Muscat	LTB	0.250[e]	2.43	0.197 ± 0.017a	1.72 ± 0.11c	0.576 ± 0.028b
	α-terpineol	floral	–	75.0[e]	2.00	0.248 ± 0.022a	1.78 ± 0.18b	1.81 ± 0.14b
higher alcohols	1-hexanol	mown grass	–	5.00[f]	1.29	0.295 ± 0.03a	1.26 ± 0.09b	0.334 ± 0.01a
	1-propanol	fusel-like	–	208[b]	51.5	26.3 ± 4.7a	48.8 ± 5.8b	38.1 ± 3.5b
	2-methyl-1-butanol	fusel-like	–	7.50[b]	26.4	6.59 ± 1.05a	25.8 ± 2.5b	6.73 ± 0.43a
	3-methyl-1-butanol	fusel-like	–	7.50[b]	168	41.9 ± 5.2a	162 ± 16c	55.3 ± 3.8b
others	methanol	–	–	167[b], 200[g]	92.2	108 ± 18b	75.9 ± 9.2a	99.5 ± 10.6b
	acetic acid	vinegar-like	–	50.0[e]	16.0	247 ± 23b	9.67 ± 0.84a	8.04 ± 0.54a

[a] Except ethanol (% *v/v*), all compounds are expressed in g/hL a.a. "d. – n.q." means detected in at least one replicate, but not quantified. "n.d." means not detected in any replicate. "–" means there is not enough information. "LTB" means Larger-The-Better. "STB" means Smaller-The-Better.
[b] Christoph and Bauer-Christoph (2007).
[c] Clutton and Evans (1978).
[d] Pino, Tolle, Gök, and Winterhalter (2012).
[e] Cacho, Moncayo, Palma, Ferreira, and Culleré (2012).
[f] Apostolopoulou, Flouros, Demertzis, and Akrida-Demertzi (2005).
[g] European legal limit (European Commission, 2008).

terms for statistical significance of linear and quadratic main factor effects and the 2-way interaction factor effects (Montgomery, 2013). Non-significant effects ($p > .05$) were ignored to obtain more accurate estimation models. The RSM estimated response for each compound was calculated using the following second-degree polynomial function with four factors:

$$\hat{Y} = b_0 + \text{block1} + b_1\cdot\text{HTV} + b_2\cdot\text{HDV} + b_3\cdot\text{pH} + b_4\cdot\text{CFR} + b_{1,1}\cdot\text{HTV}^2 + b_{2,2}\cdot\text{HDV}^2 + b_{3,3}\cdot\text{pH}^2 + b_{4,4}\cdot\text{CFR}^2 + b_{1,2}\cdot\text{HTV}\cdot\text{HDV} + b_{1,3}\cdot\text{HTV}\cdot\text{pH} + b_{1,4}\cdot\text{HTV}\cdot\text{CFR} + b_{2,3}\cdot\text{HDV}\cdot\text{pH} + b_{2,4}\cdot\text{HDV}\cdot\text{CFR} + b_{3,4}\cdot\text{pH}\cdot\text{CFR} \quad (1)$$

where $\hat{Y}$ is the estimated response for each compound (concentration in heart-cut fraction). *HTV, HDV*, *pH* and *CFR* are the coded factor values (± 1). *block1* is the blocking variable; $b_{i,j}$ are regression coefficients with different subscripts stand for: 0 is the intercept of the function, 1 is the HTV, 2 is the HDV, 3 is the pH and 4 is the CFR.

As has been introduced in Section 2.1, adding a blocking variable to the model allows us to minimize the effect of a known nuisance variable by arranging the experimental runs in similar groups. In our case, we separate the experiments into two groups (blocks) according to their order of execution. In sum, blocking modifies the origin of the coordinates of a group of samples to minimize a nuisance variation, allowing a better fit of the relevant variables of the study. In this study, experiments 1–10 were used to determine $b_0 + block1$, while experiments 11–20 were used to determine b_0.

Therefore 40 experimental points were extracted from the 20 experimental assays, because for every assay 2 heart fractions were analyzed (heart-1 and heart-2), specifically 30 data points (without counting central point replicates) and 16 regression constants (counting the blocking variable).

For compounds with low levels, concentration values below the detection limit were considered as 0 g/hL a.a., and values between detection and quantification limits were considered as the average of both limits.

2.7.2. Desirability function approach

Multi-objective optimization aims to calculate one optimal solution that groups several objectives simultaneously. Derringer and Suich (1980) suggested transforming the estimated responses (RSM) into a range of acceptability values between 0 (undesirable) and 1 (very desirable). For optimizing, desirability functions are based on three response types: Nominal-The-Best (NTB-type) to obtain a target value, Larger-The-Better (LTB-type) to maximize the response, and Smaller-The-Better (STB-type) to minimize the response. A more detailed mathematical explanation can be found in Costa, Lourenço, and Pereira (2011).

Starting from the assumption that each compound has a positive or negative aroma effect, LTB- and STB-type functions were used in this study. Curvature between inflection points of the function was not considered. In order to transform the estimated response to a linear desirability function, the following concentration points were used for each compound:

- Lower limit point: the compound odor threshold, assigned to a desirability value of 0 (for the LTB-type) or 1 (for the STB-type). This limit was selected since it makes no sense to do an organoleptic optimization of a compound below the consumer perception.
- Upper limit point: the maximum concentration analyzed in all CCD assays, assigned to a desirability value of 1 (for the LTB-type) or 0 (for the STB-type).

Therefore, the individual desirability of each compound increased (LTB-type) or decreased (STB-type) proportionally to the concentration range above the odor threshold, to maximize or minimize the response according to its positive or negative odor effect on the spirit,

respectively. Fig. S1 (Supplementary information) shows a graphical example of the implementation of the desirability function in this study. Odor description, desirability function-type, odor thresholds and maximum concentration for each compound are shown in Table 2.

To group several individual functions in a single multi-objective solution, Derringer and Suich (1980) suggested obtaining an overall desirability by calculating the geometric mean of the individual desirability of the compounds involved in each optimization. Thus, optimization aims to find the values of the factors that maximize overall desirability.

2.8. Sensory analysis

Sensory analysis was performed in the tasting room of the Facultat d'Enologia of Universitat Rovira i Virgili in compliance with standard NF V09-105 (AFNOR, 1987). The training period was conducted in 14 sessions of 1 h each with a selection of 17 assessors. During training sessions, samples of ethyl alcohol of agricultural origin (40% *v/v*) (Alcohol Suave, Bodegas y Destilerías Lehman S.A., Tortosa, Spain) were spiked at several levels of ethyl acetate as a 'glue-like' descriptor (0–300 mg/L range), linalool as a 'terpenic' descriptor (0–12 mg/L range) and ethyl hexanoate as a 'fruity' descriptor (0–4 mg/L range). Moreover, assessors were taught to differentiate spirits fractions by identifying the 'tail-like' descriptor using tail-cut fractions from spirit samples of previous research (Matias-Guiu et al., 2016) diluted at several levels.

For the sensory characterization of optimal distillation strategies (3 Muscat and 3 Macabeo), assessors scored samples using 4 aroma attributes ('terpenic', 'fruity', 'glue-like' and 'tail-like') and a hedonic test, both using 11-point scales from 0 to 10. Two sessions were held to replicate the analysis for each assessor, using Latin square designs (Montgomery, 2013). During the first 10 min of both sessions, assessors analyzed the optimizations produced with the Muscat 2016 wine. Then, after 10 min of rest, Macabeo 2016 wine optimizations were analyzed for another 10 min. For data analysis, the Product Characterization tool of XLSTAT-Sensory statistical package was applied to check if the scores given by the judges were significantly different (ANOVA model: Score = product effect + judge effect + session effect). In both training and analysis, 5 mL of samples were served in black glass cups and assessors had access to drinking water.

2.9. Statistical analysis

The CCD, RSM and the desirability function approach were performed with STATISTICA 7.0 statistical package. ANOVA, Tukey's HSD test ($p < .05$), Spearman correlation test, principal component analysis (PCA) and product characterization (an XLSTAT-Sensory tool) were performed with XLSTAT 2017 statistical add-in for Microsoft Office.

3. Results and discussion

3.1. Center point analyses

3.1.1. Volatile composition of head and heart fractions

Center point (six replicates) was applied to analyze the distillation kinetics of volatile compounds and their variance. Table 2 presents the studied compounds (18 quantified compounds out of 20 calibrated, shown in Table S1) grouped according to their distillation behavior and physicochemical characteristics (Cortés, Gil, & Fernández, 2009; Jouret et al., 1998; Matias-Guiu et al., 2016). For all the studied compounds, the table includes their odor descriptors, odor desirability function-type, odor thresholds, maximum levels found in all assays of CCD and their concentration through the distillation of the center point.

In the center point, compositions of all compounds showed significant differences between at least two fractions. Head compounds group (acetaldehyde, acetal and ethyl acetate (C_2)) and fruity esters group (ethyl butyrate (C_4), ethyl hexanoate (C_6), ethyl octanoate (C_8) and ethyl decanoate (C_{10})) were mostly distilled during the head-cut, due to their high vapor pressure and/or high solubility in ethanol. In spirits distillations, the head-cut is implemented to reduce the content of negative impact aromas (such as of acetaldehyde and ethyl acetate) and toxic compounds (such as methanol) in the product (Christoph & Bauer-Christoph, 2007). The C_4-C_{10} ethyl esters are known for their high positive impact on spirits aroma, having low odor thresholds and providing fruity notes (Christoph & Bauer-Christoph, 2007). Even though methanol showed higher concentrations in the head-cut than in heart-1, it is not considered to be a head compound, since it was present at high levels in both the first and the last distillation fractions (Carvallo, Labbe, Pérez-Correa, Zaror, & Wisniak, 2011) and its acceptance level depends on its legal regulation (European Commission, 2008) rather than its aroma impact. Acetic acid also showed high concentrations in the head-cut due to its formation by the hydrolysis of ethyl acetate (Christoph & Bauer-Christoph, 2007), despite its high boiling point (118 °C) (Environmental Protection Agency, 2012) and high water solubility ($K_{OW} = -0.17$), although, in the heart-cut it presented significantly lower values than its threshold.

The higher alcohols group (1-propanol, 1-hexanol, 2-methyl-1-butanol and 3-methyl-1-butanol) and the terpenic compounds group (linalool and α-terpineol) tended to distill during heart-1, due to their higher boiling point and/or solubility in water with respect to head and fruity ester compound groups. At high levels, higher alcohols are known for their negative impact on the spirit's aroma (fusel-like flavors). In turn, terpenic compounds are known for their high positive impact, providing the typical flowery notes from Muscat wines (Christoph & Bauer-Christoph, 2007). In our distillates, some of the compounds of both groups, like 1-propanol and α-terpineol, showed much lower concentrations than their odor thresholds (Table 2).

Tail compounds (furfural, ethyl lactate and β-phenylethanol) distilled mainly in the last fraction (heart-2), given their high boiling points and/or water solubilities. Tail compounds are considered a defect in young wine spirits, especially furfural compounds that give burnt and sweet aroma notes. However, they can add positive characteristics to other type of spirits, e.g. β-phenylethanol may provide a positive rose flavor and furfural may contribute to toasted wood aroma (Christoph & Bauer-Christoph, 2007).

Methanol, recognized as a toxic compound, presented much lower concentrations than the legal limit of 200 g/hL a.a. for wine spirits in all collected fractions (European Commission, 2008). In addition, ethyl carbamate, a carcinogen compound of Group 2A according to the International Agency for Research on Cancer (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2010), was not detected in any fraction with an analytical detection threshold of 0.2 mg/L (40% alc. *v/v*).

3.1.2. System variance

Traditionally, in the spirits industry, distillation columns do not operate under adiabatic conditions and this hinders the production of distillates with consistent composition. In this study, heat insulation significantly improved the experimental reproducibility of the distillation runs. However, it was difficult to completely avoid or control external variables with this distillation system (García-Llobodanin et al., 2011). The relative standard deviations calculated from the data of Table 2 for head-cut were high, especially for ethyl lactate (28%), ethyl octanoate (38%), ethyl butyrate (40%) and ethyl hexanoate (44%). Nevertheless, relative standard deviations in the compositions of the fractions that give rise to the product (heart-1 and heart-2) were below 12% in all compounds. The effect of room temperature and distillation time on the composition of center point replicates was checked by simple regression with no significant differences ($p < .05$) (data not shown).

Table 3
Compounds heart-cut concentration models. Significant regression coefficients values ($p < .05$) with their standard errors of linear (L), quadratic (^2) and 2-way interaction (−) effects by HTV, HDV, pH and CFR rescaled factors (± 1), and equation's adjusted correlation coefficient (*R*-adj).[a]

compound/ coefficient	Intercept	Block1	HTV (L)	HDV (L)	pH (L)	CFR (L)	HTV(^2)	HDV(^2)	pH(^2)	CFR(^2)	HTV-HDV	HTV-pH	HTV-CFR	HDV-pH	HDV-CFR	pH-CFR	*R*-adj
ethanol (% *v/v*)	65.3 ± 0.1*	−0.14 ± 0.116	−3.90 ± 0.13*	−0.692 ± 0.148*	0.190 ± 0.148	n.s.	1.30 ± 0.22*	n.s.	−0.477 ± 0.227*	n.s.	−0.208 ± 0.179	n.s.	n.s.	n.s.	n.s.	n.s.	0.986
acetaldehyde	80.5 ± 1.3*	−4.38 ± 1.52*	−30.5 ± 1.8*	−24.6 ± 2.1*	7.86 ± 2.08*	−8.78 ± 2.08*	11.5 ± 3.1*	n.s.	n.s.	n.s.	8.29 ± 2.52*	n.s.	2.88 ± 2.52	4.35 ± 2.33*	n.s.	n.s.	0.972
acetal	16.8 ± 0.5*	0.951 ± 0.534*	−7.04 ± 0.54*	−5.57 ± 0.64*	−1.75 ± 0.64*	−1.8 ± 0.64*	2.65 ± 0.94*	n.s.	3.85 ± 1.14*	−1.19 ± 1.14	1.93 ± 0.77*	n.s.	n.s.	−1.27 ± 0.71*	−0.982 ± 0.714	n.s.	0.952
ethyl acetate	13.1 ± 0.5*	1.05 ± 0.54*	−4.44 ± 0.57*	−6.62 ± 0.67*	−2.56 ± 0.67*	−1.04 ± 0.67	1.66 ± 0.99	n.s.	2.99 ± 1.03*	n.s.	2.54 ± 0.81*	n.s.	n.s.	n.s.	−0.938 ± 0.748	1.41 ± 0.75*	0.933
ethyl butyrate	0.091 ± 0.003*	0.014 ± 0.007*	−0.037 ± 0.008*	−0.062 ± 0.01*	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.024 ± 0.012*	n.s.	n.s.	−0.017 ± 0.011	−0.017 ± 0.011	0.017 ± 0.011	0.832
ethyl hexanoate	0.469 ± 0.014*	0.062 ± 0.016*	−0.155 ± 0.017*	−0.159 ± 0.02*	n.s.	0.030 ± 0.020	0.058 ± 0.03*	n.s.	−0.071 ± 0.031*	n.s.	0.052 ± 0.024*	n.s.	n.s.	n.s.	−0.041 ± 0.022*	0.063 ± 0.022*	0.930
ethyl octanoate	0.67 ± 0.021*	0.133 ± 0.025*	−0.215 ± 0.03*	−0.133 ± 0.035*	n.s.	n.s.	0.081 ± 0.051	n.s.	n.s.	n.s.	n.s.	0.048 ± 0.042	n.s.	n.s.	n.s.	0.067 ± 0.039	0.871
ethyl decanoate	0.109 ± 0.001*	n.s.	−0.008 ± 0.003*	−0.005 ± 0.004	n.s.	−0.007 ± 0.004*	n.s.	n.s.	n.s.	n.s.	0.005 ± 0.004	n.s.	n.s.	−0.005 ± 0.004	0.004 ± 0.004	0.005 ± 0.004	0.546
ethyl lactate	20.0 ± 0.2*	−1.78 ± 0.26*	6.66 ± 0.31*	1.95 ± 0.36*	−1.74 ± 0.36*	n.s.	−2.62 ± 0.54*	n.s.	n.s.	n.s.	n.s.	−0.958 ± 0.441*	n.s.	n.s.	n.s.	n.s.	0.975
furfural	0.313 ± 0.013*	n.s.	0.125 ± 0.018*	0.059 ± 0.021*	n.s.	n.s.	−0.049 ± 0.032	n.s.	n.s.	n.s.	0.033 ± 0.026	n.s.	n.s.	n.s.	n.s.	n.s.	0.796
β-phenylethanol	1.49 ± 0.01*	−0.133 ± 0.017*	0.512 ± 0.021*	0.116 ± 0.024*	n.s.	n.s.	−0.202 ± 0.036*	n.s.	n.s.	n.s.	0.051 ± 0.03	−0.032 ± 0.03	n.s.	n.s.	n.s.	n.s.	0.979
linalool	1.3 ± 0.02*	−0.055 ± 0.019*	−0.321 ± 0.021*	−0.071 ± 0.024*	0.511 ± 0.024*	−0.043 ± 0.024*	0.12 ± 0.036*	n.s.	−0.077 ± 0.037*	n.s.	n.s.	−0.173 ± 0.029*	n.s.	n.s.	n.s.	0.029 ± 0.027	0.982
α-terpineol	1.82 ± 0.01*	−0.145 ± 0.017*	n.s.	0.067 ± 0.022*	−0.238 ± 0.022*	n.s.	n.s.	n.s.	−0.128 ± 0.034*	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.918
1-hexanol	0.909 ± 0.006*	−0.045 ± 0.007*	−0.260 ± 0.009*	n.s.	0.012 ± 0.01	−0.011 ± 0.01	0.097 ± 0.015*	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.985
1-propanol	45.1 ± 0.3*	−4.37 ± 0.35*	−3.13 ± 0.42*	n.s.	0.692 ± 0.491	−0.73 ± 0.491	1.06 ± 0.73	n.s.	n.s.	n.s.	n.s.	−0.706 ± 0.595	n.s.	n.s.	n.s.	n.s.	0.938
2-methyl-1-butanol	18.6 ± 0.2*	−1.43 ± 0.18*	−5.36 ± 0.22*	n.s.	0.401 ± 0.261	n.s.	2.00 ± 0.39*	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.978
3-methyl-1-butanol	122 ± 1*	−10.0 ± 1.1*	−30.1 ± 1.4*	n.s.	2.47 ± 1.59	−1.91 ± 1.59	11.2 ± 2.4*	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.976
methanol	85.8 ± 0.5*	−8.42 ± 0.57*	6.36 ± 0.7*	n.s.	n.s.	−1.48 ± 0.81*	−2.71 ± 1.21*	n.s.	n.s.	n.s.	n.s.	−1.23 ± 0.99	n.s.	n.s.	n.s.	n.s.	0.954
acetic acid	9.49 ± 0.18*	0.396 ± 0.266	−0.689 ± 0.292*	−2.79 ± 0.34*	n.s.	−0.786 ± 0.341*	n.s.	1.03 ± 0.52*	n.s.	n.s.	1.19 ± 0.41*	n.s.	n.s.	n.s.	n.s.	n.s.	0.857

[a] Except ethanol, all compounds are expressed in g/hL a.a. HTV means the percentage (%) of Heart-2. HDV means Head-Cut Volume. CFR means Cooling Flow Rate. * $p < .001$; n.s. means no significant.

3.2. Response surface analysis

Linear, quadratic and 2-way interaction regression coefficients, as well as adjusted correlation coefficients of the model for the rescaled factors (Eq. (1)), are shown in Table 3. In Supplementary information, Table S2 shows other statistical parameters that measure the goodness of fit of the models and Fig. S2 presents contour plot examples that can help the interpretation of the models, explained by regression coefficients of Table 3.

Some compounds presented a statistically significant lack of fit *F*-test ($p < .05$) due to their low concentrations in heart-2 (C_4, C_6, C_8, C_{10} ethyl esters) and heart-1 (β-phenylethanol) fractions (Table S2). This can be explained because when the concentrations of the replicates are around quantification limit, a large deviation is produced between analytical values above the limit and those below; when the concentrations of all replicates are below the quantification limit, replicates have identical or very similar concentration values, which imply a pure error that tends towards zero. In both situations, the lack of fit *F*-test may be significant. Therefore, in these cases, the goodness of fit is analyzed by the analysis of variance of sums of squares (< 0.0001 for all models) and the adjusted correlation coefficient.

Blocking coefficients were significant in almost all models. Most volatile compounds presented positive blocking coefficients (acetal and C_2, C_4, C_6, C_8 ethyl esters) except for acetaldehyde. The remaining compounds had a negative coefficient, except for acetic acid, which was in equilibrium with ethyl acetate. Thus, the system's rectification could change through the days of experimentation by an unknown external factor that we could not control. In Supplementary information, Fig. S2 shows counter plot examples that can help the interpretation of the models explained by regression coefficients of Table 3.

To determine the effects of the studied factors on distillation time during the head-cut, Tukey's (HSD) test pairwise comparisons after a multi-way ANOVA ($p < .05$) were performed with head-cut distillation time (dependent variable) and pH, CFR and HDV factors (explanatory variables). Significant differences were found between 30 and 100 mL/min CFR levels and between all HDV levels. The pH showed no significant effects. Thus, higher CFR (higher reflux) and higher HDV (larger head-cut volume) increased distillation time (data not shown).

3.2.1. Distillation-cuts (HTV and HDV) factors

As can be seen in Table 3, HTV and HDV linear regression coefficients of each compound presented identical signs (+ or −), as long as both effects were significant, since both factors depend on distillation kinetics previously explained in Section 3.1.1.

Ethanol, head compounds, fruity ethyl esters and linalool tend to distill in higher concentrations at the beginning of the distillation (Matias-Guiu et al., 2016). Hence, larger HDV increased their extraction during the head-cut and consequently reduced their levels in the heart-cut. In addition, since the concentration of these compounds in the boiler is significantly reduced during the last fractions, a larger HTV dilutes them in the heart cut. Consequently, both factors present negative linear coefficients. On the contrary, tail compounds and α-terpineol tend to form and distill in later fractions of the process. Thus, larger HDV increased their concentrations in the heart-cut because there is a displacement of the tail-cut, since heart-cut keeps the recovered volume, as well as an increase of the distillation time. Likewise, larger HTV increased tail compounds levels in the heart-cut by adding the last distillation fractions. Therefore, both factors presented positive linear coefficients. Higher alcohols and methanol presented no significant effects by HDV. The HTV negatively affects the concentration of higher alcohols by dilution and depletion over time in the boiler (Matias-Guiu et al., 2016) while methanol concentration is positively affected since its relative concentration (g/hL a.a.) increases in the last fractions (Carvallo et al., 2011).

3.2.2. pH factor

The distillation of wine occurs in an acidic hot environment with pH between 2.8 and 4.0 (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006), and temperatures ranging between 78 and 100 °C. This medium favors the formation or reaction of many volatile compounds present in wine. Therefore, the pH of the raw material can be an essential factor for distillation strategies, which, in turn, can be easily modified by the producer.

Table 3 shows that all head compounds presented linear effects with pH, with a positive regression coefficient for acetaldehyde and negative coefficients for acetal and ethyl acetate. In acidic media, acetaldehyde and ethanol react to form acetal (Kłosowski & Czupryński, 2006). Furthermore, ethyl acetate is formed by acetic acid esterification, catalyzed in acid media. Therefore, low pH accelerated the formation of ethyl acetate in the boiler (wine) and increased its concentration in the vapor phase (product) since it is much more volatile than acetic acid. Acetal and ethyl acetate also presented positive quadratic effects with pH, showing lower levels in the 2.45–3.20 pH range. Hence, low pH favored acetal and ethyl acetate concentration in the heart-cut and decreased acetaldehyde concentration.

In the case of fruity esters, their values were below their quantification limits in the last fractions, due to depletion over time. For this reason, the sum of squares regression did not find linear significant differences with pH, given the small variation of their concentration in heart-2. Nevertheless, variations due to pH can be explained with 2-way interaction effects. Fruity esters showed a positive coefficient of HTV-pH interaction for ethyl octanoate, positive coefficients of pH-CFR interaction for all fruity esters, and negative coefficients of HDV-pH interaction for ethyl butyrate and ethyl decanoate. Low pH could favor the formation of fruity esters from their carboxylic acids, as happened with ethyl acetate–acetic acid equilibrium; thus low pH favors removing fruity esters in the boiler due to their formation at the beginning of distillation. Running out of these esters due to pH interaction effects is more noticeable with high values of HTV and CFR (longer esterification time). On the contrary, fruity esters exhaustion is reduced when the head-cut volume is small, since there is a much shorter time for esterification (negative HDV-pH interaction coefficients). Therefore, low pH accelerates the formation of fruity esters by esterification, behavior that would decrease their levels in the spirit if the head-cut volume is too large.

In relation to tail compounds, ethyl lactate had a negative linear effect with pH, like ethyl acetate. Even though pH should favor the generation of furfural during distillation due to Maillard reactions (Mottram, 2007; Peña y Lillo, Agosin, Belancic, & Latrille, 2005; Yemiş & Mazza, 2012), this effect was not significant. Linalool and α-terpineol presented positive and negative linear effects with pH, respectively, since linalool and other terpenic compounds tend to transform to α-terpineol in catalyzed hot acid media (Baxter et al., 1978; Bedoukian, 1986; Ohta et al., 1991; Osorio et al., 2004). Terpenic compounds also presented positive quadratic effects with pH, showing lower levels in the 1.70–2.45 pH range. In the case of higher alcohols and ethanol, they presented positive effects with pH, probably due to their reaction by esterification at low pH.

3.2.3. Cooling flow rate (CFR) factor

Previous work had shown that high internal refluxes during the heart-cut can significantly alter the distillation behavior throughout the distillation (Matias-Guiu et al., 2016). The present study focused on head-cut reflux strategies; hence, CFR was applied during the head-cut fraction only and in a narrow flow range, to avoid masking the effects of other factors.

Head compounds were efficiently removed during the head-cut with high CFR values, due to their high volatilities and high solubilities in ethanol (Rodríguez-Bencomo et al., 2016), and therefore showed negative linear effects with CFR.

Table 4
Distillation conditions, desirability values and predicted and analytical composition of head off-flavors reduction; terpenic enhancement and fruity esters enhancement optima calculated with RSM and desirability function approaches.[a]

distillation conditions	head off-flavor reduction	terpenic enhancement	fruity esters enhancement	head off-flavor reduction	terpenic enhancement	fruity esters enhancement	head off-flavor reduction	terpenic enhancement	fruity esters enhancement
HTV (%)	100	16.7	66.7	100	16.7	66.7	100	16.7	66.7
HDV (mL)	20.0	20.0	5.00	20.0	20.0	5.00	20.0	20.0	5.00
pH	1.70	3.20	2.95	1.70	3.20	2.95	1.70	3.20	2.95
CFR (mL/min)	100	100	100	100	100	100	100	100	100
	predicted values (RSM) for Muscat 2015 heart cut			*analytical values for Muscat 2016 heart cut*			*analytical values for Macabeo 2016 heart cut*		
desirability value	0.993	0.806	0.658						
ethanol (% *v/v*)	61.1	67.6	64.8	56.8 ± 0.0 a	62.9 ± 0.0 c	61.2 ± 0.2 b	56.5 ± 0.2 a	63.3 ± 0.2 c	61.6 ± 0.5 b
compounds (g/hl a.a.)									
acetaldehyde	**27.1**	**77.4**	**88.0**	15.5 ± 0.3 a	24.9 ± 3.1 b	37.1 ± 2.6 c	21.5 ± 0.6 a	50.5 ± 3.2 b	63.7 ± 3.8 c
acetal	11.7	12.7	19.1	8.01 ± 0.07 a	9.47 ± 0.8 a	17.2 ± 1.4 b	10.1 ± 0.2 ab	7.38 ± 0.01 a	14.2 ± 2.7 b
ethyl acetate	**8.44**	**8.38**	**18.1**	41.9 ± 1 c	12.3 ± 1.8 a	30.2 ± 1.1 b	36.4 ± 5.5 c	9.10 ± 0.30 a	19.4 ± 0.8 b
ethyl butyrate	0.000	0.022	**0.172**	0.235 ± 0.003 a	d. – n.q.	0.296 ± 0.005 b	0.218 ± 0.046	d. – n.q.	0.256 ± 0.005
ethyl hexanoate	0.119	0.386	**0.648**	1.06 ± 0.03 b	0.800 ± 0.008 a	1.25 ± 0.03 c	0.848 ± 0.056 b	0.706 ± 0.027 a	1.19 ± 0.01 c
ethyl octanoate	0.287	0.751	**0.795**	1.50 ± 0.01	1.53 ± 0.06	1.50 ± 0.14	1.16 ± 0.02 a	1.33 ± 0.13 a	1.64 ± 0.02 b
ethyl decanoate	0.097	0.104	0.106	0.319 ± 0.054	0.450 ± 0.077	0.330 ± 0.048	0.203 ± 0.037 a	0.252 ± 0.013 a	0.338 ± 0.014 b
ethyl lactate	28.7	15.2	18.6	52.2 ± 1.8 b	13.4 ± 0.5 a	16.4 ± 0.1 a	3.90 ± 0.15 c	1.12 ± 0.14 a	1.84 ± 0.26 b
furfural	0.480	0.244	0.279	d. – n.q.	d. – n.q.	d. – n.q.	d. – n.q.	n.d.	d. – n.q.
β-phenylethanol	2.00	1.17	1.50	3.93 ± 0.21 b	2.76 ± 0.2 a	3.00 ± 0.06 a	2.85 ± 0.02 b	1.97 ± 0.17 a	2.18 ± 0.03 a
linalool	0.543	**2.03**	1.52	0.128 ± 0.003 a	2.17 ± 0.14 c	1.62 ± 0.03 b	n.d.	n.d.	n.d.
geraniol	d. – n.q.	d. – n.q.	d. – n.q.	n.d.	0.273 ± 0.013 b	0.185 ± 0.001 a	n.d.	n.d.	n.d.
α-terpineol	2.00	1.52	1.54	1.01 ± 0.06	0.977 ± 0.027	0.944 ± 0.002	n.d.	n.d.	n.d.
1-hexanol	0.723	1.13	0.831	0.840 ± 0.032 a	1.14 ± 0.05 b	0.886 ± 0.004 a	1.37 ± 0.05 a	1.94 ± 0.12 b	1.56 ± 0.07 a
1-propanol	42.4	48.1	43.8	24.8 ± 0.3 a	27.9 ± 0.8 b	25.3 ± 0.3 a	18.6 ± 0.1	21.2 ± 1.3	19.2 ± 0.6
2-methyl-1-butanol	14.9	23.5	17.3	35.0 ± 0.8 a	49.2 ± 2 b	38.5 ± 0.1 a	19.0 ± 0.8 a	27.0 ± 1.9 b	21.8 ± 0.7 a
3-methyl-1-butanol	99.1	148	113	133 ± 2 a	179 ± 7 b	142 ± 0 a	121 ± 4 a	166 ± 11 b	135 ± 5 a
methanol	89.2	79.7	85.9	47.9 ± 0.8 b	44.2 ± 0.6 a	46 ± 0.9 ab	44.4 ± 0.8	41.8 ± 2.4	41.5 ± 1.1
acetic acid	7.46	6.62	11.9	9.98 ± 1.18	8.08 ± 1.08	10.7 ± 0.8	9.17 ± 0.61	8.77 ± 1.46	11.4 ± 0.4

a Optimal distillation conditions and desirability values were calculated using the responses in bold. "n.d." means no detected. "d. – n.q." means detected but not quantified.

Ethyl hexanoate showed a positive linear effect with CFR, indicating that high rectification held up its distillation during the head-cut, favoring its recovery in the heart-cut (Matias-Guiu et al., 2016). The C_4-C_8 fruity esters also showed pH-CFR and HDV-CFR interaction effects. Positive pH-CFR coefficients indicate that high rectification avoids C_4-C_8 fruity esters distillation during the head-cut and slows down their formation by esterification (at high pH). Negative HDV-CFR coefficients indicate that both factors slowed down the distillation process and, consequently, increased the time for the esterification reaction during the head-cut. Ethyl decanoate (C_{10}) presented the opposite effects with CFR and pH-CFR coefficients, although its correlation coefficient was the lowest observed (R_{adj} = 0.546), therefore analysis of these results should be done with care.

Linalool showed a negative linear effect with CFR, but a positive pH-CFR interaction. High rectification increases the distillation time and therefore the degradation of linalool. However, this effect diminished with high pH since it slows down the reaction (Baxter et al., 1978; Bedoukian, 1986; Ohta et al., 1991; Osorio et al., 2004).

Higher alcohols and methanol presented a negative effect with CFR, except for 2-methyl-1-butanol, indicating that high refluxes during the head-cut favored their recovery in the heart-cut. Tail compounds were not affected by CFR, and acetic acid had the same behavior as its ester form (ethyl acetate).

3.3. Multi-objective optimizations

Desirability individual functions were constructed according to odor desirability, odor threshold and the maximum levels found during the experimental distillations (Table 2). To compute specific overall desirability functions, only compounds with a maximum concentration above their aroma threshold were considered. Three optimizations were calculated to obtain specific products with defined organoleptic characteristics: head off-flavors reduction (acetaldehyde and ethyl acetate STB-type), terpenic enhancement (linalool LTB-type + acetaldehyde and ethyl acetate STB-type) and fruity ester enhancement (C_4-C_8 esters LTB-type + acetaldehyde and ethyl acetate STB-type). Acetaldehyde and ethyl acetate were included in all optimizations, to minimize organoleptic defects. Ethyl decanoate (C_{10}) was not included in fruity ester enhancement since it presented a considerably low fitting correlation coefficient (R_{adj} = 0.546). Results of the calculated optimal distillation conditions are shown at the top of Table 4.

3.3.1. Head off-flavors reduction (HOR)

This strategy should reduce the acetaldehyde and ethyl acetate contents in the heart-cut. The largest HTV (240 mL) should dilute these compounds in the heart-cut, the largest HDV (20 mL) should favor their recovery in the head-cut, the lowest pH (1.70) should enhance acetaldehyde degradation, and the highest CFR (100 mL/min) should concentrate these compounds in the head-cut.

3.3.2. Terpenic enhancement (TEN)

This strategy should significantly increase the content of linalool in the heart-cut. Linalool is the only terpenic compound that showed concentrations above its aroma threshold (Table 2) and the most important for Muscat spirits (Agosin, Belancic, Ibacache, Baumes, & Bordeu, 2000; Cacho, Moncayo, Palma, Ferreira, & Culleré, 2013). Low HTV (16.7%) should concentrate linalool in the heart-cut, the largest HDV (20 mL) should clean the heart-cut from acetaldehyde and ethyl acetate, the highest pH (3.20) should reduce linalool degradation, and the highest CFR (100 mL/min) should reduce linalool loss in the head-cut.

3.3.3. Fruity esters enhancement (FEN)

This strategy included operating conditions that, according to the models, would enhance the fruity esters in the heart-cut. Medium HTV (66.7%) should balance the reduction of head off-flavors and fruity esters, due to dilution; lowest HDV (5 mL) should reduce their loss in the head-cut, high pH (2.95) should reduce fruity ester esterification, and highest CFR (100 mL/min) would reduce losses of fruity esters during distillation of the head-cut.

3.4. Evaluation of optimal strategies

Two different wines (Muscat and Macabeo of 2016 vintage) were distilled with the three optimal strategies to assess RSM models and to confirm chemical analyses with a sensory panel. The main difference between both wines is that Macabeo wine is known for having no detectable terpenic compounds.

3.4.1. Optimum chemical analyses

Table 4 shows the predicted heart-cut composition of Muscat 2015 wine distilled under the calculated optimal conditions (RSM). In addition, this table shows the mean concentration of heart-cut, standard deviation and significant differences of Muscat and Macabeo 2016 wines distilled with the same optimal conditions. Most of the time, the assessed strategies performed according to what was predicted by the RSM models. Heart-cuts of both wines distilled with the FEN strategy showed in most cases the highest values of C_4-C_{10} ethyl esters. The TEN strategy applied to the Muscat 2016 wine yielded the highest levels of linalool and geraniol in the heart-cut. Geraniol was not taken into account during RSM, since Muscat 2015 wine and spirits showed geraniol levels below its quantification limit. Macabeo had no detectable terpenic compounds in both spirits and wine (data not shown). The HOR strategy showed the lowest values of acetaldehyde; however, it also showed the highest values of ethyl acetate and unexpected high values of other ethyl esters. As explained in Section 3.2, we could infer from the RSM models that ethyl esters increase with low pH; however, RSM models predict a decrease of their concentration with high head-cut and heart-cut volumes, which was not observed in 2016 wine distillates. As can be seen throughout Table 4, the rest of the compounds have a similar ratio of concentrations between optimal strategies. Thus, deviation of ethyl esters in head off-flavor reduction can be due to compositional changes of wines. Chemical analyses of the three initial wines were carried out to understand this behavior (data not shown) without consistent conclusions. Furthermore, ethyl esters obtained low *p*-value in the lack of fit *F*-test, initially attributed to their low levels in heart-2; therefore, the model may generate a wrong prediction of the ethyl esters composition for the HOR strategy.

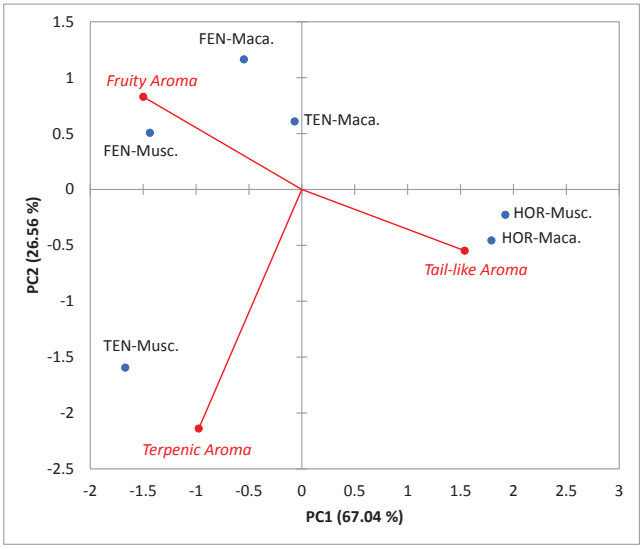

Fig. 2. PCA biplot of the sensory profile of optimal distillation strategies (HOR, FEN and TEN) using Muscat (Musc.) and Macabeo (Maca.) wines of 2016 vintage and filtering the non-discriminant descriptors ($p < .1$).

3.4.2. Optima sensory analysis

Samples of the optimal strategies using both wines (Muscat and Macabeo of vintage 2016) were analyzed by 17 trained assessors by rating 'terpenic', 'fruity', 'glue-like' and 'tail-like' aroma descriptors, plus a hedonic rating test.

In order to reflect the aroma differentiation between samples, sensory data was analyzed by PCA (Fig. 2). Two principal components (PC1 and PC2) explained 93.6% of the variance. 'Glue-like' aroma was not included, as it presented no significant differences. The PC1 axis places 'fruity' and 'terpenic' aroma descriptors against 'tail-like' descriptor, and PC2 places 'fruity' descriptor against 'terpenic' and 'tail-like' descriptors. This arrangement in the biplot appears to be related to the compound groups associated with descriptors, explained in Section 3.1.1. The optimal strategies were well differentiated by PCA. Muscat and Macabeo FEN samples presented high intensity of fruity aroma, and Muscat TEN sample presented high intensity of terpenic aroma. Macabeo TEN sample was located near Macabeo FEN sample, but with less fruity intensity. As expected, Macabeo spirits samples showed no terpenic aroma. Muscat and Macabeo HOR samples presented high intensity of tail-like aroma, since this strategy contained the last fractions of the distillation to dilute acetaldehyde and ethyl acetate in the heart-cut.

Finally, the preference test was analyzed with ANOVA and then Tukey's HSD test (to check the acceptance between samples) and with the Spearman correlation test (to check the correlation between aroma attributes and consumers acceptance). Hedonic data analysis can only be taken into account as a suggested trend, given the small number of assessors and their previous training. Tukey's pairwise comparisons (data not shown) showed significant differences ($p < .05$) between the Muscat TEN and FEN samples (highest ratings), and Muscat HOR samples (lowest rating). Macabeo samples showed no significant differences. Hedonic rating correlations ($p < .05$) showed that samples with terpenic and fruity aromas were scored positively, and samples with glue-like and tail-like aromas were scored negatively (Fig. S3). These hedonic results illustrate how developing and implementing distillation strategies can favor the production of genuine beverages that retain or enhance flavors coming from the initial fermented beverage, like terpenes (grape origin) and fruity ethyl esters (alcoholic fermentation origin).

4. Conclusions

High rectifications during distillation of the head-cut resulted in improved spirits, characterized by low content of head compounds and high content of fruity and terpenic compounds. The effect of distillation volumes and pH should be considered and adjusted when different groups of volatile compounds are needed to optimize the results, depending on which aromas should be enhanced or reduced. A larger heart-cut decreased all studied compound levels, except tail compounds (off-flavors), α-terpineol (without odor impact at spirit levels) and methanol (toxic compound). A larger head-cut decreased the concentration of head compounds (off-flavors), at the cost of reducing C_4-C_{10} ethyl esters and linalool levels (positive odors) and increasing the level of tail-cut compounds (longer distillation time). Low pH favored the decomposition of linalool and acetaldehyde to form α-terpineol and acetal, respectively, and favored the formation of ethyl esters by esterification. Sensory analysis corroborated the optimization of aroma compounds in spirits by chemical modeling using RSM. These results reinforce the versatility of this experimental system and deepen its ability to modify the aroma profile of spirit beverages.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2017.11.062.

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Figure Captions

Figure S1. Graphical example of the curve of the desirability function to maximize (LTB-type) or minimize (STB-type) the sensory impact of a compound.

Figure S2. Graphical example for the interpretation of the regression models of Table 2 using contour plots.

Figure S3. Spearman correlations bar chart between aroma descriptors and hedonic rating ($p < 0.05$), carried out with 17 trained assessors.

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Table S1. Parameters of calibrated compounds for chemical analysis, ordered according to their chromatographic retention time.

Compounds	CAS	Supplier company	Minimum assay (%)	Calculated Kovats retention indices
Acetaldehyde	75-07-0	Sigma-Aldrich, Saint Louis, USA	99.5	730
Acetal	105-57-7	Sigma-Aldrich, Saint Louis, USA	98.0	872
Ethyl acetate	141-78-6	Sigma-Aldrich, Saint Louis, USA	99.0	878
Methanol	67-56-1	PanReac Química, S.A.U. Castellar del Valles, Spain	99.9	917
Ethyl butyrate	105-54-4	Sigma-Aldrich, Saint Louis, USA	99.7	996
1-propanol	71-23-8	Sigma-Aldrich, Saint Louis, USA	99.5	1033
Ethyl hexanoate	123-66-0	Sigma-Aldrich, Saint Louis, USA	99.0	1167
2-methyl-1-butanol	137-32-6	Sigma-Aldrich, Saint Louis, USA	98.0	1206
3-methyl-1-butanol	123-51-3	Sigma-Aldrich, Saint Louis, USA	98.0	1213
1-hexanol	111-27-3	Sigma-Aldrich, Saint Louis, USA	99.0	1352
Ethyl lactate	687-47-8	Sigma-Aldrich, Saint Louis, USA	98.0	1361
Ethyl octanoate	106-32-1	Sigma-Aldrich, Saint Louis, USA	99.0	1383
2-octanol	123-96-6	Sigma-Aldrich, Saint Louis, USA	97.0	1408
Furfural	98-01-1	Sigma-Aldrich, Saint Louis, USA	99.0	1490
Acetic acid	64-19-7	J.T.Baker Chemicals, Deventer, Holland	99.0	1501
Linalool	78-70-6	Sigma-Aldrich, Saint Louis, USA	97.0	1540
Ethyl decanoate	110-38-3	Sigma-Aldrich, Saint Louis, USA	99.0	1593
α-terpineol	98-55-5	Sigma-Aldrich, Saint Louis, USA	96.0	1723
Ethyl carbamate	51-79-6	Sigma-Aldrich, Saint Louis, USA	99.0	1748
Geraniol	106-24-1	Sigma-Aldrich, Saint Louis, USA	97.0	1885
β-phenylethanol	60-12-8	Sigma-Aldrich, Saint Louis, USA	99.0	1995

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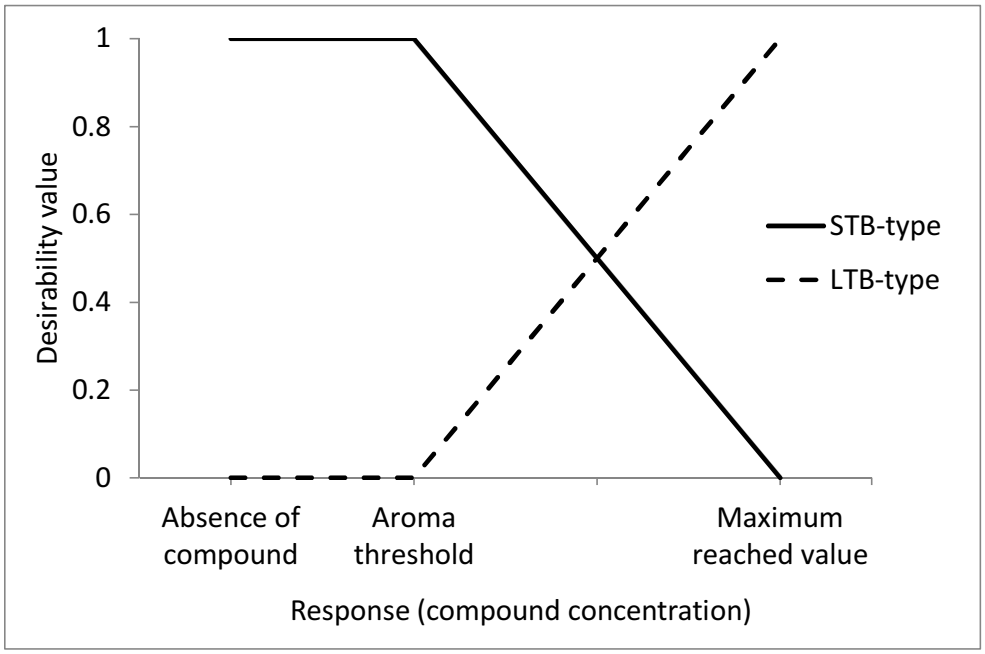
Table S2. Goodness of fit statistics parameters for models of Table 3 [a].

Response	Full R^2	R^2	Adj. R^2	MSE	RMSE	MAPE	DW	Cp	AIC	SBC	PC	Press	Q^2	MS PE	MS LoF	LoF *p*-value	AV *p*-value
Ethanol	0.988	0.987	0.986	0.161	0.401	0.409	2.32	8	-102	-85.4	0.017	10.6	0.984	0.401	0.108	0.999	< 0.0001
Acetaldehyde	0.979	0.976	0.972	31.8	5.64	4.97	2.14	10	217	238	0.033	2339	0.965	28.4	32.858	0.413	< 0.0001
Acetal	0.966	0.961	0.952	2.95	1.72	6.66	1.86	12	75.6	101	0.059	235	0.935	1.86	3.319	0.141	< 0.0001
Ethyl acetate	0.952	0.945	0.933	3.23	1.80	8.12	2.42	11	80.1	103	0.080	241	0.916	1.56	3.765	0.052	< 0.0001
Ethyl butyrate	0.887	0.852	0.832	0.001	0.026	15.7	2.21	8	-428	-412	0.193	0.051	0.792	0.000	0.001	0.000	< 0.0001
Ethyl hexanoate	0.945	0.940	0.929	0.003	0.055	10.7	1.31	10	-339	-318	0.084	0.238	0.906	0.001	0.004	0.018	< 0.0001
Ethyl octanoate	0.904	0.885	0.871	0.009	0.094	10.9	1.44	7	-277	-263	0.146	0.613	0.848	0.002	0.011	0.002	< 0.0001
Ethyl decanoate	0.649	0.592	0.537	0.000	0.010	6.68	1.19	8	-550	-533	0.533	0.006	0.494	0.000	0.000	0.038	< 0.0001
Ethyl lactate	0.984	0.977	0.975	0.971	0.985	4.75	1.79	7	4.77	19.4	0.029	67.5	0.970	0.550	1.094	0.099	< 0.0001
Furfural	0.853	0.807	0.793	0.003	0.058	14.1	2.10	5	-337	-327	0.228	0.224	0.766	0.003	0.003	0.535	< 0.0001
β-phenylethanol	0.984	0.982	0.979	0.004	0.066	4.48	1.44	7	-319	-305	0.023	0.305	0.976	0.002	0.005	0.020	< 0.0001
Linalool	0.987	0.984	0.982	0.004	0.065	3.88	1.88	10	-319	-298	0.022	0.310	0.977	0.004	0.004	0.431	< 0.0001
α-terpineol	0.943	0.924	0.918	0.004	0.060	2.45	1.52	5	-334	-323	0.090	0.237	0.908	0.004	0.003	0.718	< 0.0001
1-hexanol	0.989	0.986	0.985	0.001	0.028	2.01	1.94	6	-425	-413	0.017	0.050	0.983	0.001	0.001	0.977	< 0.0001
1-propanol	0.953	0.944	0.938	1.77	1.33	2.04	2.04	7	40.8	55.4	0.070	121	0.928	3.01	1.406	0.965	< 0.0001
2-methyl-1-butanol	0.984	0.980	0.978	0.499	0.706	2.67	1.93	5	-36.9	-26.4	0.024	32.6	0.976	27.9	15.971	0.922	< 0.0001
3-methyl-1-butanol	0.982	0.978	0.976	18.6	4.31	2.39	1.92	6	181	194	0.027	1232	0.973	0.766	0.425	0.909	< 0.0001
Methanol	0.966	0.958	0.954	4.86	2.20	1.86	1.95	6	101	113	0.052	325	0.948	9.142	3.635	0.986	< 0.0001
Acetic acid	0.888	0.871	0.857	0.850	0.922	7.07	2.03	7	-3.18	11.5	0.163	59.1	0.831	0.535	0.942	0.146	< 0.0001

[a] "Full R^2" means determination coefficient for the model without filtering factors. "R^2" means determination coefficient for the model. "Adj. R^2" means adjusted determination coefficient for the model. "MSE" means mean squared error. "RMSE" means root mean square of the errors. "MAPE" means mean absolute percentage error. "DW" means Durbin-Watson statistic. "Cp" means Mallows Cp coefficient. "AIC" means Akaike's information criterion. "SBC" means Schwarz's bayesian criterion. "PC" means Amemiya's prediction criterion. "Press" means predicted residual error sum of squares. "Q2" means cross-validated R^2. "MS pure error" means mean squared error of pure error. "MS LoF" means mean squared error of lack of fit. "LoF *p*-value" means the p-value of the lack of fit F-test. "AV p-value" means the p-value of the analysis of variance of the model.

Figure Graphics

Figure S1.



18 Figure S2

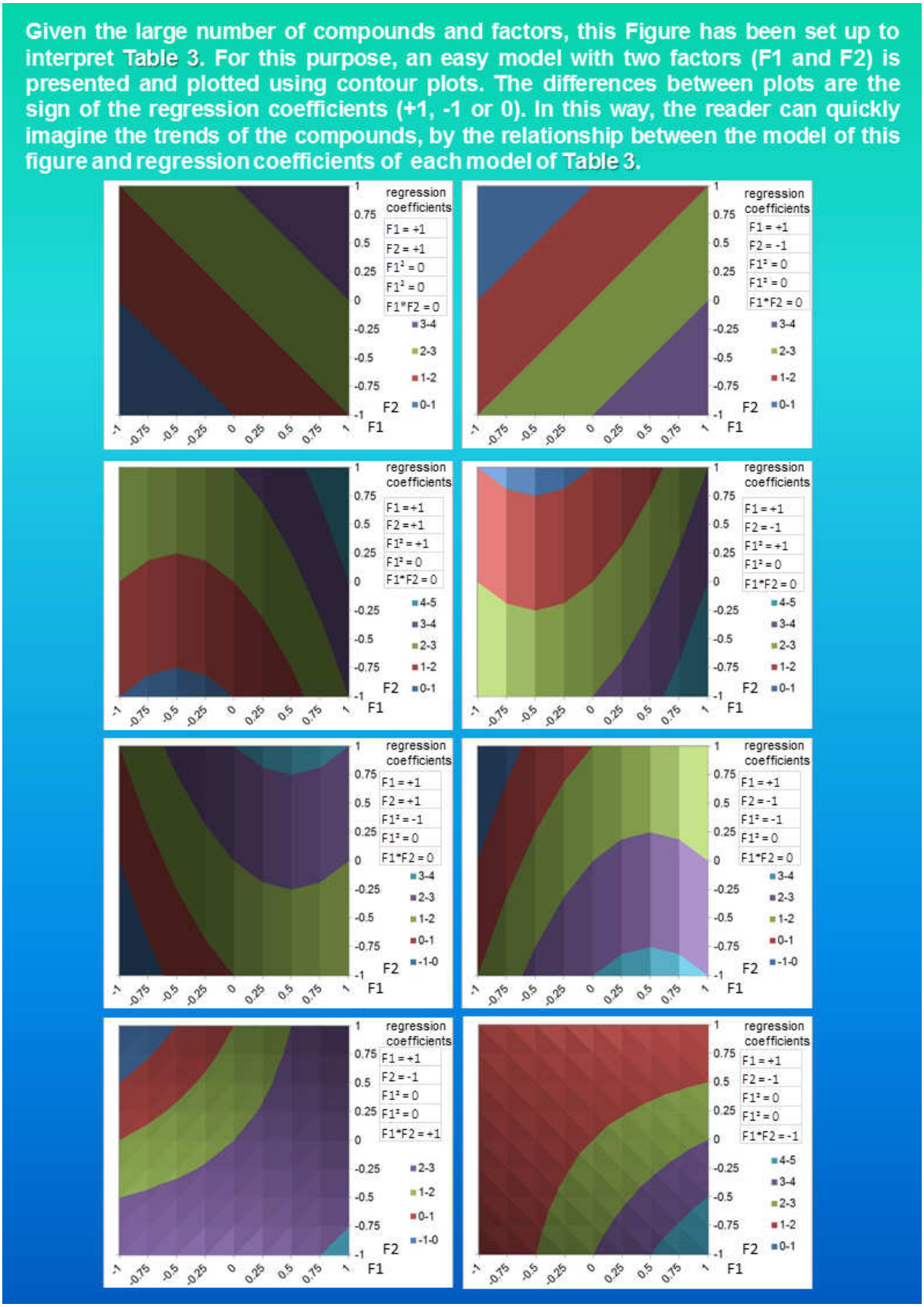


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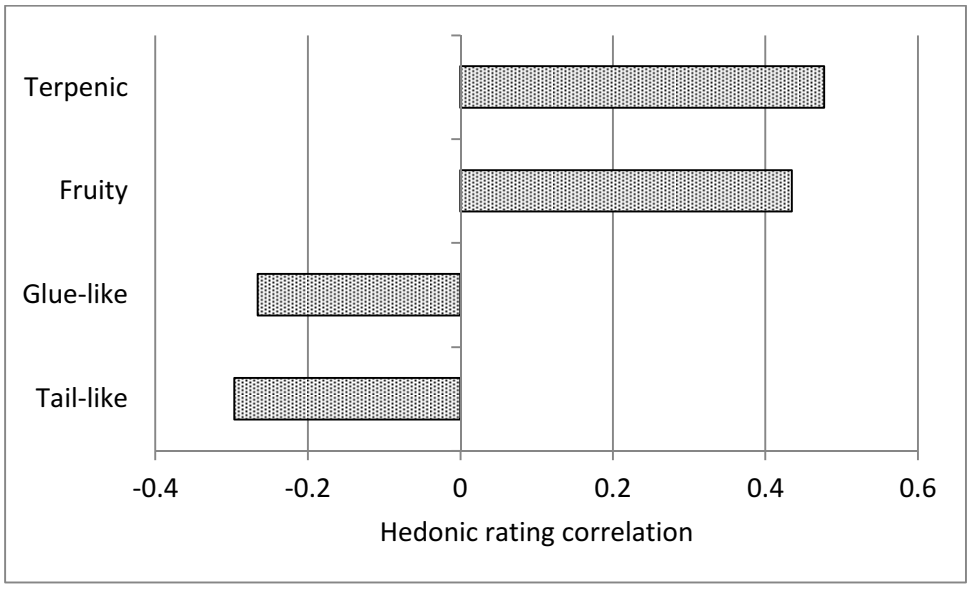
Figure S3.


Terpenic
Fruity
Glue-like
Tail-like
-0.4
-0.2
0
0.2
0.4
0.6
Hedonic rating correlation