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Floral aroma improvement of Muscat spirits by packed column distillation with variable internal reflux

Pau Matias-Guiu [a], Juan José Rodríguez-Bencomo [a,*], Ignacio Orriols [b], José Ricardo Pérez-Correa [c], Francisco López [a]

[a] Departament d'Enginyeria Química, Facultat d'Enologia, Universitat Rovira I Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain
[b] Estación Enológica de Galicia, Ponte San Clodio – Leiro, 32427 Leiro, Spain
[c] ASIS, Departamento de Ingeniería Química y Bioprocesos, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna 4860, Casilla 306, Santiago 22, Chile

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ABSTRACT

The organoleptic quality of wine distillates depends on raw materials and the distillation process. Previous work has shown that rectification columns in batch distillation with fixed reflux rate are useful to obtain distillates or distillate fractions with enhanced organoleptic characteristics. This study explores variable reflux rate operating strategies to increase the levels of terpenic compounds in specific distillate fractions to emphasize its floral aroma. Based on chemical and sensory analyses, two distillate heart sub-fractions obtained with the best operating strategy found, were compared with a distillate obtained in a traditional alembic. Results have shown that a drastic reduction of the reflux rate at an early stage of the heart cut produced a distillate heart sub-fraction with a higher concentration of terpenic compounds and lower levels of negative aroma compounds. Therefore, this sub-fraction presented a much more noticeable floral aroma than the distillate obtained with a traditional alembic.

1. Introduction

Wine spirit is an alcoholic beverage obtained from the distillation of fermented grape musts. The quality of the distillate depends on both the raw materials and the distillation process used.

The grape variety used to produce the wine could provide varietal compounds, such as terpenes and terpenols in the case of Muscat or Malvasía grape varieties, that give wine floral aroma characteristics (Etiévant, 1991). *Pisco* is one of the most relevant terpenic spirit, so distillers aim to preserve the floral and fruity aromas, a factor traditionally associated with the variety and quality of grapes (Agosin, Belancic, Ibacache, Baumes, & Bordeu, 2000). However, large chemical composition differences between aromatic *Piscos* have been observed (Cacho, Moncayo, Palma, Ferreira, & Culleré, 2012). Among floral and fruity aroma compounds, linalool is the most relevant compound in *Pisco* (Bordeu, Formas, & Agosin, 2004), although its characteristic aroma is also related to the sensory perception of other molecules (Peña y Lillo, Agosin, Andrea, & Latrille, 2005). In addition, terpenic compounds present high reactivity in catalyzed and hot acid media (Iwai et al., 2014; Ohta, Morimitsu, Sameshima, Samuta, & Ohba, 1991; Osorio, Pérez-Correa, Belancic, & Agosin, 2004) and tend to distil in early fractions of the distillation (Peña y Lillo et al., 2005), thus these compounds cannot be easily concentrated in the heart cut (commercial distillate fraction). Muscat distillates such as *Pisco* contain other non-terpenic compounds with important sensory attributes (Herraiz, Reglero, Herraiz, & Loyola, 1990), whose distillation behaviors vary throughout the process (Jouret, Cantagrel, & Galy, 1998).

The traditional distillation with a copper *Charentais* alembic (French Style) allows limited intervention during the distillation process (only the heating power in the boiler can be manipulated) to modify the composition of the distillate. A more flexible system is the batch distillation column (German Style) in which the reflux rate can be varied in a wide range. However, none of these systems allows a rapid variation of the internal reflux of the system during distillation. An interesting alternative is the use of a boiler coupled with a rectification column, equipped with an internal partial condenser that allows rapid control of the reflux rate of the column by manipulating the cooling flow rate (García-Llobodanin, Roca, López, Pérez-Correa, & López, 2011).

Several studies have compared the spirits obtained by classical alembics and columns with an internal partial condenser. Kiwi and pear fermented juices and grape pomace have been tested with both methods of distillation (Arrieta-Garay et al., 2013;

* Corresponding author.
E-mail address: jrbencomo@gmail.com (J.J. Rodríguez-Bencomo).

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Arrieta-Garay, Blanco et al., 2014; Arrieta-Garay, López-Vázquez et al., 2014) and showed that column distillates presented better fruit and floral characteristics and less solvent-like and toxic compounds (head compounds). In addition, García-Llobodanin et al. (2011) found differences between both methods. The partial reflux column system produced heart fractions of distillate with high levels of esters and higher alcohols, although they observed a lack of reproducibility of the distillation. No previous studies have tested specific variable reflux policies focused on concentrating or removing specific positive or negative compounds in certain distillate fractions.

Therefore, the aim of this study was to develop variable reflux strategies to concentrate terpenic compounds in the heart fraction of the distillate. Hence, non-aromatic wine was doped with several terpenic compounds to study the extraction/distillation kinetics. Moreover, using chemical and sensory analyses, Muscat wine (non- doped) spirits obtained with the optimum column strategy and with a traditional alembic were compared.

2. Material and methods

2.1. Wines

Experiments were performed at the Department of Chemical Engineering of the Rovira i Virgili University. Two white wines were used: a *Vitis vinifera* Macabeo produced in the experimental cellar "Mas dels Frares" of the University (Tarragona, Spain), and a *Vitis vinifera* Muscat kindly donated by Dalmau Hermanos y Cía. Suc. S.A. (Tarragona, Spain). The basic oenological parameters of Macabeo and Muscat wines were: alcohol degree 10.8 and 12.6% (v/v), pH 3.31 and 3.32, and glucose + fructose concentration <0.10 and 0.43 g/L, respectively. Since Macabeo wine contains very low amounts of terpenic compounds, it was doped with six representative terpenic compounds; limonene, linalool, α-terpineol, β-citronellol, geraniol and nerol, all of them of food grade quality (Sigma-Aldrich; Saint Louis, USA). The doses were 4 mg/L for the three most volatile compounds (limonene, linalool, α-terpineol) and 6 mg/L for the others, according to their volatility and the results of preliminary tests. These levels are much higher than those usually found in Muscat wine; the aim was to enhance the sensitivity of the chemical analysis to clearly observe the impact of the different strategies on the evolution of the terpenic compounds during distillations. Physical-chemical characteristics and terpenic compound levels of the wines (doped Macabeo and Muscat) before distillation are shown in Table 1.

2.2. Distillation systems

Column distillation system assays were performed in a distillation boiler (50 L) heated with two electrical resistances and coupled with a stainless steel distillation column with a copper mesh. The distillation column was equipped with a total condenser (on the top) and a partial condenser with variable flow (controlled with a peristaltic pump) to control the internal reflux of the column. In addition, the system was equipped with several temperature sensors (in the boiler, at different levels of the distillation column and in the partial cooling water system). Details of the distillation column have been previously described in García-Llobodanin et al. (2011). The process was controlled with Lab-view software (LabVIEW 8.6.1, National Instruments). Before experimentation, the peristaltic pump of the partial condenser was calibrated between 0 and 200 mL/min.

Traditional distillation system assays were performed in a 20 L copper *Charentais* alembic heated by an electrical hotplate.

2.3. Distillation processes

First, column distillation assays were performed with doped Macabeo wine, in order to determine the behavior of the terpenic compounds and other relevant compounds. Then, based on the obtained results, column and alembic distillation assays were performed with Muscat wine.

For column distillation, 25 L of wine (Macabeo or Muscat) were placed in the boiler. In case of Macabeo wine, terpenic compounds were added 12 h before distillation. Total condenser's cooling flow rate was constant at 1.7 L/min. Partial condenser's cooling flow rate ranged from 0 to 180 mL/min and was modified during distillation according to two different strategies (STR-1 and STR-2) detailed in Table 2. Electrical resistances operated at a constant power of 2400 W until the temperature below the partial condenser raised to 72 °C; then the power was reduced and kept constant at 960 W. The first 200 mL of distillate were collected in 50 mL fractions and the rest in 100 mL fractions until 3500 mL of distillate. Temperatures were monitored and recorded every 16 s at different points of the distillation systems.

For traditional distillation, 12.5 L of Muscat wine and 5 g of pumice stones were placed in the copper *Charentais* alembic boiler. Total condenser cooling flow rate was constant at 1.8 L/min. Electrical hotplate operated at a constant power of 2900 W until the first drop, then the power was reduced and kept constant at 2333 W (both values were calculated without considering heat loss). As in column distillations, first 200 mL of distillate were collected in 50 mL fractions and the rest in 100 mL fractions until 2600 mL of distillate.

Distillation assays were performed in duplicate for doped Macabeo wine and in triplicate for Muscat wine. Head cuts were decided by sensorial analysis.

2.4. Chemical analysis of wines and distilled fractions

Analyses of wine ethanol content and distillation residues were determined by ebulliometry (electronic ebulliometer, GAB instruments), wine glucose + fructose concentration by enzymatic bioanalysis (R-Biopharm AG) and wine pH with a pH-meter (Crison

Table 1
Terpenic compounds proprieties and their concentrations in the wines before distillation.

Compound	Molar mass[a] (g/mol)	Boiling point[a] (°C)	Vapor pressure[b] (mmHg at 95 °C)	Log $K_{o/w}$[a]	Doped Macabeo wine[c]	Non-doped Muscat wine[c]
Limonene	136	176	56.8	4.57	4.12 ± 0.07	n.d.
Linalool	154	197	22.8	2.97	4.03 ± 0.06	2.10 ± 0.00
α-Terpineol	154	220	7.11	2.98	4.23 ± 0.20	2.52 ± 0.14
β-Citronellol	156	224	6.74	3.91	6.07 ± 0.19	1.60 ± 0.08
Geraniol	154	230	5.38	3.56	6.13 ± 0.13	0.306 ± 0.028
Nerol	154	225	6.11	3.47	6.11 ± 0.11	0.117 ± 0.002

[a] Data extracted from EPI Suite database (Environmental Protection Agency & U. S., 2012).
[b] Vapor pressures were calculated with ASPEN PLUS V8.4 software.
[c] Concentrations are expressed in mg/L.