fermentation

MDPI

Article

The Impact of Wet Fermentation on Coffee Quality Traits and Volatile Compounds Using Digital Technologies

Hanjing Wu [1], Claudia Gonzalez Viejo [1,*], Sigfredo Fuentes [1], Frank R. Dunshea [1,2] and Hafiz A. R. Suleria [1,3,*]

[1] Digital Agriculture, Food and Wine Group, School of Agriculture and Food, Faculty of Veterinary and Agricultural Sciences, The University of Melbourne, Parkville, VIC 3010, Australia
[2] Faculty of Biological Sciences, The University of Leeds, Leeds LS2 9JT, UK
[3] Centre for Chemistry and Biotechnology, School of Life and Environmental Sciences, Deakin University, Waurn Ponds, VIC 3217, Australia
* Correspondence: cgonzalez2@unimelb.edu.au (C.G.V.); hafiz.suleria@unimelb.edu.au (H.A.R.S.); Tel.: +61-470-439-670 (H.A.R.S.)

Abstract: Fermentation is critical for developing coffee's physicochemical properties. This study aimed to assess the differences in quality traits between fermented and unfermented coffee with four grinding sizes of coffee powder using multiple digital technologies. A total of N = 2 coffee treatments—(i) dry processing and (ii) wet fermentation—with grinding levels (250, 350, 550, and 750 µm) were analysed using near-infrared spectrometry (NIR), electronic nose (e-nose), and headspace/gas chromatography–mass spectrometry (HS-SPME-GC-MS) coupled with machine learning (ML) modelling. Most overtones detected by NIR were within the ranges of 1700–2000 nm and 2200–2396 nm, while the enhanced peak responses of fermented coffee were lower. The overall voltage of nine e-nose sensors obtained from fermented coffee (250 µm) was significantly higher. There were two ML classification models to classify processing and brewing methods using NIR (Model 1) and e-nose (Model 2) values as inputs that were highly accurate (93.9% and 91.2%, respectively). Highly precise ML regression Model 3 and Model 4 based on the same inputs for NIR (R = 0.96) and e-nose (R = 0.99) were developed, respectively, to assess 14 volatile aromatic compounds obtained by GC-MS. Fermented coffee showed higher 2-methylpyrazine (2.20 ng/mL) and furfuryl acetate (2.36 ng/mL) content, which induces a stronger fruity aroma. This proposed rapid, reliable, and low-cost method was shown to be effective in distinguishing coffee postharvest processing methods and evaluating their volatile compounds, which has the potential to be applied for coffee differentiation and quality assurance and control.

Keywords: coffee arabica; fermentation; colour; volatiles; electronic nose; gas chromatography; artificial neural networks; machine learning

Citation: Wu, H.; Viejo, C.G.; Fuentes, S.; Dunshea, F.R.; Suleria, H.A.R. The Impact of Wet Fermentation on Coffee Quality Traits and Volatile Compounds Using Digital Technologies. *Fermentation* **2023**, *9*, 68. https://doi.org/10.3390/fermentation9010068

Academic Editor: Spiros Paramithiotis

Received: 8 December 2022
Revised: 5 January 2023
Accepted: 10 January 2023
Published: 13 January 2023

1. Introduction

Coffee is one of the most prevalent beverages worldwide owing to its stimulating function, rich and complex aroma and flavour, and health benefits. Coffee's sensory quality depends on various factors in the entire production chain, such as plant varieties, geographical and climate conditions, processing methods, roasting levels, storage, and brewing methods [1,2]. Generally, green coffee seeds can be obtained using one of three methods, including dry, semi-dry, and wet processing [1].

Fermentation is the critical procedure in wet processing to submerge de-pulped coffee beans underwater to remove the attached mucilage with the involvement of microorganisms [3]. The chemical composition of coffee seeds can be altered during fermentation by metabolic processes, especially the concentration of water-soluble compounds, including free amino acids, free sugars (glucose and fructose), caffeine, trigonelline, and chlorogenic acids [4]. Different microorganisms, such as yeast, bacteria, and fungi, can produce

various enzymes, alcohols, and acids from sugar consumption, which may influence the sweetness, acidity, and salt content of coffee beans [5,6]. Free amino acids and soluble carbohydrates are prominent precursors of volatile and non-volatile compounds, including carbon dioxide, ketones, pyrazines, acetic acid, glycerol, ethers, and aldehydes, which would affect the development of the coffee flavour and colour in the following roasting process [2,7,8]. Furan derivatives (25–41%) are the most volatile compounds contributing to the coffee flavour, with sweet, bread-like, and caramel aromas [9]. However, Knopp, Bytof and Selmar [7] reported that fermented coffee beans contained lower fructose and glucose than dry-processed coffee beans, which could influence the generation of furan derivatives during Maillard reactions and caramelisation because of the lack of substrates. Pyrazines, known for their hazelnut aroma, are the second most abundant volatile compounds in coffee at around 25 to 39%, which are also generated through complex interactions between sugar and amino acids [10]. Phenols or phenolic compounds are also important aromatic contributors in coffee brew. For example, chlorogenic acids in coffee beans could bring a bitter, acidic, and astringent flavour to coffee brew [11]. Duarte, Pereira and Farah [4] and Lee, et al. [12] commented that fermented coffee has more a aromatic flavour, with fruity and acidic attributes, and with fewer bitter, burnt, and woody notes. Haile and Kang [8] also reported that most indigenous microorganisms presumably lack important characteristics and cannot improve the coffee's flavour and aroma as expected. It is notable that ketones could be the most significant off-flavour makers when coffee beans are overfermented [13].

Brewing is another avenue bringing considerable impact on the sensory properties of final coffee products at the consumer end, related to the particle size of the coffee powder, infusion time, and temperature [14,15]. After grinding, the beans are reduced into small particles with a micro and mesoscale dimension, which generally ranges from micrometers to around 1000 μm [16]. Therefore, the coffee's aromatic compounds developed in the coffee seeds could be released, extracted, and dissolved into the final beverage when brewing [2]. Commonly, the particle size of ground coffee is classified into four groups: coarse, medium, fine, and very fine. The formation of smaller coffee powders provides a large particle surface that allows the rapid liberation of carbon dioxide and the reduction in the diffusion distance for soluble substances during brewing, which improves the transfer of colloidal substances to the liquid phase, as well as the physicochemical and final sensory properties [16,17].

Generally, headspace solid-phase microextraction/gas chromatography–mass spectrometry (HS-SPME/GC-MS) is used for coffee beverages to discriminate and evaluate the chemical patterns of aromatic volatile compounds [6,18]. The sensory analysis of coffee aroma is also widely conducted via quantitative descriptive analysis (QDA®) with a descriptive sensory panel [19]. However, considering the recognition threshold level and accuracy of human perceptions, it could induce stimulus errors and be less objective, sensible, and more time-consuming [20–22]. Electronic nose (e-nose) with artificial neural networks (ANNs) has been developed and used commercially as a substitute of those traditional methods when assessing aromas or other chemometrics in beer, wine, tea, juices, and meat [23–27]. Similarly, developed e-nose has also been used in coffee to assess, discriminate, and predict the sensory descriptors and geographical origin, roasting degree, and cultivar [18,28–30]. Although it has multiple advantages, including minimum levels of sample preparation required, interferences among involved chemical reagents, and the simultaneous determination of multiple compounds, the majority of commercial e-nose devices are non-portable and still cost-prohibitive for small and medium companies [31,32]. Moreover, scarce information is available on comparing natural and fermented coffee; the combination of GC-MS and e-nose coupled with machine learning modelling could be applied to distinguish and predict the differences between volatile compounds in natural and fermented coffee.

Therefore, this study aimed to assess the differences in quality traits between fermented and unfermented coffee brewed from four grinding levels of coffee powder using digital technologies, including NIR, portable, and low-cost e-nose, GC-MS, and supervised

machine learning (ML) modelling. A total of four ML models were developed using NIR (Model 1) and e-nose (Model 2) as inputs to classify the coffee types. Models 3 and 4 were developed using NIR and e-nose outputs as inputs, respectively, to predict the relative abundance based on the peak area of 14 volatile aromatic compounds measured by GC-MS.

2. Materials and Methods

2.1. Sample Preparation

A total of ten (n = 10) natural (n = 5) and fermented (n = 5) arabica coffee beans (250 g per kind) with two varieties (geisha and bourbon) were purchased online from eight different companies, traders, or retailers: (1) Tin Man Coffee Roasters, Melbourne, Australia; (2) Ninety Plus Coffee Estates, LLC, Volcán, Panama; (3) BENCH COFFEE CO. LT COLLINS, Melbourne, Australia; (4) Vacation Coffee, Melbourne, Australia; (5) Manhattan Coffee Roasters, Rotterdam, Netherlands; (6) Code Black Investments Pty Ltd., Melbourne, Australia; (7) ONA Coffee, Melbourne, Australia; and (8) Proud Mary Coffee Roasters PTY Ltd., Melbourne, Australia; they were used in the intended research project. For each sample, 40 g of whole coffee beans were taken, separated into four parts (10 g per part), and ground into a powder with each particle size (250, 350, 550, and 750 µm) accordingly using a Breville automatic coffee grinder (Breville® Smart Coffee Grinder Pro BCG820BSS, Breville Pty Ltd., Sydney, Australia). To avoid variation from grinder heating, interval breaks were applied to cool down the machine every eight grinding operations. For each measurement, 2.5 g of ground coffee with each particle size was brewed using a Breville Creatista® Plus espresso machine (Breville Pty Ltd., Sydney, Australia) under the Espresso mode of a constant pouring volume of 25 mL at 78 °C. This step of each sample was repeated in triplicate.

2.2. Physicochemical Characterisation of Coffee Brew

The research was conducted at the University of Melbourne, Parkville campus, Melbourne, Australia, at the Digital Agriculture, Food and Wine (DAFW) and Food science labs.

2.2.1. pH Measurement

The pH values of brewed coffee samples were measured in triplicate using the LAQUAtwin Compact pH meter (LAQUAtwin, HORIBA's, Kyoto, Japan). A total of three buffer solutions (pH 4.0, 7.0, and 9.0) were used for machine calibration.

2.2.2. Salt Determination

The salinity levels of brewed coffee samples were determined using an ATAGO digital pocket salt meter (PAL-ES2, Tokyo, Japan) through the conductivity of the solution in triplicate. The measurement range of the meter was 0.00 to 10.0% (g/100 g of salt concentration).

2.2.3. Colour Measurement

The colour of natural and fermented coffee samples with different roasting levels was measured using a handheld colourimeter NIX (Nix Pro Colour Sensor™, Nix Sensor Ltd., Ontario, CA, USA) in triplicate. The colour coordinates (L*, a*, and b* colourimetric) were recorded and analysed. The colour difference (ΔE) was calculated using the following equation:

$$\Delta E = \sqrt{\left(L^*_{aF} - L^*_{aUF}\right)^2 + \left(a^*_{aF} - a^*_{aUF}\right)^2 + \left(b^*_{aF} - b^*_{aUF}\right)^2}$$

where *aF* is the average value of fermented coffee, and *aUF* is the average value of unfermented coffee.

2.3. Near-Infrared Spectroscopy (NIR) Analysis

A portable NIR device, the microPHAZIR™ (RX Analyzer; Thermo Fisher Scientific, Waltham, MA, USA), was used to evaluate the samples according to Gonzalez Viejo,

et al. [33], with a spectral range of 1596 to 2396 nm, in triplicate and three measurements per replicate. A Whatman® filter paper (Whatman plc., Maidstone, UK; qualitative grade 3, 7.0 cm) was submerged in each coffee sample to be measured. A white background was placed at the top to avoid signal noise from the environment during the measuring. The absorbance values from the dry and empty filter paper were subtracted from the wet filter paper with the samples to obtain only the chemical fingerprinting of the coffee sample, as described by Gonzalez Viejo et al. [33]. Data obtained from the NIR device were analysed using Savitzky Golay filters by The Unscrambler X ver.10.3 (CAMO Software, Oslo, Norway) software to obtain the first derivative data.

2.4. Identification and Quantification of Volatiles by HS-SPME-GC-MS

Volatile compounds in coffee samples were analysed by headspace/gas chromatography–mass spectrometry (HS-SPME-GC-MS) based on Gonzalez Viejo, Tongson and Fuentes [31] and Wu, Lu, Liu, Sharifi-Rad and Suleria [11] with some modifications. GC-MS analysis was conducted via a gas chromatograph (6850 series II Network GC System, Agilent Technologies, Santa Clara, CA, USA) coupled to an HS-SPME system (PAL RSI I20, Zwingen, Switzerland) and a mass spectrometer (5973 Network Mass Selective Detector, Agilent Technologies, Santa Clara, CA, USA). A 30 m DB-Wax capillary column (Agilent Technologies, Santa Clara, CA, USA) with a 0.25 mm internal diameter anda 0.25 µm film thickness was chosen with the combination of 65 µm PDMS/DVB fibre (Fused Silica, Sigma Aldrich, Castle Hill, NSW, Australia). The carrier gas was helium with a 60 kPa column head pressure. Coffee samples were incubated for 15 min at 60 °C, followed by 15 min extraction and 6 min desorption. The GC oven programme was set as follows: 40 °C for 5 min continued with an increase to 190 °C at the rate of 5 °C/min for 8 min; subsequently, the temperature reached 240 °C at a rate of 10 °C/min and was maintained for 10 min. The acquisition was in SCAN mode (35–350 m/z). The solvent delay time was 2 min.

The coffee sample (2.5 mL) mixed with 20 µL 100 mg/L 3-heptanone as the internal standard was added into vials and then injected as the temperature gradient programme above. The linear retention index (LRI) was calculated according to the alkane standard (C_7–C_{30}) with the following equation, which compares the retention time of one target compound (RT_x) with those of n-alkanes with n and n + 1 carbon eluted before and after the target compound (RT_n):

$$\text{LRI (target compound)} = 100 \times \frac{\text{RTx} - \text{RT}_\text{n}}{\text{RT}_{\text{n+1}} - \text{RT}_\text{n}} + \text{n}$$

The LRI and mass spectrum of volatile compounds detected in coffee samples are compared to the data in the NIST Chemistry WebBook spectrum library (NIST2017) and NIST mass spectra database (Washington, DC, USA), respectively. Semi-quantification was conducted by comparing the response area of the target compound and internal standard with the known concentration after the LRI and compound MS were confirmed.

2.5. Electronic Nose (E-Nose) and Data Extraction

A low-cost and portable e-nose developed by the Digital Agriculture Food and Wine Group at the University of Melbourne (DAFW-UoM) was used to assess the coffee samples, according to Gonzalez Viejo et al. [31,32,34]. The device was composed of nine different gas sensors: (i) MQ3: Alcohol (ethanol), (ii) MQ4: Methane (CH_4), (iii) MQ7: Carbon monoxide (CO), (iv) MQ8: Hydrogen (H_2), (v) MQ135: NH_3/alcohol/benzene, (vi) MQ136: Hydrogen sulfide (H_2S), (vii) MQ137: NH_3, (viii) MQ138: Benzene/alcohol/NH_3, and (ix) MG811: Carbon dioxide (CO_2). Samples were exposed to sensors for 1 min after 30 s machine baseline readings. The outputs were analysed by a customised Matlab® R2021a (Mathworks, Inc., Natick, MA, USA) developed by the DAFW-UoM, which displayed the curves to select the most stable area of the signals and subdivided it into 10 sections to calculate 10 mean values per curve automatically.

2.6. Statistical Analysis and Machine Learning (ML) Modelling

All results were pure results subtracted by blanking or control values and expressed as mean ± standard error of three independent analyses. All the statistical analyses were conducted using Minitab 19 (Minitab® for Windows Release 19, Minitab Inc., Chicago, IL, USA) and GraphPad Prism 9 (GraphPad Prism version 9.0 for Windows, GraphPad Software, La Jolla, CA, USA). One-way analysis of variance (ANOVA), along with Tukey's honest significant differences (HSD) as a *post hoc* test ($\alpha = 0.05$), were used to assess significant differences between samples.

A total of four ML models (Figure 1) were constructed using a Matlab® R2019b code to assess 17 training algorithms and to find the most accurate models with no under- or overfitting in a loop [35]. Models 1 and 2 were developed for classification using the absorbance values obtained by NIR spectra within 1596 and 2396 nm and e-nose outputs as inputs, respectively, to predict the type of coffee and the grinding size of the coffee powder: (i) fermented, 250 µm, (ii) fermented, 350 µm, (iii) fermented, 550 µm, (iv) fermented, 750 µm, (v) unfermented, 250 µm, (vi) unfermented, 350 µm, (vii) unfermented, 550 µm, and (viii) unfermented, 750 µm (Figure 1a,b). Model 1 was constructed using the Bayesian regularisation algorithm, and Model 2 was constructed using the Levenberg–Marquardt algorithm. Samples were divided using a random data division (*dividerand*) algorithm as 70% for the training stage, 15% for testing, and 15% for validation using a performance algorithm based on the mean squared error (MSE).

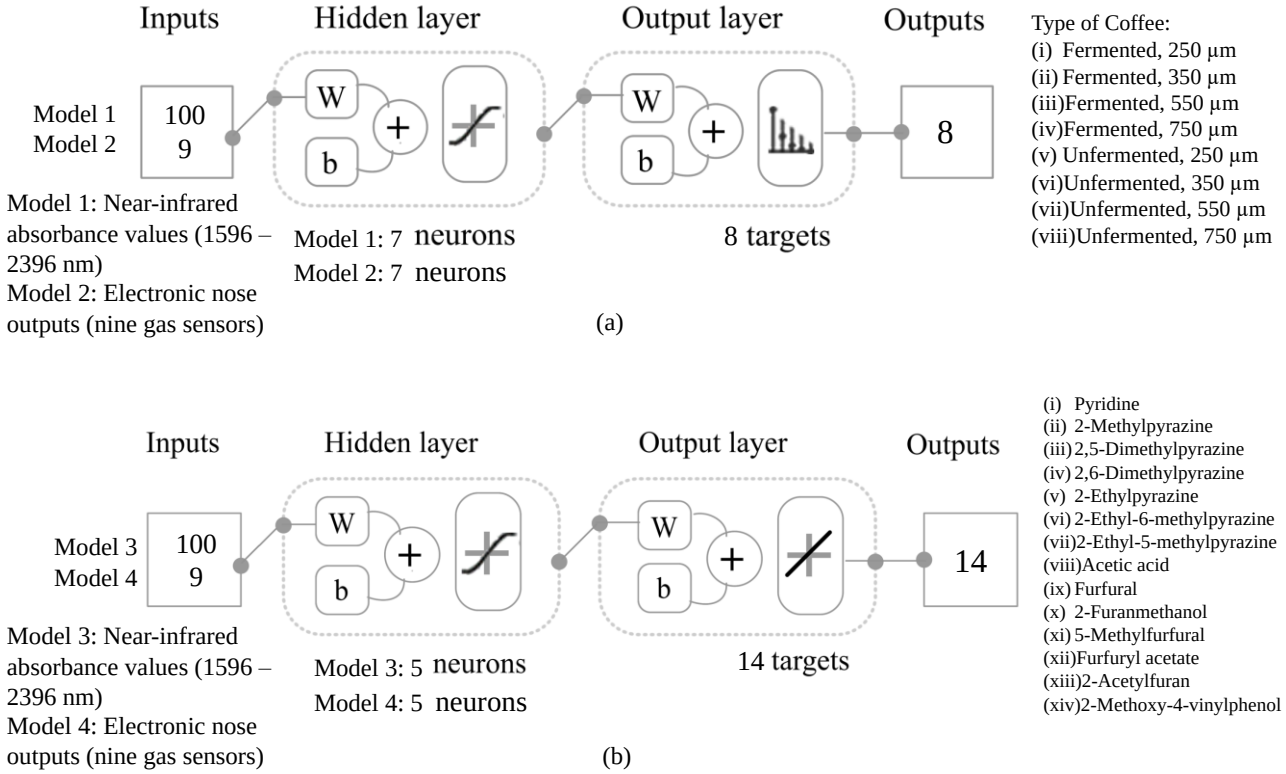

Figure 1. Diagrams of the machine learning (**a**) classification Models 1 and 2, and (**b**) regression Models 3 and 4, showing the specific inputs, targets, and number of neurons used.

Models 3 and 4 were developed using regression artificial neural networks (ANNs) with the absorbance values of the NIR data and e-nose outputs as inputs, respectively, to predict the peak area of 14 volatile aromatic compounds. Both models were developed using the Bayesian regularisation algorithm. Data were randomly divided into 70:30 for training and testing, respectively, using a performance algorithm based on the MSE. A neuron number trimming exercise was conducted with 3, 5, 7, and 10 neurons to assess the best performance.

3. Results and Discussion

3.1. Physicochemical Estimation

3.1.1. Measurement of pH and Salt Content

The pH values of the fermented and unfermented coffee brewed from four grinding sizes of coffee beans were measured as shown in Table 1. The unfermented coffee brewed from the finest-size (250 µm) coffee powder had relatively higher pH values at 4.89 ($p < 0.05$). Brewing coffee is an extraction process that may be influenced by the diameter of the ground coffee particles [16]. The surface area of the coffee particles increases with the decreasing particle size. Thus, the soluble coffee compounds could be quickly extracted from the surface and near-surface volume of the fine coffee grind matrix [36]. More acidic compounds, such as chlorogenic acids, may be dissolved and contribute a greater acidity to the coffee brew [37]. However, no significant differences ($p > 0.05$) could be observed among the coarse-ground fermented and unfermented coffee brews.

Table 1. pH and salt content of unfermented and fermented coffee brew with four coffee bean grinding sizes.

Sample		Size 1 (250 µm)	Size 2 (350 µm)	Size 3 (550 µm)	Size 4 (750 µm)
pH					
Unfermented coffee beans	UFC1	$4.79^{aC} \pm 0.03$	$4.77^{bB} \pm 0.01$	$4.76^{cD} \pm 0.01$	$4.77^{bC} \pm 0.01$
	UFC2	$4.86^{abB} \pm 0.01$	$4.81^{bA} \pm 0.01$	$4.85^{aA} \pm 0.02$	$4.83^{bB} \pm 0.03$
	UFC3	$4.94^{aA} \pm 0.03$	$4.79^{bB} \pm 0.03$	$4.80^{bBC} \pm 0.02$	$4.77^{bC} \pm 0.02$
	UFC4	$4.89^{aB} \pm 0.03$	$4.78^{cB} \pm 0.01$	$4.83^{bB} \pm 0.02$	$4.85^{aB} \pm 0.02$
	UFC5	$4.95^{aA} \pm 0.03$	$4.83^{bA} \pm 0.01$	$4.82^{aB} \pm 0.02$	$4.93^{aA} \pm 0.03$
	Average	4.89 ± 0.03	4.80 ± 0.01	4.81 ± 0.02	4.83 ± 0.02
Fermented coffee beans	FC1	$4.83^{bB} \pm 0.03$	$4.82^{bA} \pm 0.02$	$4.75^{cD} \pm 0.01$	$4.87^{aB} \pm 0.02$
	FC2	$4.77^{aD} \pm 0.02$	$4.74^{aC} \pm 0.02$	$4.74^{aD} \pm 0.01$	$4.73^{aD} \pm 0.02$
	FC3	$4.80^{aC} \pm 0.03$	$4.83^{aA} \pm 0.02$	$4.79^{aC} \pm 0.01$	$4.82^{aB} \pm 0.01$
	FC4	$4.80^{bcC} \pm 0.01$	$4.79^{cB} \pm 0.01$	$4.81^{bB} \pm 0.02$	$4.84^{aB} \pm 0.01$
	FC5	$4.69^{bE} \pm 0.02$	$4.66^{bD} \pm 0.01$	$4.83^{aB} \pm 0.04$	$4.66^{bE} \pm 0.02$
	Average	4.78 ± 0.02	4.77 ± 0.01	4.78 ± 0.02	4.78 ± 0.02
Salt content					
Unfermented coffee beans	UFC1	$0.11^{aBC} \pm 0.01$	$0.11^{aBC} \pm 0.01$	$0.11^{aB} \pm 0.01$	$0.10^{bAB} \pm 0.01$
	UFC2	$0.12^{aB} \pm 0.01$	$0.11^{aBC} \pm 0.01$	$0.09^{bC} \pm 0.01$	$0.08^{bBC} \pm 0.01$
	UFC3	$0.13^{aB} \pm 0.01$	$0.12^{bB} \pm 0.01$	$0.10^{cBC} \pm 0.01$	$0.09^{dB} \pm 0.01$
	UFC4	$0.13^{bB} \pm 0.01$	$0.14^{aA} \pm 0.01$	$0.09^{cC} \pm 0.01$	$0.07^{dC} \pm 0.01$
	UFC5	$0.11^{bBC} \pm 0.01$	$0.13^{aB} \pm 0.01$	$0.10^{cBC} \pm 0.01$	$0.07^{dC} \pm 0.01$
	Average	0.12 ± 0.01	0.12 ± 0.01	0.10 ± 0.01	0.08 ± 0.01
Fermented coffee beans	FC1	$0.12^{aB} \pm 0.01$	$0.11^{aBC} \pm 0.01$	$0.09^{bC} \pm 0.01$	$0.09^{bB} \pm 0.01$
	FC2	$0.12^{ab} \pm 0.01$	$0.11^{bcBC} \pm 0.01$	$0.13^{aA} \pm 0.01$	$0.10^{cAB} \pm 0.01$
	FC3	$0.10^{aC} \pm 0.01$	$0.10^{aC} \pm 0.01$	$0.10^{aBC} \pm 0.01$	$0.07^{bC} \pm 0.01$
	FC4	$0.19^{aA} \pm 0.01$	$0.14^{bA} \pm 0.01$	$0.11^{cB} \pm 0.01$	$0.11^{cA} \pm 0.01$
	FC5	$0.11^{aBC} \pm 0.01$	$0.10^{aC} \pm 0.01$	$0.09^{bC} \pm 0.01$	$0.09^{bB} \pm 0.01$
	Average	0.13 ± 0.01	0.11 ± 0.01	0.10 ± 0.01	0.09 ± 0.01

All values represent the average of three replicates from unfermented (UFC) and fermented (FC) coffee beans with five different brands. Different depicted significant differences between samples based on the ANOVA and Tukey's honest significant difference (HSD) *post hoc* test ($p < 0.05$). Different lowercase letters a–d indicate significant differences for particle size. Different capital letters A–E indicate significant differences for sample types.

The pH values of all the fermented coffee beans were significantly ($p < 0.05$) lower than that of the unfermented brews, which indicates that the coffee brew made from fermented coffee beans could have a relatively higher acidity. The pH value and titratable acidity are considered two conventional ways to express the acidity of coffee, since the perceived acidity of coffee is a result of the proton donation of acids to receptors on the human tongue [38]. During the fermentation, microorganisms may act on the pectinaceous sugars and other quantities of reducing or nonreducing sugars existing in coffee mucilage, which contributes to the production of lactic, butyric, acetic, and other higher carboxylic acids and tends to reduce the pH of the final coffee brew [8].

There was no significant difference ($p > 0.05$) in the salt content of the unfermented and fermented coffee brew in Table 1. However, the salt content in coffee slightly decreased along with the reduced size of the gounds. The sodium present in the brewed samples was low (0.07–0.19). During daily consumption, a small amount of salt is a usual alternative to other additives, such as sugar and milk, in coffee to bring out the sweetness, maintain the pleasant aromas, and dampen the bitterness remarkably [39,40].

3.1.2. Colour Measurement

The colour values (L*, a*, and b*) of all the coffee samples and the colour difference (ΔE) between the average value of the fermented and unfermented coffee are shown in Table 2. The fermented coffee brewed from 550 μm coffee powder showed the highest colour difference (ΔE = 91.10) to that of unfermented coffee. Overall, fermented coffee with all grinding sizes exhibited significantly higher lightness but lower redness and yellowness values (L* = 63.77, a* = 2.51, b* = 48.96) than unfermented coffee (L* = 58.36, a* = 5.74, b* = 53.16). The coffee colour is mainly developed through the Maillard reaction and caramelisation during roasting, with the primary involvement of sugar [41]. However, the sugar content in fermented coffee could be highly reduced due to the action of microorganisms during fermentation [8]. Therefore, less sugar remaining in the coffee beans could induce a lighter, less brown, but yellower appearance after roasting, since the brown pigment formation is due to the Maillard reaction through the interactions between sugar and amino acids.

In grinding size, there was a decrease in lightness but an increase in redness with the reduced particle size. Brewing coffee also contributes to the extraction of various substances from coffee powder, such as phenolic compounds, caffeine, carbohydrates, lipids, and acids. Smaller particle sizes could further contribute to the better release and dissolution of brown pigments, such as melanoidins [42]. It is reasonable that coffee brewed from coarse powder presented a brighter appearance than fine coffee powder.

Table 2. Colour measurements of unfermented and fermenetd coffee brew with four coffee bean grinding sizes.

Sample		Size 1 (250 µm)			Size 2 (350 µm)			Size 3 (550 µm)			Size 4 (750 µm)		
		L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
Unfermented coffee beans	UFC1	$50.24^{de} \pm 0.93$	$8.05^{e} \pm 0.59$	$54.52^{ab} \pm 1.99$	$53.57^{d} \pm 1.53$	$6.24^{d} \pm 1.25$	$53.74^{b} \pm 0.99$	$58.36^{bc} \pm 0.96$	$4.76^{ab} \pm 1.64$	$54.01^{ab} \pm 2.66$	$59.98^{bcde} \pm 1.74$	$5.44^{bc} \pm 1.49$	$56.69^{a} \pm 2.10$
	UFC2	$57.56^{bc} \pm 0.18$	$6.71^{f} \pm 1.89$	$52.46^{bc} \pm 1.44$	$60.13^{bc} \pm 0.82$	$4.17^{d} \pm 1.69$	$51.01^{b} \pm 0.94$	$58.57^{b} \pm 1.52$	$5.55^{a} \pm 0.60$	$52.96^{ab} \pm 0.90$	$57.70^{def} \pm 1.20$	$7.57^{ab} \pm 0.88$	$56.76^{a} \pm 1.47$
	UFC3	$49.63^{ef} \pm 1.21$	$12.83^{bc} \pm 1.02$	$47.60^{e} \pm 1.79$	$56.80^{cd} \pm 0.68$	$10.33^{bc} \pm 1.32$	$63.27^{a} \pm 0.79$	$57.80^{bc} \pm 1.70$	$7.03^{a} \pm 1.72$	$58.05^{a} \pm 1.98$	$69.14^{a} \pm 1.35$	$0.64^{cd} \pm 0.73$	$53.24^{ab} \pm 1.59$
	UFC4	$40.07^{g} \pm 0.27$	$13.94^{b} \pm 1.67$	$54.49^{ab} \pm 1.06$	$44.74^{e} \pm 1.47$	$12.29^{b} \pm 1.47$	$37.83^{c} \pm 1.56$	$51.65^{c} \pm 0.93$	$7.30^{a} \pm 1.90$	$52.72^{ab} \pm 1.78$	$55.02^{ef} \pm 2.72$	$3.94^{bcd} \pm 1.68$	$42.67^{bc} \pm 1.31$
	UFC5	$39.58^{g} \pm 0.39$	$18.91^{a} \pm 0.35$	$52.78^{bc} \pm 0.52$	$42.21^{e} \pm 0.63$	$17.19^{a} \pm 0.40$	$53.06^{b} \pm 0.65$	$58.20^{bc} \pm 0.66$	$6.24^{a} \pm 0.26$	$54.65^{ab} \pm 0.29$	$49.98^{f} \pm 1.59$	$11.10^{a} \pm 1.02$	$56.43^{a} \pm 0.17$
	Average	47.42 ± 0.60	12.09 ± 1.10	52.37 ± 1.36	51.49 ± 1.03	10.04 ± 1.23	51.78 ± 0.99	56.92 ± 1.15	6.18 ± 1.22	54.48 ± 1.52	58.36 ± 1.72	5.74 ± 1.16	53.16 ± 1.33
Fermented coffee beans	FC1	$50.31^{de} \pm 0.60$	$8.40^{e} \pm 0.37$	$50.07^{d} \pm 1.53$	$52.45^{d} \pm 0.91$	$7.02^{cd} \pm 0.21$	$52.65^{b} \pm 0.72$	$57.06^{bc} \pm 2.28$	$7.18^{a} \pm 1.64$	$53.18^{ab} \pm 1.28$	$65.03^{abcd} \pm 1.25$	$2.58^{bcd} \pm 0.36$	$45.73^{abc} \pm 1.60$
	FC2	$51.93^{d} \pm 0.37$	$10.27^{d} \pm 0.51$	$56.25^{a} \pm 0.87$	$54.44^{e} \pm 1.46$	$8.97^{a} \pm 0.72$	$57.17^{ab} \pm 1.94$	$58.41^{bc} \pm 0.75$	$6.98^{a} \pm 1.05$	$57.01^{ab} \pm 1.70$	$60.42^{bcde} \pm 1.63$	$4.60^{bcd} \pm 0.79$	$54.61^{ab} \pm 1.68$
	FC3	$58.94^{a} \pm 1.22$	$2.36^{gh} \pm 0.61$	$48.92^{de} \pm 2.12$	$64.73^{ab} \pm 0.82$	$-0.42^{e} \pm 0.86$	$42.03^{c} \pm 1.82$	$63.16^{ab} \pm 1.40$	$-0.36^{c} \pm 0.96$	$42.64^{c} \pm 0.80$	$67.24^{ab} \pm 1.02$	$-0.67^{d} \pm 2.12$	$40.49^{c} \pm 1.17$
	FC4	$59.63^{a} \pm 2.18$	$3.40^{g} \pm 1.21$	$49.97^{d} \pm 0.75$	$69.79^{a} \pm 1.24$	$-2.40^{e} \pm 0.61$	$39.50^{c} \pm 2.59$	$66.45^{a} \pm 1.30$	$0.48^{bc} \pm 0.96$	$49.04^{bc} \pm 2.67$	$59.28^{cde} \pm 1.20$	$6.46^{ab} \pm 1.51$	$56.94^{a} \pm 1.80$
	FC5	$58.78^{ab} \pm 0.92$	$1.29^{h} \pm 0.04$	$52.38^{bc} \pm 1.37$	$69.92^{a} \pm 1.26$	$-0.21^{e} \pm 1.46$	$50.43^{b} \pm 2.92$	$69.92^{a} \pm 2.26$	$-0.21^{bc} \pm 1.46$	$50.43^{abc} \pm 2.92$	$66.90^{abc} \pm 0.53$	$-0.44^{d} \pm 0.45$	$47.03^{abc} \pm 1.39$
	Average	55.92 ± 1.06	5.14 ± 0.55	51.52 ± 1.33	62.27 ± 1.14	2.59 ± 0.77	48.36 ± 1.99	63.00 ± 1.59	2.81 ± 1.21	50.46 ± 1.87	63.77 ± 1.13	2.51 ± 1.05	48.96 ± 1.53
ΔE			11.01			13.54			91.1			15.92	

All values represented as the average of three replicates from unfermented coffee (UFC) and fermented coffee (FC) with five different brands. ΔE represents the colour difference between the average value of fermented and unfermented coffee. Different letters a–h depict significant differences between samples based on the ANOVA and Tukey's honest significant difference (HSD) *post hoc* test ($p < 0.05$).

3.2. Near-Infrared Spectroscopy (NIR) Analysis

The first derivative data of the NIR absorbance scans for fermented and unfermented coffee were acquired, as shown in Figure 2. As observed in this figure, the peak values for all coffee brews were between 1700–2000 nm and 2200–2396 nm, in which compounds such as water, proteins, carbohydrates, and volatile compounds, including amides, could be found. For the main overtones, compounds such as ketones (1698 nm), aliphatic hydrocarbons (1699–1700, 1732, 1767, and 2313 nm), alcohol (1737 nm), aromatic hydrocarbons (1749 nm), water (1940 nm), esters and acids (1955 nm), aryl (2299 nm), lipids (2315 nm), sucrose (2306–2312 nm), and other polysaccharides (2327–2340 nm) were found [33,43,44]. This is consistent with the results reported by Okubo and Kurata [45].

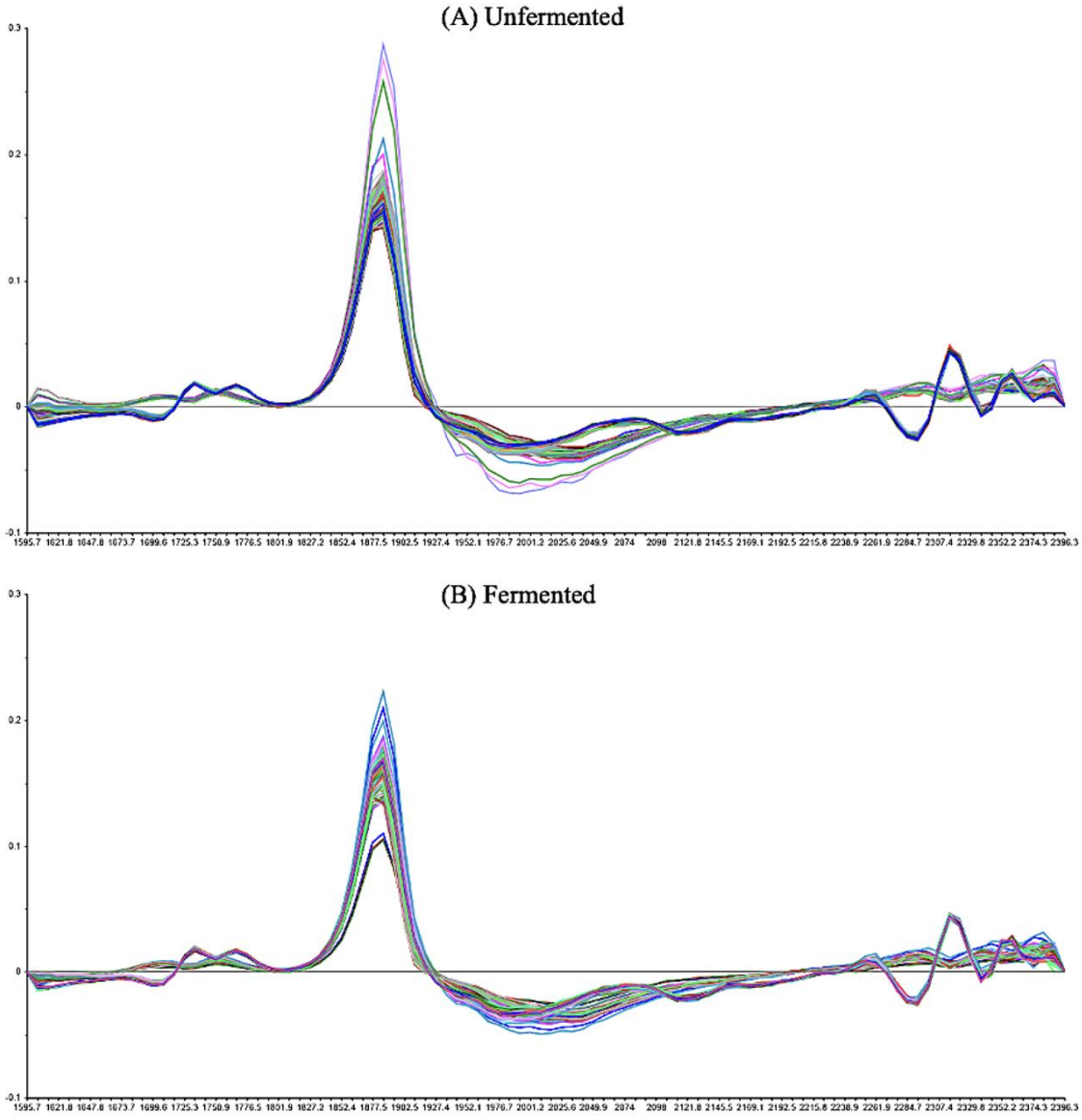

Figure 2. NIR spectra (1596–2396 nm) of unfermented (**A**) and fermented (**B**) coffee samples shown as the Savitzky–Golay first derivative. Different colours of the lines represented different replicates of sample measurement.

Although different curve trends within the same NIR wavelength range for coffee sample measurements were obtained by Esteban-Díez, et al. [46] and Ribeiro, Ferreira and Salva [43], this is probably due to the results of different brands, roasting conditions, and geographic origins [44]. Barbosa, dos Santos Scholz, Kitzberger and de Toledo Benassi [6]

also detected lipid fractions that could influence aroma formation and the release of volatile compounds during the roasting process, such as aldehydes, ketones, and alcohols, in a similar wavelength range. Unfermented coffee brews had a relatively higher absorbance than fermented coffee brew for most of the overtones from these compounds.

3.3. Electronic Nose Outputs

Figure 3 shows the volatile compound analysis results of the fermented and unfermented coffee brews with four different grinding sizes using the e-nose. Overall, except for the set brewing from the coarsest coffee powder, the fermented coffee exhibited a relatively higher total voltage accumulation of all sensors. Significant differences ($p < 0.05$) between the fermented and unfermented samples in all nine sensors could be observed. The MQ3 (ethanol) and MQ4 (methane) sensors showed a significantly higher voltage for all the coffee brews, followed by the MQ7 (carbon monoxide) sensors. The MG811 (carbon dioxide) sensor values are inverse; hence, higher values mean lower CO_2 levels.

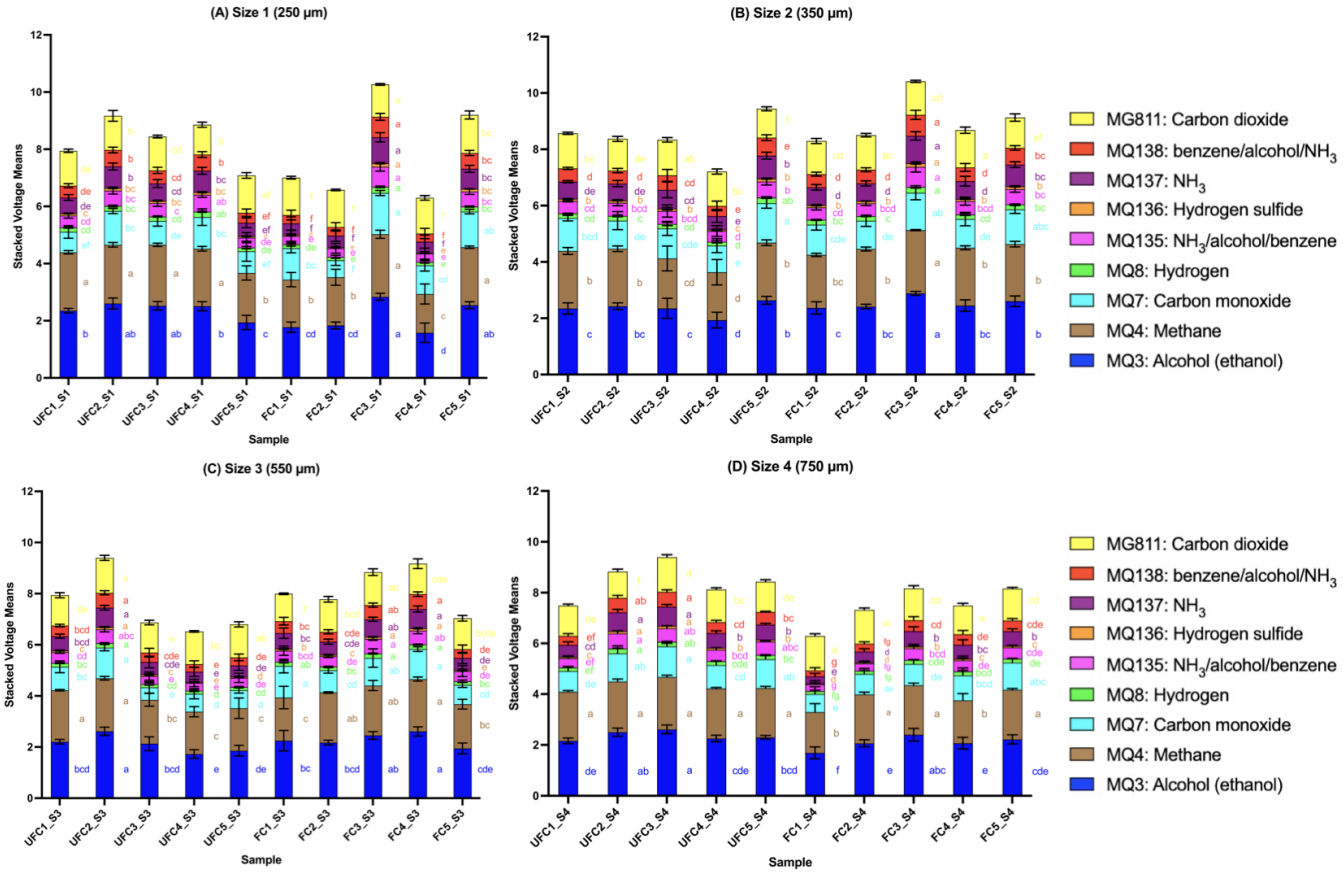

Figure 3. Stacked mean voltage of the nine different e-nose gas sensors among unfermented (UFC) and fermented (FC) coffee samples with four grinding sizes from five different brands. Differences are compared for each sensor among samples (bar colours); different letters a–g depict significant differences between samples based on the ANOVA and Tukey's honest significant difference (HSD) *post hoc* test ($p < 0.05$).

By-products such as alcohol and various acids generated by the action of microorganisms on the polysaccharides present in the mucilage of the coffee beans during fermentation could be absorbed into the cellular structure of the seed [5]. Although the voltage of alcohol detection fluctuated among all the coffee brews, it is reasonable that one of the fermented coffee brews exhibited the greatest detection level with all four grinding sizes. Carbon monoxide could be produced during coffee roasting due to the interaction between oxygen and methane. The gases could be trapped in the pore structure of the roasted coffee and be

emitted more quickly if ground into smaller particles [47]. Newton [48], Killian, et al. [49], and Gonzalez Viejo, Tongson and Fuentes [31] also commented that there is CO production during roasting, which could explain the detection of the MQ7 sensor. Gonzalez Viejo, Tongson and Fuentes [31] also claimed that the lower voltage with MQ7 in several samples is probably due to the brewing process. Noticeably, the MQ135 (NH_3/alcohol/benzene) and MQ137 (NH_3) sensors displayed fluctuating voltage among all the samples. Purine alkaloids in coffee beans, especially caffeine, could probably be degraded during roasting and generate NH_3, which may explain the detection by those three sensors [50].

3.4. Identification and Quantification of Volatile Compounds in Coffee Brew

The content range of volatile compounds identified and semi-quantified in a the fermented and unfermented coffee brew with four different grinding sizes by the HS-SPME-GC-MS method is shown in Table 3. In total, 14 compounds were identified in both types of coffee brew and shared a similar overall content of the detected volatile compounds (VOCs). As for the influence of grinding size, the average content of the overall detected VOCs decreased from around 32.80 to 25.28 ng/mL along with the coarser coffee powder size, which is consistent with previous research conducted by Yu, et al. [51]. The negative correlation between grinding size and VOC content could be related to extraction efficiency. The solid–liquid interfacial area may increase as the grinding size decreases, allowing the extraction of a higher amount of volatiles [51].

Acetic acid was the only detected organic acid in the coffee brews, which may come from the decomposition of saccharides (sucrose and fructose) during roasting [52]. Acid precursor 1-deoxyglucosone could be generated during roasting through the hydrolysis and thermal dehydration of sugars and then contribute to the formation of acetic acid [11]. The fermented coffee brew showed a lower content of acetic acid than unfermented coffee, which could again indicate the microbial consumption of sugar during the fermentation of harvested coffee beans [8]. However, Elhalis, Cox, Frank and Zhao [1] reported significantly higher ($p < 0.05$) concentrations of acetic acid in fermented coffee beans than in unfermented.

Table 3 and Table S1 show that 2-methylpyrazine was the most abundant pyrazine in the fermented coffee brew, with an average concentration of 2.20 ng/mL, similar to Elhalis, Cox, Frank and Zhao [1]. There were two clusterings that could be observed from the group of pyrazines: 2,5(6)-dimethylpyrazine and 2-ethyl-5(6)-methylpyrazine. The fermented coffee brews showed a slightly higher content of these volatile compounds. 2-Ethyl-5-methylpyrazine is generally used to distinguish roasted arabica and robusta coffee beans, which confers negative earthy notes generated through the Maillard reaction [53]. Both 2,5-dimethylpyrazine and 2,6-dimethylpyrazine were a dominant pyrazine product of the same Maillard reaction in both the fermented and unfermented coffee brews, with different locations of the functional groups and exhibiting a chocolate and nutty aroma [11,51]. This could be contributed by the formation of a series of Amadori-type conjugates through the catalysis of the Amadori rearrangement in the dipeptide/sugar adduct [54]. Significant variance could be found in the content of furans and furanic compounds between the fermented and unfermented coffee brews, especially furfural and 5-methylfurfural. Furanic compounds may be produced through the dehydration, cyclisation, and polymerisation of Amadori rearrangement products or the thermal oxidation of furans, such as 2-furanmethanol, polyunsaturated fatty acids, and ascorbic acid [11,55]. Furans are developed from the reaction between sugars and amino acids; hence, the unfermented coffee brew exhibited a relatively higher content. It could also contribute to the accumulation of other furanic compounds in the unfermented coffee brews. Gonzalez Viejo, Tongson and Fuentes [31] also identified 5-methylfurfural and furfural acetate from commercial coffee products, which could provide spice, caramel, bready, or coffee aromas. Notably, the content of furfuryl acetate was relatively higher in the fermented coffee brews, which could bring a fruity aroma. Lee, Cheong, Curran, Yu and Liu [12] also claimed that the fermentation using yeast as starter cultures could induce the production of several volatile compounds, including acetaldehyde, ethanol, ethyl acetate, isoamyl acetate, as well as a caramel and fruity flavour.

Table 3. The content range of volatile compounds identified in unfermented and fermented coffee brews by HS-SPME-GC-MS.

No.	Compound Name	Molecular Formula	Aroma	RT * (min)	Conc. (ng/mL)				
					Unfermented Coffee				
					UFC1	UFC2	UFC3	UFC4	UFC5
			Pyridines						
1	Pyridine	C_5H_5N	Sour/smoky/burnt/coffee	10.49	0.35–0.68	0.68–0.83	0.45–0.65	0.66–0.99	0.53–1.00
			Pyrazines						
2	2-Methylpyrazine	$C_5H_6N_2$	Nutty/cocoa/roasted	13.01	1.98–2.03	1.03–1.43	1.32–1.75	1.20–1.87	1.18–2.15
3	2,5-Dimethylpyrazine	$C_5H_6N_2$	Nutty/peanut/musty/earthy	14.73	0.67–0.91	0.37–0.65	0.41–0.74	0.50–0.97	0.47–1.06
4	2,6-Dimethylpyrazine	$C_6H_8N_2$	Chocolate/nutty/roasted	14.92	1.02–1.25	0.61–0.96	0.66–1.15	0.77–1.27	0.70–1.44
5	2-Ethylpyrazine	$C_6H_8N_2$	Nutty/roasted/cocoa/coffee	15.05	0.71–0.83	0.43–0.67	0.63–0.73	0.56–0.89	0.55–0.93
6	2-Ethyl-6-methylpyrazine	$C_7H_{10}N_2$	Roasted potato/roasted hazelnut	16.55	0.77–1.06	0.46–0.84	0.47–0.91	0.61–1.21	0.59–1.43
7	2-Ethyl-5-methylpyrazine	$C_7H_{10}N_2$	Coffee/roasted/nutty	16.72	0.68–0.96	0.42–0.73	0.43–0.82	0.58–1.09	0.58–1.22
			Acids						
8	Acetic acid	$C_2H_4O_2$	Sour/overripe fruit	18.34	0.80–0.98	0.43–0.83	0.52–0.77	0.52–0.88	0.46–0.89
			Furan and Furanic compounds						
9	Furfural	$C_5H_4O_2$	Sweet/woody/bready/caramellic	18.54	5.65–7.13	9.10–10.53	5.83–8.75	8.99–13.08	7.24–12.03
10	2-Furanmethanol	$C_5H_6O_2$	Sweet/brown caramellic/bready/coffee	23.62	2.74–2.99	2.72–3.69	2.48–3.48	2.71–4.29	2.62–4.10
11	5-Methylfurfural	$C_6H_6O_2$	Spice/caramel/bready/coffee	21.37	3.10–5.72	5.04–7.10	3.04–5.61	4.33–8.71	3.96–8.03
12	Furfuryl acetate	$C_7H_8O_3$	Fruity/banana/ethereal	20.52	1.48–2.00	2.31–3.12	1.30–2.20	2.21–3.30	1.93–3.16
			Ketones						
13	2-Acetylfuran	$C_6H_6O_2$	Sweet/nutty/roasted/coffee	19.64	1.33–1.52	2.05–2.47	1.44–2.10	1.73–2.67	1.15–2.26
			Phenols						
14	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	Sweet/spicy/clove-like/smoky	34.77	0.33–0.78	0.25–0.36	0.33–0.43	0.31–0.43	0.34–0.39

Table 3. *Cont.*

No.	Compound Name	Molecular Formula	Aroma	RT * (min)	Conc. (ng/mL)				
					Fermented Coffee				
					FC1	FC2	FC3	FC4	FC5
			Pyridines						
1	Pyridine	C_5H_5N	Sour/smoky/burnt/coffee	10.49	0.37–0.49	0.47–0.61	0.34–0.42	0.57–0.72	0.29–0.36
			Pyrazines						
2	2-Methylpyrazine	$C_5H_6N_2$	Nutty/cocoa/roasted	13.01	2.21–2.63	1.59–2.24	1.63–2.37	1.46–2.05	1.61–1.87
3	2,5-Dimethylpyrazine	$C_5H_6N_2$	Nutty/peanut/musty/earthy	14.73	0.79–1.17	0.53–0.97	0.55–0.97	0.52–0.99	0.59–0.67
4	2,6-Dimethylpyrazine	$C_6H_8N_2$	Chocolate/nutty/roasted	14.92	1.19–1.61	0.93–1.46	0.38–1.44	0.87–1.38	1.05–1.14
5	2-Ethylpyrazine	$C_6H_8N_2$	Nutty/roasted/cocoa/coffee	15.05	0.79–1.06	0.61–1.00	0.58–0.93	0.57–0.91	0.63–0.87
6	2-Ethyl-6-methylpyrazine	$C_7H_{10}N_2$	Roasted potato/roasted hazelnut	16.55	0.78–1.30	0.71–1.28	0.59–1.08	0.69–1.26	0.84–0.94
7	2-Ethyl-5-methylpyrazine	$C_7H_{10}N_2$	Coffee/roasted/nutty	16.72	0.75–1.19	0.58–1.07	0.59–1.04	0.62–1.13	0.72–0.81
			Acids						
8	Acetic acid	$C_2H_4O_2$	Sour/overripe fruit	18.34	0.70–0.75	0.37–0.84	0.46–0.75	0.60–0.76	0.39–0.83
			Furan and Furanic compounds						
9	Furfural	$C_5H_4O_2$	Sweet/woody/bready/caramellic	18.54	7.63–8.66	7.91–10.32	5.09–7.29	6.76–9.29	5.65–5.89
10	2-Furanmethanol	$C_5H_6O_2$	Sweet/brown caramellic/bready/coffee	23.62	3.01–3.46	3.40–4.14	2.18–3.14	2.64–3.84	2.51–2.83
11	5-Methylfurfural	$C_6H_6O_2$	Spice/caramel/bready/coffee	21.37	3.43–4.70	4.84–7.36	2.17–3.94	3.92–6.49	3.63–4.07
12	Furfuryl acetate	$C_7H_8O_3$	Fruity/banana/ethereal	20.52	1.49–2.04	3.82–5.00	0.87–1.67	2.01–2.99	1.88–2.22
			Ketones						
13	2-Acetylfuran	$C_6H_6O_2$	Sweet/nutty/roasted/coffee	19.64	1.47–1.86	1.63–2.30	0.91–1.57	1.33–2.05	1.41–1.45
			Phenols						
14	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	Sweet/spicy/clove-like/smoky	34.77	0.40–0.53	0.36–0.47	0.08–0.44	0.35–0.42	0.37–0.40

* RT is short for retention time. All values represent the average of three replicates from unfermented (UFC) and fermented (FC) coffee samples with five different brands.

In the class of phenols, 2-methoxy-4-vinylphenol was only identified with a slightly higher content in the fermented coffee brews. It is consistent with previous research conducted by Elhalis, Cox, Frank and Zhao [1] that the concentration of 2-methoxy-4-vinylphenol was slightly higher in the fermented roasted coffee beans compared to the mechanically de-mucilaged beans.

3.5. Machine Learning Modelling

Table 4 shows that Model 1 has a high overall accuracy (93.9%) to classify coffee samples according to their processing type and grinding size using the NIR absorbance values between 1596 and 2396 nm as inputs. The training MSE value (0.04) was lower than that of the testing (0.05). The similar MSE value of the validation and testing shows no under- or overfitting of the data. Furthermore, Model 2, developed to classify the type of coffee samples using the e-nose outputs as model inputs, presented a high overall accuracy (91.2%). There were no observed signs of under- or overfitting because the training MSE value (0.02) was lower than the validation (0.07) and testing (0.07), and the latter two had the same value.

Table 4. Classification artificial neural network results for Models 1 and 2. Abbreviations: MSE: means squared error.

Stage	Samples	Accuracy	Error	Performance (MSE)
Model 1: Inputs: NIR; Targets: type of coffee				
Training	126	99.7%	0.3%	0.04
Testing	54	91.6%	9.4%	0.05
Overall	180	93.9%	6.1%	-
Model 2: Inputs: electronic nose; Targets: type of coffee				
Training	420	98.4%	1.6%	0.02
Validation	90	92.4%	7.6%	0.07
Testing	90	92.4%	7.6%	0.07
Overall	600	91.2%	8.8%	-

The receiver operating characteristic (ROC) curves of Models 1 and 2 are shown in Figure 4, which were both closer to the top left edge for the true-positive-rate values (sensitivity). Interestingly, the coarser the coffee powders were, the lower the sensitivity of their ROC curves. It is probably because of the similarities shared in the physicochemical characteristics between fermented and unfermented coffee with higher grinding sizes.

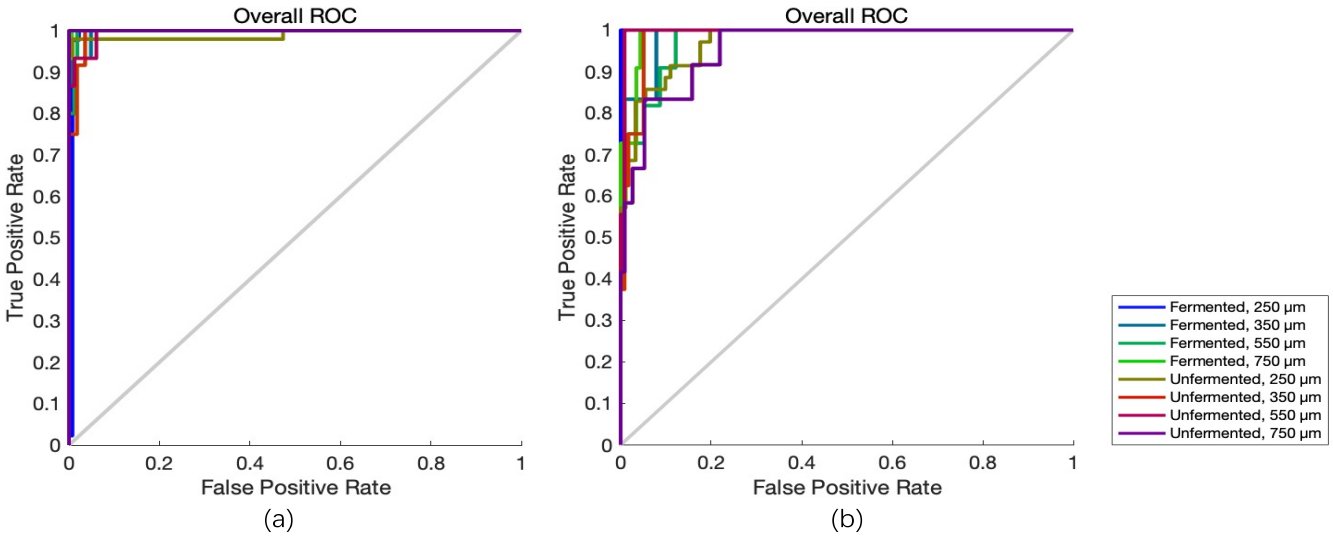

Figure 4. Receiver operating characteristic (ROC) curves for (**a**) Model 1 and (**b**) Model 2.

Table 5 shows that Models 3 and 4 had a similar and high overall accuracy (R = 0.96; R = 0.99). These models were developed using the NIR absorbance values within 1596–2396 nm and e-nose outputs as inputs, respectively, to predict 14 volatile compounds detected by GC-MS. According to the performance MSE values, there were no signs of the under- or overfitting of the models, as the training-stage MSE values were lower than the testing-stage values for both models.

Table 5. The results of the artificial neural network regression Models 3 and 4. Abbreviations: R: correlation coefficient; MSE: means squared error.

Stage	Samples	Observations	R	Slope	Performance (MSE)
Model 3: Inputs: NIR; Targets: volatile aromatic compounds					
Training	126	1764	0.99	0.99	0.07
Testing	54	756	0.89	1.00	1.34
Overall	180	2520	0.96	1.00	-
Model 4: Inputs: electronic nose; Targets: volatile aromatic compounds					
Training	420	5880	0.99	0.98	0.11
Testing	180	2520	0.98	1.00	0.25
Overall	600	8400	0.99	0.98	-

Figure 5a shows the overall Model 3 with 95% prediction bounds; there were 3.49% outliers (88 out of 2520 data points), with the majority from furfural (33 out of 88 outliers), followed by 5-methylfurfural (28 out of 88 outliers). Likewise, Figure 5b shows the overall Model 4, with 3.57% outliers (299 out of 8400 data points) according to the 95% prediction bounds, where most outliers were also from furfural (119 out of 299 outliers), followed by 5-methylfurfural (76 out of 299 outliers). Gonzalez Viejo, Tongson and Fuentes [31] reported the very high accuracy of their models (R = 0.99) using e-nose results as inputs to predict the peak area of volatile compounds in coffee detected by GC-MS. Gonzalez Viejo, et al. [56] also constructed highly accurate ML regression models using the NIR (R = 0.97) and e-nose (R = 0.99) data of sourdough bread as inputs to assess 16 volatile aromatic compounds.

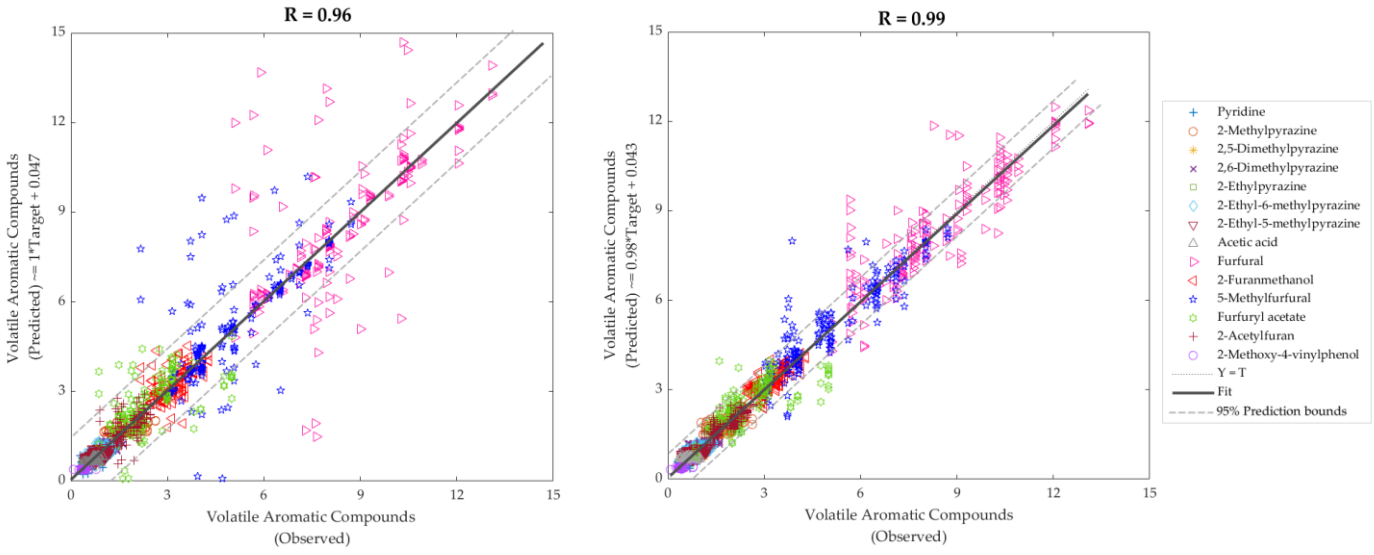

Figure 5. Overall regression Models 3 (**a**) and 4 (**b**) predicted 14 volatile aromatic compounds from GC-MS analysis, where the x-axis represents the observed data, while the y-axis depicts the predicted values. Abbreviations: VAC: volatile aromatic compounds; R: correlation coefficient.

The models developed show that the NIR (Models 1 and 3) and e-nose (Models 2 and 4) measurements of the coffee were able to find patterns within the input data to predict the post-harvesting processing method and grinding size, as well as the volatile aromatic compounds. Further studies may focus on developing machine learning models to predict the intensity of the sensory descriptors related to fermented and unfermented coffee using the e-nose outputs as inputs. This could provide a more critical prediction among postharvesting processing, sensory perception, and consumer acceptability. The NIR and e-nose used in this study are portable, affordable, and convenient, and was shown to be objective, reliable, and rapid in evaluating the coffee's quality traits. These methods may also be used to develop methods to assess authentication and provenance for the coffee industry, local family coffee farms, and retailers.

4. Conclusions

Conclusively, the wet fermentation and grinding size of coffee beans may significantly influence the flavour, aroma, and physicochemical properties of coffee brew by changing the contents of phytochemical and critical volatile compounds, such as acids, esters, and aldehydes. The fermented coffee exhibited a lighter appearance, relatively lower pH, but lower detection of acetic acid, which is probably due to other organic acids. The total e-nose detection of fermented coffee beans was relatively higher. Although the content of overall volatile compounds detected by GC-MS in the unfermented coffee was higher, several compounds, such as 2-methylpyrazine (2.20 ng/mL) and furfuryl acetate (2.36 ng/mL), had a higher concentration in the fermented coffee, which could contribute to a stronger fruity flavour. The ANN models using the results of the NIR (Model 3) and e-nose (Model 4) as inputs and GC-MS as the ground truth predicted the composition of 14 volatile compounds with very high accuracy ($R > 0.95$). The impact of fermentation on the coffee's quality traits and volatile compounds was comprehensively, rapidly, and objectively assessed in this study. Moreover, the postharvest processing methods, brewing method, and the volatile compound patterns of coffee beverages could also be predicted to some extent with minimal laboratory equipment. The lower cost of the digital technologies used in this study coupled with ML modelling have a high potential to be used for coffee differentiation assessment, processing prediction, and quality assurance for local coffee farms, roasters, and retailers. More specific and perceived relations among postharvesting processing methods, physiochemical properties, volatile aromatic compounds, and the consumers' acceptability of coffee could be further investigated using specific overtones of NIR spectra, an assessment of the intensity of sensory descriptors, the composition of volatile aromatic compounds, and machine learning algorithms.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/fermentation9010068/s1, Table S1: The content of volatile compounds identified in unfermented and fermented coffee brew with four coffee bean grinding sizes by HS-SPME-GC-MS.

Author Contributions: Conceptualization, H.W., C.G.V. and H.A.R.S.; methodology, H.W., C.G.V. and S.F.; software, H.W. and C.G.V.; validation, C.G.V. and H.A.R.S.; formal analysis, H.W.; investigation, H.W., C.G.V., F.R.D. and H.A.R.S.; data curation, H.W. and C.G.V.; writing—original draft preparation, H.W.; writing—review and editing, H.W., C.G.V. and H.A.R.S.; visualization, H.W. and C.G.V.; supervision, C.G.V. and H.A.R.S.; funding acquisition, H.A.R.S. All authors have read and agreed to the published version of the manuscript.

Funding: Hafiz A. R. Suleria is the recipient of an Australian Research Council Award (ARC-DECRA—DE220100055) funded by the Australian Government. This research was funded by the University of Melbourne under the McKenzie Fellowship Scheme (grant no. UoM-18/21), the Future Food Hallmark Research Initiative Funds (grant no. UoM-21/23) and Collaborative. H.W. is the recipient of a University of Melbourne Research Scholarship provided by the University of Melbourne (Grant reference: 767803).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to acknowledge Ranjith R. Unnithan and Bryce Widdicombe from the School of Engineering, Department of Electrical and Electronic Engineering of The University of Melbourne for their collaboration in the electronic nose development.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Elhalis, H.; Cox, J.; Frank, D.; Zhao, J. The role of wet fermentation in enhancing coffee flavor, aroma and sensory quality. *Eur. Food Res. Technol.* **2021**, *247*, 485–498. [CrossRef]
2. Bhumiratana, N.; Adhikari, K.; Chambers, E., IV. Evolution of sensory aroma attributes from coffee beans to brewed coffee. *LWT-Food Sci. Technol.* **2011**, *44*, 2185–2192. [CrossRef]
3. Pereira, L.L.; Guarçoni, R.C.; Pinheiro, P.F.; Osório, V.M.; Pinheiro, C.A.; Moreira, T.R.; Ten Caten, C.S. New propositions about coffee wet processing: Chemical and sensory perspectives. *Food Chem.* **2020**, *310*, 125943. [CrossRef] [PubMed]
4. Duarte, G.S.; Pereira, A.A.; Farah, A. Chlorogenic acids and other relevant compounds in Brazilian coffees processed by semi-dry and wet post-harvesting methods. *Food Chem.* **2010**, *118*, 851–855. [CrossRef]
5. Silva, C.F.; Schwan, R.F.; Dias, Ë.S.; Wheals, A.E. Microbial diversity during maturation and natural processing of coffee cherries of Coffea arabica in Brazil. *Int. J. Food Microbiol.* **2000**, *60*, 251–260. [CrossRef]
6. Barbosa, M.d.S.G.; dos Santos Scholz, M.B.; Kitzberger, C.S.G.; de Toledo Benassi, M. Correlation between the composition of green Arabica coffee beans and the sensory quality of coffee brews. *Food Chem.* **2019**, *292*, 275–280. [CrossRef]
7. Knopp, S.; Bytof, G.; Selmar, D. Influence of processing on the content of sugars in green Arabica coffee beans. *Eur. Food Res. Technol.* **2006**, *223*, 195–201. [CrossRef]
8. Haile, M.; Kang, W.H. The role of microbes in coffee fermentation and their impact on coffee quality. *J. Food Qual.* **2019**, *2019*, 4836709. [CrossRef]
9. Cao, X.; Wu, H.; Gonzalez Viejo, C.; Dunshea, F.R.; Suleria, H.A. Effects of Postharvest Processing on Aroma Formation in Roasted Coffee—A Review. *Int. J. Food Sci. Technol.* **2022**. [CrossRef]
10. Zakidou, P.; Plati, F.; Matsakidou, A.; Varka, E.-M.; Blekas, G.; Paraskevopoulou, A. Single origin coffee aroma: From optimized flavor protocols and coffee customization to instrumental volatile characterization and chemometrics. *Molecules* **2021**, *26*, 4609. [CrossRef]
11. Wu, H.; Lu, P.; Liu, Z.; Sharifi-Rad, J.; Suleria, H.A. Impact of roasting on the phenolic and volatile compounds in coffee beans. *Food Sci. Nutr.* **2022**, *10*, 2408–2425. [CrossRef] [PubMed]
12. Lee, L.W.; Cheong, M.W.; Curran, P.; Yu, B.; Liu, S.Q. Coffee fermentation and flavor—An intricate and delicate relationship. *Food Chem.* **2015**, *185*, 182–191. [CrossRef] [PubMed]
13. Toci, A.T.; Farah, A. Volatile fingerprint of Brazilian defective coffee seeds: Corroboration of potential marker compounds and identification of new low quality indicators. *Food Chem.* **2014**, *153*, 298–314. [CrossRef] [PubMed]
14. Steen, I.; Waehrens, S.S.; Petersen, M.A.; Münchow, M.; Bredie, W.L. Influence of serving temperature on flavour perception and release of Bourbon Caturra coffee. *Food Chem.* **2017**, *219*, 61–68. [CrossRef] [PubMed]
15. Cordoba, N.; Pataquiva, L.; Osorio, C.; Moreno, F.L.M.; Ruiz, R.Y. Effect of grinding, extraction time and type of coffee on the physicochemical and flavour characteristics of cold brew coffee. *Sci. Rep.* **2019**, *9*, 8440. [CrossRef]
16. Severini, C.; Derossi, A.; Ricci, I.; Fiore, A.G.; Caporizzi, R. How much caffeine in coffee cup? Effects of processing operations, extraction methods and variables. *Quest. Caffeine* **2017**, 45–85.
17. Baggenstoss, J.; Perren, R.; Escher, F. Water content of roasted coffee: Impact on grinding behaviour, extraction, and aroma retention. *Eur. Food Res. Technol.* **2008**, *227*, 1357–1365. [CrossRef]
18. Zhang, K.; Cheng, J.; Hong, Q.; Dong, W.; Chen, X.; Wu, G.; Zhang, Z. Identification of changes in the volatile compounds of robusta coffee beans during drying based on HS-SPME/GC-MS and E-nose analyses with the aid of chemometrics. *LWT* **2022**, *161*, 113317. [CrossRef]
19. Dzung, N.H.; Dzuan, L.; Tu, H.D. The role of sensory evaluation in food quality control, food research and development: A case of coffee study. In Proceedings of the 8th Asean Food Conference, Hanoi, Vietnam, 8–11 October 2003; pp. 862–866.
20. Fuentes, S.; Gonzalez Viejo, C.; Torrico, D.D.; Dunshea, F.R. Development of a biosensory computer application to assess physiological and emotional responses from sensory panelists. *Sensors* **2018**, *18*, 2958. [CrossRef]
21. Kemp, S.E.; Hollowood, T.; Hort, J. *Sensory Evaluation: A Practical Handbook*; John Wiley & Sons: Hoboken, NJ, USA, 2011.
22. Czerny, M.; Christlbauer, M.; Christlbauer, M.; Fischer, A.; Granvogl, M.; Hammer, M.; Hartl, C.; Hernandez, N.M.; Schieberle, P. Re-investigation on odour thresholds of key food aroma compounds and development of an aroma language based on odour qualities of defined aqueous odorant solutions. *Eur. Food Res. Technol.* **2008**, *228*, 265–273. [CrossRef]
23. Gonzalez Viejo, C.; Fuentes, S. Low-cost methods to assess beer quality using artificial intelligence involving robotics, an electronic nose, and machine learning. *Fermentation* **2020**, *6*, 104. [CrossRef]

24. Huang, C.; Gu, Y. A Machine Learning Method for the Quantitative Detection of Adulterated Meat Using a MOS-Based E-Nose. *Foods* **2022**, *11*, 602. [CrossRef] [PubMed]
25. Fuentes, S.; Summerson, V.; Gonzalez Viejo, C.; Tongson, E.; Lipovetzky, N.; Wilkinson, K.L.; Szeto, C.; Unnithan, R.R. Assessment of smoke contamination in grapevine berries and taint in wines due to bushfires using a low-cost E-nose and an artificial intelligence approach. *Sensors* **2020**, *20*, 5108. [CrossRef]
26. Rasekh, M.; Karami, H. E-nose coupled with an artificial neural network to detection of fraud in pure and industrial fruit juices. *Int. J. Food Prop.* **2021**, *24*, 592–602. [CrossRef]
27. Xu, M.; Wang, J.; Zhu, L. The qualitative and quantitative assessment of tea quality based on E-nose, E-tongue and E-eye combined with chemometrics. *Food Chem.* **2019**, *289*, 482–489. [CrossRef] [PubMed]
28. Michishita, T.; Akiyama, M.; Hirano, Y.; Ikeda, M.; Sagara, Y.; Araki, T. Gas chromatography/olfactometry and electronic nose analyses of retronasal aroma of espresso and correlation with sensory evaluation by an artificial neural network. *J. Food Sci.* **2010**, *75*, S477–S489. [CrossRef]
29. Romani, S.; Cevoli, C.; Fabbri, A.; Alessandrini, L.; dalla Rosa, M. Evaluation of coffee roasting degree by using electronic nose and artificial neural network for off-line quality control. *J. Food Sci.* **2012**, *77*, C960–C965. [CrossRef]
30. Flambeau, K.J.; Lee, W.-J.; Yoon, J. Discrimination and geographical origin prediction of washed specialty Bourbon coffee from different coffee growing areas in Rwanda by using electronic nose and electronic tongue. *Food Sci. Biotechnol.* **2017**, *26*, 1245–1254. [CrossRef]
31. Gonzalez Viejo, C.; Tongson, E.; Fuentes, S. Integrating a Low-Cost Electronic Nose and Machine Learning Modelling to Assess Coffee Aroma Profile and Intensity. *Sensors* **2021**, *21*, 2016. [CrossRef]
32. Viejo, C.G.; Fuentes, S.; Godbole, A.; Widdicombe, B.; Unnithan, R.R. Development of a low-cost e-nose to assess aroma profiles: An artificial intelligence application to assess beer quality. *Sens. Actuators B Chem.* **2020**, *308*, 127688. [CrossRef]
33. Gonzalez Viejo, C.; Fuentes, S.; Torrico, D.; Howell, K.; Dunshea, F.R. Assessment of beer quality based on foamability and chemical composition using computer vision algorithms, near infrared spectroscopy and machine learning algorithms. *J. Sci. Food Agric.* **2018**, *98*, 618–627. [CrossRef] [PubMed]
34. Duran, C.G.V. The Effect of Bubble Formation within Carbonated Drinks on the Brewage Foamability, Bubble Dynamics and Sensory Perception by Consumers. Ph.D. Thesis, The University of Melbourne, Melbourne, Australia, 2020.
35. Gonzalez Viejo, C.; Torrico, D.; Dunshea, F.; Fuentes, S. Emerging Technologies Based on Artificial Intelligence to Assess the Quality and Consumer Preference of Beverages. *Beverages* **2019**, *5*, 62.
36. Fuller, M.; Rao, N.Z. The effect of time, roasting temperature, and grind size on caffeine and chlorogenic acid concentrations in cold brew coffee. *Sci. Rep.* **2017**, *7*, 17979. [CrossRef]
37. Rao, N.Z.; Fuller, M. Acidity and antioxidant activity of cold brew coffee. *Sci. Rep.* **2018**, *8*, 16030. [CrossRef] [PubMed]
38. Wang, N.; Lim, L.-T. Fourier transform infrared and physicochemical analyses of roasted coffee. *J. Agric. Food Chem.* **2012**, *60*, 5446–5453. [CrossRef]
39. Bakke, A.J.; Stubbs, C.A.; McDowell, E.H.; Moding, K.J.; Johnson, S.L.; Hayes, J.E. Mary Poppins was right: Adding small amounts of sugar or salt reduces the bitterness of vegetables. *Appetite* **2018**, *126*, 90–101.
40. Ley, J.P. Masking bitter taste by molecules. *Chemosens. Percept.* **2008**, *1*, 58–77. [CrossRef]
41. Noda, K.; Amano, Y.; Shimamura, Y.; Murata, M. Distribution of pyrrolothiazolate, a pigment formed through the Maillard reaction between cysteine and glucose, in foods and beverages and some of its properties. *Food Sci. Technol. Res.* **2020**, *26*, 735–742. [CrossRef]
42. Rojo-Poveda, O.; Barbosa-Pereira, L.; Mateus-Reguengo, L.; Bertolino, M.; Stévigny, C.; Zeppa, G. Effects of particle size and extraction methods on cocoa bean shell functional beverage. *Nutrients* **2019**, *11*, 867. [CrossRef]
43. Ribeiro, J.S.; Ferreira, M.M.; Salva, T. Chemometric models for the quantitative descriptive sensory analysis of Arabica coffee beverages using near infrared spectroscopy. *Talanta* **2011**, *83*, 1352–1358. [CrossRef]
44. Barbin, D.F.; Felicio, A.L.d.S.M.; Sun, D.-W.; Nixdorf, S.L.; Hirooka, E.Y. Application of infrared spectral techniques on quality and compositional attributes of coffee: An overview. *Food Res. Int.* **2014**, *61*, 23–32. [CrossRef]
45. Okubo, N.; Kurata, Y. Nondestructive classification analysis of green coffee beans by using near-infrared spectroscopy. *Foods* **2019**, *8*, 82. [CrossRef] [PubMed]
46. Esteban-Díez, I.; González-Sáiz, J.; Sáenz-González, C.; Pizarro, C. Coffee varietal differentiation based on near infrared spectroscopy. *Talanta* **2007**, *71*, 221–229. [CrossRef] [PubMed]
47. LeBouf, R.F.; Aldridge, M. Carbon monoxide emission rates from roasted whole bean and ground coffee. *J. Air Waste Manag. Assoc.* **2019**, *69*, 89–96. [CrossRef] [PubMed]
48. Newton, J. Carbon monoxide exposure from coffee roasting. *Appl. Occup. Environ. Hyg.* **2002**, *17*, 600–602. [CrossRef]
49. Killian, B.; Rivera, L.; Soto, M.; Navichoc, D. Carbon footprint across the coffee supply chain: The case of Costa Rican coffee. *J. Agric. Sci. Technol. B* **2013**, *3*, 151.
50. Anaya, A.L.; Cruz-Ortega, R.; Waller, G.R. Metabolism and ecology of purine alkaloids. *Front. Biosci.-Landmark* **2006**, *11*, 2354–2370. [CrossRef]
51. Yu, J.-M.; Chu, M.; Park, H.; Park, J.; Lee, K.-G. Analysis of volatile compounds in coffee prepared by various brewing and roasting methods. *Foods* **2021**, *10*, 1347. [CrossRef]

52. Diviš, P.; Pořízka, J.; Křikala, J. The effect of coffee beans roasting on its chemical composition. *Potravin. Slovak J. Food Sci.* **2019**, *13*, 344–350. [CrossRef]
53. Toledo, P.R.; Pezza, L.; Pezza, H.R.; Toci, A.T. Relationship between the different aspects related to coffee quality and their volatile compounds. *Compr. Rev. Food Sci. Food Saf.* **2016**, *15*, 705–719. [CrossRef]
54. Wang, F.; Shen, H.; Liu, T.; Yang, X.; Yang, Y.; Guo, Y. Formation of pyrazines in Maillard model systems: Effects of structures of lysine-containing dipeptides/tripeptides. *Foods* **2021**, *10*, 273. [CrossRef] [PubMed]
55. Caporaso, N.; Whitworth, M.B.; Cui, C.; Fisk, I.D. Variability of single bean coffee volatile compounds of Arabica and robusta roasted coffees analysed by SPME-GC-MS. *Food Res. Int.* **2018**, *108*, 628–640. [CrossRef] [PubMed]
56. Gonzalez Viejo, C.; Harris, N.M.; Fuentes, S. Quality Traits of Sourdough Bread Obtained by Novel Digital Technologies and Machine Learning Modelling. *Fermentation* **2022**, *8*, 516. [CrossRef]