

# Cachaça Production: from sugar cane to spirit

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## Abstract

Why was the work done: Cachaça, the oldest distilled beverage in the Americas, has great historical and cultural significance. A review of cachaça production is important to preserve tradition, standardise industry processes, promote innovation and quality. This review offers a comprehensive overview of current knowledge and advancements in cachaça production, covering regulation, process control, product quality and future developments.

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What are the main findings: The production of Cachaça observes well defined regulations, with its processes encompassing both field and industrial practice. The review focuses on sugar cane cultivation, fermentation, distillation, and ageing in wooden barrels. It underscores the significance of regional factors such as climate, soil, and the varirty of sugar cane in shaping the sensory profile of cachaça. While a range of sugar cane cultivars have been developed and grown in different environments, further research on the adaptation of sugar cane crop is necessary. Fermentation of cachaça is spontaneous utilising the microbiota in the sugar cane juice. However, the use of wild sugar cane yeasts, complemented with commercial strains is increasingly used by producers. With regard to distillation, production of the spirit using copper still pots and ageing in tropical wood barrels remain prevalent in the industry.

Why is the work important: This review contributes to ongoing efforts to enhance the quality of cachaça. Whilst the importance of traditional production methods is recognised, this review embraces advancements in technology coupled with insights to future perspectives.

#### Keywords:

sugar cane, cachaça, production, tropical wood, barrel, ageing, quality

# Cachaça: from sugar cane to spirit

Cachaça is a Brazilian spirit produced from sugar cane juice which is fermented and distilled (Bortoletto 2023). Cachaça is only produced in Brazil and has an alcohol content of 38-48% (v/v) (Brazil 2022a). The production of cachaça includes both field and industrial practice. Field practices include planting of sugar cane, harvesting and transportation, with industrial practice involving reception, extraction of juice, fermentation, distillation, standardisation, and ageing. Overall, the primary processes in Cachaça production are fermentation and distillation.

During fermentation, yeasts transform the sugars in sugar cane juice into wine with the formation of ethanol, carbon dioxide and other metabolites. The composition of sugar cane juice reflects the cultivars and adaptation to the environment. The juice contains around 10<sup>3</sup> yeast cells/mL that play a role in fermentation. The environmental yeast are diverse and include Saccharomyces, Schizosaccharomyces, Pichia, Debaryomyces, Kloeckera, Zygosaccharomyces and Candida (Rosa et al. 2009). Cachaça fermentation is performed over several fermentation cycles using open, batch fermenters. Although the primary yeast -Saccharomyces cerevisiae - is prevalent during fermentation batch fermentations are easily contaminated by environmental microorganisms. Therefore, producers acid wash the yeast inoculum to limit bacterial contamination. The distillation process uses a column or copper still pots (Lima et al. 2022; Bortoletto 2023) and the distilled product contains alcohols, aldehydes, acids, ketones, and esters (Alcarde et al. 2012). However, freshly distilled cachaça exhibits undesirable bitterness and harshness, which are reduced by maturation through ageing (Alcarde et al. 2014).

Cachaça is aged in stainless steel or wooden barrels. The former do not contribute any ageing characteristics to cachaça, whereas wooden barrels promote chemical changes in cachaça including flavour and colour (Alcarde et al. 2014; Bortoletto 2023). Although, oak barrels predominate for ageing of cachaça, other tropical woods have been used including umburana, wild peanut, jequitibá, araruva, jequitibá rosa, cherry tree, purple ipê and chestnut tree (Bortoletto et al. 2021). The use of tropical woods must maintain quality and authenticity standards of cachaça, although each wood contiibutes different physiochemical and sensorial characteristics to cachaça (Silva et al. 2009; Bortoletto et al. 2021).

To ensure the yield, productivity and quality of sugar cane cachaça (and brandy), production is regulated by Ordinance Nº 539, which defines the physiochemical, sensorial characteristics and quality standards (Brazil 2022). Over time, the cachaça sector has improved the technologies for sugar cane production (handling, varieties, harvesting and transport), and cachaça production (extraction, fermentation, distillation and ageing). However, the production processes requires improvement to enhance process control, yield, productivity, and product quality. This review considers cachaça production and considers its technical improvement from sugar cane to a high quality spirit with consideration of contradictions, critical comments, and perspectives.

## Legislation

During the 19th century, coffee growing had a negative effect on the production and market for cachaça (Rosa et al. 2009). In 1992, the Brazilian government created 'Pró-Cachaça', an incentive program to encourage cachaça producers to return and invest in technologies enabling large scale production (Lima et al. 2022). In 1997, legislation was put in place defining sugar cane spirits such as 'cachaça,' 'caninha,' or 'aguardente de cana' (Brazil 1997). In 2002, decree 4072 reserved the term 'cachaça' for sugar cane spirits made in Brazilian territory (Brazil, 2002). In 2005, the Ministry of Agriculture, Livestock and Supply approved the technical regulation that defines the quality standards to produce cachaça (Brazil 2005) and in 2013 cachaça was recognised as a Brazilian spirit (Medeiros et al. 2017).

The technical regulation (ordinance 13/2005) boosted cachaça production. However, in 2022, a new regulation was published that establishes the identity and quality standards for sugar cane spirit including 'cachaça' and 'aguardente de cana' (Brazil 2022b). This focussed on the quality parameters that assure the identity and quality of cachaça. This was an important step in boosting the production of cachaça. Currently cachaça is produced in all Brazilian states and is the second most consumed alcoholic beverage in the country. The sugar cane sector contributes to the preservation of the diverse genetic resources, cultural heritage, historical legacy in Brazil. Cachaça helps shape the socioeconomic landscape of the country, is a versatile ingredient in culinary practice and an ingredient in the preparation of the national drink, 'caipirinha'.

#### Styles

Cachaça is an alcoholic beverage with an ABV (alcohol by volume) of 38 to 48%. Cachaça is classified into four categories: 'cachaça', 'cachaça adoçada' (sweetened cachaça) and 'aged'. Aged cachaça is divided into 'cachaça descansada' (short aged) and 'aged cachaça (premium cachaça and extra premium cachaça) (Brazil 2022b).

## Sugar cane and its cultivars

'Cachaça is produced from the wort of sugar cane juice with proper sensorial characteristics' (Brazil 2022a). Sugar cane is a tropical crop that grows well in hot climates at temperatures between 18 and 35°C (Rossato et al. 2013). Sugar cane cultivars result from crossbreeding of species or other cultivars and adapt to different soils, climate and environment. As a result, these factors influence the chemical composition and maturation of the sugar cane plants (Rosa et al. 2009; Lima et al. 2022). Sugar cane cultivars contain 75 to 89% water and 11-25% soluble solids (including carbohydrates, amino acids, minerals, vitamins, and lipids). Sugar cane juice contains glucose, fructose, and sucrose as the primary sugars (Rosa et al. 2009; Martini et al. 2010). Poor adaptation of sugar cane cultivars results in a low concentration of soluble solids and can negatively affect the yield and quality of cachaça (Vilela et al. 2021).

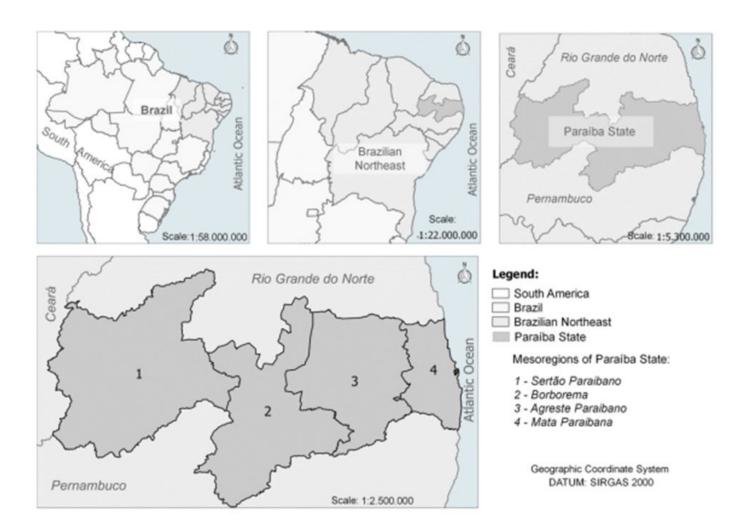
Sugar cane used for cachaça production is typically manually cropped and harvested, and is distinct from sugar cane destined for biofuel or sugar where mechanical harvesting is used (Rosa et al. 2009; Rossato et al. 2013). Large scale sugar cane plantations have embraced the adoption of new and improved sugar cane cultivars. In contrast, smaller producers have maintained the cultivation of older genotypes characterised by low yields and productivity. This is attributed to the limited adaptability with heightened susceptibility to diseases, insects, and pests exhibited by older genotypes (Ravaneli et al. 2006; Rosa et al. 2009). Recently, small scale sugar cane producers have undergone a transformative shift thanks to the emergence and advancement of novel sugar cane cultivars. These cultivars have enhanced adaptability to varying weather conditions, efficient straw removal, resistance against lodging, low fibre content, resilience to pests, insects, diseases and exhibit enhanced productivity (Ravaneli et al. 2006). This has significantly influenced small scale producers and their practices in cultivating sugar cane, such that they use new sugar cane cultivars to guarantee the quality and yield of cachaça (Martini et al. 2010).

In Brazil, three research institutes - Planalsucar/ Ridesa (RB), Copersucar Sugar cane Technology Centre (CTC) and Instituto Agronômico de Campinas (IAC) - have breeding programmes for the development of new sugar cane cultivars. Of these, RB cultivars cover 68% of the sugar cane growing area in Brazil, with the RB92579 cultivar the most cropped sugar cane in the Northeast region due to easy adaptation and high productivity (Martini et al. 2010; Alcarde et al. 2012). In the Paraíba state, the RB867515 cultivar is used by small and large producers due to its adaptation to growth conditions, yield and productivity. Further, this cultivar shows excellent microbiological and physical-chemical characteristics (Martini et al. 2010; Alcarde et al. 2014).

With the exception of Amapá and Roraima, sugar cane is produced in all Brazilian states. Paraíba, is divided into four mesoregions, with sugar cane cropping in two mesoregions, Ageste Paraibano (3), and Mata Paraibana (4) (Figure 1). The Mata Paraibana mesoregion is characterised by hot and humid tropical climate that contains a large area for sugar cane cultivation due to its weather and relief. However, most of the sugar cane production is destined for bioethanol and sugar production (Medeiros-Silva et al. 2019; Vilela et al. 2021). The Agreste mesoregion is characterised by medium to low temperatures with irregular rainfall and produces most of the cachaça in Paraiba (Medeiros-Silva et al. 2019).

#### Figure 1.

#### Paraíba state in Brazil with mesoregion divisions (Adapted from Medeiros-Silva et al. 2019).



Serafim et al (2016) sampled cachaça from five Brazilian states, produced by spontaneous fermentation and distilled in copper stills pot. The authors reported that there were chemical differences in cachaças which were not aged in wooden barrels. Vilela et al. (2021) examined thirty-eight cachaça samples from Paraíba state and identified differences in their chemical profile. The differences of these cachaças were associated with the characteristics of each region, including weather, soil, environment, sugar cane cultivars, and the type of wild yeast native to each region.

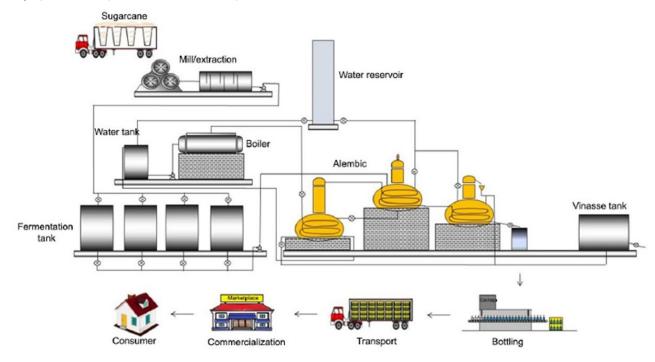
# Juice extraction, wort composition, and microbiota

Sugar cane harvesting should be during the optimal harvesting period or 'maturation index' (MI), corresponding to the highest sucrose concentration in the culms (Rosa et al. 2009). The sugar cane cultivars can reach maturation at different times and are classified as early (< 12 months), average ( $\approx$  12 months) or late (> 12 months). These three periods are driven by the type of sugar cane cultivar and its adaptation to the environment (Martini et al. 2010). Not all producers use the maturation index for harvesting but identify a soluble solids concentration >18°Brix as suitable (Rosa et al. 2009). Sugar cane juice is ground (mechanically crushed) to extract 65-75% (at a small-scale), or up to three times for a 90% extract (Rosa et al. 2009; Martini et al. 2010). Increasingly grinding is being replaced by milling and then grinding (Figure 2).

Yeasts are inoculated into sugar cane juice (or 'must') (Martini et al. 2010; Bortoletto 2023) that supports microbial growth and fermentation through sugars (glucose, fructose, and sucrose), nitrogenous material (amino acids, peptides, proteins, nitrogenous ions, nucleic acids), vitamins, organic acids, lipids, inorganic elements (potassium,

#### Figure 2.

Cachaça production (from Silva et al. 2020)



phosphorus, magnesium, zinc, copper, iron, manganese) (Briggs et al. 2004). Sugar cane juice contains about 10<sup>3</sup> yeast/mL, which multiply during fermentation. Although *Saccharomyces cerevisiae* is prevalent, other yeasts have been identified including *Schizosaccharomyces*, *Pichia*, *Debaryomyces*, *Kloeckera*, *Zygosaccharomyces* and *Candida* (Rosa et al. 2009; Monjito et al. 2014). With the correct yeast handling practice, the cell number increases to 30 x 10<sup>6</sup>/mL in 48 hours (Monjito et al. 2014).

Sugar cane juice also inevitably contains bacteria, contaminants which convert sugar and ethanol to lactic and acetic acid (Borges et al. 2014). These acids are thought to be associated with the formation of volatile compounds although there is little evidence for this (Rosa et al. 2009). In contrast, *Saccharomyces* yeast produce acetic, lactic, citric and succinic acids (Briggs et al. 2004). Researchers and producers have been considering options for inactivating wort microbiota as these can impact on the quality of cachaça. This would improve fermentation control and the quality of cachaça.

#### Fermentation

In the production of cachaça (Figure 2), fermentation is performed by yeasts which convert sugars into

ethanol, carbon dioxide and secondary metabolites. Saccharomyces cerevisiae is widely used for cachaca production due to its resistance to toxicity, high fermentative capacity, resistance to stress, and the formation of desirable compounds (Briggs et al. 2004; Martini et al. 2010; Duarte et al. 2013; Ribeiro-Filho et al. 2021). Cachaça yeasts are indigenous to the sugar cane plant, and reflect the cultivars, weather, soil, and environment (Vilela et al. 2021). Typically, cachaça fermentation is spontaneous using the yeast from sugar cane (Vicente et al. 2006; Martini et al. 2010; Portugal et al 2017). However, producers are increasingly using commercial yeasts to inoculate the juice (Duarte et al. 2013; Monjito et al. 2014). Although commercial yeasts enable faster fermentation, yeasts from different environments are important in the quality and diversity of cachaça.

The sugar cane plant is rich in yeast from the eleventh internode to the top with reducing sugars and elevated acidity (Martini et al. 2010; Borges et al. 2014). Strains of *Saccharomyces cerevisiae* have been isolated from sugar cane with favourable characteristics in adaptation/survival to environmental factors including pH, temperature, oxygen, osmotic stress, nutritional limitation (carbon, amino acids and inorganic elements) and ethanol yield (Alcarde et al. 2014). Commercial yeasts are an attractive alternative to better

control fermentation (Rosa et al. 2009; Alcarde et al. 2014; Paredes et al. 2018). Despite this, some producers prefer to continue use the yeasts from sugar cane juice microbiota.

Yeast strains for cachaça production have been isolated according to fermentation rate, stress consumption, tolerance, sugar flocculation, no hydrogen sulphide, low acetic acid, ethanol tolerance, high ethanol formation and desired aroma compounds (Vicente et al. 2006; Nova et al. 2009; Paredes et al. 2018). Further, a mix of yeasts (Saccharomyces cerevisiae and non-Saccharomyces) were used to assess fermentation performance, flavour and aroma. It was observed that Pichia caribbica and Saccharomyces cerevisiae improved fermentation, increasing ethanol content and the aroma profile (Duarte et al. 2013; Borges et al. 2014). Similarly, Saccharomyces cerevisiae and Meyerozyma caribbica were reported to increase the content of esters and higher alcohols (Amorim et al. 2016).

# Secondary metabolites produced during fermentation

Yeast metabolites are either non-volatile or volatile. Sugars (including mono-, di-, tri-, and polysaccharides), inorganic salts, nucleotides, amino acids, proteins, polyphenols, small peptides contribute to the flavour of the beverage. Whereas volatile compounds (esters and higher alcohols) are responsible for aroma. Although the raw material can influence flavour formation, yeast metabolism generates a multitude of compounds, which, together with the partition coefficient of compounds during distillation, influence the aroma profile of cachaça and. Yeast compounds can be grouped into six groups including organic acids, higher alcohols, carbonyl compounds, sulphur compounds, phenolic compounds, and volatile esters (Saerens et al. 2010). Higher alcohols and esters are important aroma compounds. Higher alcohols are generated from amino acid metabolism and esters from higher alcohols and acetyl-CoA (Briggs et al 2004).

### Distillation

During distillation, compounds are separated according to their boiling point (Alcarde et al. 2012). Distillation can be performed as a continuous, semi-

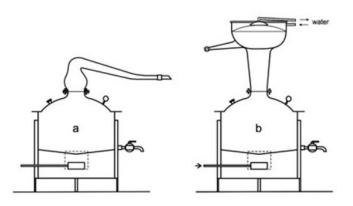
continuous or discontinuous batch process (Rosa et al. 2009: Alcarde et al. 2012;). The continuous process uses fractional distillation with stainless steel columns that are used for large scale production of cachaça or for bioethanol (Rosa et al. 2009; Bortoletto 2023). Discontinuous distillation or 'simple' or 'double distillation' with a copper still pot (alembic) are used in the small scale production of cachaça (Figure 3). A copper still can result in an increase in the concentration of copper in cachaça, an issue which is managed by effective cleaning. Cachaça distillation is controlled by alcohol content and is seperated into three fractions - 'head', 'heart' and 'tail' (Alcarde et al. 2012; Serafim et al. 2013; Portugal et al. 2017).

The heads fraction contains desirable volatile compounds, a high ethanol content but more undesirable compounds (including methanol) (Alcarde et al. 2009; Nova et al. 2009; Serafim et al. 2013; Rota et al. 2013). The hearts fraction is used for cachaça, and represents 80-85% of the distillate, with ethanol and other volatile compounds reflecting the requirements of legislation (Alcarde et al. 2009; Serafim et al. 2013; Borges et al. 2014; Bortoletto et al. 2021). The tails fraction contains a low level of ethanol and desirable compounds, with a high levels of acetic acid, furfural, and hydroxymethylfurfural (Nova et al. 2009; Rota et al. 2013; Granato et al. 2014; Bortoletto and Alcarde 2015; Portugal et al. 2017). Further, during distillation or double distillation, the underiable compound ethyl carbamate (from the reaction of ethanol and cyanide) is retained in the tails fraction (Alcarde et al. 2012). It should be noted that continuous distillation in stainless steel columns does **not** result in separation into the three fractions (Nova et al. 2009; Alcarde et al. 2012).

Post processing, cachaças from copper still pots or stainless steel columns are described on tasting as aggressive, alcoholic, hard, bitter with negative sensory characteristics (Rosa et al. 2009; Alcarde et al. 2014). The use of copper still pots minimise some of these characteristics as copper removes sulphur compounds, generated during fermentation from sulphur containing amino acids (Alcarde et al. 2014; Silvello et al. 2021). During the first three to six months of maturation in stainless steel or wooden barrels, some of the highly volatile compounds are lost, which improves the sensory characteristics (Alcarde et al. 2014; Silvello et al. 2021).

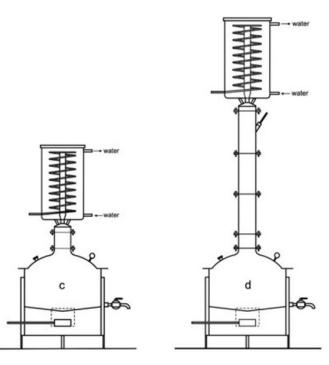
#### Figure 3.

Copper pot stills used to produce Cachaça: (a) hot head; (b) head cooler; (c) dephlegmator; and (d) rectifier (adapted from Alcarde et al. 2012).



Discontinuous double distillation can also be used to reduce the hard and bitter characteristics of unaged cachaça (Alcarde et al. 2012). Double distillation uses a second distillation, using (1) hearts fraction, (2) a mix of head and tails fraction) or (3) a mix of 50% (heads and tails) + 50% of freshly fermented wort. Double distillation reduces acidity, aldehydes, esters, methanol, higher alcohols, copper and ethyl carbamate and is good for ageing (Alcarde et al. 2012). Indeed, double distillation generates a more standardised beverage, improving its sensorial quality and consistency (Alcarde et al. 2012; Rota et al. 2013).

Increasing the number of distillations results in a more neutral spirit with fewer congeners (acetic acid, aldehyde, ethyl acetate, propyl alcohol and furfural) and contaminants (methanol, butan-2-ol, copper and ethyl carbamate). Moving from double distillation to five rounds of distillation, creates a soft and flavourless product, which can be developed by ageing in wooden barrels. However, for traditional unaged cachaça, a simple or double distillation can generate a product with the desirable and complex flavour profile of cachaça. This process takes five hours and further research is required establish the optimal duration and configuration of copper still pots for aroma formation during distillation.



## Ageing

Whilst ageing is a standard process step in the production of cachaça, it is not mandatory (Rosa et al. 2009) but significantly improves flavours (Rosa et al. 2009; Caetano et al. 2022). However, as noted above, freshly distilled cachaças can be hard and bitter. Accordingly, a short storage period (three to 12 months) in steel or wooden barrels is recommended to improve the sensory characteristics of cachaça (Alcarde et al. 2014; Silvello et al. 2021). Further, the poor sensory characteristic of fresh or young cachaças can be mollified by the addition of sucrose (6 g/L to young or 30 g/L to fresh). In the latter case, the addition of sucrose requires labelling as 'sweetened' cachaça (Brazil 2022b).

Cachaça is classified as 'cachaça', 'sweetened cachaça', 'aged cachaça', 'premium cachaça', and 'extra premium cachaça' (Brazil 2022b). 'Aged' cachaça must contain 50% of cachaça which has been aged for at least 12 months in wooden 700 L barrels, whereas 'premium cachaça' contains 100% aged spirit. The 'extra premium' cachaça is 100% aged spirit but aged for three years or more.

Like whiskey, cachaça is aged using oak barrels (Rosa et al. 2009; Castro et al. 2020). There are several oak

species including peduncular oak (*Quercus robur* L, *Quercus pedunculata* Ehrh), sessile oak (*Quercus petraea* L, *Quercus sessiliflora* Sm), American white oak (*Quercus alba* L) and North American red (*Quercus rubra*) (Chatonnet and Dubourdieu 1998). Ageing in oak barrels contributes attractive compounds including cumurins, scopoletin, gallic acid, ellagic acid, and vanillin (Chatonnet and Dubourdieu 1998; Bortoletto et al. 2016; Castro et al. 2020). However, as oak is not a native Brazilian wood, its use has become expensive through importation costs (Silva et al. 2009).

As a result other Brazilian tropical wood species have been used for cachaça ageing including castanheira-do-Pará (Pará or Brazil nut tree), umburana/ amburana (Amburana cearenses), balsamo (Myroxylon balsamum), Jatoba (Hymenaea courbaril), wild peanut, araruva, jequitibá rosa, peroba rosa (Aspidosperma polyneuron), cherry tree, ipê (Brazilian walnut), chestnut tree, grápia, pau-pereira, and freijó (Bortoletto and Alcarde 2013; Bortoletto et al. 2016; Bortoletto et al. 2021). The use of tropical woods contributes a different physicochemical composition and sensory characteristics to cachaça (Alcarde et al. 2010; Bortoletto et al. 2021). Ageing cachaça using tropical wooden barrels opened a new market to the diversity of tropical wooden barrels and possibilities for blending, resulting in different flavours and sensory character (Bortoletto et al. 2021).

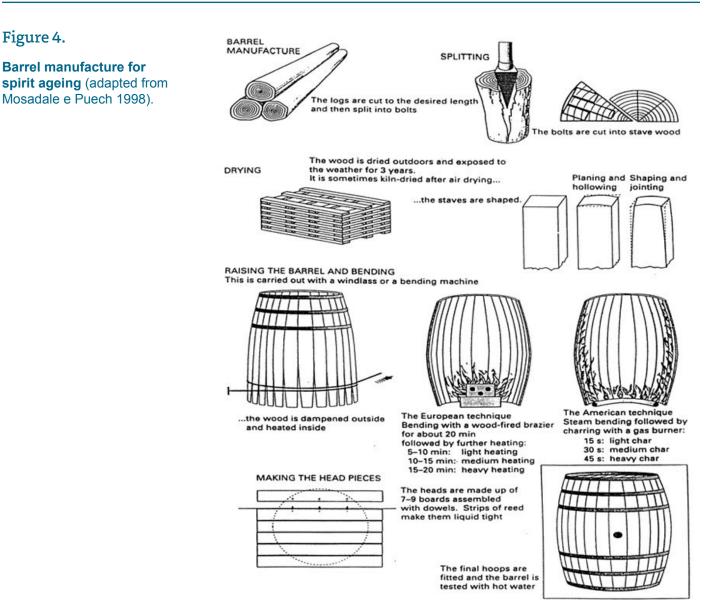
During ageing, compounds in cachaça interact with cellulose, hemicellulose, and lignin in the wood, undergoing decomposition facilitated by alcohol and water. Lignin degradation is responsible for the generation of compounds with low molecular weight including phenolic compounds (Carvalho et al. 2020; Castro et al. 2020; Silvello et al. 2021) which have been widely studied due to antioxidant properties (Bortoletto 2023). Phenolic compounds are secondary metabolites obtained from plants, bacteria, or fungi with high antioxidant capacity (Carvalho et al. 2020) and are divided into flavonoids (isoflavonoids. anthocvanidins. flavonoids. flavonols, flavanone, and flavones), and nonflavonoids (hydroxycinnamic and hydroxybenzoic acids, stilbenoids, lignoids and coumarins). In foods, phenolic compounds contribute colour, astringency, aroma and oxidative stability (Carvalho et al. 2020; Castro et al. 2020).

Ageing cachaça in tropical wooden rather than oak barrels results in a similar spectrum of compounds but with differences in concentration (Zacaroni et al. 2011). Castanheira (Pará or Brazil nut) barrels contribute phenolic compounds such as gallic acid, and ellagic acid (Zacaroni et al. 2011; Bortoletto et al. 2016). Barrels made from the timber tree umburana contribute curamin, eugenol, cinnamon laurel, catechin and vinylic acid (Alcarde et al. 2014). Barrels made from balsamo contribute phenolic compounds such as ellagic acid and vanillin (Alcarde et al. 2010; Bortoletto et al. 2016). However, barrels made from Brazilian walnut (ipê) contribute syringic acid, vanillic acid and coniferaldehyde (Alcarde et al. 2014; Bortoletto et al. 2016). Similarly, the phenolic acids from peroba wood are vanilin and syringic acid (Santiago et al. 2017). Gallic acid and syringaldehyde are the main phenolic compounds found by ageing in jatobá barrels (Bortoletto et al. 2016; Santiago et al. 2017).

An evaluation of tropical wooden barrels by Bortoletto et al (2016) reported that cachaça aged in oak provide a sweet, smooth taste with a vanilla aroma and a yellow colour. A similar colour was observed in cachaças aged in barrels made from umburana, cabreúva and jatobá. In contrast, barrels made from feijó, peanut wood, araruva, and jequitibá did not influence the colour of aged cachaça (Alcarde et al. 2010; Santiago, et al. 2017). Balsamo barrels contributed a sharp and pleasant aroma with a reddish-yellow colour (Bortoletto et al. 2016; Santiago et al. 2017). Ageing in barrels from peanut wood, pear tree, jatobá, and eucalyptus contributed similar characteristics to oak barrels including colour, together with polysaccharides and lignin, which improve the sensory character (Souza et al. 2012).

#### Wooden barrels

No two wooden barrels are the same, reflecting the background of the tree (genetic and topographical), the part of the tree from which the wood was taken and subsequent variations in the production process (Gollihue et al. 2021). The manufacture of wooden barrels is outlined in Figure 4. France and the United States are the largest producers and exporters using oak from French forests (*Quercus petraea, Q. robur*) and American oak (*Q. alba*) (Cadahía et al. 2009; Carpena et al. 2020). The wood used in barrels for



spirit maturation must meet requirements for porosity, permeability, and chemical composition (Cadahía et al. 2009). Cylinder cuts are used to form the staves, which are dried, cut to shape and are heated to be more malleable (Mosedale and Puech 1998). After assembly of the barrel by the Cooper, he internal surface is charred or 'toasted' to be light, medium or heavy using different methods in Europe and the USA (Figure 4).

Toasting changes the structure, and composition of wood, which impacts on the spirit during ageing (Mosadale and Puech 1998; Bortoletto et al. 2021). The toasting process is divided into three types: 1) 'light' which contributes a yellow colour to the beverage 2) 'medium' which results in a red colour and 3) 'heavy' gives a dark brown colour. Barrels toasted using heavy toasting result in smoky aromas which may not be desirable (Mosadale and Puech 1998; Bortoletto et al. 2016; Bortoletto et al. 2021).

#### Flavour and aroma compounds

Cachaça contains both volatile (aromas), and nonvolatile (flavour) compounds (Portugal et al. 2017; Bortoletto 2023). Cachaça flavour and aroma is influenced by numerous factors including sugar cane cultivar, yeast microbiota, fermentation conditions, distillation method and – where applied - ageing (barrel wood and toasting) (Bortoletto and Alcarde 2013; Granato et al. 2014, Bortoletto et al. 2016). Cachaça spirit contains a multitude of secondary compounds including aldehydes, esters, acids, alcohols, and phenols (see Table 1). Even at low concentrations compounds influence flavour and aroma through complex interactions which can be both synergistic and antagonistic.

#### Table 1.

#### Volatile compounds identified in cachaça aged in different types of wooden barrel.

CLASS	COMPOUNDS	DESCRIPTORS	WOOD
Ethyl esters	ethyl pentanoate; ethyl hexanoate; ethyl heptanoate; ethyl octanoate; ethyl nonanoate; ethyl decanoate; ethyl undecanoate; ethyl dodecanoate; ethyl tridecanoate; ethyl tetradecanoate; ethyl pentadecanoate; ethyl hexadecanoate; ethyl octadecanoate; diethylsuccinate; diethyl malate	Alcohol, apple, banana	Cerejeira, Castanheira
Acetate esters	ethyl butyrate; propyl acetate; isobutyl acetate; hexyl acetate; isoamyl acetate; heptyl acetate; octyl acetate; nonyl acetate; decyl acetate; dodecyl acetate; tetradecyl acetate; hexadecyl acetate	Perfume, rancid	Amendoim, Araruva
Propyl esters	propyl octanoate; propyl dodecanoate; propyl hexadecanoate	Sweet	Carvalho, Cerejeira
Decanoate esters	pentyl decanoate; heptyl decanoate	Vinegar	Cabreúva, Castanheira, Cerejeira
2-Methylpropyl (isobutyl) Esters	2-methylpropyl octanoate; 2-methylpropyl decanoate; 2- methylpropyl tetradecanoate	Soap	Castanheira, Cerejeira
3-Methylbutyl (isopentyl) esters	3-methylbutyl acetate; 3-methylbutyl hexanoate; 3-methylbutyl octanoate; 3-methylbutyl decanoate; 3-methylbutyl dodecanoate	Orange peel Papaya	Castanheira
Phenylethyl esters	pentyl acetate; phenethyl acetate; phenethyl butanoate; phenethyl haxanoate; phenethyl octanoate	Roses	Cabreúva
Propan-2-yl (isopropyl) esters	propan-2-yl dodecanoate; propan-2-yl tetradecanoate; propan-2-yl hexadecanoate	Solvent, sugar cane	Amburana
Aldehydes Fatty alcohols	acetaldehyde; furfural; heptanal; octanal; nonanal; decanal; undecanal; dodecanal; tridecanal; tetradecanal; pentadecanal; hexadecanal; octadecanal	Honey	Grápia, Carvalho, Cerejeira, Ipê, Jequitibá
n-Alcohols	propanol; pentanol; hexanol; heptanol; octanol; nonanol; decanol; undecanol; dodecanol; tridecanol; tetradecanol; pentadecanol; hexadecanol; 2-methyl-1-butanol; 3-methyl-1- butanol	Butter, citrus	Carvalho
2-Alcohols	propane-1,2-diol; heptan-2-ol; octan-2-ol; noman-2-ol; decan-2-ol; undecan-2-ol; dodecan-2-ol; tridecan-2-ol; pentacan-2-ol; furfuryl alcohol	Coconut, fruity	Castanheira, Cerejeira
Acids	acetic acid; propionic acid; isobutyric acid; butyric acid; hexanoic acid; heptanoic acid; 2- ethyl caproic acid; octanoic acid; noanoic acid; decanoic acid; benzoic acid, ellagic acid. vanillic acid, gallic acid	Vinegar, pungent, acidic, dairy-like	Bálsamo, Ipê, Carvalho, Jequitibá, Amburana
Phthalates Fatty acid ester	pentyl decanoate; heptyl decanoate; 2-methylpropyl butyl benzene-1,2-dicarboxylate; bis(2-methylpropyl) benzene-1,2-dicarboxylate; dibutyl benzene-1,2-dicarboxylate	Waxy, wood	Cabreúva, Carvalho
Ketones	heptan-2-one; octan-2-one; nonan-2-one; decan-2-one; undecan-2-one; dodecan-2-one; tridecan-2-one; pentadecan-2-one; hexadecan-2-one; heptadecan-2-one	Green apple, green leaves	Cerejeira
Alkanes	nonane; undecane; tridecane; tetradecane; pentadecane; heptadecane; octadecane; nonadecane; docosane	Bitter, lemon	Cerejeira

Information dervied from Alcarde et al. 2010; Bortoletto et al. 2021; Catão et al. 2011; Dias et al. 1998; Nóbrega 2003; Cardeal and Mariott 2009; Silva et al. 2009; Souza et al. 2009; Duarte et al. 2011; Duarte et al. 2013; Amorim et al. 2016; Gonçalves et al. 2016; Santiago et al. 2016; Zacaroni et al. 2017; Nascimento e Silva et al. 2020.

Esters are important aroma compounds and are formed during fermentation, distillation, and ageing (Bortoletto et al. 2016; Portugal et al. 2017; Oliveira et al. 2020). Ethyl carbamate (EC) is a carbamic acid ester formed during fermentation, distillation, and ageing (Nóbrega et al. 2009; Machado et al. 2013; Bortoletto and Alcarde 2016) and is a concern due to its carcinogenic properties (Machado et al. 2013; Gonçalves et al. 2016). Higher alcohols contribute to cachaça aroma and are generated by yeast via the Ehrlich pathway together with aldehydes and short-chain fatty acids (Hazelwood et al. 2008). Acetaldehyde contributes positively to the aroma of cachaça (Ribeiro-Filho et al. 2021). Other aldehydes such as furfural and hydroxymethylfural can be formed when sugar cane crop is burned before harvesting and generated during distillation due to a poor separation of yeast after fermentation (Bortoletto 2023). The alcohol, methanol is undesirable as it can cause health problems even at low concentrations (Alcarde et al. 2014).

## Quality control

Cachaça is influenced by the geographical origin, field and industrial practice (Alcarde et al. 2012; Bortoletto 2023;) but the quality of the spirit must be controlled and standardised (Brazil 2022b). The geographical origin inevitably results in variation but promotes diverse flavour profiles, contributing to the complexity of the cachaça. Similarly, field practice encompasses the sugar cane supply chain from choosing a cultivar to harvesting. The industrial processes are key to minimising undesirable organic or inorganic contaminants such as copper, dimethyl sulphide, and ethyl carbamate.

#### Copper

The Brazilian legislation limits copper in cachaça to 5 mg/L (Brazil 2022b). Sugar cane contains copper and the juice contains ca. 0.06 mg copper/L) which is required by yeast during fermentation. The divalent cation acts as an essential cofactor for enzymes

(including cytochrome C oxidase, lactase, and Cu, Zn superoxide dismutase) and is important for yeast metabolism during iron homeostasis (De Freitas et al. 2003). However, copper present in the must/ wort does not contribute to the copper content of the spirit as it remains in the 'tail' fraction post distillation. Distillation using stainless steel columns does not contribute copper, whereas cachaça distilled in copper still pots does. Here, oxidation of internal walls of the copper still generate a copper salt, which dissolves in cachaça (Rosa et al. 2009; Alcarde et al. 2014; Böck et al. 2022). Therefore, copper content can increase to levels that are of concern (>5 mg/L). Accordingly, to reduce copper exposure and copper content within legal limits, the internal walls of copper pot stills should be cleaned before distillation (Rosa et al. 2009; Oliveira et al. 2020; Böck et al. 2022).

## Dimethyl sulphide

Dimethyl sulphide is not regulated by Brazilian legislation, but generates sulphur off-flavours in the spirit (Rosa et al. 2009). Dimethyl sulphide is generated by yeast during fermentation but is captured during distillation in copper still pots. However, cachaça distilled in stainless steel columns contains dimethyl sulphide and can result in product with sulphur off-flavours (Alcarde et al. 2014). These may be mitigated by the addition of up to 6 g/L of sucrose to reduce the perception of off-flavours.

### Ethyl carbamate

Sugar cane is a cyanogenic crop characterised by containing cyanogenic glycosides. Although little is known about the metabolic pathway of ethyl carbamate (EC) formation during fermentation of sugar cane juice (Rosa et al. 2009; Lachenmeier et al. 2010). Ethyl carbamate is a concern, potentially carcinogenic and an undesirable compound in cachaça (Nóbrega et al. 2009; Alcarde et al. 2012; Machado et al. 2013; Mendonça et al. 2016; Santiago et al. 2017).

The formation of EC is influenced by the raw material, fermentation and distillation practice (Lachenmeier et al. 2010; Alcarde et al. 2012; Santiago et al. 2014; Mendonça et al. 2016). During fermentation, urea supplementation increases EC formation (Nóbrega et al. 2009; Ljungdahl and Daignan-Fornier 2012) with the amino acid arginine a precursor of urea, carbamyl phosphate, and cyanide (Jiao et al. 2014). The nitrogenous precursor interacts with ethanol to form ethyl carbamate (Jiao et al. 2014; Santiago et al. 2014). Studies reveal that the use of commercial yeast strains reduce the formation of ethyl carbamate (Lima et al. 2012; Santiago et al. 2017) as did wild yeasts from sugar cane juice supplemented with corn flour or rice bran (Santiago et al. 2014; Mendonça et al. 2016; Santiago et al. 2017).

Ethyl carbamate is formed during fermentation, but its concentration increases during distillation (Nóbrega et al. 2009; Lachenmeier et al. 2010). Separation of the distilled spirit into three fractions (heads, heart, and tails) enables the reduction of ethyl carbamate as the heads fraction retains much of the ethyl carbamate (Alcarde et al. 2012; Nova et al. 2009; Rota et al. 2013; Santiago et al. 2017). Cachaça distilled in stainless steel columns is associated with the low levels of ethyl carbamate, but distillation in a copper pot results in a higher concentration of EC which can be reduced by longer distillation (Nóbrega et al. 2009; Lima et al. 2012;). Double, triple, or multiple distillation reduces the concentration of congeners (acetic acid, aldehyde, ethyl acetate, propyl alcohol and furfural) and, importantly, compounds of concern (methanol, butane-2-ol, copper and ethyl carbamate) (Alcarde et al. 2012; Bortoletto et al. 2016).

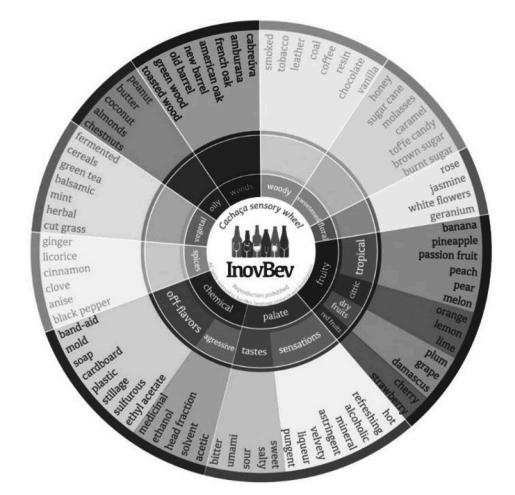
It was thought that ethyl carbamate increases during the ageing process. However, there is no evidence that ethyl carbamate increases to levels above the international limit of 150  $\mu$ g/L during ageing (Santiago et al. 2014; Bortoletto et al. 2016; Mendonça et al. 2016). In passing, cachaça stored in colourless glass bottles for six months results in an increase in the EC content due the exposure to natural light (Zacaroni et al. 2015).

#### Sensory analysis

Cachaça is a spirit with a distinctive sensory character with flavours from fermentation, distillation, and the ageing process. The aroma and flavour of cachaça offer a unique and complex matrix, which requires greater knowledge of its sensory attributes (Bortoletto et al. 2021). Sensory analysis determines the main attributes of the beverage and can facilitate the improvement and standardisation

#### Figure 5.

#### Sensory wheel for cachaça (Bortoletto 2023).



of quality through monitoring (Serafim et al. 2013). The application of sensory analysis has enabled the identification of the positive and negative attributes of cachaça including descriptors such as aggressive, hard, bitter, sulphur off-flavour, oiliness, yellow colour intensity, warming, sweetness, acidity, smooth, floral, fruity (vanilla aroma), woody, and alcohol (Serafim et al. 2013; Bortoletto et al. 2016). A sensory wheel has been created for cachaça to describe the profile of aged cachaça (Bortoletto 2023). The sensory wheel for cachaça contains four sensory categories, fifty descriptors (including three for visual evaluation), thirty-three specific aromas, five tastes and nine sensations (Figure 5). Sensory wheels are tools to unify technical attributes to describe the characteristics of a product (Silvello et al. 2020). The lexicon of the sensory wheel enables the qualitative and quantitative description of different examples of cachaça.

#### Future trends

Further studies are required to improve understanding of the adaptation of sugar cane cultivars, the characteristics of sugar cane juice (including microbiota), and the influence on fermentation, distillation, and ageing of cachaça. Further, given the ecological diversity and varieties of sugar cane, the understanding of yeast handling for cachaça production is poor. Selecting and characterising the indigenous yeasts (physiology, genetic identity and diversity, metabolome etc) from different sugar cane cultivars and producers can create special cachaças with a mix of yeasts to create novel sensory characteristics. Fermentation would benefit from studies targeted at 1) the dominance and persistence of yeasts, 2) fermentation kinetics, 3) nutrient transport, 4) yeast drying, 5) hydration of dried yeast, and 6) storage of dried yeast.

The distillation process for cachaca takes inspiration from production of 'bagaceira' (Portuguese brandy) and whiskey. There are opportunities for the improvement in cachaca distillation such as the volatilisation kinetics of compounds during distillation in copper and/or stainless steel stills. Similarly, the use of different tropical woods for barrel ageing of cachaca ageing opens the door to new opportunities. Underpinning any developments or innovations is the application of sensory science to fingerprint the spirit and assure quality. Finally, the application of new analytical techniques such as fluorescence and infrared spectroscopy can be applied for the quality control of cachaca. Such methods are worthy of development as they non-destructive and have application in on-line monitoring.

# Conclusions

Cachaça production is defined process with supporting regulation. Field practice involves planting of sugar cane, harvesting and transportation whilst industrial practice involves extraction, fermentation, distillation, juice ageing, and standardisation. Cachaça's sensory characteristics are determined by the climate, soil, environment, sugar cane cultivar and associated microbiota. Fermentation practice contributes to the sensory characteristics of cachaça, determined by indigenous or starter commercial yeasts. Cachaça fermentation is performed in open vessels resulting in the loss through gas washing of some aroma volatiles. Producers prefer to use a copper pot still for cachaça distillation with the increasing use of different tropical wood for barrels ageing. The options for different toasting regimes of barrels influences the flavour and aroma of cachaça providing opportunities for differentiation of the spirit.

# Author contributions

**Vanessa Pedro Da-Silva:** conceptualisation, writing (original draft, review and editing).

Jéssica Barbosa de Souza: writing (original draft). Ângela Lima Meneses de Queiroz: writing (original draft).

Normando Ribeiro-Filho: conceptualisation, writing (original draft, review and editing). Taliana Kenia Alves Bezerra: conceptualisation, writing (review and editing).

# Declaration of competing interest

The authors declare there are no conflicts of interest.

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