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# Potential of lees from wine, beer and cider manufacturing as a source of economic nutrients: An overview

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## ABSTRACT

Lees are the wastes generated during the fermentation and aging processes of different industrial activities concerning alcoholic drinks such as wine, cider and beer. They must be conveniently treated to avoid uncontrolled dumping which causes environmental problems due to their high content of phenols, pesticides, heavy metals, and considerable concentrations of nitrogen, phosphate and potassium as well as high organic content. The companies involved must seek alternative environmental and economic physicochemical and biological treatments for their revalorization consisting in the recovery or transformation of the components of the lees into high value-added compounds. After describing the composition of lees and market of wine, beer and cider industries in Spain, this work aims to review the recent applications of wine, beer and cider lees reported in literature, with special attention to the use of lees as an endless sustainable source of nutrients and the production of yeast extract by autolysis or cell disruption. Lees and/or yeast extract can be used as nutritional supplements with potential exploitation in the biotechnological industry for the production of natural compounds such as xylitol, organic acids, and biosurfactants, among others.

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#### 1. Definition, composition and importance of lees

Lees are the wastes generated during the fermentation and aging processes of different industrial activities involving alcoholic drinks such as wine, cider and beer (Pérez-Bibbins et al., 2014). They are composed by solid and liquid fractions, whose composition depends on their regions of origin and their agronomic and edaphoclimatic characteristics.

The solid fraction contains all the deposits precipitated at the bottom of the tanks, which primarily consist on microbial biomass (yeasts and bacteria), insoluble carbohydrates (cellulosic or hemicellulosic materials), phenolic compounds that contribute to color and flavor, lignin, proteins, metals, inorganic salts, organic acid salts (mainly tartrates in the case of wine lees) and other materials such as pips, fruit skins, grains and seeds. The type of phenolic compounds depends on the origin of grape, apple and barley variety as well as the climate. Phenolic compounds contribute to color,

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flavor, astringency, bitterness, enzymatic or nonenzymatic browning, haze formation and aging behavior (Ziegler, 1990; Bustos et al., 2004a).

The liquid phase mainly consists in the exhausted fermentation broth, namely wine, cider and beer. In consequence, the liquid phase is rich in ethanol and organic acids. Lactic acid from the malolactic fermentation, where malic acid is dicarboxylated into lactic acid by bacteria metabolism (*Oenocuccus oeni*) (Moreno-Arribas and Lonvaud-Funel, 2000), and acetic acid, which is the product of the bacterial metabolism of *Gluconobacter oxydans*, *Acetobacter pasteurianus* and *Acetobacter aceti* present in wine mature stages (Joyeux et al., 1984; Bustos et al., 2004a), can be also present in significant amounts in liquid lees.

# 2. Composition of lees and market of wine, beer and cider industries in Spain

### 2.1. Wine and vinification lees

Spain is the third wine producing country in the world, occupying the 12.1% of the worldwide production in 2012 (30.4 millions

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of hl) after France (16.4%) and Italy (15.9%), with 41.4 and 40.1 millions of hl respectively. The Iberian Peninsula is an ideal place for producing different kinds of wines. The International Organisation of Vine and Wine (OIV) reported 1.018 millions of hectares for vine growing in Spain, remaining as the largest area of vineyards of the European Union (OIV-OEMV (2013), www. winesfromspain.com). Spain has 89 production areas of quality wines with 69 Designation of Protected Origin (DOP), which 67 are DOP, 2 with Designation of Qualified Origin, 6 are Heading Quality Wines with Geographical Indication and 14 are Wine of "Pago". The first authorized designations were approved in 1932 and are: Xères-Jerez-Sherry, Manzanilla de Sanlúcar de Barrameda, Málaga, Montilla-Moriles, Rioja, Tarragona, Priorato, Alella, Utiel Requena, Valencia, Alicante, Ribeiro, Cariñena, Penedés, Condado de Huelva, Valdepeñas, La Mancha, Navarra and Rueda. The most common grape varieties in Spain are Airén (23.5%), Tempranillo (20.9%), Bobal (7.5%), Garnacha Tinta, Monastrell, Pardina, Macabeo and Palomino, where Tempranillo, Bobal, Garnacha Tinta and Monastrell are red varieties and the rest are white varieties.

Vinification, the process involving all the steps for wine elaboration, is a seasonal activity that accounts approximately 3 months preferably during the autumn (Torrijos and Moletta, 2003). This activity is considered one of the most important agricultural activities in Spain, representing up to 10% of the total agricultural production (Rivas et al., 2006), and producing large volumes of wastes that can be estimated in  $18 \times 10^6 \text{ m}^3/\text{year}$ , a value 6 times higher than the wine wastewater produced in France or Italy.

As a result of the winemaking process in wineries, one ton of grapes approximately generates 0.13 t marc, 0.06 t lees, 0.03 t of stalks and 1.65 m<sup>3</sup> of wastewater (Oliveira and Duarte, 2014). According to the European Council Regulation No. 79/337, wine lees are defined as "the residue that forms at the bottom of recipients containing wine, after fermentation, during storage, after authorized treatments, as well as the residue obtained following the filtration or centrifugation of this product" (Pérez-Serradilla and Luque de Castro, 2008). Meanwhile, vinasses are the liquid fraction waste from the distillation process of the wine lees, which is carried out to recover ethanol and elaborate distilled beverages. Their effluents show a high organic matter content, which is responsible for their high Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) (de Bustamante and Temiño, 1994; Beltrán et al., 1999), as well as a acidic and reducing properties (de Bustamante, 1990). These acid characteristics provoke that their disposal into soils lead to the karstification of the calcareous component of the terrain and the formation of CH<sub>4</sub> and CO<sub>2</sub> in anaerobic environments, which, if the environment is closed, can produce explosions (de Bustamante and Temiño, 1994). On the other hand, the free spill of vinasses and/or wine lees in water environments results in local fish kill and damage in the aquatic biota (Niranjan and Shilton, 1994). In spite of this, particularly some small wine-producers do not obey the laws in force, making illegal waste discharge to water body, sewage or uncontrolled deposition, for which fines can reach up to  $60,000 \in (Oliveira and$ Duarte, 2014).

The composition of wine lees depends on the winemaking technology (see Table 1) although, according to de Bustamante and Temiño, 1994 the main characteristics are a pH between 3 and 6, a COD that can be higher than 30,000 mg/L, an organic matter content between 900 and 35,000 mg/L, potassium concentrations that can be higher than 2500 mg/L, phenolic components in quantities up to 1000 mg/L, and discharge temperatures of 90 °C.

Red wine is made by fermenting the grape must in contact with skins and seeds, thus releasing high levels of soluble phenolic compounds (Bustos et al., 2004a), which can polymerize and form

#### Table 1

Composition of cider, beer, white and red wine (for 100 g of edible portion).

| Components                           | Beer           | Cider         | White<br>wine  | Red wine       |
|--------------------------------------|----------------|---------------|----------------|----------------|
| General composition                  | 2.00           |               | 0.50           | 0.00           |
| Alcohol (ethanol)(g)<br>Total energy | 3.96<br>176 KI | 3.7<br>209 KI | 8.58<br>252 KI | 9.82<br>294 KI |
| Total chergy                         | (42 Kcal)      | (50 Kcal)     | (61 Kcal)      | (71 Kcal)      |
| Total fat (total lipids) (g)         | 0              | 0             | 0              | 0              |
| Total protein (g)                    | 0.5            | Trace         | 0.1            | 0.23           |
| Water (humidity) (g)                 | 92.4           | 90.3          | 91.2           | 89.7           |
| Carbohydrates                        |                |               |                |                |
| Sugars (g)                           | 3.12           | 6             | 0.1            | 0.3            |
| Fiber (total dietary) (g)            | 0              | 0             | 0              | 0              |
| Fat                                  |                |               |                |                |
| Fatty acids, total                   | 0              | 0             | 0              | 0              |
| monounsaturated (g)                  |                |               |                |                |
| Fatty acids, total                   | 0              | 0             | 0              | 0              |
| polyunsaturated (g)                  |                | 0             | 0              | 0              |
| Cholostorol (mg)                     | 0              | 0             | 0              | 0              |
| cholesterol (llig)                   | 0              | 0             | 0              | 0              |
| Vitamins                             |                | -             |                |                |
| Vitamin A <sup>a</sup> (µg)          | -              | Trace         | -              | -              |
| Vitamin D ( $\mu g$ )                | 0              | 0<br>Tra ao   | 0              | 0              |
| Vitalilli E <sup>-</sup> (liig)      | 0 42           | 1 ace         | 0              | 0              |
| (Vitamin B3) (mg)                    | 0.43           | 0.01          | 0.08           | 0.09           |
| Riboflavin (Vitamin B2) (mg)         | 0.03           | 0.01          | 0.05           | 0.02           |
| Thiamine (Vitamin B1) (mg)           | 0              | 0.01          | 0.01           | 0.01           |
| Vitamin B12 (µg)                     | 0.15           | 0             | 0              | 0.01           |
| Vitamin B6 (mg)                      | 0.06           | 0.01          | 0.02           | 0.02           |
| Vitamin C (ascorbic acid)<br>(mg)    | 0              | 0             | 0              | 0              |
| Minerals                             |                |               |                |                |
| Calcium (mg)                         | 8              | 8             | 9              | 7.6            |
| Total iron (mg)                      | 0.01           | 0.49          | 0.6            | 0.9            |
| Potassium (mg)                       | 37             | 72            | 82             | 93             |
| Magnesium (mg)                       | 9.6            | 3             | 10             | 11             |
| Sodium (mg)                          | 4.4            | 7             | 2              | 4              |
| Phosphorous (mg)                     | 55             | 3             | 15             | 14             |
| Iodide (µg)                          | 8              | 0             | 0              | 0              |
| Total selenium (µg)                  | 1.2            | Trace         | 0.3            | 0.2            |
| Zinc (Cinc) (mg)                     | 0.01           | Trace         | 0.07           | 0.05           |

BEDCA. Base de Datos Española de Composición de Alimentos [computer file]. <http://www.bedca.net>.

Ortega et al. (2004).

<sup>a</sup> Equivalents of retinol as retinos and carotenoids activities.

<sup>b</sup> Alpha tocopherol equivalents from E vitamers activities.

complexes with proteins and polysaccharides during winemaking and precipitate again. Therefore, red wine lees also contain skins, pips and polymeric phenolic compounds.

In white wine making technology the must is extracted from the unfermented grapes and separated from the seeds and skins before fermentation. In consequence, white lees do not contain the phenolic compounds from pips and skins. These lees are rested in tanks or barrels to precipitate the solid particles to the bottom.

Additionally, white and red wine lees composition differs depending not only on the kind of wine but also on the number of decanting steps performed. Total solids, ashes, nitrogen and carbon contents are generally higher in the first decanting step in white/red wine lees because they have more concentration of dead yeast and solids in suspension (such as other microorganisms and organic matter) than in the second one. Carbon and nitrogen contents are usually higher in white non-distilled lees (C = 10.9 g/100 g dry basis, N = 0.7 g/100 g dry basis) in comparison with the values observed after distillation (C = 6.4 g/100 g dry basis, N = 0.4 g/100 g dry basis). Conversely, the behavior observed with red lees was opposite, with the higher contents quantified after distillation (C = 11.7 g/100 g dry basis; N = 1.2 g/100 g dry basis).

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