University of “São Paulo”
“Luiz de Queiroz” College of Agriculture

Development of an electronic nose for characterizing the level of maturation of
cachaça

Giovanni Casagrande Silvello

Thesis presented to obtain the degree of Doctor in
Science. Area: Food Science and Technology

Piracicaba
2021

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A todas as pessoas que acreditaram em si mesmas
ao se arriscarem em novas áreas do conhecimento.

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BIOGRAFIA

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EPÍGRAFE

*"[...] data is know-what,
information is know-why,
knowledge is know-how
and
intelligence is know-when".*

Tang, Yanine e Valenzuela (2016)
[<https://doi.org/10.1108/IJIS-07-2016-0022>]

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RESUMO

Desenvolvimento de um nariz eletrônico para determinação do grau de maturação de cachaças

Para agregar qualidade à cachaça torna-se fundamental o envelhecimento em barris de madeira visando ampliar o perfil químico e a complexidade sensorial da bebida. O grau de maturação do destilado é influenciado por diversos fatores, nos quais se destacam em importância: a espécie de madeira usada na fabricação do barril, a aplicação ou o grau de queima interna da madeira, o número de usos do barril e o tempo de envelhecimento. A determinação do grau de maturação do destilado pode ser realizada usando a concentração e as relações entre os compostos fenólicos marcadores de envelhecimento extraídos da madeira do barril. Esta determinação depende atualmente de análises cromatográficas custosas, o que inviabiliza o acompanhamento frequente e periódico da evolução do grau de maturação. O desenvolvimento de um nariz eletrônico, equipamento composto por conjunto de sensores de gases, microcontrolador e algoritmo de classificação, pode viabilizar econômica e operacionalmente o monitoramento do processo de envelhecimento da cachaça para a indústria de bebidas, para produtores e laboratórios com menor estrutura analítica. O objetivo desse estudo foi caracterizar o processo de envelhecimento de cachaça a partir de um nariz eletrônico, correlacionando as leituras desse equipamento com a concentração dos compostos fenólicos oriundos da degradação da lignina durante a maturação da bebida em tonéis de madeiras. Foram estudadas cachaças envelhecidas por até 60 meses em barris de diferentes espécies de madeira (carvalhos e tropicais), sem ou com queima interna (em diferentes intensidades) e diversas condições de uso (novo, segundo uso e extenso uso). A avaliação foi baseada em análises de compostos marcadores de envelhecimento (derivados da degradação da lignina) por CLAE (Cromatografia Líquida de Alta Eficiência) e obtenção da leitura das amostras obtida pelo conjunto de sensores do protótipo do nariz eletrônico. A nova metodologia criada para a determinação do grau de envelhecimento da cachaça, em função de leituras do nariz eletrônico associada a um algoritmo de rede neural artificial, atingiu mais de 90 % de exatidão ao classificar diferentes amostras com diferentes graus de maturação. O desenvolvimento desta tecnologia apresenta potencial para avaliação de características relacionadas à composição química volátil e aos aspectos sensoriais de bebidas alcoólicas destiladas.

Palavras-chave: Cachaça, Envelhecimento em barril, Grau de maturação, Nariz eletrônico

ABSTRACT

Development of an electronic nose for characterizing the level of maturation of cachaça

Aging in wooden barrels is essential to add quality to cachaça aiming to improve its chemical profile and sensory complexity. The degree of maturation of the distillate is influenced by several factors such as wood species used to manufacture the barrels, application or degree of internal burning, number of times the barrel is used, and aging time. The maturation level of cachaça can be determined using the concentration of aging-marker phenolic compounds extracted from the wood of the barrel and their relations with each other. Since this determination currently depends on costly chromatographic analysis, the periodic monitoring of the level of maturation is impracticable. The development of an electronic nose, an equipment composed of an array of gas sensors, a microcontroller, and a classification algorithm, can make the surveillance of sugar cane spirit aging process economically and operationally feasible for the cachaça industry, producers, and laboratories relying on a simpler analytical structure. This study aimed to characterize the aging process of cachaça using an electronic nose by correlating the results obtained using this equipment with the lignin degradation mechanism during the maturation period of this distilled spirit in wooden barrels. Aged cachaça was studied for up to 60 months of ageing in barrels made from different oak species, with or without internal burning (at different intensities) and three use conditions (new, second use, and extensive use). The aged cachaça was analyzed based on the contents of aging markers (derived from lignin degradation) using high performance liquid chromatography and the 'smellprint' obtained using the electronic nose prototype sensors array. The innovative technology developed for determining the maturation level of cachaça, based on the electronic nose readings, associated with an artificial neural network algorithm, reached over 90% of accuracy for the classification of samples of different maturation classes. The development of this technology has a good potential to evaluate other characteristics related to the chemical volatile composition and sensory aspects of distilled beverages.

Keywords: Sugarcane spirit, Barrel-aging, Maturation level, Electronic nose

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ABBREVIATIONS

AI	Artificial Intelligence
ANN	Artificial Neural Networks
CA	Cluster Analysis
CART	Classification and Regression Trees
DFA	Discriminant Function Analysis
E-nose	Electronic Nose
GC-MS	Gas Chromatography – Mass Spectrometry
GMM	Gaussian Mixed Model
GMP	Good Manufacturing Practices
HPLC	High Performance Liquid Chromatography
KNN	K-Nearest Neighbors
LDA	Linear Discriminant Analysis
LDP	Lignin Degradation Product
ML	Machine Learning
MOS	Metal Oxide Semiconductor
PCA	Principal Components Analysis
PCR	Principal Components Regression
PE	Processing Element
R&D	Research and Development
RF	Random Forest
SGD	Stochastic Gradient Descent
SVM	Support Vector Machine

1. INTRODUCTION

The aging of distilled beverages in wooden barrels, imperative for high quality products such as brandy, whisky, wine spirits, and eventually rum, has been used for centuries to improve their flavor (Bortoletto, Silvello, & Alcarde, 2018). The aging process is one of the most important factors to define the quality of distilled spirits, and although it is not mandatory in the production of Brazilian sugar cane spirit (cachaça) (Bortoletto & Alcarde, 2013), it is becoming a recurrent practice among the producers of appreciated cachaça brands, focusing on product innovation and highest added value.

Cachaça exports reached more than 60 countries in 2017, adding up to US\$ 15.8 million in revenues to Brazil (Instituto Brasileiro da Cachaça, 2019). This amount corresponds to an increase by 13.4% in relation to the year before. In the same period, an increase by only 4.3% was registered for exports in general, indicating a proportionally greater increase in revenue generated by cachaça alone compared to the export volume growth. This reflects a scenario of more added value and cachaça of better quality, enhancing its international visibility.

Cachaça production may pursue good manufacturing practices to achieve higher quality production. The aging of this distilled beverage is a critical control point (Bortoletto et al., 2018) due to factors such as endogenous (wood species, cachaça composition prior to aging) and exogenous variations (cellar environment, aging period). Furthermore, the qualitative analysis of the distillate during the aging process is difficult, given that it involves subjective decisions and a complex cognitive process performed by expert tasters or a panel that might be in constant sensory training to properly characterize this distillate and meet its quality standards.

Recent studies to investigate the changes in composition of distilled beverages during the aging process in wooden barrels have shown the formation pathways of aging congeners through lignin degradation (Cernîșev, 2017; Rodríguez-Solana, Salgado, Domínguez, & Cortés-Diéguez, 2014). Those reactions and the concentrations of compounds in the final distillate correspond to the actual quality parameters of the beverages, even applicable for fraud detection (Wiśniewska, Dymerski, Wardencki, & Namieśnik, 2015). The rate of lignin degradation relies on numerous factors besides the aging period, such as the number of previous uses of the barrel, warehouse temperature, and initial content of ethanol in the spirits (Conner, 2014). Moreover, Driver (2014) commented that a new tendency in the whisky market indicates that age will be less

important as a determinant of quality when other means of differentiation, innovation, and a greater standard quality are implemented.

An electronic nose (or digital olfactometer) is a new device that encompasses analytical reliability and affordability, is easy to use, and offers a considerable potential solution that enables quality assessment for different processes in the beverage industry. As idealized by Jack (2014), an instrument capable of reporting real-time flavor data during the production stages of aged distilled spirits would create a favorable scenario for quality warranty. A qualitative approach may be more suitable for flavor analysis, once high-precision quantification methods are already well established (chromatography) and likely achievable. Therefore, devices that are able to capture smellprints, combined to a pattern recognition trained algorithm, are suitable solutions for flavor assessment (Ghasemi-Varnamkhasti et al., 2018; Hines, Boilot, Gardner, & Gongora, 2004; Wilson & Baietto, 2009) applicable to beverage industries. Viejo, Torrico, Dunshea, and Fuentes (2019) supported the integration of novel methods and technologies involving cheaper analytical instruments and automated techniques, such as computer vision, artificial intelligence, and machine learning algorithm, to model and predict quality of beverages based on different measurable parameters. Assays successfully used in beverage industries have displayed a large potential for quality assurance and increasing efficiency (Folz & Mol, 2019; Schlenker, 2019).

The development of such devices, dedicated to supply small producers of cachaça with a tool for productive control and monitoring based on electronic nose technology, may encompass metal oxide semi-conductor gas sensors responsible for transforming chemical stimuli, coming from samples headspace, into digital signals for interpretation by pattern recognition machine learning techniques. The applicable algorithms demand data from known samples to train over the classification task (supervised learning), which may have high quality and be representative considering the intended task to obtain satisfactory performance results and consolidate a robust system (Géron, 2019).

1.1. Objectives

1.1.1. General Objectives

The present project aimed to create a new method for the qualitative classification of cachaça aged in wooden barrels, based on compounds derived from lignin degradation, named aging markers, due to their proved importance and application among international researchers. The contribution of specific wood compounds was evaluated in samples aged in different types of barrels. This research also aimed to develop a new accessible device, based on electronic nose technology, capable of distinguishing the maturation class of cachaça samples according to their aroma profile detected by gas sensors.

The major objective of this study was to supply cachaça producers with a method and an equipment to evaluate the evolution of their distillates obtained by aging in wooden barrels. This evaluation may help their decision making either for maintaining the barrel aging process longer for greater evolution of the distillate, or for interrupting this process, standardizing, and bottling the aged distillate. Both the maturation classes and the electronic nose were conceived as techniques that may provide qualitative information about the cachaça aged in wooden barrels as a parameter for monitoring the aging process.

1.1.2. Specific Objectives

The specific objectives of this project were:

- Use unsupervised machine learning techniques to evaluate similarities and discrepancies among cachaça samples aged in different barrels;
- Group cachaça samples aged in different barrels according to their composition and aging period to establish “maturation classes”;
- Develop an electronic nose and optimize the system to evaluate distilled beverages avoiding ethanol poisoning of the sensors;
- Evaluate all samples available in the Laboratory of Technology and Quality of Beverages of “Luiz de Queiroz” College of Agriculture, University of São Paulo, using an electronic nose prototype;

- Relate all the maturation classes of cachaça samples to their flavor profile assessed by an electronic nose prototype;
- Employ machine learning and artificial intelligence to obtain a model that accurately classifies cachaça samples according to their maturation classes based on their flavor profile;
- Explore the possibilities of commercial application of an electronic nose device applied to the evaluation of cachaça aged in wooden barrels.

1.2. Literature Review

1.2.1. Electronic nose technology overview

Electronic nose devices, also called e-noses, artificial noses, digital olfactometers, or aroma sensors, were first reported in the 1980's (Persaud & Dodd, 1982), and a growing interest persisted in the following decade (Pearce & Gardner, 1998; Schaller, Bosset, & Escher, 1998). The development of such apparatus underpinned the technological and scientific progress over the fields of electronic systems and sensors as well as data analysis, leading to the emergence of numerous new instrumental devices intended to be used for medical applications, food safety, and analysis of contaminants, aroma, and flavor (Keller, 1995; Schaller et al., 1998). Currently, the development of electronic nose devices is more expressively directed to the engineering and chemistry fields (Figure 1), considering faster analytical detection of volatile fraction, early detection of compounds, increased sensitivity of sensors, and instrumental simplification (Wardencki, Chmiel, & Dymerski, 2013).

Figure 1. Evolution of number of publications focusing on the development of electronic nose devices per area of knowledge (data obtained from Scopus–Elsevier database – June 2020).

Electronic noses that have recently been built for analyzing food are capable of classifying levels of spoilage of different food matrices such as meat (Sarno & Wijaya, 2019; Wijaya, Sarno, Zulaika, & Sabila, 2017), adulteration of saffron (Kiani, Minaei, & Ghasemi-Varnamkhasti, 2016a), post-harvest quality of peaches (Voss, Stevan, Jr., & Ayub, 2019), wine spoilage (Gamboa, Albarracin, Silva, Lima, et al., 2019), beer quality during storage (Ghasemi-Varnamkhasti et al., 2011), and classification of beverages (Ragazzo-Sanchez, Chalier, Chevalier, Calderon-Santoyo, & Ghommidh, 2008).

Odor analysis using electronic sensors is based on human olfaction, a system that has resulted from thousands of years of evolution (Shipley, Zimmer, Ennis, & McLean, 1996). Olfaction is the sense that enables mammals to interact with their environment through the chemical stimulation of sensory receptors (Katz et al., 2008) on olfactory sensory neurons, which make part of the nose epithelium, by odorous ligands (Buck & Axel, 1991). The activation of the olfactory receptors by an odor compound triggers G-protein in the epithelium cell membrane branched to neurons and generates an electric potential difference transmitted through the neurons to the brain, where it is interpreted as information (X. Zhang et al., 2018). Son, Lee, Ko, and Park (2017) reported that these receptors (around 400 in a human nose) display diverse affinities with distinct odorants, and due to lack of odor standards, human description of smells rests on personal experience and capability, therefore limited to subjective conditions.

In addition, both the olfactory ability and memory are peculiar to each person (Son et al., 2017) and natural scents are composed by various odors and combinatorial patterns of interaction among odorants (Francl, 2015), making odor standardization a complex task. Thus, Son et al. (2017) proposed a concept that merges human olfactory receptors and electronic circuits for the electrical transduction of signals. The complex interpretation of odor may be approached as multifactor information named smellprint (Wardencki et al., 2013), which represents stimuli from a combinatory perspective, rather focused on quantification of individual compounds concentration in a matrix.

This multiplex bioelectronic nose relies on a sensor array network that generates a representation of odor patterns, mimicking the human response to chemical stimuli obtained through olfaction. This composes a database of stimuli captured from different samples over a common matrix. Machine learning, statistics, and other mathematical tools are employed to detect data patterns and relevant features in known training datasets that enable classification of new samples analyzed by an e-nose (Wardencki et al., 2013).

Concerning the new advances on food monitoring and quality assurance by the use of electronic noses, it represents an advantageous technology that combines an inexpensive, fast, reliable, and real-time implementable method compared to other traditional analytical techniques such as chromatography or sensory analysis with panel of assessors, which represent precise techniques despite being more expensive, time-consuming, and demanding well-trained labor (Sanaeifar, ZakiDizaji, Jafari, & de la Guardia, 2017). The potentially high effectiveness of an e-nose device relies on the identification of smellprint patterns of foods and beverages according to their volatile compounds. This corresponds to a task accomplished after establishing a proper sensor array to compose the olfactometer hardware, as well as a suitable data treatment method to optimize information considered for the analysis of sample classification (Viejo et al., 2019).

Recent efforts of the beverage industry already indicate a potential for e-nose devices (Viejo et al., 2019). Maciejewska, Szczurek, and Kerényi (2006) confirmed the successful monitoring of wine fermentation process using an MOS-based electronic nose installed for analyzing volatile composition and gas released by fermentative activity. The prototype responses were highly correlated to fermentation quality parameters such as volatile acidity, ethanol, and ethyl acetate contents, quantified instrumentally and also by human sensory assessment. Gamboa, Albarracin, Silva, Lima, et al. (2019) implemented a qualitative e-nose solution for the classification of levels of acetic bacteria spoilage in

wines. Phetchakul and Sutthinet (2014) developed an equivalent apparatus for monitoring beer fermentation that enabled quality standardization through aroma evaluation performed hourly for 10 days.

Considering the applicability of e-nose technology, this transforming market pull instrument underpins the advances in the alcoholic beverage industry. In this scenario, companies that adopt new technologies for operational optimization, from raw materials to selling strategies, are more likely to compete globally due to faster and more precise decision-making attitudes when encountering new opportunities (Otles & Sakalli, 2019). This technological optimization is also supported by consumer and market-oriented values such as traceability, sustainability, and transparent connection in different stages of the productive chain.

1.2.2. Sensors and hardware

An electronic nose device is composed of different parts of hardware, and the sensor array is the core of this type of system due to its ability to perceive the physical world and translate the information into electronic signals, similarly to the odorant receptors present in human olfaction. The sensor array receives the odor stimulus and translates it into a smellprint (Wardencki et al., 2013). The development of sensors suitable for safety and microbiological analysis of food and beverages, as well as applied to the medical area, have fostered progress in the field of materials technology, seeking to find a suitable material, with high sensitivity and selectivity. These features are achieved through an optimized manufacturing process to obtain proper surface and bulk properties (Eranna et al., 2004). The types of sensors developed for applications in e-nose devices include metal oxide semiconductor (MOS), MOS field effect transistor, quartz crystal microbalance, surface acoustic wave, conducting polymer, as well as electrochemical, optical, and biomimetic sensors (Dey, 2018; Nanto & Stetter, 2003).

The most investigated and most commonly used type of gas sensor for e-noses are MOS sensors, characterized by semiconductive solid-state materials with a reactive element for detection when in contact with gas molecules. The surface interaction is responsible for changes in the density of charge carriers available in the semiconductor matrix, a phenomenon that depends on receptor (recognition) and transduction functions, as well as on sensor construction (Jain, 2011). The recognition factor is associated with the sensitivity of the sensors to gases and volatile compounds. The conductivity of the

material increases proportionally to the concentration of gas molecules that react on its surface (Dey, 2018; Jain, 2011).

Sanaeifar et al. (2017) reported that despite the disadvantages of MOS-type sensors, such as a limited range of coating material variation and susceptibility to poisoning, this type of sensor is quite common in e-nose projects (Table 1) for food analysis due to their low cost, high reproducibility, short recovery time, and good durability. Their reliability is therefore favorable and their susceptibility to material cumulative defect is less important compared to sensors that reach higher operation temperatures (Dey, 2018; Setvín, Wagner, Schmid, Parkinson, & Diebold, 2017).

The MOS-based sensor array is a viable solution for analyzing different matrices, based on their volatile odor compound compositions, since it achieves high accuracy for classification tasks and satisfactory performance on quantitative analysis as well. Satisfactory results rely on sensor characteristics such as response and recovery time, reversibility, cost, life cycle, stability over time, reproducibility, sensitivity, and selectivity (Huang, Liu, Zhang, & Wu, 2015). These features directly influence the choice over number and type of sensors selected for a specific application of the electronic nose device (Sanaeifar et al., 2017).

Table 1. Researches using MOS based sensor array for the development of electronic devices intended for food analysis.

Manufacturer	Sensor array	Application	Result	Reference
Hanwei Electronics, Figaro Engineering	MQ2, MQ3, MQ4, MQ5, MQ6, MQ7, MQ8, MQ9, MQ135, TGS822, TGS2600, TGS2602, TGS2603	Detection of alcohol content in beer (regression model)	$R^2 = 0.888$; RMSE* = 0.45	Voss, Mendes, Jr., Farinelli, and Stevan, Jr. (2019)
Hanwei Electronics	MQ3, MQ4, MQ6 (doubled)	Detection of wine quality concerning acetic acid content (classification task)	Training accuracy = 99.04%; validation accuracy = 96.78%	Gamboa, Albarracin, Silva, Lima, et al. (2019)
Airsense Analytics GmbH	W1C, W1S, W1W, W2S, W2W, W3C, W3S W5C, W5S, W6S	Discrimination of kiwifruit different ripening stages (classification task)	Cross-validation accuracy = 99.40%	Du, Wang, Wang, Zhu, and Hong (2019)
Hanwei Electronics, Figaro Engineering	MQ3, MQ136, TGS2600, TGS2602, TGS2610, TGS2611, TGS2620, TGS813, TGS822, TGS822TF	Detection of type of Chinese liquor based on aroma quality (classification task)	Accuracy = 98.78%	Wu et al. (2019)
Hanwei Electronics, Figaro Engineering	MQ3, MQ4, MQ8, MQ135, MQ136, TGS813, TGS822	Differentiation of three classes of cumin seed (classification task)	Accuracy = 80.10%	Ghasemi-Varnamkhasti et al. (2018)

Hanwei Electronics, Figaro Engineering	MQ3, MQ4, MQ8, MQ135, MQ136, TGS813, TGS822	Characterization of rice aging process and classification of storage duration (classification task)	Accuracy = 97.40% (non- aromatic rice type)	Rahimzadeh, Sadeghi, Ghasemi- Varnamkhasti, Mireei, and Tohidi (2019)
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*RMSE, root mean square error.

Despite the great advantages of MOS-based sensors for e-nose applications, the most important drawback of this type of system is sensor drift, a slow and random variation in sensor response over time when exposed to the same gas under the same conditions (Gutierrez-Osuna, 2002). This is in agreement with the findings of H. Liu and Tang (2013) and Wang, Yin, Ge, and Yu (2019), which confirm the importance of sensor drift control to increase the robustness of electronic noses. The drift condition may accrete additive and multiplicative noises to the signals obtained for a sample, observable respectively as baseline disturbance and sensitivity decrease (Gutierrez-Osuna, 2002). These hardware shortcomings, however, are supported by software and data pre-processing solutions (T. Liu, Li, Chen, et al., 2018; Wang et al., 2019; L. Zhang, & Zhang, 2018).

Another part of an electronic nose is the sensor chamber, which contains the sensors and is isolated from the environment to obtain a more controlled space for interaction between the volatile odor compounds and the surface of the sensors. A flow system to control the air passage that carries the sample headspace is frequently used and can be of different types: air pump (Tang et al., 2010), compressed reference gas (Rahimzadeh et al., 2019), and flushing fan (Voss, Mendes, Jr., et al., 2019; Wijaya, Sarno, Zulaika, et al., 2017). Valves are employed to control the sample headspace injection and purge at the appropriate moments. A sample container is commonly used to concentrate vapors containing odor compounds in the headspace fraction, which are further carried to the sensor chamber. A microcontroller integrates the parts of the operation and converts sensor signals into information for data collection, transmission, and storage in a computer for further data processing and analysis.

1.2.3. Sample preparation and injection

Odor profile readings are taken after an equilibrium state is attained in the sensor array chamber. This status is achieved in different conditions, depending on sample preparation method. Sample handling is crucial for determining the quality of e-nose analysis (Sanaeifar et al., 2017). The headspace gas sampling may be one of the most effective methods for carrying volatile compounds from the sample chamber to the sensor array chamber. Moreover, for specific applications, a heat element may be required to enhance volatilization (Sanaeifar, Mohtasebi, Ghasemi-Varnamkhasti, & Ahmadi, 2016). Besides sample injection, temperature, and humidity are factors that may play important roles in electronic olfactometer performance (Sanaeifar et al., 2017; Voss, Mendes, Jr., et al., 2019). Therefore, these parameters are frequently measured and taken into account to ensure better quality of data provided by MOS sensors.

For multiple readings, between different sample injections, a reconditioning phase is necessary to bring the sensor array back to an initial state. Applying this process, it is possible to withdraw possible residual odors and avoid interference from former responses. Using a gas flow in the sensor array chamber, it is possible to achieve a standard inner condition that differs from a sample headspace, which allows elimination of volatile compounds from the sensor resistive structure and lowers the signal back to an original baseline condition. Different types of gas may be suitable for this task, from synthetic air to inert gases (e.g. N₂, CO₂) (Sanaeifar et al., 2017) or even local atmospheric air (Kiani, Minaei, & Ghasemi-Varnamkhasti, 2016b).

Susceptibilities to ambient conditions and ambient air variation are among the major drawbacks of e-nose technique according to Wijaya, Sarno, and Zulaika (2019). These uncontrolled variations, also called “noise” or “sensor drift”, may lead to inconsistent data and negatively affect pattern recognition and further classification of samples. Although recurrent, techniques of pre-processing applied over acquired data prior to statistical analysis are indispensable for increasing further analysis performance, once they reduce the influence of noise related to sensor drift (Wijaya et al., 2019).

1.2.4. Data treatment and pre-processing

After conversion of MOS sensor signals into smellprints, data treatment is required prior to processing classification algorithm in machine learning. This stage of analysis using an electronic nose device may include procedures to avoid sensor variations, caused by injection conditions or random noise. Concerning injection conditions, temperature and humidity cause variation in the system due to interference on material resistance. Because of that, manufacturers display the curves for different temperature and humidity tested conditions in sensors datasheets, as well as their respective values for signal compensation, described as a function of the measured resistance, measured temperature, and relative humidity of the gas fraction (Voss, Mendes, Jr., et al., 2019). Sensor drift corresponds to the variation in sensor response for identical measurements and eventual signal noise issues (Wijaya et al., 2019), which may not only decrease regression model prediction, but also negatively interfere in multiclass classification tasks, with greater impact as the number of classes increases (Wijaya, Sarno, & Daiva, 2017).

Other required pre-treatment data are: 1. elimination of outlier points, caused by electric circuit noise, performed by modified moving average filter, data standardization, and normalization for properly scaling sensor signals; 2. feature extraction for dimensional reduction of input data.

The process of data transformation and pre-treatment is also named data pipeline and includes data transformation and manipulation to increase ratio between information and noise (Géron, 2019).

The use of centrality measure filters has been considered an efficient pre-treatment to eliminate data outliers for electronic nose signal responses (Voss, Mendes, Jr., et al., 2019) caused by eventual circuit peaks. These filters have successfully been used in e-nose devices that employ methods such as simple moving average, modified moving average, and exponential moving average (Gamboa, Albarracin, Silva, & Ferreira, 2019; Rehman & Bermak, 2018; Voss, Mendes, Jr., et al., 2019). Another pre-processing technique consists in standardizing response vectors (Gardner & Hines, 1997), performed in association with signal normalization based on the ratio between a sample exposition response over the response obtained by dry air applied to the sensor (Gamboa, Albarracin, Silva, & Ferreira, 2019; Patil et al., 2015; Rehman & Bermak, 2018). Other signal filtering techniques employed for e-nose systems are binomial smoothing and wavelet transformation, the latter considered more suitable for online non-stationary food monitoring (Wijaya et al., 2019).

After applying the described filters and corrections to eliminate noise interference from e-nose signal responses, the technique named feature extraction is mostly applied. It preserves the useful information in datasets for predicting models while reducing the dimensionality of the dataset by combining or discarding variables containing no or redundant information.

Considering e-noses based on batch processing analysis, sample injection consists in a three-phase process. First, the sample injection in the sensor array chamber changes it from a neutral (neutral baseline obtained after sensor chamber is purged and reconditioned) to an unstable state. Second, a dynamic phase is achieved when great amplitude of signal occurs and its slope depends on the specificity of the sensor in relation to the sample composition. Third, a stationary signal is obtained after the volatile fraction of the sample and the sensor array reach an equilibrium state, and the analog readings display their maximum values for a specific sample in that sample run (Rahimzadeh et al., 2019).

The importance of combining these three-phases, namely initial conductance, steady-state conductance, and dynamic slope of the conductance to the area below the conductance curve, has been emphasized in some studies. As a result of this combinatory response, a great correlation is obtained with the type of odor and frequently leads to the recovery of most of the information contained in the samples headspace (Gamboa, Albarracin, Silva, Lima, et al., 2019; Haddi et al., 2011). The process to obtain features from different phases involves different mathematical procedures, characterizing different levels of abstraction (Haddi et al., 2014), for steady-state (equilibrium phase between sensors and chamber environment) and transient-state (changing

sensor chamber composition). Both steady-state and transient-state have been proven to be efficient measures for e-nose devices (Rahimzadeh et al., 2019; S. Zhang et al., 2007). The former is based on the area generated above the signal line of each of the sensors, whereas the latter is the rate of the reaction between the MOS material and the headspace compounds defined by the slope in a window of observations.

1.2.5. Classification algorithms

The new dataset resulting from pre-processing, containing the most relevant information extracted from sensor signals, is firstly divided into two data subsets for training and testing the classification model based on the stratification principle. The stratified subsampling takes into account the improvement of model representativeness by preserving the proportion of classes found in both data subsets, training and testing (Sechidis, Tsoumakas, & Vlahavas, 2011).

Training data subset may proceed to classification analysis. Concerning a static pattern analysis for e-nose sample reading, Hines et al. (2004) listed the most commonly employed statistical techniques based on linear calibration, such as partial least squares for quantitative analysis and principal component regression, as examples of supervised pattern analysis, as well as discriminant function analysis as a nonlinear calibration method. Concerning non-parametric techniques, supervised or not, other methods such as principal component analysis (PCA), cluster analysis, and artificial neural networks have also been employed. More traditional multivariate analyses and techniques are used in so-called chemometrics methods, consisting in signal interpretation for chemical composition responses, favorably regarded in food and beverage odorant analysis (W. Dong, Zhao, Hu, Dong, & Tan, 2017).

A common non-parametric technique, PCA is a supervised and nonlinear analysis applied to a great range of odor analysis (Gancarz et al., 2017; Hidayat et al., 2019; Kiani et al., 2016a; H. Liu, Li, Yan, Zhang, & Gu, 2018; Ragazzo-Sanchez et al., 2008). This statistical tool is used to visualize distinctions among samples through information extraction contained in the variables that mainly affects the values of samples (W. Dong et al., 2019). It can also reduce the dimensionality of the data matrix, retaining most of the information of the original data, and explain the relationship of objects due to correlation structure maintenance (Kaya, Yildiz, & Ünlütürk, 2015).

Furthermore, PCA may also be explored as a first approach to data visualization and a preliminary indicator of electronic nose capability to separate the behavior of samples and classes in a lower-dimensional scale (Hidayat et al., 2019). Although this method of visualization promotes a lower-dimension representation, it focuses on representing dissimilar data observations far apart

in the space, a drawback considering a dataset with manifold nonlinear characteristics. In this case, the t-distributed stochastic neighbor embedding technique is suitable, since it keeps the low-dimensional representations of higher similarity data points close together (van der Maaten & Hinton, 2008).

Recent advances applied to data analysis of electronic nose devices involve the implementation of machine learning algorithms, considered a subset of artificial intelligence, due to their ability to learn without explicit programming. Luxton (2016) defined machine learning as the exposure of machines to data and experiences in order to improve their performance regarding specific tasks. Machine learning algorithms are alternative solutions to replace programming tasks that require an extensive list of rules to solve a specific issue, or that do not present a precise answer considering traditional approach, or that require adaptability promoted by frequent new data input, managing massive databases (Géron, 2019).

Machine learning developed in recent years applied to food and beverage industries may be decisive for the economic success of new companies, due to the ability to improve the efficiency of processes and the assessment of product quality in a faster, more accurate, objective, and cost-effective way (Viejo et al., 2019). Additionally, machine learning-based systems may be accurate to predict product acceptability, evaluate the most relevant sensory attributes and physicochemical composition, and other aspects related to the evaluation of product quality (Buss, 2018; Sharma, 2019).

Different machine learning algorithms have been successfully used for classifying electronic nose signals (J. J. Dong et al., 2014; Gamboa, Albarracin, Silva, Lima, et al., 2019; Gila, García, Bellincontro, Mencarelli, & Ortega, 2020; Gutierrez-Osuna, 2002; H. Liu, Li, Yan, et al., 2018; Schaller et al., 1998; Shurmer & Gardner, 1992; Tohidi, Ghasemi-Varnamkhasti, Ghafarinia, Mohtasebi, & Bonyadian, 2018; Uçar & Özalp, 2017; Wijaya et al., 2019; Xu, Wang, & Gu, 2019), including techniques such as regressions (linear, polynomial, or logistic) for quantitative prediction, support vector machines for linear or nonlinear classification, ensemble learning and random forest for classification performed by multiple classifiers and resulting in optimized solution, local grouping of samples by k-nearest neighbors analysis for unsupervised learning algorithms, and deeper techniques such as artificial neural networks (Géron, 2019).

Given that regression models explored for electronic nose analysis are generally structured for multiple variables, due to the possibility of contributions of numerous types of sensors, a dependent variable is defined by more than two input variables (Voss, Mendes, Jr., et al., 2019). Regression models may explore linear and nonlinear behavior, depending on data distribution, and the advantages related to polynomial, exponential, logarithmic, or other nonlinear models are the

interpretation of observations and the performance of prediction tasks (Archontoulis & Miguez, 2015). Support vector machine is a supervised learning model broadly employed for analysis of gas sensor response. This technique is based on linear discrimination of samples using optimal hyperplane, although kernel functions may be applicable to solve nonlinear classification problems (Sarno & Wijaya, 2019) observed in e-nose system analysis (Distante, Ancona, & Siciliano, 2003). Random forest, also called random decision forests, is an ensemble learning technique suitable for classification tasks and regression, with operation based on multiple decision trees created along the training stage. Considering that the bootstrap method is performed for samples, these bootstrap observations undergo classification and regression trees. The results coming from all the classification and regression trees are submitted to a voting step, based on the majority rule, which outputs the observation class (H. Liu, Li, Yan, et al., 2018). K-nearest neighbors is a non-parametric classification algorithm, with a locally approximated function, which considers that a sample belongs to a group according to its proximity measured (Euclidian distance) by the majority votes of the closest k neighbor observations (Ali, Neagu, & Trundle, 2019; Banerjee, Roy, Tudu, Bandyopadhyay, & Bhattacharyya, 2019).

Recent researches rely on artificial neural networks for classifying task solution considering the features of smellprints (Gamboa, Albarracin, Silva, Lima, et al., 2019; Ghasemi-Varnamkhasti et al., 2018; Rahimzadeh et al., 2019; Voss, Mendes, Jr., et al., 2019). These types of classification algorithms correspond to a non-supervised method, capable of achieving a superior ability of self-organization, generalization, and noise tolerance compared to the conventional methods cited above. Artificial neural networks are fundamentally distributed, adaptive, and generally nonlinear learning machines formed by so-called processing elements, equivalent to biological neurons (Anderson, 2019), connected by definable parameters named weights, in charge of conducting a flowing signal to a final processing element (output) containing the sum of previous elements (Guresen & Kayakutlu, 2011). The final layer contains the number of processing elements equivalent to the number of classes of interest, so that the highest activation value at the end indicates the class attributed to a specific sample (input). The weight values are established during the training stage of the model, and the model performance is directly proportional to the training data size (Specht, 1990).

Artificial intelligence methods applied in the beverage industry may be favorable to carry continuous processes, obtaining new data from them, and permitting online learning to enhance performance, reliability, and accuracy compared with human enforcement (Nayik, Muzaffar, & Gull, 2015). Even though most applications of automation in food and beverage industries still remain restricted to mechanical activities, such as packaging and transporting facilities (Iqbal, Khan,

& Khalid, 2017), Holmes, Russell, and Allen (2012) sustain the use of artificial intelligence in different automated segments such as inspection and quality control. All the aspects concerning the feasibility of an electronic nose device capable of classifying distilled beverage samples are supported by previous researches, which investigated different alcoholic matrices, such as differentiation of whiskies (Nakamoto, Fukuda, Moriizumi, & Asakura, 1991), differentiation among several beverages (Shurmer, Gardner, & Corcoran, 1990), quality assessment of fermented beverages (Gamboa, Albarracin, Silva, Lima, et al., 2019; Ghasemi-Varnamkhasti et al., 2011; Linehan & Nizami, 2007; Viejo et al., 2016), implementing different classification techniques. The main factors related to the current proposed e-nose system is the quality of input data, following optimized methods for analysis of sugar cane spirit samples, and representativeness of features extracted from sensor signals that feed the classification algorithm.

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2. ELECTRONIC NOSE TECHNOLOGY: INNOVATION MANAGEMENT FOR COMMERCIAL APPLICATION IN THE CACHAÇA INDUSTRY

ABSTRACT

In this chapter we experiment with the effort of building a technology roadmap with an early growth stage company located in the State of São Paulo, Brazil. Roadmaps are easy to design yet flexible tools that can allow decision makers to explore a myriad of possible strategies. However, the challenges ahead of new companies facing uncertain growth scenarios demand that framework conditions be sufficiently addressed, and that innovation culture and technology management tools become integrated with the technology roadmapping strategy. Based on the empirical evidence collected from the startup studied, along with the literature and interviews with key stakeholders, this chapter develops a pathway to support technology and innovation plans for startups in similar growth stages and provides directions for future research in the area, given the scarce evidence available from new high-tech companies' efforts in planning and developing new products.

Keywords: Technology Roadmap; Cachaça; Industry 4.0.

2.1. INTRODUCTION

Production and service provision systems of any kind present an irreversible tendency towards the introduction of innovations that help them devise new business models, products, processes and services with impacts both inhouse and in the market. Such a tendency triggers strategies and actions encompassing the development of technology solutions that can meet a firm's commitment towards the promotion of quality improvements, market expansion and profitability. However, despite the myriad of successful cases and experiences available both in the literature and in the media, a number of production segments remain either resistant or have simply failed to understand how to capture the benefits of an effective management of the process involving the development, diffusion and adoption of new technologies. This is the case of several companies operating in the agriculture value chain in developing countries, such as Brazil, one of the world's largest agricultural players.

Following significant productivity gains achieved in agriculture and livestock production in the last three decades, Brazilian firms in every segment of agriculture are facing the challenges of growing in a somewhat highly uncertain and budget-constrained scenario that may continue in the coming years (Chaddad, 2016), with significant impact in both the business model and the corporate strategies of the companies (Phillips, et al., 2013). As a response, state and federal public

agencies are promoting financing schemes for the upskill of workers, tax deductions for firms carrying Research and Development (R&D) or acquiring capital goods, and sunk cost funds for joint translational research with universities and firms (Matos, et al., 2017).

As a result, small hightech firms in the agricultural segment, known as Agtechs, are growing in importance in the country as a response to, on the hand, policy stimuli, and, on the other hand, to meet the demand of agriculture firms looking for cost-effective solutions that help them deal with productivity bottlenecks, increased competition, international penetration, and new product development challenges.

This chapter focuses on the technology planning and management efforts of an early growth stage firm operating in one segment that has been, for decades past in Brazil, a synonym of technological backwardness and social distress: the Cachaça industry. This has changed a lot though (MAPA, 2011).

Cachaça is the exclusive denomination of sugar cane spirits produced in Brazil and is the most consumed distilled beverage in Brazil, and fourth in the world. The figures are not precise though estimates point out to 11 thousand producers being responsible to 4 thousand different brands of sugar cane spirits manufactured throughout this continental country (IBRAC, 2019). Also, in 2014 the sector generated 600 thousand direct and indirect jobs and total revenues of US\$ 6 billion, followed by approximately 950 million liters of sugarcane spirits (*aguardente* and cachaça) produced nationwide, with an annual consumption of 6.3 L per person (Bortoletto and Alcarde, 2015). Following a recent ‘premiumization’ tendency that is also affecting distilled spirits with effects in the increasing demand for quality products from both local and international consumers, producers are demanding solutions that help them tackle challenges such as chemical composition requirements for the entry in foreign countries, for meeting quality standards as production volumes grow, for qualification of the workforce, and for sourcing advanced machinery and equipment to increase productivity.

The startup in this study is IT Beverages. The company, derived from a PhD research carried at the School of Agriculture “Luiz de Queiroz” of the University of São Paulo, Brazil’s most acclaimed agricultural research university, was financed by the São Paulo Research Foundation (FAPESP) and aims to deliver a two-fold value proposition to Cachaça producers, by combining a low-cost and technology intensive solution to optimize decision-making in the critical wood-aging process of cachaça manufacturing. The solution proposed is based on the concept of an “electronic nose”, which is expected to have potential applications in other distilled spirits segments too.

In order to achieve the mission of providing automated solutions for the production of distilled spirits following the Industry 4.0 concept for digitalization, automation, process integration

and production chain traceability, IT Beverages needs to rely on innovation management methodologies to reduce risks in product development, design, testing and prototyping, all areas with potential room for misalignment with market expectations, and therefore failure. The process encompassed an investigation of internal factors that support innovation in the company, culminating in the identification of company's specific aspects that, according to the literature, strengthen a culture for innovation, along with external factors related to required technology development approaches and future scenario propositions. This process introduced a learning experience to the company that, combined with data obtained from semi-structured interviews with 15 participants in the University and in the industry, generated a technology roadmap that organizes key information supporting the firm's technology development strategies. The aim of the roadmap is to provide decision-makers with clear visualization of the phases and bottlenecks in the technology development process that permeates the firm's mission towards automation of key phases in the production of distilled spirits. This process is summarized in Figure 2 and is explained further along this chapter.

Figure 2. Constructive pathway considered for elaboration of IT Beverages' Roadmap. (a) Sawhney, Wolcott, and Arroniz (2006); (b) Maidique and Zirger (1984); (c) Garcia and Calantone (2002); (d) Rao and Weintraub (2013); (e) Munnir and Phillips (2005); (f) Martins and Terblanche (2003); (g) Bidasaria et al. (2014); (h) Goffin and Pfeiffer (1999); (i) Lu and Weng (2018); (j) Schuh et al. (2017); (k) Phaal et al. (2004).

This chapter addresses an empirically observable and relevant innovation management phenomenon, at the intersections of product development and technology management literatures. By analysing technology development strategies in an AgTech startup, this chapter attempts to fill a gap in the literature, given the scarcity of documented similar experiences from developing countries. Such scarcity of academic case studies exploring these themes is, on the one hand, influenced by the reluctance of entrepreneurs in providing information revealing details of the

technological approaches underlying their business models (Botelho and Almeida, 2010; Alves, et al., 2018). On the other hand, by the difficulties of reproducing the findings of a single case study based on an exploratory research (Edmondson and McManus, 2007). Regarding the first aspect, the company founder is one of the authors of this chapter, which guarantees accountability over the information and data disclosed for this research. The second, which is critical per se as a single case study does not allow for broader generalizations, entails an effort from authors to make the results outlined in the paper supportive for future studies involving public policies and enterprise development strategies for Agtechs, which given the importance of the theme is not restricted to audiences from developing countries.

As 95 % of the startups fall short of meeting financial and product development projections and in 99 % of the cases the reason pointed out by entrepreneurs and investors was lack of planning and experience skills (OECD, 2019), we believe the discussions carried in this chapter can stimulate debates on the barriers and challenges for technology management practices in Agtech startups. Therefore, this chapter analyses different technology and innovation management practices and discloses key elements for the implementation of a technology solution applied to the distilled beverages industry.

This research paper is structured as follows. First, we analyse the innovation opportunities in the segment of interest and identify a new technology that can fill an important gap in the production of distilled spirits derived from sugar cane. Then, we identify the factors underlying innovative thinking in the company, including internal factors based on the concept of Innovative Building Blocks (Rao and Weintraub, 2013). We then explore the current state of innovative mindsets among employees, along with strategies required for an effective technology implementation. The following step involves an in-depth analysis of the technological landscape, which allows the understanding of possibilities and scenarios that generate strategies leading to value creation. This step culminated in the analysis of the current status of the distilled beverages industry, which resulted in the identification of a lagged scenario whereby new solutions are increasingly needed to keep up with the pace of industry 4.0 challenges and opportunities in the value chain of distilled spirits production.

Next, the Roadmap method is then presented, merging all previous information with the strategic thinking required to design a chronological cadence of fundamental steps to achieve IT Beverages' goals. The future projection of events takes place as a linkage among technology generation requirements and product release. We also understand that, as a long-term perspective, innovation processes must be able to adapt to new trends and circumstances that appear along the way. Therefore, and departing from a speculative point of view, mindfulness and open innovation

circumstances are envisaged as part of a construct to help overcome difficulties in the technology development process of a startup. We dedicate the last section of the paper to present the final remarks and recommendations.

2.2. ORGANISATION AND INNOVATION: IDENTIFYING INNOVATIVE USE OF TECHNOLOGY IN OPERATIONS, PRODUCTS AND SERVICES

The first step investigated existing technology processes available. The objective was to understand which alternative paths the company could follow to achieve a certain desired future position in the market. Concerning the main bottlenecks related to technology, processes, marketing and internal organization, we questioned stakeholders in the academy and in the industry on the strategies needed by IT Beverages to offer innovative IT-based products and solutions in the distilled beverages market. The discussion carried evolved towards the understanding that any IT-related solution aiming to promote industrial transformation relies on the connectivity of ubiquitous technologies (Internet of Things, IoT) in order to integrate business processes and engineering functions that promote efficient and sustainable production systems (Wang, et al., 2016; Ciuffoletti, 2018; Wang, et al., 2019).

As a response, the company chose the development of a new technology covering areas such as raw-materials, quality assurance, real-time process control, and bottling standardization. The idea behind the envisaged solution is based on existing gas sensors forming the e-nose concept, or ‘digital olfactometry’, which will collect a myriad of key data throughout the Cachaça production process.

An e-nose is an equipment that emulates human olfaction using gas sensors in a sample chamber (Figure 3). The electronic signal is imported into a classification algorithm that uses Artificial Intelligence (AI) for the characterization of a beverage sample according to a database (Loutfi, et al., 2015). The e-nose technology will primarily focus on wood-barrel aging processes for Cachaça manufacturing, which today represents a subjective process relying on the expertise of one trained employee, the ‘Master blender’. A subjective or low-precision input data for process control can lead to errors, resulting in lower system performance response or on an increase in production costs (Kahn, et al., 2003; Leo, et al., 2002). The use of an AI-based algorithm aims not to substitute, but to provide the team with new inputs based on data collected upstream the production value chain.

Figure 3. Schematics of e-nose basic prototype operational system.

According to Coherent Market Insights (2018), a consultancy, a 11.7 % compound annual growth rate is expected for the e-nose market until 2026, covering industries as varied as food and beverages, environment and health (Market Research Engine, 2019). Although there are already companies in this market such as *Alpha MOS*, *Odotech* and *E-Nose py*, their technologies focus on analytical solutions for general-purpose applications based on huge datasets applied to different food matrices and isolated compounds. This creates opportunities not yet exploited, such as in the distilled beverages industry. The considerations emanated from this evaluation led us to one question, which answers obtained influence strategies required for the identification of alternative paths and risks in the e-nose technology deployment processes. Which type of innovation does IT Beverages aim to introduce in its target market?

Abernathy and Clark (1985) offered an interesting perspective for product classification, called “niche creation”. This classification entails a well-specified technology being renewed to target a new and specific market application. We can also describe this niche creation idea for the distilled beverages segment as a product innovation based on technical contents (Maidique and Zirger, 1984), which is an innovation based on existing components recombined to display a completely new functionality. As a product innovation targeting a market niche in a developing country, an e-nose for the Cachaça industry is idealized as a discontinuous innovation, or a “game changer” following Rice and Morone (1998) definition, since it encompasses technical and market assumptions leading to potential increases in performance through new algorithms and AI tools, and proposed cost reductions to clients of at least 30 %.

Recently, some local startups have been developing solutions to existing problems in the Brazilian beverages industry, which match Atuahene-Gima (1995) “newness to customer”

classification of an innovative offer. To name a few, *Smart Yeast* is developing microbiological products applied to the fermentation process; *Tecdef* and *InovBev* act in the technology, legal and regulatory upskill of personnel in both the distilled and fermented beverages industries; *Cachaça Gestor* provides IT management tools for inventory and sales control. By interviewing entrepreneurs in the startups mentioned in this paragraph, it became clear that IT Beverages success involves the identification of a “newness to customer” solution (Atuahene-Gima, 1995) that can bring potential discontinuity in a marketplace not yet covered by established firms (Garcia and Calantone, 2002). As a result of this investigation, we encountered no single startup offering an assimilated digital olfactometry solution applied to the beverages industry.

Sawhney and Arroniz (2006) presented 12 dimensions to successful innovation, summarised by what the firm is offering, to whom the firm is providing the innovation, how the firm is providing it and where. Based on this conceptual tool for innovation/innovativeness quantification, they proposed an “innovation radar” encompassing all 12 elements into a somewhat ‘big picture’ framework. Following the interviews carried and the inputs from the literature, we were able to depict an innovation radar for the company, as presented in Figure 4.

Figure 4. Innovation radar (Sawhney, et al., 2006) elaborated for IT Beverages based on interviews and authors’ elaboration.

The innovation radar was built under IT Beverages’ current position, considering average rates given by the stakeholders interviewed from academy and industry. These stakeholders were confronted with future perspectives whereby an e-nose concept should be deployed. The radar analysis displays a strong innovation capacity related to Offerings and Solutions, which is related

to the type of technology under development, as compared to current technology solutions available for the Brazilian Cachaça industry.

The Platform component also presented lower rates. This result relates to Brazilian Small and Medium Enterprises historical low rates of technology adoption and innovation (De Negri and Rauhen, 2018). The Cachaça industry is no exception, as producers also appear reluctant to implement IT solutions, mostly due to low computer literacy (Daniel, 2016) and difficulties to properly balance the trade-offs between implementation costs and the benefits obtained by a technology adoption (Choi and Moon, 2013; Martins, et al., 2018). As a result, the Customers component also displayed a lower score. As a response to these potential risks affecting the e-nose technology implementation process, IT Beverages incorporated the principles described by Kearns, Taylor and Hull (2005) in its deployment plan, by including frequent prototype tests and aggregation of human factors such as the user experience into the adaptive improvements of its e-nose technology.

The Customer Experience component indicates a possibility for changing this scenario through the development of a user-friendly interface, followed by a successful adoption of IT Beverages' products by key-customers that may encourage the use of e-nose by more resistant cachaça producers. IT Beverages' proposed grounding structure for operations led to a higher Process and Organization rating, given the novelty of the e-nose proposition to this industry. The Supply Chain item entices significant challenges to the effectiveness of technology implementation, given the myriad of risks and bottlenecks involved in the deployment of a package such as e-nose comprising embedded semiconductors, software and hardware (See Figure 3). Consequently, the critical Networking component is required by means of addressing partnerships with other companies that offer complementary services and solutions in the beverages industry, some of which were already mentioned in this Section of the paper.

2.3. ANALYSIS OF COMPANY'S INNOVATIVE CAPACITY IN USING, ADOPTING AND GENERATING INNOVATION

It is widely acknowledged that the culture of an organization is an important driver for innovation and creativity (Lundy and Cowling, 1996). A creative organization encourages valuable ideas in different spheres of the company, encompassing products, processes, services and procedures (Martins and Terblanche, 2003) towards the promotion of a vision and mission oriented to the future (Covey, 1993). In a study carried by Rao and Weintraub (2013), corporate culture was found more important to innovation than labor, capital, government, or national culture. With this

in mind, the processes leading to planning the development and implementation of a technological innovation requires that the organization understands what constitutes an innovation culture and how culture can lead to innovation. Our understanding of a company culture is as simple as Lundy and Cowling (1996, p. 169) view, to whom organization culture is “the way we do things around here”.

According to Rao and Weintraub (2013), an organization culture framework encompasses six main blocks: Resources, Values, Processes, Behaviors, Success and Climate, of which at least one has to be fully consolidated for innovation. After surveying with the stakeholders interviewed, we build an innovation readiness summary presented in Table 2. This summary allowed for the identification of some bottlenecks to be addressed by the company, which are discussed further.

Table 2. Building blocks (Rao and Weintraub, 2013) for IT Beverages organization culture implementation, ordinated according to innovation readiness score.

Bottleneck importance	Building block	Composing factors
More relevant	Resources	People, Systems, Projects
	Success	External, Enterprise, Individual
	Behaviors	Energize, Engage, Enable
	Processes	Ideate, Shape, Capture
↓	Climate	Safety, Simplicity, Collaboration
Less relevant	Values	Entrepreneurial, Creativity, Learning

As the case in point refers to an early growth stage company, it comes with no surprise that Resources is the factor demanding more attention. In fact, IT Beverages counts with limited resources such as Time, Money and Space (Rao and Weintraub, 2013). As a response, a detailed business plan presenting e-nose’s business model and its value proposition strategy to potential sources of financing can reduce the risks that this factor becomes detrimental to the company’s sustainable growth.

Despite belonging to different blocks, “Behaviors” and “Success” relate both to approaches of individuals in the organization. The Behavior block point out to the need of recruiting workforce whose profile, attitudes and values are aligned with the company’s mission. The Success block, on the other hand, involves the establishment of a culture in the organization that embeds learning opportunities within its reward and feedback mechanisms, regardless of results achieved.

For dealing with a costful, though essential learning instrument to any organization, like failure, a positive approach is required to enhance the team's knowledge over failed undertakings of which learning generated can capitalize on successful projects later. As a response, the company plans to enact internal symposiums with members of the organization, industry and academy for the exchange of ideas and experiences. The ecosystem to which IT Beverages belongs is important to this end. The company is in the premises of a very dense environment comprising Agtechs in varied areas of the agriculture value chain, public and private research universities, large national and multinational firms, and support organizations like science parks and startup accelerators. This is all within a 10 km radius from IT Beverages location. This certainly contributes to Values not being a quite serious bottleneck to the firm's growth, according to respondents.

After creating an environment that sustains innovation creation, it turns out necessary to develop and implement the ideas generated. After considering that a favourable innovation culture is in place, the effectiveness of the implementation process requires precious investments of time, financial resources, internal training, users' support, continuous monitoring, team's meetings and evaluation (Klein and Knight, 2005). Concerning New Product Development (NPD) efforts, intra technical innovations displays better performance according to five main factors originally pointed by Cooper and Kleinshmidt (1999), such as process, strategy, organization, culture and management commitment. Based on an extensive review of the literature and field research, Adams, Bessant and Phelps (2006) proposed a framework based on seven categories, known as: Inputs, Knowledge Management, Innovation Strategy, Organizational Culture, Portfolio Management, Project Management, and Commercialization.

The measure of inputs for innovation implementation is accessible through human resources count, which is the number of people directly involved in developing new solutions, equipment and analysis, divided by their absolute numbers (Cooper, et al., 2001). Knowledge management processes cover the phases of opportunity identification, analysis, and idea generation, followed by concept selection and development (Koen, et al., 2001) Innovation strategy analysis can be accessed by measurements of alignment between company's structure and production systems (Bessant, 2003), or between strategic objectives and innovation goals (Tipping and Zeffren, 1995). Portfolio management entails firms' efforts towards effective allocation of material, human and financial resources. This occurs by implementing a framework – either qualitative, quantitative or mixed – leading to operational and financially effective new products or service platforms (Cooper, et al., 2001). Project Management practices require the application of measures that identify, analyze and monitor planned against realized activities, usually with cost, schedule, operability and safety as main success indicators (Morrow, 2011). The Communications component

implies that an open channel is in place and that it encompasses all stakeholders involved in the innovation project, internal or external, and that the company has a defined framework allowing that the right information is available to the right person at the right time (Parthasarthy, 2002). The definition of roles and responsibilities is a key element to this end.

The last stage of innovation implementation entails the launch of a new product. According to Adams et al. (2006), the “Commercialization” category consists on turning an innovative product into a commercial success through relentless marketing, distribution, and sales strategies. Measurement tools for commercialization of innovation are scarcely available in the literature, even though Verhaeghe and Kfir (2002) highlight market analysis, planning and constant monitoring as strategic capabilities contributing to more successful products that manage to reach their target markets.

Therefore, IT Beverages needs to gather intangible and tangible resources, processes and tools that can help it achieve successful implementation of its e-nose innovation. Departing from the challenging establishment of a culture of innovation around its internal resources, a critical issue consists on identifying the parameters required for monitoring its innovation development and implementation processes. Hence, the evolution of its organizational structure may be frequently monitored and, eventually, reassessed to guarantee alignment to its desired goals.

From the literature review and interviews with key stakeholders, who outlined potential risks and barriers for a successful implementation of a technology such as e-nose, the innovation management tools required to increase chances for a more effective technology delivery were identified and summarised in Table 3.

Table 3. Management measurement components for IT Beverages innovation implementation according to categories proposed by Adams et al. (2006).

FRAMEWORK CATEGORY	MEASUREMENT IN IT BEVERAGES
INPUTS	- number of innovation team members
	- ratio of number of members involved with innovation development over total employees in the company
	- financial amount for innovation projects
	- ratio of innovation budget over general budget
KNOWLEDGE	- number of patents registered
MANAGEMENT	- number of ideas proposed to upper management

	<ul style="list-style-type: none"> - ratio between all ideas generated and those that became products/ solutions - number of active projects - number of concluded projects - number of filed/discontinued projects - sum of all projects (all-in) - ratio between filed projects and total number of projects
INNOVATION STRATEGY	<ul style="list-style-type: none"> - deadline commitment for milestone (percentage of in-time achieved over all deadlines) - innovative alignment and engagement of employees (qualitative aspect) - innovative alignment of projects
PORTFOLIO MANAGEMENT	<ul style="list-style-type: none"> - selection of higher Product Innovation Index (Pi2)
PROJECT MANAGEMENT	<ul style="list-style-type: none"> - cost efficiency: quotient between expenses in current state of a project and budget allocated - time efficiency: quotient between time expended in current state of a project and foreseen workhours - team efficiency: quotient between achieved tasks in a current state of a project and overall tasks in same timeframe - number of meetings for new ideas discussion - ratio between new ideas meetings and overall meetings
COMMERCIALIZATION	<ul style="list-style-type: none"> - online Purchase Intention forms - prospecting market gaps through social medias - creating an interactive interface for collecting data of interest

The set-up of the internal innovation management competences, as indicated in Table 2, is key to any hitech organization, either new or established in the market. However, as pointed out by Munnir and Phillips (2005), the success of a new technology and its diffusion is not necessarily associated with the newness of the technology and the effectiveness with which it is designed, tested and implemented. Instead, they argue, it is also related to the discursive activities surrounding

the market and how the firm manages to reach the social context whereby the innovation will be deployed. In a context of internationalization of innovative activities, being mindful towards a firms' key attributes is of interest to any startup dealing with technological, organizational, financial and market uncertainties. A Mindful firm "attends to an innovation with reasoning grounded in its own organizational facts and specifics" (Swanson and Ramiller, 2004, p. 553). The key attributes of a mindful organization, according to Sternberg (2000, p. 12) are: (a) openness to novelty; (b) alertness to distinction; (c) sensitivity to different contexts; (d) implicit, if not explicit, awareness of multiple perspectives; and (e) orientation in the present.

Mindfulness in organizations entails developing cognitive behaviors that help a company deal with harsher environmental conditions such as growing competition, elevated customers' expectations, and market factors leading to "demand for high performance standards, lower errors tolerance, turbulence and complexity" (Weick, et al., 1999, p. 104). The adoption of new technologies at IT Beverages is strongly rooted on hardware and software development. Besides, it consists on a domain facing growing national and international visibility, such as the adoption of AI and algorithms of data science, all indispensable for IT Beverages' e-nose technology. A significant market-making effort will be required, which entails marketing, pricing, and positioning strategies, in order to positively intervene in the cultural barriers towards the utilization of such technologies from Brazilian cachaça producers.

Embedded sensors in industrial plants are key concepts of industry 4.0 (Jang, 2016; Kang, et al., 2016; Lu and Weng, 2018; Lee, et al., 2015). Creating a connected environment in an industrial facility leads to process optimization, real-time production and control, and effectiveness in equipment utilization (Schug, 2018; Evans, et al., 2015). Therefore, food and beverages companies are currently more concerned about implementing new technologies for process monitoring and efficiency improvements, with new windows of opportunities appearing in different segments of the production chain (Schug, 2018; Rodriguez Gamboa, et al., 2019). Being mindful towards these coming challenges is therefore key to the e-nose development and implementation successes. We will exploit this further in the following Sections.

2.4. INNOVATIVE TECHNOLOGIES SUITABLE FOR IT BEVERAGES: INDUSTRY 4.0 INNOVATION IMPLEMENTATION

AI can be an important ally to innovations in the beverages industry, given its pervasive role in technology-based production processes and influence on decision-making and monitoring of production systems (Lee, et al., 2015; Wang, et al., 2019).

Product estimation quality is based on patterns emanating from the comparison with similar samples available. The concept behind IT Beverages technology is that a significant amount of observed data will feed a database containing related AI learning processes over cachaça Quality Assurance (QA), allowing the system to recognize new “smelling patterns” (or odorprintings) out of all data points previously collected. The requirements for such technology integration consist on extensive data collected over assimilated industrial processes, along with connectivity to enable AI incremental learning (Wang, et al., 2016; Encinas, et al., 2017).

According to Wang et al. (2016), the radical change addressed by Industry 4.0 relies on ubiquitous information systems (IoT) connected in real-time, leading to a scenario of operational flexibility and potentially increased efficiency and sustainability (end-to-end engineering integration). Such intricate processes have little chances to successfully occur within the boundaries of a single startup. Concerning the implementation of the e-nose technology, after the development and validation steps for a thorough characterization of cachaça aged in wood barrels, its application all the way through different processes within the cachaça industry will depend on establishing solid partnerships. IT Beverages is therefore building local ties with important players in the academy and in the market such as the University of São Paulo’s Laboratory of Technology and Chemical Quality of Alcoholic Beverages, consultants and Brazilian distilling facilities and bottling companies. At this point, financial and legal support is required, demanding suitable mindful strategies for weighing up pros and cons of sharing sensitive information with potential investors, collaborators, business partners and customers.

Therefore, the e-nose concept will evolve upon sensitive and critical data collected from different distilleries which, after a consented data sharing policy, enter a Computing, Communication and Control process, or 3C process, as remarked by Wang et al. (2016).

Another starting point for implementing an AI-based solution within an industrial facility involves the development of a multiagent system (MAS), which consists on an intermediate intelligent decision-making structure that merges human and computer-controlled processes. This concept is known as “augmented intelligence” (Ford, 2015), and involves human and machine working complementarily (Kurzweil, 2005). Considering Schug et al. (2017) maturity process, six steps are required towards the implementation of an autonomous system: computerization, connectivity, visibility, transparency, predictive capacity, and adaptability. The first two correspond to the traditional digitalization efforts required to industrial automation. The last four, in sequence, represent the building blocks of an Industry 4.0 autonomous system.

In addition, the implementation of a new technology under industry 4.0 foundations may also consider four aspects described by Lu and Weng (2018), which are sensors, integration,

intelligent and response systems. Considering a market that suffers from competition from internationally established spirits like whiskey and gin, coupled with rudimentary industrial practices that, in a myriad of low tech producers, can generate contaminants (Bortoletto, et al., 2018), the few modernized Brazilian producers of Cachaça are eager to adopt solutions that can address such specific and complex (Martins, et al., 2018). Also, government schemes are now coming into being, with the Ministry for Agriculture engaged in a myriad of programs to support this industry development through new regulations, supply chain, marketing, R&D and innovation support initiatives (MAPA, 2011). The opportunity envisaged by IT Beverages encompasses an effort to help the industry adopt the concept of connectivity and data handling to improve product quality, process efficiency, and equipment effectiveness.

2.5. INNOVATION STRATEGY: LINKING PEOPLE, OPERATIONS, PRODUCTS/SERVICES AND IT WITH GROWTH AND COMPETITIVE EDGE

According to Bidasaria et al. (2014), a lead role of R&D initiatives targeting innovations consist on merging both technical and commercial skills to support complex decision-making based on knowledge and expertise from across all company sectors. This is no easy task as it demands a thorough implementation strategy supporting opportunity framing, scope selection and definition (Cooper, et al., 2001), which can be harsh for early growth firms with limited resources.

Roadmaps have emerged as an attempt to help companies face challenges in project planning and implementation. A Roadmap is an efficient and flexible method for implementing different types of projects within plural niches of knowledge, in variable time-frame terms, and with multiple purposes, provide decision-makers with flexibility and adaptability during critical path execution (Rinne, 2004). In this chapter, we focus our attention on the concept of technology roadmap introduced by Phaal et al. (2004, p. 5), defined as “a structured (and often graphical) means for exploring and communicating the relationships between evolving and developing markets, products and technologies over time”. Both technology roadmap and roadmap terms are used interchangeably in this chapter.

As a strategy formulation tool relying on critical multilayer and multilevel features (Bidasaria, et al., 2014), roadmaps merge development of attitudes and built-in project, product, process, company and/or market characteristics in a defined time-line, clarifying and explaining the intricate processes leading to the development and consequent implementation of a technological innovation (Lu and Weng, 2018).

According to Phaal et al. (2004), the elements used to build a technology roadmap are not limited to but are strongly dependent on the following: i) Time-frame, normally the horizontal Cartesian dimension in a Roadmap, designed to suit a particular situation. The scale used depends on companies' present vision and position; ii) Top vertical layers, related to market approach, or "know-why", designating factors leading to value creation; iii) Bottom layers indicate companies' "know-how", which correspond to consolidated or in-development technology and applied knowledge; iv) Intermediate layers comprise the carriage agent who delivers knowledge and technologies to meet market needs, namely "product development strategy"; v) Linkages among components of different layers may be useful to provide a perspective of existing dependency or relation between concomitant or successive processes. Also, codes and notations may help visualization of specific paths.

Based on the review of product and technology management literatures, the taxonomy and features of technology roadmapping and the interviews carried, we present IT Beverages' Technology Roadmap in Figure 5. The purpose of this Roadmap is to link technology needs with new product development efforts in order to support IT Beverages mission of being a major player on technology development and automation in the Brazilian distilled beverages industry. Observe that product and technology development, along with required processes and resources are highlighted to contextualize each phase necessary to achieve IT Beverages aim, as well as marketing and market aspects determining major risks to value capture and creation. The Technology Roadmap presented in Figure 5 emphasizes the myriad of critical technology and product development bottlenecks discussed earlier, as well as market forces affecting product demand and acceptance the company decision-makers will need to tackle before the firm can meet its five-years expectations.

Figure 5. IT Beverages' Roadmap built for development of technologies until 2025 and providing solutions and products for Beverages Industry 4.0.

The selected areas determining the layers of IT Beverages' technology roadmap are based on the criteria proposed by Phaal et al. (2004), consisting on a two-fold market dynamic, namely as Market-Push and Market-Pull. Market-pull ("Marketing" layer in the roadmap) focuses on value creation through innovative products and marketing actions that enhance value perception. Market-push embeds a series of actions produced by the company's mission and the main technologies ("Technology" layer), resources and processes required for the company to meet its desired outcomes. Lying between both top and bottom layers, the intermediate "Processes/Resources" layer correspond to the materials and methods employed to develop the envisaged technological solution. The "Processes" component represents the path through which financial, human and intellectual resources intertwine to create and improve technology development practices. A critical process identified in this layer involves the financial resources for the consolidation of IoT cloud computing infrastructure and the AI algorithm improvements, along with their sub-components (Štefanič, et al., 2019). Because of the inherent risks in these processes, IT Beverages will count on its partnership with the Laboratory of Technology and Chemical Quality of Alcoholic Beverages to obtain further resources from FAPESP's sunk-cost funding scheme for early-stage startup and university translational research, the PIPE Program in its two phases (PIPE I and PIPE II), as highlighted in the roadmap. The "Products" layer provides the linkage between required technologies, thereby merging the visualized components that provide an edible solution to the market. This layer also provides a notion of which resources are needed for IT Beverages to meet the distinct needs of the distilled beverages industry under the umbrella of Industry 4.0 specifications.

As depicted in the Roadmap, IT Beverages' critical success components rely on developing and delivering a Minimal Viable Product, or MVP, herein represented as E-nose version 1.0, and provide all conditions for increasing its value capture from the target market. Further, a fundamental structural change on IT Beverages' operation involves major financial and human resources to consolidate the company position in order to display a series of new capabilities provided by improved versions of the E-nose software and hardware. Also, creating a connected environment that integrates client's critical processes in view to obtain a comprehensive structure for information traceability and the organization of quality olfactometry data will rely on solid partnerships with industry players to improve a critical path such as the market consolidation of the automation system underlying the e-nose main technology offer.

2.6. INNOVATIVE SCENARIOS: FUTURE CASES OF IT INNOVATION DEPLOYMENT

Concerning a favorable scenario where IT Beverages becomes a key provider of high-tech automation solutions in the distilled beverages industry, the company sustained growth envisaged by the Technology Roadmap will also rely on building other complementary assets. A possible strategy in regard for companies in early growth stages facing uncertain critical paths both in product development and in market acceptance is open innovation. Open innovation corresponds to an interactive practice between a company and its environment, assumed in order to take advantage of external knowledge to foment internal innovative ideas and solutions (Chesbrough, 2003; van de Vrande, et al., 2006).

As a future oriented construct, IT Beverages open innovation approach encompasses two key areas, highlighted in the Technology Roadmap presented in Figure 4: i) Partnerships for collection and quality assurance of olfactometry data; ii) Release of ‘public coding challenges’ in order to aggregate successful innovative approaches and solutions from other industry areas (e.g. marketing information, production management, business modelling, pricing etc.).

Basic monitoring of main parameters influencing the quality of cachaça production processes takes place concurrently with e-nose’s data collection structures using sensors containing significant amounts of data. On top of that, data validity procedures rely on the quality and validity of the data previously collected. In order to obtain samples of interest, strategic partnerships with local producers becomes essential, as it relies on teams collecting field data with appropriate sampling procedures that assure a precise correlation between e-nose readings and applicable field conditions.

However, there can be risks in disclosing e-nose detailed project information to users in online platforms. IT Beverages’ strategy consists in gathering strategic data from key players in industry and academy to improve either one or more of the following steps: i) control of processes, such as properly blending aged beverages to standardize products; ii) distillation fractioning based on online information of volatile profile of the distillate; iii) develop software to assist on recommendations of volume of each distillate to compose a final product through mixture; iv) signalize quality of fractions during distillation based on field data.

The next phase involves testing and grading facilities required for basic Good Manufacturing Practice (GMP), including issuance of motions of understanding and non-disclosure agreements over a shared information policy. After data acquisition contribution, the collaborators are invited to join a group benefiting over IT Beverages technology built using their own data. Therefore, the analytical readings obtained and accurately analysed are subsequently transformed into market and production-oriented data that feed an AI algorithm.

Along the consolidation of the proof of concept phase, the results obtained will be traded with partners as a technology intensive and accurate analysis made over their distilled beverages production processes. Exemplifying, e-nose is expected to provide partners and then clients with feedbacks such as: “Mix 20 % of the volume of barrel A with 80 % of the volume of barrel B to obtain a beverages that matches the standard sensory profile of previous batch” or “High level of acetic acid detected in the distillate. Recommendation: collect this lower quality fraction in another container so as not to impair the quality of the beverage”.

To aggregate market and sales information to the AI system, opened back-end challenges will be addressed with a global developers’ network to discuss solutions that merge beverages production and market demand (Viejo, et al., 2019). The challenges proposed will consider data available from social networks, such as user preferences over partner products (through citations of brand profiles or tags), as well as data on customer behavior over different beverages and brands along the year. The challenges will be oriented towards the creation of AI-based tools for market-oriented solutions, such as determining automated production schedule, inventory management and optimized product offer along different seasons of the year, in order to minimize operating costs.

As a result of the challenges based on shared data, open innovation can be useful to generate knowledge and technology assessment over market behaviour, production trends, consumer habits, industry production capacity, autonomous portfolio management methodologies, and optimization techniques for data collection. Lichtenthaler (2011) describes this approach as an outside-in process, also denominated external knowledge exploration, whereby he indicates the need for adequate management mechanisms, concerning appropriate tools, processes and structures that lead to a successful implementation of open innovation.

2.7. FINAL REMARKS

Technology roadmaps enable diagnosis of organizational challenges for technological innovation and provide the company with directions on how to best implement innovative technologies. However useful and critical to support strategy at corporate levels, in the context of early growth firms the practical effects of the critical synthesis of the knowledge acquired through roadmaps can be hampered if certain conditions are not met. Startups need to desperately tap into all resources, such as working capital, qualified personnel, equipment and machinery, all of them very scarce or non-existent in these firms. As we discussed previously, also critical is recognizing that company culture can be as important for innovation as other tangible resources. Not least, the

choices over the paths through which the identification, selection, definition, development and operation of the technology will occur, along with managing the chosen path within acceptable cost, schedule, risk and operability constraints are also detrimental for a successful innovation implementation. Roadmaps therefore embed a dense network of methods, tools and resources that new companies need to address in order to introduce successful high-tech solutions in their markets.

By reviewing the literature and carrying out interviews with 15 individuals from the university, potential customers, partners, and members of the company team, we managed to build a critical analysis of the efforts required to support technology development strategies in a new high-tech firm. As a result, this application of related theories and perceptions from key stakeholders helped the early growth stage company build capacity to gain insight from technology management and industrial developments, thereby championing practices and solutions that supported the elaboration of a technology roadmap.

The first practice utilized, the innovation radar, promoted an overview of the organization's potential for generating new ideas and highlighted existing areas for improvement. This exercise demonstrated that consciousness on the potential areas for internal innovation practices was vital to help the firm come up with more creative processes leading to market innovation. Aspects concerning culture fitting and mindful approaches were recognized as elucidative for achieving the results expected in the five-year timeframe considered in the roadmap. In addition, understanding global approaches to behaviors that lead to innovation has contributed for the implementation plan. Such approaches relate particularly to organization culture, to which a major challenge is to align the firm's goals with expectations and motivations of human resources. These practices support the setup of a deeper sense of embeddedness and satisfaction required for building a corporate innovation mentality that tolerates failure and stimulates learning, accompanied by measurable success indicators supporting decision-making at all levels.

Roadmapping the development of an electronic nose in the company studied supported the determination of an exploratory step-by-step approach, consisting on the visualization of necessary resources along time and the identification of key improvements and developments required for achieving a technology deployment strategy. As a result, it was possible to define a parallel schedule for financial and marketing strategies supporting the firm's objective, as presented in the technology roadmap. During execution, the roadmap flexibility will prove vital for dealing with environmental conditions and technical issues that may appear in the course of the company growth, representing new inputs that need to be assessed and incorporated into the technology roadmap, if deemed appropriate.

On top of discussions carried in this chapter, the company management concluded that the complex and uncertain path ahead of it demanded reviewing practices and strategies related to some restrictive business policies that can hamper sustained growth. The reason was simply the recognized difficulty to count on key in-house human and material resources that, although important, could not be sourced on a short or midterm basis due to budgetary constraints and the overall local supply conditions of specialized workforce and suppliers. In this regard, open innovation was considered a possible growth perspective. Besides internal technology improvements, the aspect of external collaboration enriches community engagement and brings in, at a relative low cost, external perspectives that can contribute to the generation of new solutions. This strategy, obviously, can come at a cost if the firm does not set up policies to ensure roles and responsibilities over the sharing of key and sensitive data with both internal and external supporters.

The case studied in this chapter focused on identifying a pathway supporting technology development efforts in a pre-revenue small high-tech firm. By starting with technology prospection, it was possible to describe the dynamics of the company's industry, such as recent structural changes, anticipated future developments and the global landscape, thereby elucidating the current role and status of innovation in the company. The success of this phase required a comprehensive coverage of the challenges and opportunities the organization faces, along with the corporate response to technology implementation and utilization. Having identified the innovative technologies suitable to the business purposes, the company studied was able to explain the potential benefits of adopting each of the proposed technologies, including anticipated improvements in productivity, products and services, collaboration, and project management. Next, the evaluation of corporate implementation of technologies inside the company required that the firm identified the impact of failure on the company's innovation practices, and that it understands how technology management metrics contribute to successful implementation of innovations in the organization.

The company studied recognized that the roadmap was important to support its way through deploying the e-nose technology in the market within five years. As a next step, market-oriented prospecting after the roadmap become vital to enhance communication with the market and, consequently, aggregate value to the firm's future portfolio of products. The technology roadmap defined the timeframe for these actions, but the concrete pathway to be assumed was not defined yet.

Finally, as a single case study based on a literature review and on the evidence collected by the authors from investors, researchers, potential clients and other entrepreneurs, this study

does not allow for wider generalizations. However, given its scope as an exploratory study, we believe the discussion and results outlined will offer support to guide future studies in technology management in the context of startups. The authors also understand that upon attempting to provide this balance between theory and practice, we risk alienating either one or all our intended audiences of entrepreneurs, academics, and policymakers. At the same time, we hope they appreciate the value of the approach developed and that, consequently, this study will serve peripherally to encourage and strengthen the development of a better understanding of the capital requirements of entrepreneurial firms between academics and practitioners.

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3. MATURATION LEVEL DETERMINATION

ABSTRACT

The evolution of distillate beverages during barrel aging process is related to extraction and transformation of wood barrel compounds. Even though time represents an important factor for distillates quality, other reported attributes concerning wood barrel features, such as wood species, internal toast and previous use, are determinant to accrete mature characteristics to the beverage. We evaluated the level of lignin derived products (LDPs), through HPLC UV-Vis analysis, in sugar cane spirit (cachaça) from different barrels, and compared those results to reported aging classes for distillates through multivariate principal component analysis (PCA). Unsupervised machine learning techniques of clustering were applied to identify similarities among samples and form cohesive groups concerning wood derived phenolic compounds. As an effort to provide a new metric for wood aged distillates, four new classes of maturation were determined as a qualitative parameter, with their characteristics described, based on quantitative parameters equivalent to guaiacyl and syringyl compounds, as well as a regression model for new samples classification (86.9 % of prediction accuracy).

Key-words: wood aging, distillate, cachaça, maturation level, machine learning.

3.1. Introduction

3.1.1. Wood interaction and compounds

Newly distilled spirits are described as aggressive, alcoholic, harsh, and bitter, sensory characteristics that may not be appealing to consumers. Aging distillates in wood barrels improves the sensory characteristics of these beverages, as a result of the inherent reactions of polymerization, esterification, hydrolysis, and oxidation (Litchev, 1989; Onishi et al., 1977). The barrel aging process is associated to wood structural transformation promoted by action of both water and ethanol from distillates (Singleton, 1995). Lignin degradation is the pathway responsible to generate low molecular weight phenolic compounds (Table 4) that influence on the chemical composition and, consequently, the sensory characteristics of the aged distillate (Alcarde et al., 2014; Bortoletto et al., 2016), also improving distillates' antioxidant activity (Canas et al., 2008; Goldberg et al., 1999). The lignin degradation is a complex process, influenced by numerous factors such as wood species, geographical origin, tree age, and type, barrel manufacturing techniques such as seasoning and the level of internal toasting, number of previous uses of a barrel, time in contact with the beverage during aging process, distillate composition (acidity and ethanol content), and

environment cellar conditions encompassing air moisture and temperature (Baldwin et al., 1967; Farrell et al., 2015; Prida & Puech, 2006; Rodríguez-Rodríguez & Gómez-Plaza, 2011; Spillman et al., 2008).

Table 4. List of volatile and semi-volatile compounds found in wood barrel aged cachaças, and their respective sensory descriptors (Bortoletto & Alcarde, 2013) and thresholds.

Precursor	Compound	Aroma descriptor	Threshold
Ligning	Coniferaldehyde	Cinnamon	90 ppm ^g
Ligning	Vanillin *	Vanilla	200 ppb ^b
Ligning	Vanillic acid	Cream/ Vanilla	30 ppm ^g
Ligning	Sinapaldehyde	Spicy	80 ppm ^h
Ligning	Syringaldehyde *	Pepper	25 ppm ^h
Ligning	Syringic acid	-	25 ppm ^h
Lipid	Whisky-lactone *	Coconut	67 ppb ^a
Ligning	Eugenol *	Clove/ Spicy	6 ppb ^a
Ligning	Guaiacol *	Medicinal/ Smokey	9.5 ppb ^a
Polysaccharide	Furfural	Almonds	88 ppm ^e
Polysaccharide	5-hydroxymethylfurfural *	Caramel	16 ppm ^f
Polysaccharide	Maltol	Caramel/ Toasted	36 ppm ⁱ

* - compounds that exceed threshold in wood aged distilled beverages (Alcarde et al., 2014; Cernîșev, 2017), a – (Escudero et al., 2007), b- (Guth, 1997), c – (De Simón et al., 2008), d – (Boidron et al., 1988), e – (do Nascimento et al., 2000), f – (Chatonnet et al., 1997), g – (Maga & Lorenz, 1973), h – (Singleton, 1995), i – (Lee et al., 2001).

Thus, characterizing wood aged distillates relies on their chemical composition, resulting from the interaction among the alcoholic matrix compounds, and the wood barrel. The transformations induced by wood barrel aging process of distilled beverages have been elucidated along years (Nishimura & Matsuyama, 1989; Reazin, 1981). Final quality of aged spirits depends on numerous internal factors, from beverage composition to process undergoing environment conditions. These factors embrace modifications of distilled beverage according to notoriously complex pathways (Rodríguez-Solana et al., 2014; van Jaarsveld & Hattingh, 2012): wood compounds extraction, decomposition of wood macromolecules, volatile compounds loss, oxidation of extracted compounds and distillate inherent components, interaction of wood and beverage components.

Through polymerization, esterification, acetalization, hydrolysis, and oxidation reactions (Litchev, 1989; Onishi et al., 1977), the original distillate undergoes transformations related to visual aspect, taste, aroma, and flavor characteristics (Dodero et al., 2010). These reactions that promote sensory differentiation during barrel aging are impacted not only by wood species, but also by wood geographical region, and mainly by cooperage techniques during barrel construction such as seasoning and toasting (Canas, 2017; Le Floch et al., 2015; Prida & Puech, 2006; Rodríguez-Solana et al., 2014).

The different classes of wood derived flavor active compounds, responsible for barrel aged distillates aroma characteristics, have been widely researched (Le Floch et al., 2015). Among the classes of interest, volatile phenols (Madrera et al., 2003; J. -L. Puech, 1988), lactones (De Rosso et al., 2009; Maga, 1996), norisoprenoids (Sefton et al., 1990) are included, as well as non-volatile compounds such as extractable carbohydrates in wood (Le Floch et al., 2015), lignin derived acids (Rodríguez-Solana et al., 2014), and polyphenols with resistance to oxidation reactions along aging process (De Rosso et al., 2009).

The content of those wood derived compounds and their ratio, which is responsible to determine the main smellprint of an aged distillate, is notably dependent on wood species. Oak wood presented higher content of volatile phenolic aldehydes, terpenes, and lactones (De Rosso et al., 2009), as well as higher concentration of antioxidative phenolic compounds (Jung et al., 2016) compared to other species tested, namely Chestnut, Mulberry, Cherry, and Acacia. So that, many aspects of Oak wood turn it suitable for long-time aging periods, and it provides richest aroma composition compared to other wood species.

The internal thermal treatment of barrels accretes favorable sensory characteristics to the distillate by increasing availability and solubility of wood compounds. As reported by Otsuka et al. (1974) and Maga (1996), methyl octalactones concentration in wood extracts considerably increase after wood thermal processing, mainly due to heat induced oxidation of their precursors. Severe thermal treatment results on aerobic and anaerobic pyrolysis (MacNamara et al., 2001), degrading lignin in the adjacent layer to the charcoal and generating flavor compounds such as vanillin (Singleton, 1995). Barrel toasting is responsible also for generate aroma compounds from hemicellulose degradation, formed by caramelization pathway of sugar monomers released by hydrolysis induced by high temperatures (Le Floch et al., 2015). Besides the thermal degradation pathway, lignin-derived phenolic aldehydes increase along barrel aging period due to ethanol-lignin reactive complex named ethanolysis (Puech, 1988).

Barrel condition is a notable factor responsible to accrete favorable sensory attributes. Casks are normally reused for distillate aging practice according to distillers' perception of wood-

aged characteristics aggregated (Conner et al., 1993). Piggott and Conner (Piggott & Conner, 2003) reported that reused charred barrels displayed a migration of phenolic aldehydes and lactones content from an inner part of the wood stave to a more superficial one, namely the charred surface. So that, the resulting aged spirit from a second-use charred barrel would present intermediate phenolic aldehydes and lactones, lower than a new charred, and higher than a toasted barrel (Baldwin et al., 1967; MacNamara et al., 2001). Although, exhausted barrel, which were refilled more than two times, presented low content of extractable ligning degradation compounds and lactones in the surface, presenting a substantial concentration only in a wood stave depth of 25 mm (Conner et al., 1993).

3.1.2. Maturation level as a quality indicator

The lignin macromolecule has branches of coniferyl (guaiacol compounds) and sinapyl (syringol compounds) alcohols. Coniferyl alcohol generates coniferaldehyde, which is converted to vanillin and, in turn, oxidized to vanillic acid. Sinapyl alcohol gives rise to sinapaldehyde, which is transformed into syringaldehyde and later oxidized to syringic acid (Figure 6) (Puech, 1981).

Figure 6. Transformations of lignin-derived aromatic compounds during the aging process of distilled spirits.

Considering the differences in regard of distillates composition due to barrel condition, namely compounds that contribute to sensory characteristics, the period of aging process represents a relevant factor but may not fully reflect the perceived quality of a wood-aged distillate. Distillates that are mandatorily aged in wood barrels have a legal time threshold to be aged, such as whiskies (Russell et al., 2014) and brandies, even though there is no specification concerning barrel characteristics, which may favor distillate evolution considering less used barrels.

Cernîșev (Cernîșev, 2017) evaluated the evolution of brandies, concerning lignin degradation products ratios and concentrations, in a broad variety of aging time-length (one to 50 years). He reported the decrease of cinnamic aldehydes (sinapaldehyde and coniferaldehyde) along brandies' barrel aging process, likely due to oxidation pathway. Diversily, benzoic aldehydes (syringaldehyde and vanillin) and acids (syringic and vanillic acids) increased during the period. The

transformation of benzoic aldehydes into the respective benzoic acids presented a similar reactions rate, fact in accordance with previous remarks that ratio between syringaldehyde and vanillin remain almost constant along distillates aging in wood barrels (Canas et al., 2013; Cernîșev, 2017; Quaresma et al., 2004; Rodríguez-Solana et al., 2014). Cernîșev (Cernîșev, 2017) provided a classification of samples into “maturation classes” of brandies, according to their aging-markers composition and evolution along time (Table 5).

Table 5. Concentration of lignin degradation aging markers (mg/ L) and classes of aged brandies considering ratios and sums of those compounds (Cernîșev, 2017).

Aging marker	Young(< 5 years)	Moderate-aged (5 to 10 years)	Old (10 to 20 years)	Extra old (>20 years)
Coniferaldehyde	4.4	4.3	3.9	2.4
Vanillin	4.0	8.6	12.3	16.7
Vanillic acid	0.7	1.7	3.5	4.5
Sum of guaiacyl group	9.1	14.6	19.7	23.6
Ratio vanillin / coniferaldehyde	0.9	2.0	3.2	7.0
Ratio vanillic acid / vanillin	0.18	0.2	0.28	0.28
Sinapaldehyde	10.0	7.8	3.5	1.6
Syringaldehyde	8.1	17.6	23.2	27.8
Syringic acid	1.3	4.9	8.4	8.3
Sum of syringil group	19.4	30.3	35.1	37.7
Ratio syringaldehyde / sinapaldehyde	0.81	2.2	6.6	17.4
Ratio syringic acid / Syringaldehyde	0.16	0.28	0.4	0.3
Sum of vanillic and syringic acids	2.0	6.6	11.9	12.8
Ratio syringaldehyde / vanillin	2.0	2.04	1.9	1.7
Ratio syringic acid / vanillic acid	2.0	2.8	2.5	1.8

Besides the qualitative aspect related to aging markers parameters and the possibility of classification of wood aged distillates considering sums and ratios of congeners, these parameters may be useful for interpreting barrel aging process. Considering unusual and distorted observations of those parameters (ratios and sums of aging markers), it would be possible to distrust the process of wood extraction (e.g. barrel aging versus wood chips extraction) and even indicate addition of flavoring agents and other adulterants in the beverage (Buxton & Hughes, 2013).

Aged distilled beverages present specific production ordination, including parameters' thresholds related to barrel volume, minimum time, and maximum ethanol content. Sugar cane spirit regulation is made by the Ministry of Agriculture, Livestock and Food Supply (MAPA, abbreviation in Portuguese), which contains guidelines for raw material and manufacturing process, including definitions, even though aging practices guidelines are not well defined. A recent proposed Ordinance (Portaria nº90/ August of 2016) contains particular ordination for wood-aging process, involving a more restrictive process and conditions for denominating "barrel aged": wood-barrel size limited to 700 L; minimum aging period of 1 year; determination of permitted wood species for barrel construction; inspection, and labeling rules.

As reported in the 1st Article of this Ordinance, the Ministry inspection and control of aging process in sugar cane spirit industry would be made through computerized system available at MAPA website (MAPA, 2016). If entirely approved, this legal demand may be implemented regarding analysis of the aging parameters, based on wood copounds extractation and transformation. A maturation index would be a favorable metric indicate aged distillate quality and defining maturation classes would be a useful parameter to increase sugar cane spirit quality. As reported by Lachenmeiner (Lachenmeier, 2016), confirmation of storage period is an important issue associated to adulteration of cask-aged spirits, so methods as HPLC (Canas et al., 2019; Jaganathan & Dugar, 1999) and HNMR (Petrakis et al., 2005) were proposed. Those indicated methods provide accurate results; however, they are costly, require a well-trained operator and represent a difficultly applicable method for online analysis (Sanaeifar et al., 2017).

So that, emerging technologies that present a high level of accuracy and reliability started taking place in food industry to test adulteration in a range of food-matrices recently (Jo et al., 2016; Kiani et al., 2017; Kilcast, 2013; Wu et al., 2019). The development of portable, low-cost and efficiency equipment represents an advantage on reaching and dismisses the need for a laboratorial structure, financial support for machinery and consumables, access to specialized workforce, and reinforces capability and time of testing samples and may help online decision-making. This type of device, namely a portable electronic nose, is possibly a suitable tool addressed to sugar cane spirits industry, offering a solution that attends new regulations for barrel aging classification (qualitative approach) and helps monitoring and decision-making based on cachaça's quality along the process.

3.1.3. Maturation level analytical aspects

Most current instrumental resources employed in wood-aged spirits analysis, include basically liquid and gas chromatography, which are suitable for analytical quantification tasks, although, as reported by Sefton et al. (1993), some desirable characteristics, such as “vanilla oak” is not exclusively related to vanillin content in the spirit, but the flavor descriptor perception may be enhanced considering synergistic action (Singleton, 1995). As reported by Jaarsveld and Hattingh (2012), furfural, vanillin and lactones presented high positive correlation to sweet-associated aromas, and consequently to better overall-appreciation score of wooden brandies by tasters.

Analytical responses of quantitative nature may be crucial as quality parameters of aged beverages, although they do not describe entirely the flavor characteristics of beverages and their properties. Many studies examined odors and tastes additive contribution to overall flavor characteristics, comparing mixtures of components to their individual perception (Garcia-Medina, 1981), and results pointed to a lack of independency between tastes and odors. Prescott (Prescott, 1999) indicates that the combination of those two factors may cause significant changes over odor perception through the different olfaction forms (orthonasal and retronasal).

These observations are consistent with the psychological phenomena described as ecological view of perception (Gibson, 1966), which relies on a greater importance of identifying objects through a sensation than the physiological origin of the sensation itself. Thereby, the identity of a food or beverage matrix may be object of individual identification of the intrinsic sensory properties (Prescott, 1999), which undergo a cognitive construction of a perception integrating different physiological responses. According to Prescott (1999), this cognitive construction relies on hedonic and global judging by consumers, representing a subjective approach to a sample classification susceptible to information conflict, such as olfactory location illusion (Marks, 1991).

Later interest on flavor perception science (Verhagen, 2007) was supported by elucidating multisensory integration. As Auvray and Spence (2008) state, the integration between distinct human sensory systems is responsible for defining flavor perception: taste, smell, the trigeminal system, and touch, adding visual and auditory cues, although may correspond to anatomically separated systems, are responsible for triggering a series of interactive cognitive responses over a food matrix (Abdi, 2002). Because of such stimuli complexity, even trained panelists yield varied responses to the same stimulus (Civille et al., 2015), so that sensory professional may be aware and responsible for assessors' training in attempt to minimize discrepancies between subjects and create a more homogenous mental process between them.

Continuous assessors' training is necessary as maintenance to have solid standards and consistent results, which may be significantly costly for larger and even economically unfeasible for medium-sized and smaller food and beverages industries (Giacalone, 2017). Furthermore, the expert panel may display great performance for product or raw-material standardization assessment, however the trained subjects' evaluation may be restricted to that, once their experience with products may differ from consumer's process or they may be biased towards detection of less important sensory attributes (Ares, 2015).

Concerning analytical techniques for chemical analysis, aging markers' quantitative analysis have been performed by High Performance Liquid Chromatography (HPLC) for the last decades, specially focused on wood degradation compounds compounds (Cernîșev, 2017), such as phenolic aldehydes and acids found in wood-aged spirits (Bortoletto & Alcarde, 2013; Canas et al., 2008; OIV-MA-BS-16, 2009). As pointed out by Cernîșev (2017), some concerns about this methodology are the long analysis time, poor separation efficiency and pre-column short-life caused by irreversible adsorption of wood extract compounds, such as lignin oligomers and polysaccharides.

Other compounds than lignin-derived may be considered as aging marker in barrel-aged spirits, namely methyl-ketones (Watts & Butzke, 2003) reported as accurate aging predictors for cognac age determination. Reazin (1981) approached high-volatility compounds transformation during Bourbon whiskey aging process, evaluating oxidative pathway of ethanol generating acetals, which contribute to pleasant and desirable sensory characteristics in matured whiskeys (Nykänen & Suomalainen, 1983). Meanwhile, lignin-derived aldehydes and acids derived from wood barrels have been more widely approached as aging markers (Aline M. Bortoletto & Alcarde, 2013; Canas et al., 2008; Cernîșev, 2017; Rodríguez-Solana et al., 2014), and most related to sensory aspects changes over maturation of spirits (Nishimura & Matsuyama, 1989), entailed by wood casks extract and breakdown of compounds (Singleton, 1995).

The lignin degradation products, hydrolysable in aqueous ethanolic medium (Mosedale & Puech, 1998), are either formed from toasting or charring, or by wood lignin degradation. For uncharred or previously used casks, this second pathway is thought to be the major route of formation of lignin breakdown products extracted into the spirit (Nishimura et al., 1983). De Rosso et al. (2009) broadly approached the extraction of volatile and semi-volatile compounds by a model spirit interacting with Oak wood. The authors found the richest composition and the highest content in significant volatile phenols, benzoic aldehydes, and fatty acids extracted from Oak wood compared to other 4 wood species - Acacia, Chestnut, Cherry and Mulberry - usually employed in cooperage industry. Diversily, Garcia-Moreno et al. (2020) reported greater concentration of those

phenolic compounds in Chestnut wood barrels with medium toast, compared to barrels of Oak woods from different origins (American, French, and Spanish) with both intense and medium toast.

Conner, Reid and Richardson (2001) tested whiskies aged along different periods of time in new and refilled barrels, comprising olfactometry associated to headspace SPME extraction over diluted samples (20 % ethanol), being able to recover alcohols (3-methyl-1-butanol and phenylethanol), esters (ethyl hexanoate, 2-phenylethyl acetate, cis oak lactone), and volatile phenolic compounds (benzaldehyde, 4-ethyl-2-methoxyphenol, vanillin and eugenol). The authors conclude that headspace method avoids matrix interaction issues and are more related to odor activity and sensory properties.

Zhao et al. (2009) investigated the volatile composition different brandies of distinct aged qualities (*VO, VSOP, XO) by GC-MS with HP-SPME extraction, identifying and quantifying more than 140 compounds (alcohols, ketones, aldehydes, acids, esters, aromatic compounds, phenols, furans, acetals, terpenes and norisoprenoids, lactones and sulfurs). The authors concluded that esters and alcohols primarily corresponded to quality parameters, or markers, for samples and their concentrations were decisive for quality level.

Sánchez-Guillén et al. (2019) recently successfully established predictive models for Brandy de Jerez, aged in barrels from different previous uses, considering an aging system called 'solera', based on HPLC responses of phenolic compounds (gallic acid, 5-HMF, furfural, and ligning-degradation products) and organic acids (tartaric, mallic, succinic, lactic, formic, and acetic). The chemical parameters analysed by the authors were correlated to seasoning and average aging time, displaying a favorable accuracy to estimate period of aging (in years) for some samples, however the model based strictly on semi-volatile compounds estimated periods close to 3 years of barrel aging for samples aged for 1 year.

3.2. MATERIAL AND METHODS

3.2.1. Samples

Sugar cane spirit was produced at Pilot-scale Distillery of the Department of Agri-Food Industry, Food and Nutrition, in College of Agriculture "Luiz de Queiroz" – ESALQ (University of São Paulo) in 2013. Sugar cane variety SP 81-3250 was grown at ESALQ and the plants, immediately after harvesting, were forwarded to sugar cane juice extraction employing a three-roll mill. The juice was conducted towards a decanter for elimination of solid impurities (soil and bagasse fractions). Sugar cane juice soluble solid concentration was further adjusted to 18 °Brix in

a juice-standardization tank by addition of water, leading to the wort that underwent fermentative process.

The wort was pumped to 1,500L-stainless steel fermentation vessels where yeast strain CA-11 (LNF Latino Americana, Bento Gonçalves, RS, Brazil) was pitched following manufacturer instruction and recommendations. After achieving maximum attenuation (24 h at 30 °C) fermented sugar cane juice underwent double-distilling procedure described by Piggot and Conner (2003), in a 1000 L steam heated copper still, assembled with a 2-plates neck followed by a dephlegmator. First distillation corresponded to exhaustion of the ethanol contained in fermented juice without fraction separation, obtaining the so-called “flegma”. The successive distillation relies on fractioning “flegma” into three portions: the foreshots corresponding to 2 % of total “flegma” volume; the sugar cane spirit, obtained by distillate recovery until alcohol content reached 60 % (v-v-1) at the condenser output; and the feints, corresponding to distillate collected from 60 % ethanol content until exhaustion of ethanol.

The barrels for aging the spirit, with capacity to 225 L, were made from French and American Oak woods (*Quercus petraea* and *Quercus alba*, respectively), medium toasting (Tonelleries de Bourgogne, Meursault, France), and high toast for French Oak. The double-distilled sugarcane spirit (63.5% ethanol v/v) was aged in the barrels (in triplicate) at room temperature (22 ± 3 °C) and a relative humidity of $55 \pm 10\%$, and protected from vibrations. Samples of 25 mL were collected at the same level from the center of the barrels at 3, 6, 9, 12, 18, 24, 36, 48, 60, and 72 months of aging period for the analysis of maturation-related congeners for first filled barrels, 3 to 60 months, with the previous interval described, for second filled barrel aging, and 3, 6, 12, 18, 24, 36, 48, 60, 72, 120, and 144 for extensively used barrel samples.

3.2.2. Maturation level determination

3.2.2.1. High performance liquid chromatography analysis (HPLC)

In order to obtain the maturation degree (Cernîșev, 2017) for samples, the quantification of aging congeners was performed over the samples analyzed using high-performance liquid chromatography (HPLC; Shimadzu, model LC-10AD), equipped with two Shimadzu LC-20AD pumps, a UV–vis detector Shimadzu SPD-20A, a system controller CBM-20A and an autosampler. The standard compounds used in this study were vanillin, vanillic acid, syringaldehyde, sinapaldehyde, syringic acid and coniferaldehyde, all supplied by Sigma-Aldrich (St Louis, MO, USA), purity >99 %. The HPLC method employed in this study had two mobile phases composed

of water: acetic acid, 98:2 (v/v) (Solvent A), and methanol–water–acetic acid, 70:28:2 (v/v/v) (Solvent B) with gradient elution (Table 2), flow-rate of 1.25 mL/min and volume of injection 20 μ L. A pre-column Shimadzu VP-ODS (1 cm $\times$ 4.6 μ m) and a C18 reversed-phase column model, Shim-pack VP-ODS (4.6 mm $\times$ 25 cm $\times$ 5 μ m), both thermostated at 40 °C, were used. The UV detector was programmed at variable wavelengths (Table 6). The sample preparation involved previous filtering using Millex-HV filter with PVDF membrane (diameter 13 mm, pore size 0.45 μ m). The quantification of the compounds was performed based on external calibration curves of six standard concentrations (Bortoletto & Alcarde, 2013). In total, 62 samples were obtained for the analysis of phenolic compounds by HPLC.

Table 6. HPLC method gradient elution and wavelengths specifications (Bortoletto & Alcarde, 2013).

Time (min.)	Solvent A (%)	Solvent B (%)	Wavelength (nm)
0	100	0	271
6	100	0	280
25	60	40	276
34	60	40	320
37	60	40	320
40	100	0	271
45	100	0	271

Solvent A - water: acetic acid, 98:2 (v/v); Solvent B - methanol–water–acetic acid, 70:28:2 (v/v/v).

3.2.2.2. Data analysis

Data entry corresponded to results of aging congeners analyzed by HPLC. Complementarily to the current dataset (62 samples of cachaças aged under different conditions), four observations were included based on each of maturation classes stated by Cernișev (2017), considering the mean values of phenolic compounds concentration for each class (young, moderate, old, and extra old). Those observations were imputed as supplementary information for data analysis.

The parameters considered were based on HPLC results of aldehydes derived from lignin degradation pathway, namely, content of coniferaldehyde, vanillin, vanillic acid, sinapaldehyde, syringaldehyde, and syringic acid, parameters correspondent to other wood structural transformation during cooperage, gallic acid, 5-hydroxymethylfurfural, and furfural (Le Floch et al., 2015; J. -L Puech, 1988; Rodríguez-Solana et al., 2014). Also, hyper parameters (combination of previous parameters) were defined as sum of guaicyl compounds (coniferaldehyde, vanillin, vanillic acid), sum of syringyl (sinapaldehyde, syringaldehyde, and syringic acid), sum of benzoic acids (vanillic and syringic acids), sum of intermediate compounds from guaiacyl and syringyl blocks (vanillin and syringaldehyde), and sum of initial compounds (coniferaldehyde and sinapaldehyde), plus ratio parameters: vanillin/ coniferaldehyde, vanillic acid/ vanillin, syringaldehyde/ sinapaldehyde, syringic acid/ syringaldehyde, syringaldehyde/ vanillin, syringic acid/ vanillic acid, coniferaldehyde/ sinapaldehyde, vanillin/ syringaldehyde. The choice of those variables was based on their reported importance for classification of wood aged distilled beverages

(Aylott & MacKenzie, 2010; Canas et al., 2019; Cernîşev, 2017; MacNamara et al., 2001; Quaresma et al., 2004). Supplementary variables (previous use of barrel, wood species, toast, and aging time) were added to evaluate how those factors are related to distribution of samples and their correlation to classes established by Cernîşev (2017).

An exploratory data analysis was conducted as paired investigation of variables (Schloerke et al., 2020) and their potential to sort samples according to their classes of barrel usage, aging time, and maturation class. Next, a Random Forest (RF) machine learning algorithm (Cutler et al., 2012) was implemented to select variables, among parameters, hyper parameters and ratios, from their calculated weights (Géron, 2019). Ten variables with greater importance score (vanillic acid, syringic acid, vanillin, syringaldehyde, coniferaldehyde, sinapaldehyde, sum of vanillin and syringaldehyde, sum of guaiacyl compounds, sum of syringil compounds, and sum of benzoic acids) were selected to undergo unsupervised classification task performed by two different clustering algorithms: k-means and Gaussian mixture model (GMM) (Géron, 2019; Maugis et al., 2009). Both clustering algorithms were tested with two distinct input data, for comparison purposes, corresponding to: a) scaled selected variables; and b) scores obtained from PCA performed over selected variables dataset.

K-means cluster analysis was performed by factoextra R package (Kassambara & Mundt, 2020) in datasets a) and b) after obtaining optimized number of clusters and agglomeration methods. GMM clustering was optimized based on Bayesian Information Criterion (Scrucca et al., 2016) for fitting model and number of clusters. Clustering results of the different tested methods over datasets a) and b) had their convergence tested. A new consensual cluster was generated after equally considering the overall likeliness to belong to a specific cluster.

Pairwise comparison of clusters results was performed employing the Goodman Kruskal's tau statistics, which enables obtaining a metric for association between categorical variables of different lengths (Agresti, 2012; Goodman & Kruskal, 1959). So that, Goodman Kruskal analysis took into account the variables previous use of barrels, aging period, Cernîşev classes, and the current obtained clusters (k-means, GMM, and consensual cluster).

3.3. RESULTS AND DISCUSSION

3.3.1. Variable selection and data treatment

Raw data was explored to evaluate general distribution of variables considering observations belonging to one of four classes determined by Cernîşev (2017): 'young', 'moderate',

‘old’ and ‘extra old’. In total, 18 samples of cachaça were classified as ‘young’, 20 as ‘moderate’, 20 as ‘old’, and 4 as ‘extra old’. The initial distribution analysis considered separately the variables, ratios and sums described in section 2.2.2. Data analysis. The variables and hyperparameters were highly correlated (over 0.80), likely containing redundant information. So that, Random Forest machine learning algorithm (Cutler et al., 2012) was implemented considering all input parameters and maturation class as the output. A ranked list of parameters, sorted by importance, was generated as response and led to a reduction from 22 to ten active parameters (vanillic acid, syringic acid, vanillin, syringaldehyde, coniferaldehyde, sinapaldehyde, sum of vanillin and syringaldehyde, total guaiacyl compounds, total syringil compounds, and total benzoic acids), increasing computation efficiency for clustering calculations and avoiding significant information loss. The exploratory analysis of selected variables is presented in Figure 7.

Figure 7. Pairwise evaluation of selected variables, their correlation (in black) and mean scaled values for each one of the Cernișev’s maturation classes (Cernișev, 2017) (colored).

In order to obtain optimized uncorrelated variables for further graphic representation of samples, a PCA was performed on selected variables data, leading to five components (Figure 8) containing 99.7 % of total variance. The selected variables were more correlated to first three dimensions, being the first dimension (77.8 % of total variance) more correlated to vanillic acid, syringic acid, vanillin, syringaldehyde, sum of vanillin and syringaldehyde, total guaiacyl compounds, total syringil compounds, and total benzoic acids, the second dimension (16.8 % of

total variance) associated to coniferaldehyde and sinapaldehyde, and third dimension (3.4 % of total variance) (Figure 9) also correlated to vanillic acid content.

Figure 8. Pairwise evaluation dimensions from PCA performed over selected variables, their correlation (in black) and mean scaled values for each one of the Cernîșev's maturation classes (Cernîșev, 2017) (colored).

Figure 9. Graphical representation of selected variables in first PCA plan (94.5 % of total variance).

3.3.2. Maturation classes determination

After variables were optimized to PCA responses of cachaça aging markers, considering the most important features related to maturation level of distillates based on Cernîșev's findings (Cernîșev, 2017), unsupervised learning (Géron, 2019) techniques of clustering, namely k-means and GMM, were tested to evaluate how the samples are grouped based on their chemical composition. Both clustering algorithms were tested with two distinct input data: a) scaled selected variables; and b) scores obtained from PCA performed over selected variables dataset.

The clustering algorithm displayed different behavior for classification of samples. Optimized k-means implemented over datasets a) and b) grouped identically (Goodman Kruskal's $\tau = 1$ in Table 7). Despite presenting a 100% consensus, the k-means grouping tasks represented lower discriminant capacity when compared to GMM trials, which was measured considering distribution of samples per cluster (Figure 10). As the purpose of the present research is to classify wood aged distillate samples and discriminate them by maturation level, only the GMMs were considered to generate consensual cluster, in order to obtain final classes related to maturation level.

Table 7. Pairwise comparison through Goodman Kruskal's tau values for different clustering methods (k-means and GMM) applied to selected variables and PCA scores.

	GMM - Sel. Vars.	GMM - PCA	k-means – Sel. Vars.	k-means – PCA
GMM - Sel. Vars.	-	0.63	0.84	0.84
GMM - PCA	0.59	-	0.49	0.49
k-means – Sel. Vars.	0.29	0.22	-	1.00
k-means – PCA	0.39	0.29	0.22	-

Figure 10. Comparative representation of number of samples per cluster considering different situations (I – GMM performed over selected variables, II – GMM performed over PCA results from selected variables, III – k-means method).

Regarding the optimized GMMs performed over datasets containing selected variables and PCA scores, the consensus rate between these models, namely the percentage of samples classified equally in both cluster analysis, was equal to 39.3%. The divergence was primarily related to distinct optimal number of clusters (k) considered for each dataset: 8 and 7 for datasets with selected variables and PCA scores, respectively. So that, $k = 8$ was re-dimensioned to fit into 7 clusters classification, considering Euclidian distance among centers, and enables a direct comparison between the models due to as increased consensus rate to 80.3% after the transformation.

After obtaining proportionally comparable clusters, the two sets were merged into a single consensual classification ($k=7$) based on greater probability (Bayesian model) of each sample belonging to each of new clusters proposed. Associations among the clustering methods and class variables were further investigated to better visualize the new grouping related characteristics (Table 8).

Table 8. Pairwise association measured (Goodman-Kruskal τ) between different clustering GMM methods and qualitative variables of samples describes by barrel period of aging (Time), previous use (Use), and maturation class according to Cernîşev (Cernîşev, 2017) definitions (Class).

Association (Goodman-Kruskal τ)	GMM for Selected Variables	GMM for PCA performed over Selected Variables	Merged results from both GMMs
Time	0.21	0.21	0.22
Use	0.69	0.61	0.70
Class *	0.66	0.36	0.48

Goodman-Kruskal τ – range from 0 (weak association) to 1 (strong association).

The new clustering that resulted from merging GMMs was strongly associated (0.70) to the previous use of barrel to classify sample of aged cachaça, and the association to aging time was less important (0.22), evidencing that the chemical characteristics of wood aged distillates is more related to the content of barrel readily extractable compounds than to aging time, in accordance to other studies (Alcarde et al., 2014; Canas, 2017; Conner et al., 1993; Reazin, 1981). First-filled barrels present a greater extractable fraction and enables a fast solubilization of aging congeners into the spirit matrix. The association index between the merged cluster and classes defined by Cernîşev (2017) was lower (0.48) than for qualitative variable related to experimental barrel usage, possibly due to a greater variation among cachaça samples from first, second-fill and extensive use, compared to samples investigated by the author, likely more homogeneous concerning barrel type employed for aging process (commercial samples).

Following the analysis of clusters generated after merged GMM models, characteristics of the individuals belonging to each of the clusters were evaluated, concerning barrel toast, previous use, aging time, and sum of congeners as a quantitative parameter. This information was compiled into a list of general characteristics for each of the clusters obtained ($k=7$) (Table 9). For data visualization, a PCA was performed over selected variables and observations were sorted by cluster (Figure 11).

Table 9. Qualitative variables, quantitative LDP (mg/L of anhydrous ethanol) content and general characteristics and related to each of merged GMM clusters.

Cluster number	Samples			Total LDP	General characteristics
	Toast	Use	Time (month)		
1	all	1 st	3 and 12	19.5	Short period of contact with barrels with high extractable content.
2	all	1 st	6 to 72	35.9	Shorter time with higher toast level, and longer time with lower toast level.
3	all	1 st	18 to 36	24.2	Intermediate group concerning concentration of aging markers and aging time.
4	all	1 st , 2 nd	18 to 60	14.4	French Oak, medium toast and 1 st use in same group of 2 nd use of American and French Oak, all toasts and similar time range.
5	all	1 st	48 to 72	56.8	Highest concentration of aging markers. Only French oak with high toast and American oak with medium toast.
6	all	2 nd , ext.	3 to 12	4.3	Short time of contact with barrels with low extractable content.
7	medium	ext., 2 nd	18 to 144	4.6	Mostly barrels with low extractable content and longer time of contact with barrels. A single 2 nd use, French oak, medium toast, 18 months.

Figure 11. Representation of the samples of cachaça by PCA analysis performed over selected variables, grouped in clusters (1 to 7) concerning maturation characteristics presented in Table 9.

Cluster 2 presented the higher variability, containing samples of cachaça from a large range of aging time (6 to 72 months). PCA representation evidenced the higher variability over second dimension (16.8 % of total variability), influenced mostly by coniferaldehyde and sinapaldehyde content, which are the first lignin degradation products (LDPs) from guaiacyl and syringyl blocks, related to higher scores on vertical axis (barrels of first use aging cachaças for 6 months). Cluster 1 represented intermediate scores, with intermediate variability, for dimension 2, indicating a more uniform rate of transformation and extraction of early LDPs. Clusters 3 and 4 are closely represented, due to aging similarities, regarding aging markers' content, between samples of cachaça aged in first use barrels, for 18 to 36 months and samples aged in second use barrels, for 24 to 60 months. This proximity is an indicative that those samples may present similar maturation characteristics, despite the differences between barrel previous use and aging time-length.

Clusters 6 and 7 presented the closest representation among all clusters generated, which may be a strong indication that those samples share strong similarities regarding the maturation level, considering their aging markers concentration and characteristics. Those clusters encompass samples from second use barrels, aged for 3 to 24 months and samples from extensive use barrels, aged for 3 to 144 months. The content of aging markers in samples in these clusters are in accordance with quantitative findings obtained by Conner, Paterson and Piggott (1992), that compared guaiacyl and syringyl compounds from exhausted, second filled, first filled and charred

barrels. The Concentration of LDPs for second use and exhausted barrels are similar, which sustains the cluster 6 and 7 results, that may lead to a common maturation class for cachaças.

Cluster 5 is represented by samples aged in first use barrels for 48 to 72 months, all presenting high scores on PCA's first dimension, which indicates a high content of intermediate and final LDPs, as well as higher value for hyperparameters containing sums of LDPs. Those samples of cachaças may share characteristics of high level of maturation due to high concentration of aging markers derived from a longer period of transformation promoted by barrel interaction.

Aiming to establish a new classification system of maturation level of wood barrel aged cachaças, and considering the possibility of obtaining a more succinct and generalized grouping procedure, optimized clusters were adapted, and manually grouped into named classes of maturation that may share general characteristics. So that, individuals from cluster number 2 were relocated into other already established clusters according to their Euclidian proximity: samples from first use American oak, medium toast, aged for 48 months were relocated to cluster 5; samples from first use barrels aged for 6 months were relocated to cluster 1; and samples from first use American oak, medium toast, aged for 36 months and French oak, medium toast, aged for 72 months were relocated to cluster 3. Due to proximity, considering multivariate chemical composition and characteristics observed, clusters 1 and 3 were merged together, as well as clusters 6 and 7, composing classes that express distinct maturation characteristics (Table 10). The classes are presented according to the samples that compose them, as well as average value of total LDP content calculated, and a simplified characteristic description for each one of the maturation levels.

Table 10. Classes of maturation level obtained for sugar cane spirits wood aged under different types of barrels (total LDP in mg/L of anhydrous ethanol).

Maturation Class Name	Samples	Total LDP	Characteristics
Immature	2 nd use 3 to 12 months and all extensive use	4 ± 2	Low extractability / Low transformation
Moderate	2 nd use 18 to 72 months, and French Oak medium toast 1 st use 36 to 60 months	14 ± 5	Moderate extractability / Moderate transformation
Mature	1 st use 3 to 36, and French Oak medium toast 1 st use 72 months	25 ± 9	High extractability / Low transformation
Extra Mature	1 st use, American Oak and French Oak high toast 48 to 72 months	56 ± 6	High extractability / High transformation

LPDs average values obtained for each one of the maturation classes of cachaças were compared to data reported. Cernîşev (2017), who proposed aging classes for brandies, reported that commercial young spirits (aged for less than 5 years) presented a LDP content of 29 mg/ L a.a., moderate (from 5 to 10 years) class presented average content of 45 mg/ L a.a., old (from 10 to 20 years) class presented average content of 55 mg/ L a.a., and extra old (more than 20 years) class presented average content of 61 mg/ L a.a. Extra mature cachaça class may be, therefore, comparable to distillates aged for 10 to 20 years, with maximum experimental aging period equivalent to 6 years. Mature cachaças, differently, would be represented as a young distillate considering Cernîşev's classification.

Canas (Canas, 2017) reported results for a barrel aged brandy, during 4 years in barrel with different toast levels: samples from light toast barrel presented average LDPs content of 21 mg/ L a.a., medium toast barrel presented average LDPs content of 52 mg/ L a.a., and heavy toast barrel presented 93 mg/ L a.a. Reported samples from medium toast barrels displayed LDPs values, toast level and period of aging comparable with experimental extra mature cachaças presented in this study. Light toast, diversely, had LPDs average content close to mature cachaças, which correspond to samples aged for a shorter period. Heavy toast reported by Canas (2017) presented LDPs content even higher than those observed for brandies aged for more than 20 years, reported by Cernîşev (2017). These comparisons support that maturation level may be more suitable to indicate

how developed a barrel aged distillate is, instead of considering numerous other parameters such as barrel toast, species, previous uses and aging period.

3.3.3. Regression models for maturation classes

After obtaining the maturation classes for cachaça samples (immature, moderate, mature and extra mature coded as 1, 2, 3 and 4, respectively), different regression models were applied to evaluate how the classes are correlated to average LPDs, determined by HPLC analysis. Linear and second order models were fitted to the average values of each of the variables selected, individually, and regression coefficients of determination (R^2) were calculated (Table 11).

Table 11. Average concentration of LDP parameters and fitted model coefficients of average individuals from each of the maturation classes.

Class	Immature	Moderate	Mature	Extra mature	R^2 for linear model	R^2 for 2nd order model
Con.	0.2 ± 0.1	0.5 ± 0.2	2 ± 1	1.4 ± 0.4	0.6511	0.7508
Van.	0.4 ± 0.2	1.4 ± 0.5	3 ± 1	6.2 ± 0.6	0.9048	0.9881
Van. Acid	0.6 ± 0.5	2.5 ± 1.2	5 ± 2	9.2 ± 1.9	0.9778	1.000
Sum Guaiacyl	1.2 ± 0.3	4.4 ± 0.9	10 ± 2	16.8 ± 2.8	0.9770	0.9997
Sin.	0.5 ± 0.3	0.9 ± 0.4	4 ± 4	2.6 ± 0.3	0.5598	0.6631
Syr.	2.3 ± 1.2	6.0 ± 2.8	8 ± 5	25.1 ± 5.3	0.8205	0.9603
Syr. Acid	0.5 ± 0.2	3.1 ± 1.1	3 ± 2	11.3 ± 1.2	0.7746	0.9014
Total Syringyl	3.3 ± 0.8	9.9 ± 2.3	15 ± 3	38.9 ± 8.1	0.8704	0.9723
Total Van. Syr.	2.7 ± 1.0	7.4 ± 2.5	11 ± 3	31.4 ± 9.4	0.8396	0.9671
Total Benzoic Acids	1.0 ± 0.3	5.5 ± 1.1	8 ± 2	20.4 ± 1.5	0.8949	0.9678

Fitted linear models presenting $R^2 > 0.80$ were obtained for the parameter total guaiacyl compounds (coniferaldehyde, vanillin and vanillic acid) (Equation 1) and vanillic acid concentration (Equation 2). Those two parameters were further considered in a regression model (Equation 3). Considering models presenting $R^2 > 0.70$, the parameters corresponding to vanillin content and

total benzoic acids were considered to compose the next regression model containing four input parameters (Equation 4).

$$MC = 0.1749 \times [\textit{Sum Guaiacyl}] + 1.0784 \quad (\text{Equation 1})$$

$$MC = 0.3004 \times [\textit{Vanillic Acid}] + 1.1567 \quad (\text{Equation 2})$$

$$MC = 0.1908 \times [\textit{Sum Guaiacyl}] - 0.0291 \times [\textit{Vanillic Acid}] + 1.0772 \quad (\text{Equation 3})$$

$$MC = 0.1162 \times [\textit{Sum Guaiacyl}] - 0.0534 \times [\textit{Sum Benzoic acids}] + 0.0809 \times [\textit{Vanillic Acid}] + 0.2233 \times [\textit{Vanillin}] + 1.0781 \quad (\text{Equation 4})$$

Models represented in equations 3 and 4 exhibited, respectively, $R^2 = 0.857$ (adjusted $R^2 = 0.852$) and $R^2 = 0.865$ (adjusted $R^2 = 0.856$). As result of testing the models to predict maturation classes of samples based on LDPs' content, Equation 4 (combination of sums of guaiacyl and benzoic acids, vanillin and vanillic acid) displayed the greatest accuracy among all model obtained, achieving 86.9 %, followed by Equation 1 (sum of guaiacyl compounds) and Equation 3 (combination of sum of guaiacyl compounds and vanillic acid), both displaying an accuracy equivalent to 85.2 %, and Equation 2 (vanillic acid) achieved 72.1 % of accuracy. Furthermore, the increased accuracy for a multiple input regression model is in accordance with findings reported in adulteration analysis of barrel aged distillates (Canas et al., 2019; Wiśniewska et al., 2015).

3.3.4. CONCLUSIONS

The maturation classes generated for classification of cachaça samples based on lignin degradation products (LDPs), quantified by HPLC method, are in accordance with findings reported by many authors along years: barrel internal conditions are considerably relevant for distillates quality and content of extractable compounds. New barrel with higher levels of toast presented a faster development regarding level of maturation gain. Conversely, exhausted barrel displayed low extraction of LDPs and, regardless longer period of aging, the maturation level gain was proportionally lower than first and second use barrels at a same time-length basis.

Variable selection based on Random Forest algorithm was an effective technique to obtain a lower-dimensional dataset, containing the most relevant information. Cluster analysis performed using Gaussian Mixture Models was able to discriminate samples and supported the

generation of classes of maturation based on general aging markers characteristics (unsupervised method). Hereafter, machine learning techniques may provide a more accurate classification model than linear regression, based on quantitative analytical responses HPLC UV-Vis method.

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4. OPTIMIZATION OF SAMPLE PREPARATION AND INJECTION

Abstract

Wood barrel aging distilled beverages corresponds to a process capable of aggregating flavor compounds that may change sensory profiles and improve distillates quality. The analysis of the flavor compounds to determine degree of maturation of distillate relies most on costly techniques such as chromatography, so that more affordable and less laborious technologies may be suitable for wood-derived flavor determination in beverages, such as digital olfactometry. An electronic nose system reliability may take into consideration appropriate sample preparation method in order to obtain optimal performance over detection of odor compounds. An optimized pre-injection method was established for cachaça analysis in an electronic nose system after an experimental Rotational Central Composite Design, considering the sample preparation factors: incubation temperature, ethanol content of samples, stirring and equilibrium periods. Raw data underwent the chemometric technique Multiple Co-inertia Analysis for feature extraction in prior to optimization design. The chemometric approach for data pre-treatment and analysis demonstrated favorable performance for electronic nose application. The optimal sample preparation included dilution of the aged distillate to lower ethanol content (10% v/v), sample incubation at 49 °C and excluded stirring and equilibrium stages, leading to a simpler and less time-consuming protocol.

Keywords: electronic nose; optimization design; chemometric approach; surface response; distilled beverage.

4.1. INTRODUCTION

Wood aging distilled beverages has been used along centuries in order to improve distillates' flavor, being imperative for high quality beverages such as brandy, whisky, wine spirits (Bortoletto et al., 2018), and eventually rum. The aging process is one of the most important factors that define distilled spirits quality, and although it is not mandatory in Brazilian sugar cane spirit (cachaça) production (Bortoletto & Alcarde, 2013), it is becoming recurrent among appreciated brands focused on product innovation and highest added value.

According to IBRAC (2018), exportation of cachaça reached more than 60 countries in 2017, adding up to US\$ 15.8 million in revenues. This amount corresponds to an increase of 13.4 % in relation to the period of 2016, while in the same period, it was reported an increase of only 4.3 % in exported volume, indicating a proportionally greater increase in revenue compared to the exported volume growth, reflecting a scenario of more added value and better quality cachaças gaining international visibility.

Cachaça production may pursue the Good Manufacturing Practices (GMP) to achieve higher quality production. Besides aging process has a critical control point (Bortoletto et al., 2018), considering factors such as endogenous variations (e.g. wood species and cachaça composition prior to aging) and exogenous (e.g. cellar environment and time-length), it has been difficult to qualitatively analyze the distillate along the aging process, involving subjective decisions and complex cognitive process performed by expert tasters or panel that might be in constant sensory training to execute the task of characterize the distillate and meet the quality standards.

Recent studies investigated the changes in composition of distilled beverages during aging process in wood barrels, remarking aging congeners formation pathways through lignin degradation along time (Cernîşev, 2017; Rodríguez-Solana et al., 2014). The reactions and compounds concentrations in final beverage correspond to actual quality parameters, being even applicable for fraud detection (Wiśniewska et al., 2015). The rate of lignin degradation rely on numerous factors besides aging time, such as barrel number of previous uses, warehouse temperature, and initial ethanol content of the spirit (Conner, 2014). Moreover, Driver (2014) remarks a new tendency in the whisky market quality parameters, indicating that age will be lesser weighted as determinant of quality as other means of differentiation, innovation and ‘premiumization’ may rise.

Quality assessment of aged spirits is currently based on chromatographic techniques, namely HPLC and GC (Aylott & MacKenzie, 2010; Canas et al., 2019; Madrera et al., 2003; Rodríguez-Solana et al., 2014; Simpkins, 1985; Villalon Mir et al., 1992). Those techniques generally require consumables, including solvents and pure substances, and skilled analysts, which may be financially unfavorable for smaller industries considering the number of samples involved in product development. The small cachaça producers may be strict with compliance of GMP, even though they still have scarce access to online analysis to help with instant decision making. In order to appease this situation, a suitable monitoring system for aged cachaça encompassing reliability, practicality and affordability would fulfill the current scenario and complement quality assessment procedures in industry.

Regarding the previous characteristics demanded for a new device, a potential solution to be considered is an electronic nose (or digital olfactometer). As idealized by Jack (2014), an instrument capable of reporting flavor real-time data along production stages of spirits would be a favorable scenario for quality warranty. At the perspective of flavor analysis, a qualitative approach may be more suitable, once high-precision quantification methods are already well established (namely chromatography), and likely achievable. So that, devices able to capture a “smellprint”, combined to pattern recognition trained algorithm, correspond to suitable solutions for flavor

assessment (Ghasemi-Varnamkhasti, Amiri, et al., 2018; Hines et al., 2004; A. D. Wilson & Baietto, 2009), applicable to beverages industry.

The development of such device, dedicated to small producers of *cachaça* productive control and monitoring, and based in electronic nose technology may encompass metal oxide semiconductor gas sensors responsible for transform chemical stimuli, coming from samples headspace, into digital signal for interpretation by pattern recognition machine learning techniques. The applicable algorithms demand data from known samples to train over the classification task (supervised learning), which may have high quality and be representative considering the intended task to obtain satisfactory performance results and consolidate a robust system (Géron, 2019).

Thus, flavor online analysis in industries may support considerable improvements in product standardization, monitoring and assisted decision-making to achieve higher quality and strengthen market of aged *cachaça*. In favor of obtaining representative data in an electronic nose system, it must take into consideration optimized parameter for sample preparation in prior to injection. In this scenario, the most relevant volatile odor compounds from samples may be found in headspace and detrimental factors' influence over sensors operation may be minimized (e.g. high moisture).

Suitable sampling techniques may attend demands such as recovery of compounds of interest, operational speed and simplicity (Martí et al., 2005). These characteristics take into account factors such as sample incubation temperature, stirring period, ethanol content of sample and equilibrium time, that may impact on the recuperation of volatile and semi-volatile compounds to be analyzed.

Physical parameters, such as increasing samples' temperature or longer equilibrium period, may interfere on aroma substances volatility and consequently lead to the concentration in headspace (Scholtes et al., 2015). Physicochemical properties such as sample dilution rate or ethanol content may modulate aroma compounds hydrophobicity, providing a selective release from the sample to the headspace (Seuvre & Voilley, 2017).

Stirring samples in headspace analysis represent the so-called Dynamic Headspace (DHS) method, which is observed in sample preparation techniques for electronic noses devices analysis (Aishima, 1991; Guadarrama et al., 2000; Martí et al., 2005), even presenting better performance for samples discrimination when compared to other techniques such as Static Headspace extraction (Martí et al., 2005). Static Headspace (SHS) corresponds to the most common technique among electronic noses systems (Borràs et al., 2015; Di Natale et al., 1995; Majchrzak et al., 2018; Martí et al., 2005), mainly due to its simplicity (Martí et al., 2005), and provides favorable control when associated to vapor-flow injection (Pearce, 1998; Shurmer & Gardner, 1992).

Considering the numerous possible combinations of factors and the necessity to determine optimal conditions for a specific situation, an experimental design may be appropriate to minimize the number of runs, maximize performance, obtain the best results and turn feasible the optimization task (Da Costa et al., 2013; Naozuka et al., 2011). So that, the methodology selected corresponds to rotational central composite design (RCCD), which merges statistical and mathematical procedures to model the relationships among independent variables (factors or parameters tested) and dependent variable (response) (Malaquias et al., 2018; More & Arya, 2019).

RCCD experiment is based on testing combinations of factors in different levels, considering repetition of central points along the experiment, intercalating with factorial points, for process stability verification, and axial runs for second-order model fitting and checking adequacy (Myers et al., 2009), the last representing an appropriate strategy for eventual saturation-type response displayed by gas sensors (Fleischer et al., 2000).

Despite the considerable reduction of necessary tests, RCCD may consider the feasibility of sequential runs, which may be restrictive considering experimental nature and conditions. So that, a desirable solution relies on a design technique named “confounding”, that correspond to an arranging in smaller-size blocks containing a determined number of treatment combinations in one replicate. Myers et al. (2009) states a consideration over this method based on incomplete blocks design but it is compensated by the special structure of the experimental design construction and analysis.

The present study intended primarily to define the optimal parameters for preparation of sugar cane aged spirits samples for injection in electronic nose prototype, considering incubation temperature, sample dilution, stirring and equilibrium periods. Likewise, it was planned to evaluate the sensors array susceptibility to different sample preparation parameters. The objective of obtaining optimized procedure from surface responses and a fitting model considered suitable implementation of signal data pre-treatment based on chemometric approach.

4.2. MATERIAL AND METHODS

4.2.1. Samples

Samples of Brazilian sugar cane spirit aged in different oak barrels (Table 12) were selected to perform the optimization method based on RCCD. The sugar cane spirit was produced in 2011 in the distillery of the Agri-Food Department of the College of Agriculture, University of São Paulo. Sugar cane juice was extracted, fermented and further distilled following double distillation, based on the method used in the production of whisky (Piggott & Conner, 2003). The barrels were acquired from a French cooperage. The oak woods underwent identical production process. The barrels were constructed with an average volume of 225 L. Aging process started with sugar cane spirit standardized at 55% ABV and was conducted at room temperature (22 ± 5 °C), relative humidity of 55 ± 10 %.

Table 12. Composition of LDP (mg/L) of samples employed for RCCD test session.

Wood	Toast level	Use condition	Aging period (months)	Sample Code	LDP parameter			Maturation level (Cernîşev, 2017)
					Sum S	Sum C	Sum Acs	
French Oak	Medium	Extensive	120	A	17.2	12.4	11.3	Moderate-aged (5-10 yrs)
French Oak	Medium	First fill	36	B	15.2	6.3	9.4	Young (<5 yrs)

LDP – Lignin Derived Products, Sum S – Sum of sinapaldehyde, syringaldehyde and syringic acid, Sum C – Sum of coniferaldehyde, vanillin and vanilic acid, Sum Acs – Sum of vanilic acid and syringic acid.

The characterization of the aged spirits was based on aging-marker compounds, namely products of lignin degradation, analysed by HPLC methodology (Canas, 2017; Cernîşev, 2017; Madrera et al., 2003). This method of classification of distillates includes characteristics beyond the period of barrel aging in years (e.g. 12 or 18-year-old whisky). The maturation parameter was selected as class variable (Géron, 2019) for further training of algorithms to be implemented in electronic nose data analysis.

Considering that maturation parameter is based on LDPs, which present low volatility, and that electronic nose systems are intrinsically based on volatile composition analysis, the

proposed e-nose system intends to correlate both responses and generate a classification model to estimate the samples' level of maturation based on the headspace composition. A similar association considering HPLC data and volatile profile from electronic nose for wheat contamination analysis was successfully implemented by Lippolis et al. (2014).

4.2.2. High Performance Liquid Chromatography analysis (HPLC)

In order to obtain the maturation degree (Cernîșev, 2017) for samples, the quantification of aging congeners was performed over the samples analyzed using high-performance liquid chromatography (HPLC; Shimadzu, model LC-10AD), equipped with two Shimadzu LC-20AD pumps, a UV–vis detector Shimadzu SPD-20A, a system controller CBM-20A and an autosampler. The standard compounds used in this study were vanillin, vanillic acid, syringaldehyde, sinapaldehyde, syringic acid and coniferaldehyde, all supplied by Sigma-Aldrich (St Louis, MO, USA), purity >99 %. The HPLC method employed in this study had two mobile phases composed of water: acetic acid, 98:2 (v/v) (Solvent A), and methanol–water–acetic acid, 70:28:2 (v/v/v) (Solvent B) with gradient elution (Table 2), flow-rate of 1.25 mL/min and volume of injection 20 μ L. A pre-column Shimadzu VP-ODS (1 cm $\times$ 4.6 μ m) and a C18 reversed-phase column model, Shim-pack VP-ODS (4.6 mm $\times$ 25 cm $\times$ 5 μ m), both thermostated at 40 °C, were used. The UV detector was programmed at variable wavelengths (Table 6). The sample preparation involved previous filtering using Millex-HV filter with PVDF membrane (diameter 13 mm, pore size 0.45 μ m). The quantification of the compounds was performed based on external calibration curves of six standard concentrations (Bortoletto & Alcarde, 2013). In total, 62 samples were obtained for the analysis of phenolic compounds by HPLC.

Table 13. HPLC method gradient elution and wavelengths specifications (Bortoletto & Alcarde, 2013).

Time (min.)	Solvent A (%)	Solvent B (%)	Wavelength (nm)
0	100	0	271
6	100	0	280
25	60	40	276
34	60	40	320
37	60	40	320
40	100	0	271
45	100	0	271

Solvent A - water: acetic acid, 98:2 (v/v); Solvent B - methanol–water–acetic acid, 70:28:2 (v/v/v).

4.2.3. Electronic Nose Prototype

The electronic nose device developed included metal oxide semiconductor (MOS) sensors listed in Table 14, a microcontroller, an air pump, internal ventilation unit in sensor chamber, sample flask and software required for data acquisition, processing and statistical analysis (Figure 12). The choice of MOS sensors was considered due to their considerable chemical stability, long lifetime, low humidity interference, affordable cost, high sensitivity and applicability for a wide range of chemicals and foods (Jordan Voss et al., 2019; Kiani et al., 2016a; Rodriguez Gamboa, Albarracin E, et al., 2019; Wijaya, Sarno, Zulaika, et al., 2017).

Table 14. Description of sensors employed in electronic nose prototype and their application according to manufacturer (Hanwei Electronics Co.).

Sensor	Main application
MQ2	LPG (Liquid Petroleum Gas), Methane, Propane, Butane, Hydrogen (H ₂), Alcohol, Natural Gas, flammable
MQ3	Alcohol, Ethanol, Benzene, hexane
MQ4	LPG, Methane, H ₂ , Carbon monoxide (CO), Ethanol
MQ5	H ₂ , LPG, Methane, Propane, Butane, Ethanol, CO, iso-butane, Propane
MQ6	LPG H ₂ , Methane, Propane, Butane, Ethanol, CO, iso-butane, Propane
MQ7	CO, H ₂ , LPG, Methane, Ethanol
MQ8	H ₂ , LPG, Methane, CO, Ethanol
MQ9	CO, Methane, LPG, Flammable gas
MQ135	Ammonia, Benzene, Ethanol, CO ₂ , CO, NH ₄

Figure 12. Scheme of the assembled electronic nose. a – air pump; b – sample flask; c – air drier pre filter; d – power supply; e – microcontroller for data conversion; f – gas sensors' chamber; g – MOS gas sensors; h – computer for data acquisition; i – purge pipeline; j – injection air pipeline.

4.2.4. Experimental design

The experiment investigated four factors: sample incubation temperature during established time (8 minutes), the ethanol content in samples (dilution), stirring and equilibrium periods. In order to obtain a model that considers quadratic behavior of factors in the response (Table 15), a combination of factors comprising a central point (0), its upper (+1) and lower (-1) proportional variations, and axial points ($+\alpha$ and $-\alpha$) were tested. The ranges proposed for coded levels of each factor were based on previous researches which optimized headspace extraction (Zhao et al., 2009). According to previous studies (Collier et al., 2003; Hidayat et al., 2019; Tohidi et al., 2018) sample preparation for electronic nose analysis considered as levels the following factors: incubation temperature (higher than 40°C) and ethanol content (lower than 12 % v·v-1). Lower temperature considered in experimental design was defined as room temperature (25 °C). Higher ethanol content at 40 % (v·v-1) was considered because it represents the level found in commercial distillates. Parameters such as stirring period and equilibrium period length were also proposed due to their influence on headspace extraction according to Henry's law (Burlachenko et al., 2016).

Table 15. Levels of factors analyzed in two sessions of RCCD experiments for sample preparation optimization.

Situation	Variables			
	Incubation Temperature (°C)	Ethanol Content (% v·v-1)	Stirring Period (min.)	Equilibrium Period (min.)
1	48.9 (+1)	33.9 (+1)	4.8 (+1)	2 (-1)
2	48.9 (+1)	33.9 (+1)	1.2 (-1)	2 (-1)
3	48.9 (+1)	16.1 (-1)	4.8 (+1)	8 (+1)
4	31.1 (-1)	33.9 (+1)	1.2 (-1)	8 (+1)
5	48.9 (+1)	16.1 (-1)	1.2 (-1)	8 (+1)
6	31.1 (-1)	16.1 (-1)	4.8 (+1)	2 (-1)
7	31.1 (-1)	33.9 (+1)	4.8 (+1)	8 (+1)
8	31.1 (-1)	16.1 (-1)	1.2 (-1)	2 (-1)
9	40 (0)	25 (0)	3 (0)	5 (0)
10	40 (0)	25 (0)	3 (0)	5 (0)
11	25 (- α)	25 (0)	3 (0)	5 (0)
12	55 (+ α)	25 (0)	3 (0)	5 (0)
13	40 (0)	10 (- α)	3 (0)	5 (0)
14	40 (0)	40 (+ α)	3 (0)	5 (0)
15	40 (0)	25 (0)	0 (- α)	5 (0)
16	40 (0)	25 (0)	6 (+ α)	5 (0)
17	40 (0)	25 (0)	3 (0)	0 (- α)
18	40 (0)	25 (0)	3 (0)	10 (+ α)
19	40 (0)	25 (0)	3 (0)	5 (0)
20	40 (0)	25 (0)	3 (0)	5 (0)

4.2.5. Data treatment

The response variable corresponds to the pair-wised distance between the two distinct samples evaluated according to each pre-injection procedure. Sensor signals were transformed prior to data analysis. The steady-state characteristic considered (Rodriguez Gamboa, Albarracin E, et al., 2019) was calculated as follows: signals from each sensor were corrected in relation to baseline readings ($R_t = (r_t - r_b) / r_b$), where R_t is the standardized signal, r_t represents the raw signal

for sample at the steady-state of injection, and rb is the baseline signal. Finally, signals were filtered by Weighted Median (WM) method (L. Yin et al., 1996), considering a calculation window correspondent to ten previous samples, and weight ratio between current read and median ($\alpha/(1-\alpha)$) with $\alpha = 0.1$, in order to obtain a smoother signal (Broesch, 2009).

The pre-treated sensor signals obtained were further pretreated employing a Standard Normal Variate (SNV), in order to eliminate additive effects (Bylesjö et al., 2009; Johansson et al., 1984; Rietjens, 1995), then feature extraction performed by Principal Component Analysis (PCA), which is a technique of transformation of original data, extracting most of the information into uncorrelated variables called principal components, containing most of existing variance among the data points (Kiani et al., 2016a).

The PCA scores generated for each sensor were analyzed by Multiple Co-inertia Analysis (MCOA) (Hanafi et al., 2006), which effectively enables the simultaneous comparison of numerous tables through variance optimization among individuals and correlation increase among scores of those individual tables (Bady et al., 2004). This method provides synthetic final global coordinates (scores) and percentage of variance explained (loadings) that were employed in Euclidian weighted distance calculation (de Leeuw & Pruzansky, 1978). Those resulting values obtained from ChemFlow (Rossard et al., 2016) were computed in Statistica 13.5.0 (TIBCO, 2018) software for ANOVA and Fitted Surface Response modeling analysis.

4.3. RESULTS AND DISCUSSION

4.3.1. Chemometric Approach

After MCOA performed over data originated from signals from all sensor array, coming from both samples A and B that underwent the twenty distinct design conditions, a multidimensional plan was obtained presenting presented over 95 % of total variance (Figure 13). Samples A and B pairwise comparison was done taking into consideration the variance weighted coordinates (scores), which was approached as an intra-situation variation metric.

Figure 13. Representation of multivariate coordinates (scores from MCOA performed over total sensor array signals) between samples A and B analyzed after different experimental pre-injection situations (1 to 20).

4.3.2. Sensor Array Performance

In order to verify which sensors displayed more responsiveness for paired distinction between samples, weighted mean and standard deviation of distances between samples A and B were calculated from individual (by-sensor) MCOA scores, considering all twenty situations tested (Figure 14). These metrics may relate a higher variation to a greater sensibility of each sensor to variations in experimental conditions tested.

Figure 14. Centrality and variation metrics, by sensor, of multivariate distance obtained for each injection condition tested.

The sensors that resulted on greater variation on weighted distance values obtained for the experimental conditions tested were MQ 4, 6, 7 and 135, which were respectively developed for quantification of hydrocarbons (methane, propane and butane), LPG (isobutane and propane), carbon monoxide, and aromatic compounds plus alcohol. The observed range existing for each of the sensors may be related to sample properties (Seuvre & Voilley, 2017) that directly affect sensors responses, such as favoring volatilization of molecules with properties analogous to those presented by compounds for which the sensors were developed.

Considering the observed behavior of sensors, it is possible to state that there are sensors more sensible to variations on sample treatment. So that, optimum conditions choice may take into consideration their responses. Lower values of weighted distance (lower distinction power of the sensor array) may be associated to differentiation on concentration of compounds of interest in the headspace inject into sensors' chamber.

Among the four sensors with greater variation, MQ 135 behavior may represent an important role in electronic nose assemble for cachaça analysis. Voss et al. (2019) reported that, for the ethanol quantification in beer, MQ 135 response was redundant for performance improvement of the mentioned task, possibly due to a lower affinity or specificity to ethanol detection. Regarding other volatile odor compounds (VOCs) present in aged cachaça, its contribution may be relevant for classificatory task and increase discriminant ability after optimized method for sample preparation.

4.3.3. Experiment Design

Concerning the optimization design, significant ($\alpha = 0.05$) modeling results were observed for linear effect of stirring period, linear and quadratic effects for ethanol content, and significant linear interactions for incubation temperature versus stirring and equilibrium period, and ethanol content versus stirring period. Incubation temperature isolated was not a significant factor at $\alpha = 0.05$ for model fitting analysis. This factor's higher and lower levels displayed an important increase over multivariate distance (vertical axis '*Dist*') when combined to the other inspected factors (Figure 15).

Figure 15. Incubation temperature response in combination with other factors in sample preparation for electronic nose readings.

Among the factors explored, ethanol content displayed unanimously better conditions for multivariate differentiation between samples at lower concentrations (Figure 16). This behavior may be related to sensors construction and to already reported ethanol and interferences on MQ sensors (Martí et al., 2005). Besides, major water content may benefit the volatility of non-polar compounds (Seuvre et al., 2000) that may interact more specifically with sensors that presented greater variability in different conditions tested (MQ 4, 6, 7 and 135). Concerning the ethanol content relation to stirring and equilibrium periods, both presented more important sample differentiation when ethanol content was at the lower and the other factors at higher levels.

Figure 16. Response surfaces relating sample preparation factors (ethanol content versus stirring period and equilibrium period) for electronic nose differentiation of samples.

4.3.4. Optimized Model

The model determined from coded variables (Equation 5) in RCCD experiment presented R^2 and adjusted R^2 respectively equal to 0.9344 and 0.8962, which corresponds to a favorable ratio of total variance explained by the model over experimental data.

$$Z = -0.85645 \times E + 0.07993 \times E^2 - 0.025945 \times S + 0.055023 \times I \times E - 0.087221 \times I \times Eq - 0.053161 \times E \times S \quad (\text{Equation 5})$$

In order to obtain the optimum conditions for each factor to enhance electronic nose differentiation capacity for aged sugar cane spirit samples, a desirability profile was performed considering the predicting interval ($-\alpha$ to $+\alpha$) of proposed model for coded variables (Figure 17).

Figure 17. Desirability profile obtained for factors explored in RCCD.

According to desirability results, it was possible to obtain optimum values for each factor tested during sample preparation before injection in electronic nose. The optimum un-coded values for factor correspond to incubation temperature of 49.2 °C, and zero for magnetic plate stirring period and equilibrium time. Those levels represent a maximum desirability for the model obtained. Ethanol content behavior, on the other hand, present a quadratic displaying higher desirability for 40 % (v·v-1), although, the level of 10% (v·v-1) displayed a closely high desirability level (0.967).

The adoption of lower level of ethanol content for optimized sample preparation for electronic nose readings, may not only influence positively on aging compounds' solubility (Seuvre et al., 2000) but also avoid sensors poisoning effect. The diluted sample preparation matches the approach describe for human panel sensory analysis in whisky quality assessment, where samples are standardized at around 20 % alcohol by volume in order to avoid burning sensation caused by ethanol (Jack, 2014) and increase the level of certain volatile compounds in headspace (Conner et al., 1998). This similarity may be desirable for future investigations able to compare results of sensory analysis performed by humans versus those performed by the e-nose.

Even though the isolated effects of incubation temperature were not significant for modeling, an optimum condition was observed regarding the established conditions for its

interactive factors (stirring and equilibrium periods). The desirability for incubation temperature reached a maximum at 49.2 °C, same value obtained at higher incubation temperature, which may indicate a saturation behavior of volatile compounds in headspace for electronic nose injection. It is known that cold temperature of samples during sensory analysis decreases flavor intensity perceived by panel of tasters due to direct impact on volatility of compounds of interest (Jack, 2003). Heating of whisky samples because of exothermic heat of dilution of mixture of ethanol and water enhanced the spirits' flavor for the panel evaluation (Costigan et al., 1980).

The results for stirring and equilibrium periods lead to dismissing those sample preparation procedures, which may increase analysis productivity by eliminating time-consuming steps for electronic nose system. Moreover, a part of hardware - namely a magnetic stirring plate - is dismissed according to the desirability profile. Stirring and equilibrium periods optimized at lower level may be related to headspace composition equilibrium achieved in absence of heating because of sequential sample preparation.

As expected, this fact points for an important role of molecules volatility in electronic nose differentiation between samples. The volatilization phenomenon is based on saturated vapor pressure, a physicochemical property, that corresponds to the measurable ability of compounds to migrate from a liquid matrix to vapor phase (Seuvre & Voilley, 2017).

4.4. CONCLUSIONS

The RCCD enabled, through desirability analysis over a fitted model surface result, establishing condition for sample preparation in order to maximize the differentiation power of an electronic nose system based on MOS sensors.

Injection response data must undergo pretreatment for signal noise reduction and variance feature extraction. The chemometric tools and analysis employed in this experiment were effective to extract variance causes from the electronic nose readings and the multivariate distance was an efficient metric to explore samples differentiation in this system.

The performance of distinction between two samples of cachaça from different maturation levels (lignin-derived composition) using the electronic nose device was more associated to incubation temperature and ethanol content of samples than stirring and equilibrium time. So that, further electronic nose analysis over aged sugar cane spirits will be driven according to the sample preparation procedure based on dilution of spirits to 10 % (v-v-1) of ethanol content, followed by incubation at 49 °C during 8 minutes.

A broader investigation into headspace composition after the present sample preparation procedure may be achieved considering further GC-MS analysis, which may possibly aid to determine new aging-markers and detail the potential of the electronic-nose response to specific flavor compounds found in wood-aged distilled beverages.

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5. CACHAÇA CLASSIFICATION USING THE ELECTRONIC NOSE

ABSTRACT

Aging distillates in wooden barrels is a secular technique that accretes flavor to the beverage. Cachaça is a typical Brazilian sugar cane spirit. In spite of aging is not mandatory for cachaça, this finishing process increases the spirit's quality and adds value to the product. The evolution and transformation of distillate's compounds in wood barrels depend on multiple factors, such as aging period, barrel usage, barrel internal toasting, wood species, cellar conditions. These factors are related to extraction and transformation of compounds by wood structure degradation, which is characterized as "maturation level". The maturation level may be determined by High Performance Liquid Chromatography (HPLC), although it is a costly analytical technique and therefore not accessible to some producers. In order to allow producers to monitor the maturation level of spirits during aging, an electronic nose device and a data processing model to classify samples of cachaça into four distinct categories (immature, moderate, mature, and extra mature) were developed. The electronic nose captures the smellprint of a sample through gas sensors, and the signal is processed to exhibit the correspondent level of maturation as output. The models obtained 90 % (neural network) and 95 % accuracy (random forest) in classification task. The developed system has potential to evaluate sensory and chemical properties of distillates, representing an accessible device to numerous producers.

Key-words: sugarcane spirit, barrel-aging, maturation level, innovation, electronic nose, disruptive technology.

5.1. INTRODUCTION

Wood aging distilled beverages has been used along centuries in order to improve distillates' flavor, being imperative for high quality beverages such as brandy, whisky, wine spirits (Bortoletto et al., 2018), and eventually rum. The aging process is one of the most important factors that define distilled spirits quality, and although it is not mandatory in Brazilian sugar cane spirit (cachaça) production (Bortoletto & Alcarde, 2013), it is becoming recurrent among appreciated brands focused on product innovation and highest added value.

According to IBRAC (IBRAC, 2018), exportation of cachaça reached more than 60 countries in 2017, adding up to US\$ 15.8 million in revenues. This amount corresponds to an increase of 13.4% in relation to the past year, while in the same period, it was reported an increase of only 4.3% in exported volume, indicating a proportionally greater increase in revenue compared to the exported volume growth, reflecting a scenario of more added value and better quality cachaças gaining international visibility.

Cachaça production may pursue the Good Manufacturing Practices (GMP) to achieve higher quality production. Besides aging process being a critical control point (Bortoletto et al., 2018), considering factors such as endogenous variations (e.g. wood species, cachaça composition in prior to aging) and exogenous (e.g. cellar environment, time-length), it has also a difficulty to qualitatively analyze the distillate along the aging process, involving subjective decisions and complex cognitive process performed by expert tasters or panel that might be in constant sensory training to execute the task of characterize the distillate and meet the quality standards.

Recent studies investigated the changes in composition of distilled beverages during aging process in wood barrels, remarking aging congeners formation pathways through lignin degradation along time (Cernîșev, 2017; Rodríguez-Solana et al., 2014). Those reactions and compounds concentrations in final beverage correspond to actual quality parameters, being even applicable for fraud detection (Wiśniewska et al., 2015). The kinetics of lignin degradation rely on numerous factors besides aging time-length, such as barrel number of previous uses, warehouse temperature, and initial ethanol content of the spirit (Conner, 2014). Moreover, Driver (2014) remarks a new tendency in the whisky market quality parameters, indicating that age will be lesser weighted as determinant of quality as other means of differentiation, innovation, and a greater standard quality may rise.

Quality assessment of aged spirits is currently based on chromatographic techniques, namely HPLC and GC (Aylott & MacKenzie, 2010; Aylott et al., 1994; Canas, 2017; Canas et al., 2019; Madrera et al., 2003; Rodríguez-Solana et al., 2014; Simpkins, 1985; Villalon Mir et al., 1992). Those techniques generally require consumables, including solvents and pure substances, and intensively-trained work force, which may be financially unfavorable for smaller industries considering the number of samples involved in product development. The small cachaça producers may be strict with compliance of GMP, even though they still have scarce access to online analysis to help with instant decision making. In order to appease this situation, a suitable monitoring system for aged cachaça encompassing reliability, easy-to-use and affordable would fulfill the current scenario and complement quality assessment procedures in industry.

Regarding the previous characteristics demanded for a new device, a potential solution to be considered is an electronic nose (or digital olfactometer). As idealized by Jack (2014), an instrument capable of reporting flavor real-time data along production stages in spirits production would be a favorable scenario for quality warranty. At the perspective of flavor analysis, a qualitative approach may be more suitable, once high-precision quantification methods are already well established (namely chromatography), and likely achievable. So that, devices able to capture a “smellprint”, combined to pattern recognition trained algorithm, correspond to suitable solutions

for flavor assessment (Ghasemi-Varnamkhasti, Amiri, et al., 2018; Hines et al., 2004; Wilson & Baietto, 2009), applicable to beverages industry. Viejo et al. (2019) supported the integration of novel methods and technologies, involving cheaper analytical instruments and automated techniques such as computer vision, artificial intelligence and machine learning algorithm, to model and predict quality of beverages based on different measurable parameters. Successful applied assays in beverages industry displayed a large potential for quality assurance and increasing efficiency (Folz & Mol, 2019; Schlenker, 2019).

The development of such devices, dedicated to small producers of cachaça productive control and monitoring, and based in electronic nose technology may encompass metal oxide semiconductor gas sensors responsible for transform chemical stimuli, coming from samples headspace, into digital signal for interpretation by pattern recognition machine learning techniques. The applicable algorithms demand data from known samples to train over the classification task (supervised learning), which may have high quality and be representative considering the intended task to obtain satisfactory performance results and consolidate a robust system (Géron, 2019).

5.2. MATERIAL AND METHODS

5.2.1. Samples

Sugar cane spirit was produced at Pilot-scale Distillery of the Department of Agri-Food Industry, Food and Nutrition, in College of Agriculture “Luiz de Queiroz” – ESALQ (University of São Paulo) in 2013, by the responsible team members at that moment. Sugar cane variety SP 81-3250 was grown at ESALQ and the plants, immediately after harvesting, were forwarded to sugar cane juice extraction employing a three-roll mill. The juice was conducted towards a decanter for elimination of solid impurities (soil and bagasse fractions). Sugar cane juice soluble solid concentration was further adjusted to 18 °Brix in a juice-standardization tank by addition of water, leading to the wort that underwent fermentative process.

The wort was pumped to 1,500L-stainless steel fermentation vessels where yeast strain CA-11 (LNF Latino Americana, Bento Gonçalves, RS, Brazil) was pitched following manufacturer instruction and recommendations. After achieving maximum attenuation after (24 h at 30 °C), fermented sugar cane juice underwent double-distilling procedure described by Piggot and Conner (2003), in a steam heated copper still with capacity for 1000 L, assembled with a 2-plates neck followed by a dephlegmator. First distillation corresponded to exhaustion of the ethanol contained in fermented juice without fraction separation, obtaining the so-called “flegma”. The successive

second distillation relies on fractioning “flegma” into three portions: the foreshots corresponding to 2 % of total “flegma” volume; the sugar cane spirit, obtained by distillate recovery until alcohol content reached 60 % (v·v-1) at the condenser output; and the feints, corresponding to distillate collected from 60 % ethanol content until exhaustion of ethanol.

The barrels for aging the spirit. with capacity to 225 L, were made from French and American Oak woods (*Quercus petraea* and *Quercus alba*, respectively), medium toasting (Tonelleries de Bourgogne, Meursault, France), and high toast for French Oak. The double-distilled sugarcane spirit (63.5% ethanol v/v) was aged in the barrels (in triplicate) at room temperature (22 ± 3 °C) and a relative humidity of $55 \pm 10\%$, and protected from vibrations. Samples of 25 mL were collected at the same level from the center of the barrels at 3, 6, 9, 12, 18, 24, 36, 48, 60, and 72 months of aging period for the analysis of maturation-related congeners for first filled barrels, 3 to 60 months, with the previous interval described, for second filled barrel aging, and 3, 6, 12, 18, 24, 36, 48, 60, 72, 120, and 144 for extensively used barrel samples.

5.2.2. E-nose prototype

The electronic nose device developed for this research included metal oxide semiconductor (MOS) sensors listed in Table 16, a microcontroller, an air pump, internal ventilation unit in sensor chamber, sample flask and software required for data acquisition, processing, and statistical analysis (Figure 18). The choice of MOS sensors was considered due to their considerable chemical stability, long life, low humidity interference, affordable cost, high sensitivity and applicability for a wide range of chemicals and foods (Jordan Voss et al., 2019; Kiani et al., 2016a; Rodriguez Gamboa, Albarracin E, et al., 2019; Wijaya, Sarno, Zulaika, et al., 2017).

Table 16. Description of sensors employed in electronic nose prototype and their application according to manufacturer (Hanwei Electronics Co.).

Sensor	Main application
MQ2	LPG (Liquid Petroleum Gas), Methane, Propane, Butane, Hydrogen (H ₂), Alcohol, Natural Gas, flammable
MQ3	Alcohol, Ethanol, Benzene, hexane
MQ4	LPG, Methane, H ₂ , Carbon monoxide (CO), Ethanol
MQ5	H ₂ , LPG, Methane, Propane, Butane, Ethanol, CO, iso-butane, Propane
MQ6	LPG H ₂ , Methane, Propane, Butane, Ethanol, CO, iso-butane, Propane
MQ7	CO, H ₂ , LPG, Methane, Ethanol
MQ8	H ₂ , LPG, Methane, CO, Ethanol
MQ9	CO, Methane, LPG, Flammable gas
MQ135	Ammonia, Benzene, Ethanol, CO ₂ , CO, NH ₄

Figure 18. Scheme (I) of the assembled electronic nose and current prototype (II). a – air pump; b – sample flask; c – air drier pre filter; d – power supply; e – microcontroller for data conversion; f – gas sensors' chamber; g – MOS gas sensors; h – computer for data acquisition; i – purge pipeline; j – injection air pipeline.

5.2.3. Sample preparation and injection

Sugar cane spirit samples were tested for ethanol content by micro-distillation and further quantification in Anton Paar DMA-4500 density meter. Then, samples were standardized at 10 % (v·v⁻¹) ethanol obtaining a volume equivalent of 20 mL, conditioned in 250 mL reagent bottle with screw cap and taken to water bath under controlled temperature of 49 °C for 8 minutes.

Electronic nose prototype injection system is based on a diaphragm air compressor 'Big Air', model A320, to carry either volatile compounds or fresh air to sensors chamber, and a filter containing silica gel beads (3-5 mm), to obtain a moisture free carrier gas for headspace sample. The headspace generated in sampling bottle is pumped inside the sensor array chamber through a set of pneumatic valve and inert material hose. The intake of headspace volatile gases is controlled by a manually driven valve situated on reagent bottle cap, and the pump action is controlled by the injection procedure defined in Arduino. The microcontroller signal activates the pump through a relay module, for 10 seconds (at a flow rate of 3.5 L·min.⁻¹).

5.2.4. Data acquisition

Data acquisition corresponds to the conversion of analog readings made by each of the MQ gas sensors (0 to 5 V) to a digital value equivalent to an integer value with maximum size of 10 bits (0 to 1023). The acquired signals are divided into three distinct phases: baseline recording, injection, and recover responses (Ghasemi-Varnamkhasti, Apetrei, et al., 2018; Rahimzadeh et al., 2019; L. Zhang & Zhang, 2018). Baseline record correspond to the reading of standardized air inside sensor array chamber during 30 s, obtaining sensors' reading values for standardization of further responses. Next, admission valves are opened and pump is activated (40 s), enabling the carriage of sample's head space into sensors chamber, so the system stays in injection response status during 300 s more. Finally, recover response procedure undergoes for 760 s, with valves opened and constant flow of fresh standardized air through the sensor array chamber, and data is collected to verify sensors' readings return to baseline conditions during this purging stage (Figure 19).

Figure 19. Plot of sensor array raw data representing the phases during injection of an aged cachaça sample in electronic nose system.

5.2.5. Data pre-processing and feature extraction

Raw data underwent a signal pre-treatment pipeline (Géron, 2019) in order to eliminate sensor additive noise, feature extraction, and avoid redundant information for further classification task.

During the admission of samples headspace into the sensor chamber, a natural variation on temperature and humidity may occur in the system. As indicated by Voss et al. (Jordan Voss et al., 2019), temperature and humidity dependent variations are already expected and manufacturers' datasheet provide a compensation function parameter (Table 17) in order to enhance signal quality as presented in the following equation (Equation 6), where compensated signal (r_t) is in function of the raw signal (R_t), temperature (t), umidity (u), and constants ($\alpha_0, \alpha_1, \beta, \xi$).

$$r_t = R_t / (a_0 t + a_1 t^2 + \beta + \xi) \quad (\text{Equation 6})$$

Table 17. Values of constants employed in the compensation equation (Jordan Voss et al., 2019).

Sensor	α_0	α_1	β	ξ	R^2
MQ2	-0.0266	0.0003	-0.0023	1.4700	0.9989
MQ3	-0.0229	0.0002	-0.0036	1.4640	0.9960
MQ4	-0.0103	0.0001	-0.0033	1.2760	0.9970
MQ5	-0.0145	0.0001	-0.0040	1.3350	0.9881
MQ6	-0.0126	0.0001	-0.0034	1.2920	0.9941
MQ7	-0.0157	0.0001	-0.0036	1.3580	0.9876
MQ8	-0.0106	0.0001	-0.0012	1.0880	0.9962
MQ9	-0.0158	0.0001	-0.0037	1.3590	0.9875
MQ135	-0.0258	0.0003	-0.0023	1.4660	0.9978

Then, compensated signals from each sensor were transformed in degree of reaction (Aguilera et al., 2012; Kiani et al., 2016a) through baseline correction from signals obtained immediately before sample injection in the electronic nose chamber in order to minimize sensor variations (Gutierrez-Osuna, 2002). The average baseline values (30 reading points) obtained prior to each injection were subtracted from values obtained to each sensor in each of the test results, which is called “baseline-removing pretreatment” (Y. Yin et al., 2014) or “fractional baseline correction” (Tohidi et al., 2018), where R_t correspond to the baseline treated signal, r_t is the current compensated signal value, and r_b is the current injection baseline value.

$$R_t = ((r_t - r_b)) / r_b \quad (\text{Equation 7})$$

This transformation is advantageous due to both dimensionless result and normalization processing, resulting on a per-unit and proportional variation in relation to the baseline obtained in each pre-injection for each sensor. Next, a noise reducing technique was employed to eliminate random points that may impart further pattern recognition procedure (Tohidi et al., 2018). So that, a Weighted Median (WM) filter (L. Yin et al., 1996), where R_t correspond to the baseline treated signal, M_{ep} is the median calculated over previous ten readings, Y is the filtered signal, and $\alpha = 0.1$.

$$Y = (1 - \alpha) \times M_{ep} + \alpha \times R_t \quad (\text{Equation 8})$$

Considering the entire sensor array, 9,900 observations points are obtained for each sample injection. Due to probable existing information redundancy, as well as in order to optimize

computational meaningful information, the number of variables was further reduced to 3,483 by steady-state and transient features extraction, based on pre-treatment employed by Rahimzadeh et al. (Rahimzadeh et al., 2019) represented in the Table 18.

Table 18. Steady-state and transient feature extraction techniques employed in signal treatment for pattern recognition task.

Feature type	Formula	Description
Steady state	Y_i (40s)	First response after sample injection
	Y_i (340s)	Last response of injected sample before recover phase
	$x = \int_{t1}^{t2} Y_i(t)dt$	<i>Steady-state</i> x is the accumulative summation of change in the reaction degree (Zhang et al., 2007), with varying $t1$ and $t2$ for both injection (30 and 340) and recover (341 and 930) stages
Transient	ΔG_i (injeção)	Time length for signal rise from 20 to 60% of maximum value (Llobet et al., 1997)
	ΔG_i (purga)	Time length for signal rise from 60 to 20% of maximum value (Llobet et al., 1997)
	$w = dY_i(t)/dt$	Transient w is the rate of the reaction in the reaction degree (Zhang et al., 2007), with varying t for both injection (30-70s) and recover (341-650s) stages
	$Y_i'(t) = At^2 + Bt + C$	Coefficients A , B and C represent the fitting second order model of recover stage (341-440s)

Where i corresponds to the number of sensor varying from 1 to 9.

In order to reduce even more the number of input variables, a recursive feature elimination with cross-validation (RFECV) algorithm was implemented to perform feature selection (Géron, 2019), based on the importance displayed by each specific variable to classify the samples, eliminating redundant features and variables with low contribution to the classification task. The algorithm employed was implemented using Scikit Learn (Pedregosa FABIANPEDREGOSA et al., 2011), and its parameters were: classification model Random Forest (RF), stratified 10-fold cross-validation, with model scoring based on accuracy results. The algorithm provided a list containing 1,534 optimized features.

5.2.6. Classification algorithms tested

Prior to submit the feature extracted data to different classification algorithms, procedures oriented to data visualization were performed in order to obtain an exploratory first approach to electronic nose signals data. PCA and T-SNE analysis were implemented as a resource for dimensionality reduction (Voss et al., 2019) and graphic representation of samples based on their smellprint features.

Next, data stratification was performed in order to separate observation to model training (75 %) and testing (25 % of total entries) proportionally by class of maturation level. Then, learning algorithms K-Nearest Neighbors, Support Vector Machine (SVM), Random Forest (RF) and Artificial Neural Network (ANN) were fed with the training dataset and its performance was measured by predictive accuracy performed on testing dataset. The classifiers tested that provided higher accuracy responses (RF and ANN) were further selected, and individually optimized concerning the sample stratification and their respective tuning parameters (Géron, 2019), as presented in Table 19. Tuning parameters were defined for ANN models to avoid overfitting on training and test data and obtain a model that generalizes more efficiently over validating data avoiding Gaussian noise (R. C. Wilson et al., 2019).

Table 19. Parameters tuned to obtain optimized classification algorithm for maturation level evaluated by electronic nose.

Classifier	Parameters
Random Forest (RF)	<p>Sample stratification (training, test and validation);</p> <p>Node criterion: gini, entropy;</p> <p>Number of estimators: 50 to 500 (increments of 50 estimators);</p> <p>Screening: 30-fold model validation.</p>
Artificial Neural Network (ANN)	<p>Sample stratification (training, test and validation);</p> <p>Number of layers;</p> <p>Number of nodes per layer;</p> <p>Activation function per layer;</p> <p>Optimizer: stochastic gradient descent and adadelta;</p> <p>Learning rate and momentum;</p> <p>Number of epochs;</p> <p>Model loss function.</p>

5.3. RESULTS AND DISCUSSION

5.3.1. Exploratory data visualization

An initial exploratory analysis of extracted features was performed to evaluate the distributions of values by maturation class established in this work. Figure 20 indicates the possibility of differentiation of at least one maturation class from the others. Lower-dimensional representations (PCA and T-SNE) were then performed to better evaluate the distribution of samples concerning features from electronic nose observations (Figure 21).

Figure 20. Mean values of different features obtained after during recover stage of the electronic nose analysis of maturation level of samples. (A - MQ2 sensor signal feature, B – MQ9 sensor signal feature, C – MQ5 sensor signal feature, D – MQ6 sensor signal feature, E – MQ3 sensor signal feature)

Figure 21. Lower-dimensional representations of samples of cachaca samples of different maturation levels using PCA (A) and T-SNE (B) methods.

PCA results indicated a significant ($\alpha < 0.01$) separation between Moderate and Mature classes on first dimension, between Immature and Mature classes on second dimension, and between Extra mature and Immature classes on third dimension. PCA's first dimension is mostly correlated to the intercept of MQ-9 (methane, CO and LGP gas sensor) sensor signal obtained at the initial purging stage of injection. This feature corresponds to the intercept (window of three observations) calculated around 330 seconds after signal obtaining start. MQ-9 was reported as a significant sensor for beer regression task, described by Voss et al. (Jordan Voss et al., 2019), who analyzed different beer styles with different alcohol content.

Second PCA dimension is most related to MQ-5 sensor intercept calculated around 390 seconds after signal obtaining start. The third PCA dimension is correlated again to the calculated intercept, this time for signals from sensors MQ-5 in earlier stage (around 300 seconds after start), and also MQ-8 sensor signal intercept also at 300s. For RF dataset MQ-6 sensor feature also displayed among the 20 most correlated to third dimension. In general, the distribution of the cited PCA-relevant sensors' values displayed a bimodal asymmetric behavior, in accordance with the separations previously described for each dimension. MQ-5 and 8 displayed significant impact on classification of peach, monitored during maturation cycle, as reported by Voss et al. (Voss et al., 2019), with regards to key aroma compounds from different classes (aldehydes, alcohols, esters, ketones and lactones).

PCA represented an efficient method to separate some classes of barrel aged cachaças, such as most of Mature samples from Immature or Moderate, even though the lack of clear separation for Extra Mature samples in relation to the other classes was observed for the first three PCA dimensions. Despite the fact that PCA enables dimension reduction to a human-observable scale, considering a multivariate space, van der Maaten and Hinton (2008) report this linear technique as being focused on representing dissimilar observations far apart. A more suitable representation strategy proposed by the authors for high-dimensional data would be a technique based on keeping the low-dimensional projections of very similar data points close together, which is typically not possible with a linear mapping such as PCA. For that, Maaten and Hinton (2008) proposed a new algorithm called t-SNE, a variation from Stochastic Neighbor Embedding (Hinton & Roweis, 2003), for visualizing the data resulting from a generate pairwise similarity matrix.

The t-SNE technique enables preserving most part of the high-dimensional data local structure, while also revealing global structure such as the presence of clusters at several scales. A disadvantage of method is that it is oriented exclusively for data visualization, considering the unclear aspect of optimization towards dimensionality reduction Maaten and Hinton (2008). t-SNE representation provided an alternative spatial distribution in relation to PCA. A central or inner

concentration of Mature class observations is noticeable, while the other classes grouped more peripherally. Immature class was split into two groups of samples over the first “dimension” of t-SNE, one containing labels of second fill samples that aged for no longer than 12 months, and other containing samples of extensively used barrels aged for a period of time longer than 12 months.

5.3.2. Optimization of sample stratification

The performance of classifiers is dependent on representativeness of samples employed in training stage of the ML classification task (Borovicka et al., 2012). The optimization of training and testing data subsets was performed considering different random states for the data-split preparation, considering a steady split rate of 0.75 for training subset and 0.25 for testing subset and the stratifying parameter set as the maturation class in all cases. The stratification promoted a proportional distribution of classes both in training and testing subsets. For Neural Network (NN) models, a second stratification split was performed to obtain a smaller dataset (cross-validation data with split rate of 0.2) to evaluate classification accuracy along the epochs during learning. To obtain the optimized stratified training datasets, a 50-fold cross validation was performed based on models’ accuracy, considering each learning models’ default parameters (Chollet, 2017; Pedregosa et al., 2011).

As a result, each of the classifiers implemented (Random Forest, NN with Adadelta optimizer, and NN with Stochastic Gradient Descent optimizer) was associated to a determined optimal data subset applied to model training. The general similarity among those data subsets is presented in Table 20. The training subsets that underwent different classifiers presented similarity coefficients greater than 0.81, therefore it represents a considerable overlapping among entry individuals. The most expressive similarity is observed between the Neural Network classifiers (Ada and SGD), representing over 0.83 for training subset and 0.31 for testing subset.

Table 20. Similarity of training and testing data subsets employed in each of the implemented classifiers.

Train				Test			
	RF	Ada	SGD		RF	Ada	SGD
RF	1.000	0.818	0.810	RF	1.000	0.286	0.257
Ada	0.818	1.000	0.832	Ada	0.286	1.000	0.314
SGD	0.810	0.832	1.000	SGD	0.257	0.314	1.000

To deeply assess sample subsets differences, the samples distributions were compared (Figure 22) regarding their species (American Oak – *Quercus alba*, or French Oak – *Quercus petraea*), level of toast (medium or heavy), previous uses (first, second, or extensive), and the barrel aging length (expressed in months).

Figure 22. Distribution of samples in data subsets for training (A index) and testing (B index) of different classifiers, concerning the characteristics wood species (index 1), level of toast (index 2), previous usage (index 3), and aging time length (index 4).

The optimized training subset applied in ADA classifier displayed a greater proportion of American Oak samples, compared to the other classifiers. Regarding distribution of types of toasts, RF classifier training subset displayed higher number of samples of presenting heavy toast. Concerning the levels of previous use, RF testing subset presented proportionally more second use samples, and ADA testing subset contained a higher number of samples from first use. Concerning

aging period distribution, RF was the only model that displayed absence of one aging class (84 months for training and 48 months for testing dataset).

Despite the differences described, regarding individual samples, all datasets contained proportional maturation classes observations, namely all datasets had the same number of 'immature', 'moderate', 'mature' and 'extra mature' samples. These optimized datasets obtained were further employed for classification model optimization.

5.3.3. Classification performance

The presented ANN models tested, with different optimizers (Adadelta and SGD), were established after fine tuning of parameters. Both ANN were built based on Kullback-Leibler divergence function loss, once the present electronic nose performs a classificatory task (Yang, 2019). All classificatory models (ANN and RF) were fine tuned to avoid overfitting, being NNs set to a learning threshold (early stop) of 0.001 of loss function gain after five learning epochs, and RF number of estimators determined by out-of-bag error decrease of 0.001 (entropy) after five trees added. ANN models were tuned by adjustments in neural net structure (number of nodes per layer and number of layers), optimizer learning rate and momentum, and number of learning epochs.

The training dataset accuracy for NN models were 96.1 % and 99.2 %, and testing dataset accuracy (test split realized during learning process) of 67.4 % and 74.4 %, for Adadelta and SGD optimizers, respectively. RF model achieved 90.7 % of accuracy on training dataset. The validation of those models was performed with new data, with number of observations per class proportional to those previously observed for training dataset, input to obtained models. The results of prediction on validation data are presented below as confusion matrix (Tables 21 to 23).

Table 21. Confusion matrix of predicted maturation class for cachaça samples using Neural Network model (Adadelta optimizer).

		Predicted classes				
		IMMAT	MODERATE	MATURE	EXT_MT	Accuracy (%) by class
Actual classes	IMMAT	5	2	0	0	71.4
	MODERATE	1	11	0	0	91.7
	MATURE	0	0	20	0	100.0
	EXT_MAT	0	0	0	4	100.0

Overall accuracy: 93.02 %

Table 22. Confusion matrix of predicted maturation class for cachaça samples using Neural Network model (SGD optimizer).

		Predicted classes				
		IMMAT	MODERATE	MATURE	EXT_MT	Accuracy (%) by class
Actual classes	IMMAT	6	1	0	0	85.7
	MODERATE	3	9	0	0	75.0
	MATURE	0	0	20	0	100.0
	EXT_MAT	0	0	0	4	100.0

Overall accuracy: 90.70 %

Table 23. Confusion matrix of predicted maturation class for cachaça samples using Random Forest model.

		Predicted classes				
		IMMAT	MODERATE	MATURE	EXT_MT	Accuracy (%) by class
Actual classes	IMMAT	6	1	0	0	85.7
	MODERATE	0	12	0	0	100.0
	MATURE	0	0	19	1	95.0
	EXT_MAT	0	0	0	4	100.0

Overall accuracy: 95.35 %

SGD model (Table 22) displayed the lower misclassification of sample into a more superior maturation level than the actual (one immature sample classified as moderate). Whereas this model represented the highest number of samples classified as a lower maturation level as its actual. Considering those characteristics, it is possible to evaluate the e-nose SGD model as a more conservative characteristic, avoiding type II errors despite assuming more type I errors.

RF (Table 23) was the predictive model that displayed the higher overall accuracy (over 95 %), presenting the lowest number of misclassification among the predictive models. RF misclassification (two cases) overvalued the samples, indicating their belonging to more superior maturation classes. RF was the only model to present an error on classifying ‘mature’ cachaça sample.

Adadelata model (Table 21) presented an intermediate accuracy performance (93 %) compared to the other predictive models, and its classification performance presented 100 % accuracy for ‘mature’ and ‘extra mature’ groups, only one misclassification into a lower maturation category (‘moderate’ classified as ‘immature’), and two ‘immature’ samples overvalued as ‘moderate’, corresponding to one more observation compared to the SGD and RF predictive models.

In order to compare the present electronic nose, developed for barrel aged cachaça classification according to their maturation level, other e-noses developed for alcoholic beverages analysis were evaluated, due to the inexistence of reported data for such a device developed for wood-aging characteristics analysis on alcoholic beverages, and the fewness of e-noses developed for distilled beverages analysis.

Sikorska et al. (Sikorska et al., 2007) evaluated the discriminant power of GC-MS used as an electronic nose to discriminate beer stored under different conditions, obtaining an accuracy ranging from 52 to 100 % for different classes, representing an overall accuracy for Linear Discriminant Analysis (LDA) method equivalent to 86.3 %, and 78.6 % for k-Nearest Neighbors (kNN) method. Even though the equipment employed in this study is more sophisticated, counting on a mass spectrum detector and GC, the authors reported an accuracy lower than the one found in the e-nose built during this project. This may be associated to the data analysis selected, which may indicate that a less costly hardware may be suitable for specific analytical classification tasks.

Santos et al. (Santos et al., 2017) reported models for beer classification among 8 classes, considering a portable MOS-based electronic nose, with accuracies equivalent to 87.5 % for backpropagation neural network (BP-NN) and 92.9% for probabilistic neural network (PNN) algorithms. The samples reported corresponded to different beer styles and brands, so that the e-nose described by the authors was able to provide satisfactory smell-print data and algorithm classification response.

Ghasemi-Varnamkhasti et al. (2011) evaluated beer samples aged in condition to mimic longer period, obtaining 5 classes of the same beer type, by a MOS-based electronic nose prototype. The authors reported an accuracy of 90.5 % using BP-NN algorithm, and 83.3 % with PNN to analyze PCA transformed data from smell-prints of samples, considering a suitable method for storage monitoring and shelf-life control for alcoholic beers. Liu et al. (Liu et al., 2016) also performed a discriminant flavor analysis of beer on beer samples using an electronic nose device with MOS sensors, obtaining overall accuracy equivalent to 90.1 % obtained for a predictive model based on fuzzy neural network (FNN).

Prieto et al. (Prieto et al., 2011), reported the performance of a MOS-based e-nose device developed for polyphenol content estimation based on flavor profile of red wines, obtaining 82.6 % of correlation between those characteristics with a partial least squares discriminant analysis (PSL-DA), which is noticeable to highlight the correlation of a non-volatile characteristic with wines smell-print. Similar, the e-nose developed in this study was able to provide satisfactory performance to evaluate a characteristic that is related not only with volatile profile of distilled beverages (maturation level), but also to semi-volatile aging markers commonly analyzed by HPLC method.

Considering volatile and complex characteristics derived from wood aging process, Wei et al. (2014) tested the discrimination power of an electronic nose device to evaluate wine samples aged in barrels, age with oak chips and non-aged. The device was able to successfully differentiate

samples with 88.9 % accuracy for LDA applied after PCA data transformation, and 94.4% accuracy using Mahalanobis distance calculated for PCA coordinates of samples.

Ragazzo-Sanchez et al. (2008) performed a classification analysis of different alcoholic beverages (beer, wine, tequila, vodka and whisky) using a commercial MOS-based electronic nose (model FOX 4000 with 18 gas sensors), and results were analyzed by discriminant factorial analysis (DFA). The authors reported an accuracy of 90.5 % for classification task, with misclassification solely between tequila and whisky samples. Evaluating only distilled beverages' samples (2 tequilas, 3 vodkas and 4 whiskies), the authors reported an accuracy of 88 %. As evidenced by the reported results (Ragazzo-Sanchez et al., 2008), the misclassification occurred among the wood-aged distillates, indicating that the use of a commercial e-nose and the described data analysis were not sufficient to perform distillates' classification with a higher level of accuracy.

Wu et al. (2019) developed an e-nose system with MOS gas sensors able to discriminate samples of Chinese liquors with ethanol content ranging from 46 to 53 % (v/v), obtaining accuracy values of 90.0 %, 95.5 % and 98.8 % for kNN algorithm classification performed over features extracted using PCA, discriminant PCA (DPCA) and fuzzy DPCA (FDPCA) respectively. The samples tested correspond to commercial distillates, and the authors did not report any other chemical parameter that would represent the differences among those beverages, besides ethanol content.

Rodrigues et al. (2016) reported a low-cost electronic device based on computer vision and pattern recognition features, successfully employed for cachaça analysis concerning classification of different wood types (amburana, oak and castanheira) and different aging periods. The classification algorithms were applied to computer vision data and traditional physicochemical parameters (pH, density and volatile compounds analyzed by GC). The authors reported an accuracy between 97.1 and 99.0 % for the computer vision system, versus 92.4 to 96.3 % for chemical features, to discriminate among wood types using different types of algorithms. Nevertheless, aging-period classificatory determination displayed an inferior performance: from 68.6 to 70.5 % for computer vision features, 85.7% with ensemble classification (using the power of all classification algorithms together), versus a range from 78.1 to 84.8 % for traditional chemical features. The authors highlighted the advantageous cost of their device that enables superior or equivalent results compared to results from a traditional and costly equipment structure. The electronic nose developed in this project may be a suitable technology to integrate the device described by Rodrigues et al. (Rodrigues et al., 2016), merging features from different aspects of wood-aged cachaça, based on chemical composition (e-nose) and physical properties from the distillates (computer vision).

Jo et al. (2016) performed a MS-e-nose implementation to classify vinegars aged during different periods, obtaining linear separation for all classes ($R^2 \geq 0.99$) using Discriminant Factor Analysis (DFA). This performance was achieved using a commercial Heracles Electronic Nose (Alpha MOS) integrated to classical gas chromatography.

Viejo et al. (2019) reported recent studies that applied ML algorithms to evaluate alcoholic beverages: classification of whiskies samples according to their age, cask material, distillery and variety, obtaining accuracy above 95 % using radial basis function networks (RBFN) implemented for Ramah spectra data (Backhaus et al., 2012); classification of tequilas through UV-Vis spectrometry into three classes (white, rested and aged), achieving accuracy of 89 % using quadratic discriminant analysis (QDA) performed after PCA transformation (Ceballos-Magaña et al., 2012); and classification of geographical origin of Cabernet Sauvignon wines (Brazilian and Chilean) using Support Vector Machine (SVM) algorithm, which displayed an accuracy of 89 %, based on physicochemical parameters (da Costa et al., 2016).

5.4. CONCLUSIONS

Neural network (NN) models provided lower accuracy (90.7 and 93.0 %) when compared to Random Forest algorithm (95.5 %). Despite displaying lower overall accuracy, the NN models presented higher accuracy than RF model for classification cachaça samples of higher maturation level. The accuracy for different models tested were satisfactory, considering the alcoholic matrix that was analyzed by electronic nose prototype developed in this project and the semi-volatile nature of compounds of interest (aging markers) related to maturation level.

More new observations may be tested to better evaluate classification models accuracy, and repeated observations of samples used for training may positively influence on overall system's accuracy. Further GC-MS (scan mode) analysis of samples, prepared similarly to those analyzed by the e-nose, may be useful to better assess what are the major compounds extracted in the presented methodology and correlate their concentration to specific gas sensors signals obtained by the e-nose, as well as obtaining detailed smellprint data related to cachaças of different maturation levels.

Further development for the current e-nose system developed may include: unified process for data pre-processing and classification task (single platform), evaluation of long frame temporal drift of sensor signals, analyze commercial samples in HPLC and e-nose device to validate the prototype for wider sample evaluation and classification.

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6. GENERAL CONCLUSIONS

The “maturation classes” determined in this project correspond to a classification method, applicable to barrel aged cachaças, which takes into consideration the contents of lignin derived products in the aged distillate. These classes (immature, moderate, mature, and extra mature) may be interpreted as a qualitative factor that encompasses both quantitative, namely concentration of aging markers obtained by HPLC analysis, and qualitative characteristics, namely barrel usage, wood species, barrel internal toast, and aging period. The new parameter called maturation class is intended to be an attribute that contains information about the extraction and transformation of wood degradation compounds, serving as a feature to assist monitoring of the barrel aging process. The maturation class may also be interpreted as a leveling tool for creating and standardizing different products in the barrel aged distillate industry, representing a potential complement for Brazilian regulations about barrel aged cachaça characterization.

The techniques implemented for data analysis in this project were suitable for developing a full electronic nose system intended to assess the quality of distilled beverages. The optimization of the method for sample preparation was a determinant factor for the project path. Sample preparation and injection procedures required prevention of gas sensor poisoning by ethanol, reported in the literature, and assurance of extraction of aroma compounds of interest related to barrel aged cachaça samples.

Different classification algorithms were employed to identify the electronic nose smellprint patterns in samples and relate (or train) them to the maturation classes previously established. A proper signal treatment of electronic nose signals was a key-element to reduce dimensionality of data obtained by the e-nose device, as well as to extract the most relevant features associated with the peculiar maturation classes in the samples analyzed. Artificial intelligence and machine learning algorithms provided good accuracy for sample classification according to the maturation classes, compatible or superior to that reported in the literature.

The electronic nose technology has wide potential of application in the beverage industry, suitable for different processes and different types of alcoholic beverages. Due to low assembly cost and simple operation, the scalability of e-nose technology depends on its adoption in productive facilities (market pull). The electronic nose device may be an accessible and useful equipment adopted for monitoring of production and assisting online decision making, providing qualitative and even quantitative responses to alcoholic beverage producers, based on odor parameters captured by different gas sensors.

APPENDIX

APPENDIX A. LEARNING CURVES OF ANN MODELS' ACCURACY AND LOSS WITH DIFFERENT OPTIMIZER METHODS (A – SGD, B - ADA).

APPENDIX B. LINKS TO INTERACTIVE GRAPHS ON RPUBS WEB DOMAIN.

Clusters visualization after PCA dimensionality reduction (2D-representation) - <https://rpubs.com/giovannisil/643877>

Clusters visualization after PCA dimensionality reduction (3D-representation) - - <https://rpubs.com/giovannisil/643875>

Maturation classes visualization after PCA dimensionality reduction (3D-representation) - - <https://rpubs.com/giovannisil/644178>

APPENDIX C. FIRST PAGE OF PUBLISHED CHAPTER 2

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Agricultural Engineering

Integrated technology roadmapping in startups: a case study of an AgTech in the Cachaça industryGiovanni Casagrande Silvello¹, Alex da Silva Alves^{2*}, André Ricardo Alcarde¹¹Universidade de São Paulo/ESALQ – Depto. Agroindústria, Alimentos e Nutrição, Av. Pádua Dias, 11 – 13418-900 – Piracicaba, SP – Brasil.²Universidade de São Paulo/ESALQ – Depto. Economia, Administração e Sociologia, Av. Pádua Dias, 11 – 13418-900 – Piracicaba, SP – Brasil.

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ABSTRACT: Companies develop strategies to describe where they want to go and how they will reach their destination. Business strategies are useful but may not be sufficiently detailed for areas of high importance, such as technology and innovation. In this paper we examined the effort of building a technology roadmap with an early growth stage company located in the state of São Paulo, Brazil. Roadmaps are easy to design yet flexible tools that can allow decision makers to explore a myriad of possible strategies. However, the challenges ahead for new companies facing uncertain growth scenarios demand that framework conditions be adequately addressed, and that innovation culture and technology management tools are integrated with the technology roadmapping strategy. Based on the empirical evidence collected from the startup studied, along with the literature and interviews with key stakeholders, this paper developed a pathway to support technology and innovation plans for startups going through similar growth stages and provides directions for future research in the area, given the scarcity of evidence available of new high-tech companies' efforts in planning and developing new products

Keywords: Industry 4.0, technology roadmap, cachaça, electronic-nose

Introduction

Production and service provision systems of any kind have an irreversible tendency towards the introduction of innovations that help them devise new business models, products, processes and services with impacts both inhouse and on the market. Such a tendency triggers strategies and actions encompassing the development of technology solutions that can meet a firm's commitment towards the promotion of quality improvements, market expansion and profitability. However, despite the myriad of successful cases and experiences appearing in both the literature and the

As a result, small high tech firms in the agricultural segment, known as Agtechs, are growing in importance in the country as a response to, on the one hand, policy stimuli, and, on the other, to meet the demand of agricultural firms looking for cost-effective solutions that will assist them in dealing with productivity bottlenecks, increased competition, international penetration, and new product development challenges.

This paper focused on the technology planning and management efforts of an early growth stage firm operating in one segment that has been, for decades past in Brazil, a synonym for technological backwardness and social distress: the cachaça industry.

APPENDIX D. FIRST PAGE OF PUBLISHED CHAPTER 3

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New approach for barrel-aged distillates classification based on maturation level and machine learning: A study of cachaça

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ARTICLE INFO

Keywords:

Wood aging
Distillate
Cachaça
Maturation level
Machine learning

ABSTRACT

The evolution of distillate beverages during the aging process in wooden barrels is related to the extraction and transformation of wood compounds. Even though time is an important factor for the quality of distillates, other attributes concerning wooden barrel features such as wood species, internal toast, and previous use are of paramount importance to confer maturation characteristics to the beverage. We evaluated the level of lignin-derived products (LDPs) in Brazilian sugar cane spirit (cachaça) aged in different barrels using high performance liquid chromatography with ultraviolet/visible (HPLC UV-Vis) analysis, and compared the results to aging classes reported for distillates applying multivariate principal component analysis (PCA). Unsupervised machine learning techniques of clustering were applied to identify similarities among samples and form cohesive groups concerning wood derived phenolic compounds. In an effort to provide a new metric for distillates aged in wooden barrels, four new classes of maturation were determined as a qualitative parameter. We describe their characteristics, based on quantitative parameters equivalent to guaiacyl and syringyl compounds, as well as a regression model for the classification of new samples (86.9% of prediction accuracy).

APPENDIX E. FIRST PAGE OF PUBLISHED CHAPTER 4

Journal of Agriculture and Food Research 2 (2020) 100037

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Journal of Agriculture and Food Research

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Experimental design and chemometric techniques applied in electronic nose analysis of wood-aged sugar cane spirit (*cachaça*)

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ARTICLE INFO

Keywords:

Electronic nose
Optimization design
Chemometric approach
Surface response
Distilled beverage

ABSTRACT

Wood barrel aging distilled beverages corresponds to a process capable of aggregate flavor compounds that may change sensory profiles and improve distillates quality. The analysis of the flavor compounds to determine degree of maturation of distillate relies most on costly techniques such as chromatography, so that more affordable and less laborious technologies may be suitable for wood-derived flavor determination in beverages, such as digital olfactometry. An electronic nose system reliability may take into consideration appropriate sample preparation method in order to obtain optimal performance over detection of odor compounds. An optimized pre-injection method was established for *cachaça* analysis in an electronic nose system after an experimental Rotational Central Composite Design, considering the sample preparation factors: incubation temperature, samples ethanol content, stirring period and equilibrium period. Raw data underwent the chemometric technique Multiple Co-inertia Analysis for feature extraction in prior to optimization design. The chemometric approach for data pre-

APPENDIX F. PATENT PENDING PROCESS FOR ELECTRONIC NOSE DEVELOPED

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