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Research Article

Green Chemistry Applied to Ground Coffee Volatile Compounds Modification Aiming Coffee Aroma Improvement

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Aroma has a major role in coffee acceptance by consumers. This work has assessed the application of cold plasma technology to induce modifications in ground coffee beans without resorting to solvents or additives, thus applying a green chemistry approach. Cold plasma improved and modulated coffee aroma, increasing desirable and decreasing undesirable aroma notes. Ground coffee beans were subjected to dielectric-barrier discharge (DBD) plasma at different excitation frequencies. Its volatile chemical profile was determined by GC-MS. The odor activity value technique was used to evaluate the aroma profile. Extensive chemical changes occurred with aldehydes, furans, and pyrazine compounds. This work showed that setting proper excitation frequency enables modulating changes toward oxidation and C-C bond scission. Chemical reaction pathways were postulated and discussed. DBD plasma technology enhanced the importance of the desirable cocoa note from 74.4 to 88.6% and decreased the significance of the green and fruity notes from 8.5 to 3.2% and 2.7 to 1.9%, respectively. Plasma-induced reactions can help mitigating aroma defects.

1. Introduction

Coffee is one of the world's most consumed beverages. Coffee is consumed in its roasted, ready-to-drink instant, and instant versions. Factors such as variety, origin, processing, and preparation methods changes considerably coffee flavor [1, 2]. One of the most critical aspects of roasted coffees is their aroma. Persons that drink coffee regularly are attracted to the smell of coffee, which drives their will to consume coffee.

Several studies have used descriptive sensory analysis of coffee [3–5]. These studies have described up to 127 sensory characteristics of coffee, including aroma, flavor, and texture. Between 12 and 33 aroma attributes have been reported [4, 6]. The primary trend observed by these studies is that descriptors such as coffee, roasted, cocoa, and burnt are considered coffee-like aromas. In contrast, musty, earthy, and green descriptors are characterized by noncoffee-like aromas [6]. Flavor and

aroma descriptors can trigger different emotional responses, with roast and burnt aromas associated with positive emotions and citrus aromas related to negative emotions [6], thus showing the importance of good flavor characteristics.

The flavor, aroma, and texture of the coffee bean depend on many factors, including variety, geographical origin, climatic factors, maturation of the cherry, fermentation, drying, roasting, and storage conditions [7, 8]. More recently, studies reported that pollination enhanced coffee's volatile compounds [9]. The aroma of the powdered coffee beans depends on these factors, where roasting is considered the final line of chemical modification of the aroma.

Several volatile compounds determine the aroma of powdered coffee beans, such as furans, pyridine, pyrroles, pyrazines, esters, ketones, alcohols, aldehydes, and alcohols. Pyrazines, pyridines, and pyrroles are important compounds, which are related to desired attributes such as nutty, cocoa,

and roasted notes [10]. On the other hand, some aldehydes, alcohols, and esters are related to undesired or less desirable attributes, such as green and fruity notes, usually associated with light coffee, which most customers do not accept well [11–13].

Prior works from our group reported that cold plasma induces several chemical reactions to aroma compounds in fruit juices [14, 15]. Cold plasma technology can successfully modulate fruit juices aroma that are rich on sesquiterpenoids and terpenoids. Plasma processing induces hydrolysis, dehydrogenation, isomerization, scission, hydrogenation, ring closure, and opening reactions. Furthermore, such reactions can be controlled changing the operating conditions during processing [14]. Plasma-induced reactions are identical to the reactions that occur in plants since they are based on the same free radicals that are naturally produced during stress-driven or normal metabolism [16].

This study has assessed the application of cold plasma in promoting chemical changes in powdered coffee beans to improve their aroma, increasing the desirable and decreasing the undesirable aroma notes. To accomplish this goal, ground coffee beans were subjected to DBD plasma at three excitation frequencies. The volatile compounds profile of the ground coffee beans' aroma was determined by GC-MS. The evaluation of the aroma profile was carried out by means of the odor activity value (OAV). The chemical changes observed in powdered coffee beans were presented, and the chemical pathways proposed.

2. Materials and Methods

2.1. Materials. Brazilian arabica coffee grains (Melitta, Brazil) were bought from a local vendor. The coffee grains were ground in an electric coffee grinder (Cuisinart, Brazil) for 30 s. Ribitol was purchased from Merck.

2.2. Plasma Processing. The DBD plasma treatments were carried out using an Inergiae model pulse 0300 plasma generator. Plasma was generated in a gap (15 mm) between two aluminum electrodes of 80 mm diameter. The dielectric barrier consisted of two 5.0 mm thick acrylic plates. The experiments were carried out at three plasma excitation frequencies, 50, 500, and 1000 Hz. A 20 kV electrical potential difference was applied between the electrodes. Processing time was set at 15 and 30 min. Coffee powder (25 g) was subjected to cold plasma placed on acrylic petri dishes. Untreated coffee powder consisted of the control sample. All experiments were done in triplicates.

2.3. GC-MS Analysis. A sample of 5.0 g of coffee powder was added to a 20 mL vial and equilibrated at 40°C for 20 min. A manual SPME holder with a DVB/CAR/PDMS (50/30 μm) of 2 cm length fiber was employed to adsorb the sample volatile compounds. The SPME fiber was exposed to the sample headspace for 20 min at 40°C. The volatiles were desorbed directly on the GC liner after extraction. The fiber was reconditioned at 250°C for 10 min in the GC injector. Samples were analyzed in a gas chromatograph coupled with a mass spectrum (Thermos model ISQ). The injector and the

interface temperatures were 250°C working in splitless mode. Chromatographic separations were performed using a (5%-phenyl-) methylpolysiloxane column (30 m × 0.25 mm ID × 0.25 μm film). The temperature programming started at 40°C for 4 min, increased to 80°C at 2.5°C.min^{-1}, increased to 100°C at 5.0°C.min^{-1} holding at this temperature for 1 min, and then increased to 250°C at 10.0°C.min^{-1} maintaining the final temperature for 1 min. The ion trap detector operated in the EI mode at 70 eV and 200°C with a mass scan range of 50 to 400 m/z. The carrier gas was helium set at a 1.0 mL.min^{-1} flow rate. The mass spectra were compared with the NIST and Wiley mass spectra library.

2.4. Odor Profile. The coffee powder volatile compounds were grouped according to their primary odor description. All primary descriptors were obtained in "*The Good Scent Company*" database [17]. The odor activity value (OAV) was calculated based on the mass fraction of each substance divided by its odor threshold in water [18]. The OAV of each substance were summed following their odor description. The five primary odor descriptors that give coffee its characteristic aroma were presented in the following radar plots: nutty, cocoa, fruity, green, and meaty.

The water odor threshold values were obtained in the literature [19–26].

2.5. Statistical Analysis. Statistical analysis was done using Statistica v.13 (TIBCO softwares). The experiments followed a 2^3 factorial design with processing time (0, 15, and 30 min) and excitation frequency (50, 500, and 1000 Hz) being the independent variables. Each volatile compound's mass fractions (% w/w) were considered the dependent variables. Means comparison were carried out applying the Fisher LSD test at a 95% level of confidence.

3. Results and Discussion

3.1. Volatile Compounds Profile. Table 1 shows the volatile compounds identified in coffee powders (treated and untreated), retention times (RT), odor threshold, Kováts index, and primary odor description. A total of twenty-five compounds were identified, accounting for $97 \pm 1\%$ of the total peek area. Three compounds ($3 \pm 1\%$ of the total peak area) were not identified due to being present in trace amounts.

The volatiles in coffee powder are a mixture consisting of alcohols, aldehydes, furans, pyrazines, pyrroles, and other nitrogenated and oxygenated compounds. In terms of mass fraction, coffee powder has high concentrations of 2-methylfuran, 2-methylbutanal, 3-methylbutanal, and 2,5-dimethyl furan, pyridine, 2-furan methanol, and 4-methyl pyrimidine.

Reports in the literature evidence a considerably diverse volatile profile of coffees in relation to each compound's concentration (or mass fraction). Coffee commonly presents many pyrazines, pyrroles, furans, aldehydes, ketones, and pyridines. Compared to an arabica Brazilian coffee produced at a different location, higher concentrations of 3-methylbutanal, 2-methylbutanal, 2,5-dimethyl furan, and 2-furan methanol acetate were observed in the coffee applied in this

Table 1: Volatile compounds identified in ground coffee beans and their respective retention times (RT), Kovacs index, main *m/z*, odor threshold in water, and odor description.

Compound	Retention time (min)	Kovacs index	*m/z*	Odor threshold in water (mg/L)	Odor description
2-Methylfuran	1.64	644	82, 53, 39	—	—
2-Methylbutanal and 3-methylbutanal	2.12	703	44, 58, 71	0.002	Cocoa
2,5-Dimethyl furan	2.44	712	96, 43, 53	0.1	Meaty
1,5-Hexadien-3-ol	3.02	728	57, 29, 39	0.5	Fruity
2-Methyl-1H-pyrrole	3.14	731	80, 53, 28	0.017	Nutty
Pyridine	3.27	735	79, 52, 39	2.0	Fishy
Not identified	3.50	741	79, 52, 91	—	—
Hexanal	4.60	771	44, 56, 72	0.0045	Green
5-Hydrazino-1H-1,2,3,4-tetrazole	4.92	779	72, 100, 207	—	—
Furfuryl methyl ether	5.40	792	81, 112, 53	—	Coffee
4-Methyl pyrimidine	5.52	796	94, 40, 53	—	—
Furfural	5.79	803	96, 39, 67	0.77	Bready
2-Furan methanol	6.67	827	98, 41, 81	2.0	Bready
2-Furyl methyl ketone	9.00	890	95, 110, 39	10.0	Balsamic
2,6-Dimethylpyrazine	9.17	895	108, 42, 67	10.0	Chocolate
2-Ethylpyrazine and 2,3-dimethylpyrazine	9.27	898	107, 80, 53	2.5	Nutty
5-Methyl-2-furaldehyde	11.62	962	110, 53, 81	1.11	Caramellic
3-Ethyl-2,5-dimethylpyrazine	11.94	970	135, 42, 108	0.001	Nutty
2-Pentyl furan	12.78	993	81, 138, 53	0.006	Fruity
2-Furan methanol acetate	13.32	1005	81, 98, 140	0.1	Fruity
1-Methyl-1H-pyrrole-2-carbaldehyde	13.90	1015	109, 53, 80	19.6	—
2-Ethyl-3,5-dimethylpyrazine	17.87	1085	135, 42, 108	—	Earthy
2,2′-Methylenedi furan	18.03	1087	91, 148, 39	—	—
2-Furan methanol propionate	18.54	1096	81, 98, 154	—	Fruity
1-(2-Furanylmethyl)-1H-pyrrole	23.20	1190	81, 147, 53	0.1	Vegetable

work. The content of pyridine was similar, and the contents of 5-methylfuran aldehyde, 3-furan methanol, and 2-ethyl-3-methylpyrazine were lower [27]. Compared to an arabica Colombian coffee, the results presented herein showed higher concentrations of pyridine, 2-methylbutanal, and 3-methylbutanal. While the content of 2,5-dimethyl furan and 2-furan methanol acetate were similar. Lower concentration of furfural was detected [28].

Table 2 presents the volatile profile of coffee powders subjected to DBD plasma. The studied operating conditions have significantly modified the volatile compounds content in the coffee powder aroma ($p < 0.05$) compared to the control sample (untreated coffee).

Figure 1 presents a heat map concerning the modifications in the volatile components' mass fractions with untreated coffee powder as a basis for comparison. The darker colors indicate modifications above 50% in the components' mass fraction, and lighter colors indicted modifications below 25%.

Overall, the plasma treatment induced similar molecular changes independently of the applied excitation frequency and processing time. The changes in mass fractions increased with increasing processing times. The excitation frequency presented a less significant effect in coffee powders than in camu-camu juice, where a significant effect in the plasma-induced chemical reactions selectivity was due to the excitation frequency [29]. High excitation frequencies (600 to 1000 Hz) generate more ozone and reactive oxygen species, while low frequencies (50 to 200 Hz) generate more hydroxyl and hydrogen radicals [30, 31].

The discussion on the effects of cold plasma on the profile of volatile compounds will be divided into their main chemical classes (furans, pyrazines, pyrroles, aldehydes, and alcohols) for better understanding of the changes and induced chemical reactions. This division is essential to identify within compound groups the reactions pathways that are occurring. In this work, we have analyzed the mass balance of each aroma compound to identify the possible chemical reactions observed during plasma treatment, as commonly done in reaction engineering. The proposed reaction routes were verified with chemistry reactions theory to evaluate their suitability.

The contents of alcohols and pyrroles did not change significantly after L processing. Aldehydes concentration

TABLE 2: Mass fraction (% w/w) of the ground coffee volatile compounds.

Compound	Control (untreated)	50 Hz 15 min	50 Hz 30 min	500 Hz 15 min	500 Hz 30 min	1000 Hz 15 min	100 Hz 30 min
2-Methylfuran	16.4 ± 0.5^a	15.8 ± 0.5^{ab}	8.5 ± 0.5^e	14.5 ± 0.5^b	10.7 ± 0.5^d	12.8 ± 0.6^c	11.3 ± 0.5^d
2-Methylbutanal and 3-methylbutanal	15.5 ± 0.5^a	14.0 ± 0.5^b	8.6 ± 0.5^d	12.1 ± 0.5^c	11.9 ± 0.5^c	11.4 ± 0.5^c	12.5 ± 0.6^c
2,5-Dimethyl furan	8.7 ± 0.3^a	8.3 ± 0.3^a	4.5 ± 0.3^c	6.4 ± 0.3^b	6.8 ± 0.3^b	6.6 ± 0.4^b	6.7 ± 0.3^b
1,5-Hexadien-3-ol	0.3 ± 0.1^a	0.2 ± 0.1^{ab}	0.2 ± 0.1^{ab}	0.1 ± 0.1^b	0.2 ± 0.1^{ab}	0.2 ± 0.1^{ab}	0.1 ± 0.1^b
2-Methyl-1H-pyrrole	3.0 ± 0.2^{ab}	2.6 ± 0.2^b	3.3 ± 0.2^a	3.0 ± 0.2^{ab}	3.3 ± 0.2^a	3.3 ± 0.2^a	3.0 ± 0.2^{ab}
Pyridine	8.3 ± 0.3^e	10.6 ± 0.3^c	9.3 ± 0.4^d	13.3 ± 0.5^b	10.1 ± 0.4^{cd}	15.1 ± 0.7^a	10.7 ± 0.6^c
Not identified	1.7 ± 0.2^a	0.9 ± 0.1^b	1.9 ± 0.3^a	0.4 ± 0.2^c	1.7 ± 0.2^a	0.4 ± 0.1^c	1.4 ± 0.2^b
Hexanal	4.0 ± 0.2^a	2.4 ± 0.3^b	0.8 ± 0.1^c	2.4 ± 0.2^b	1.1 ± 0.1^c	2.3 ± 0.2^b	1.0 ± 0.2^c
5-Hydrazino-1H-1,2,3,4-tetrazole	4.0 ± 0.2^a	3.6 ± 0.2^{ab}	3.1 ± 0.2^c	3.7 ± 0.2^{ab}	3.4 ± 0.2^{bc}	3.5 ± 0.2^{bc}	3.4 ± 0.2^{bc}
Furfuryl methyl ether	0.4 ± 0.1^a	0.0 ± 0.0^b	0.2 ± 0.1^{ab}	0.0 ± 0.0^b	0.2 ± 0.1^{ab}	0.0 ± 0.0^b	0.2 ± 0.1^{ab}
4-Methyl pyrimidine	7.9 ± 0.3^d	9.4 ± 0.3^{bc}	8.5 ± 0.3^{cd}	9.8 ± 0.4^{ab}	8.6 ± 0.3^{cd}	10.7 ± 0.4^a	8.6 ± 0.4^{cd}
Furfural	2.1 ± 0.2^d	3.0 ± 0.3^c	7.1 ± 0.3^a	4.0 ± 0.2^b	7.3 ± 0.4^a	4.5 ± 0.2^b	6.9 ± 0.4^a
2-Furan methanol	9.7 ± 0.4^{cd}	8.9 ± 0.4^d	22.2 ± 0.5^a	10.7 ± 0.5^c	16.6 ± 0.6^b	11.0 ± 0.4^c	15.7 ± 0.5^b
2-Furyl methyl ketone	0.6 ± 0.1^c	0.7 ± 0.1^c	1.3 ± 0.2^a	0.8 ± 0.1^{bc}	1.1 ± 0.1^{ab}	0.8 ± 0.1^{bc}	1.1 ± 0.1^{ab}
2,6-Dimethylpyrazine	2.0 ± 0.3^b	3.0 ± 0.3^a	1.9 ± 0.2^b	2.8 ± 0.3^a	1.6 ± 0.2^b	3.0 ± 0.2^a	1.6 ± 0.3^b
2-Ethylpyrazine and 2,3-dimethylpyrazine	3.0 ± 0.3^a	3.4 ± 0.3^a	3.3 ± 0.4^a	3.5 ± 0.3^a	2.1 ± 0.3^b	3.2 ± 0.3^a	2.7 ± 0.3^{ab}
5-Methyl-2-furaldehyde	1.3 ± 0.2^c	1.6 ± 0.2^{bc}	2.8 ± 0.2^a	1.8 ± 0.2^{bc}	2.4 ± 0.3^{ab}	1.8 ± 0.2^{bc}	2.6 ± 0.2^a
3-Ethyl-2,5-dimethylpyrazine	1.3 ± 0.2^a	0.2 ± 0.1^b	0.2 ± 0.1^b	0.1 ± 0.1^b	0.2 ± 0.1^b	0.2 ± 0.1^b	0.2 ± 0.2^b
2-Pentyl furan	1.4 ± 0.2^b	1.9 ± 0.2^a	0.9 ± 0.2^c	1.8 ± 0.2^{ab}	0.6 ± 0.1^c	1.6 ± 0.2^{ab}	0.5 ± 0.2^c
2-Furan methanol acetate	3.9 ± 0.3^d	5.3 ± 0.3^{bc}	7.0 ± 0.3^a	4.9 ± 0.3^c	6.0 ± 0.3^b	4.0 ± 0.3^d	5.9 ± 0.4^b
1-Methyl-1H-pyrrole-2-carbaldehyde	0.6 ± 0.1^a	0.7 ± 0.2^a	0.6 ± 0.1^a	0.2 ± 0.1^b	0.6 ± 0.1^a	0.3 ± 0.1^b	0.5 ± 0.1^{ab}
2-Ethyl-3,5-dimethylpyrazine	0.3 ± 0.1^a	0.5 ± 0.1^a	0.3 ± 0.1^a	0.5 ± 0.1^a	0.3 ± 0.1^a	0.5 ± 0.1^a	0.3 ± 0.1^a
2,2′-Methylenedi furan	0.3 ± 0.1^a	0.3 ± 0.1^a	0.2 ± 0.1^a	0.2 ± 0.1^a	0.2 ± 0.1^a	0.2 ± 0.1^a	0.2 ± 0.1^a
2-Furan methanol propionate	0.0 ± 0.0^a	0.1 ± 0.1^a	0.1 ± 0.1^a	0.2 ± 0.1^a	0.1 ± 0.1^a	0.2 ± 0.1^a	0.1 ± 0.1^a
1-(2-Furanylmethyl)-1H-pyrrole	0.0 ± 0.0^a	0.1 ± 0.1^a	0.1 ± 0.1^a	0.1 ± 0.1^a	0.1 ± 0.1^a	0.1 ± 0.1^a	0.1 ± 0.1^a

*Letters indicate significant differences among the treatments for each compound.

decreased significantly (16 to 51%), mainly when a 50 Hz excitation frequency was applied for 30 min (51%). The concentration of furans and pyrazines increased after the treatment (2 to 23% and 0 to 43%, respectively). The increase in pyrazine content occurred in the first 15 min, decreasing back to near the initial levels after 30 min of treatment. Furans showed little change in the first 15 min of treatment but raised significantly after 30 min. The decrease in pyrazines and increase in furans observed after 30 min can be attributed to the accumulation of ROS and to the higher levels of oxidation of compounds during longer treatments.

All three aldehydes' volatiles in the coffee powder decreased in content after plasma treatment. Hexanal presented the highest percentual decrease (40 to 80%), while 3-methylbutanal and 2-methylbutanal showed the highest mass change (10 to 45%), given their higher concentration in coffee aroma. The aldehydes compounds decreased more intensely at a 50 Hz than at 500 or 1000 Hz. The higher reaction rates observed at 50 Hz demonstrate that the aldehydes present in

the coffee powder reacted with hydronium, hydroxyl, or hydrogen radicals producing their respective hydrocarbons (hexane, 2-methylbutane, and 3-methylbutane) or alcohols (hexanol, 2-methyl butanol, and 3-methylbutanol). However, due to their high volatility, these products were not detected in the coffee aroma because they might have been volatize during plasma application.

Several chemical shifts were observed among furans. A significant decrease (6 to 57%) was observed in the concentration of 2-methylfuran, the main furan compound in the control sample (untreated powder). A similar decay trend occurred with 2,5-dimethyl furan and 2-pentyl furan. The highest decrease in 3-methylfuran and 2,5-dimethyl furan occurred at 50 Hz.

The highest increments were observed for furfural, 2-furan methanol and 2-furan methanol acetate (in mass basis). Furfural concentration raised 181%, while 2-furan methanol concentration increased by 86%. The excitation frequency was important to the selectivity of the reactions since the
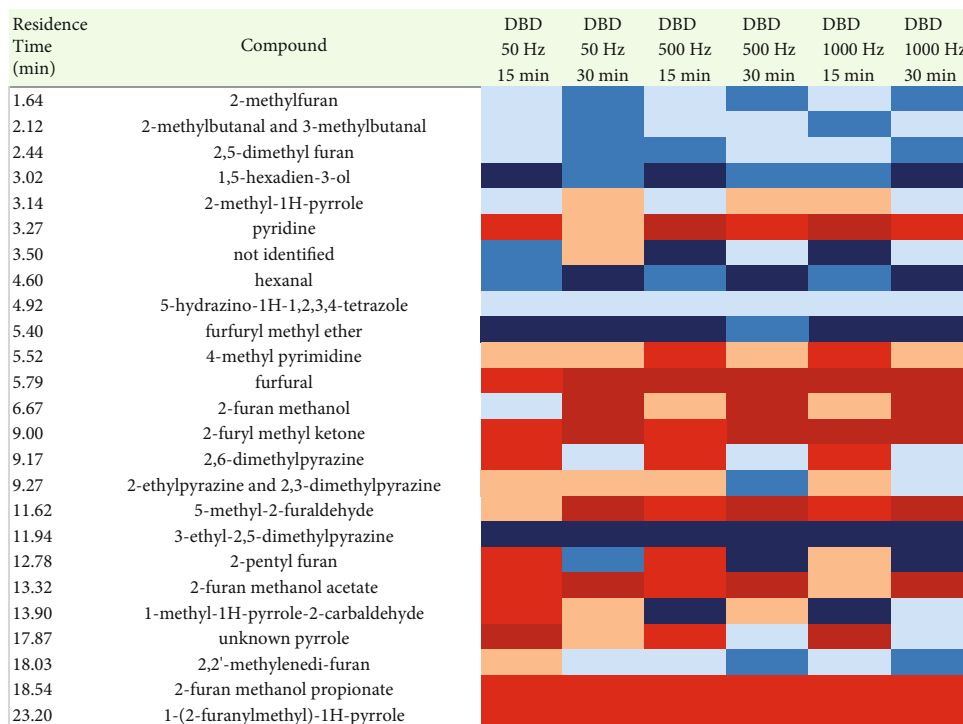
Residence Time (min)	Compound	DBD 50 Hz 15 min	DBD 50 Hz 30 min	DBD 500 Hz 15 min	DBD 500 Hz 30 min	DBD 1000 Hz 15 min	DBD 1000 Hz 30 min
1.64	2-methylfuran						
2.12	2-methylbutanal and 3-methylbutanal						
2.44	2,5-dimethyl furan						
3.02	1,5-hexadien-3-ol						
3.14	2-methyl-1H-pyrrole						
3.27	pyridine						
3.50	not identified						
4.60	hexanal						
4.92	5-hydrazino-1H-1,2,3,4-tetrazole						
5.40	furfuryl methyl ether						
5.52	4-methyl pyrimidine						
5.79	furfural						
6.67	2-furan methanol						
9.00	2-furyl methyl ketone						
9.17	2,6-dimethylpyrazine						
9.27	2-ethylpyrazine and 2,3-dimethylpyrazine						
11.62	5-methyl-2-furaldehyde						
11.94	3-ethyl-2,5-dimethylpyrazine						
12.78	2-pentyl furan						
13.32	2-furan methanol acetate						
13.90	1-methyl-1H-pyrrole-2-carbaldehyde						
17.87	unknown pyrrole						
18.03	2,2'-methylenedi-furan						
18.54	2-furan methanol propionate						
23.20	1-(2-furanylmethyl)-1H-pyrrole						

FIGURE 1: Heat map presenting the modifications in the volatile components mass fractions having the untreated coffee powder as a comparison basis.
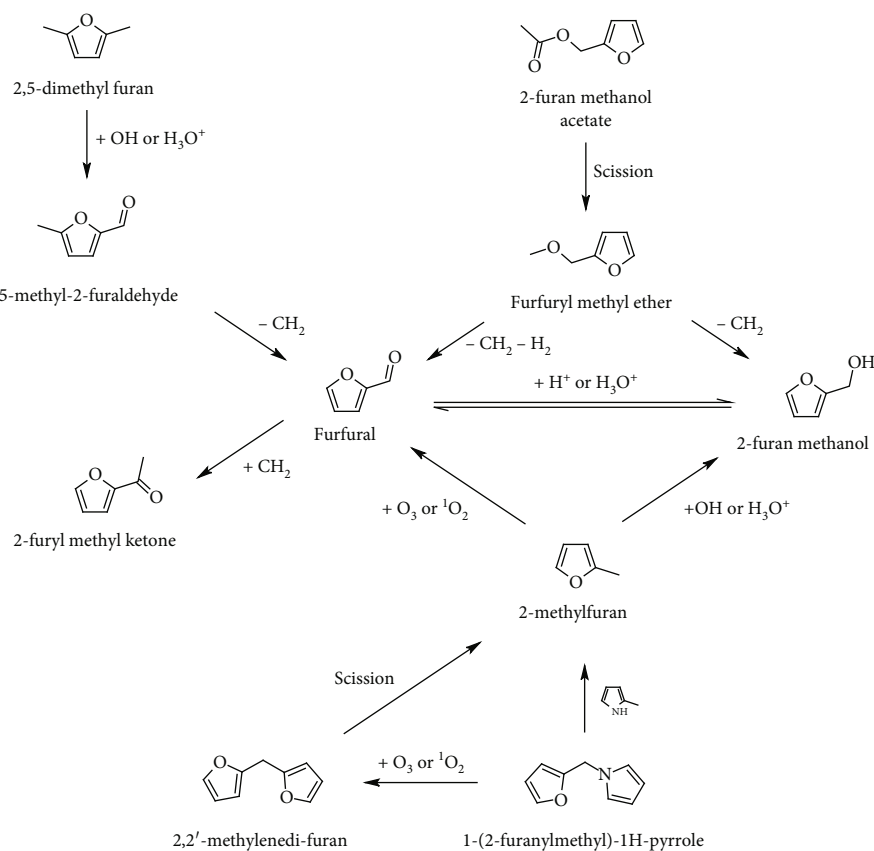
FIGURE 2: Plasma-induced chemical reactions on furans contained in powdered coffee beans.
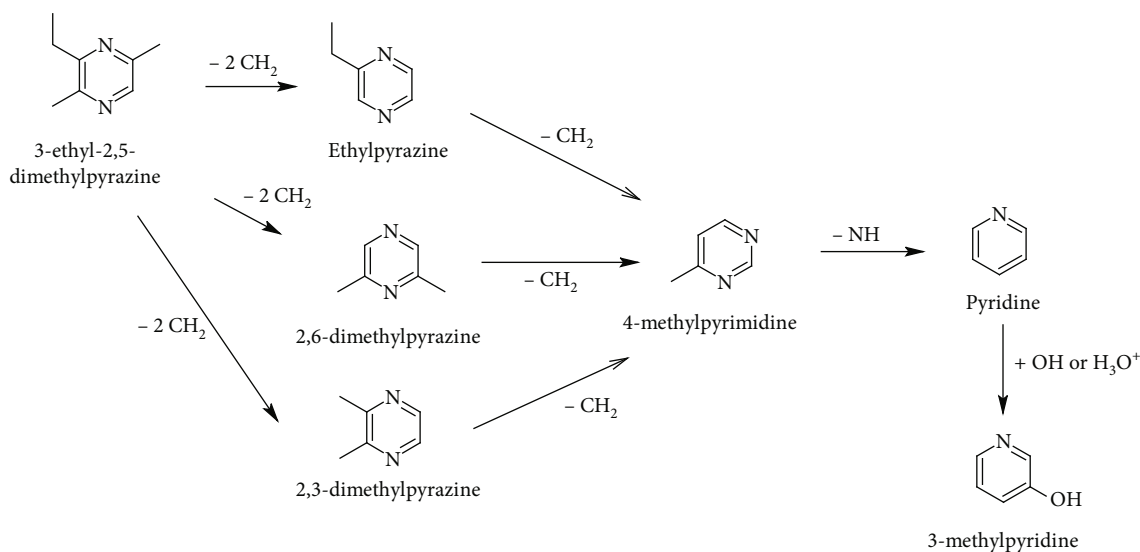
Figure 3: Plasma-induced chemical reactions on pyrazines and pyridines present in powdered coffee beans.

highest rise in furfural was attained at 500 Hz and the increase in 2-furan methanol acetate and 2-furan methanol occurred at 50 Hz.

Figure 2 presents the putative chemical reactions related to the changes observed in furans. Many compounds were converted into furfural and 2-furan methanol that showed to be two central compounds for these reactions. The reactions of 2-methyl furan into 2-furan methanol, 2,5-dimethyl furan into 5-methyl-2-furaldehyde, and furfural into 2-furan methanol occur to greater extent at low excitation frequencies because of the higher hydronium, hydroxyl, and hydrogen radical concentrations [30, 31]. At higher excitation frequencies, the conversion of 1-(2-furanylmethyl)-1H-pyrrole to $2,2'$-methylenedi-furan, 2-methyl furan to furfural, and 2-furan methanol to furfural occur to larger extent due to the higher content of ozone, oxygen singlet, and superoxide radicals [30, 31]. The scission reaction of $2,2'$-methylenedi furan and 1-(2-furanylmethyl)-1H-pyrrole to 2-methylfuran occurred at all excitations frequencies. Scission of methylene units were observed and resulted in the conversion of 5-methyl-2-furaldehyde and furfuryl methyl ether to furfural, and furfuryl methyl ether to 2-furan methanol. Photon irradiation and reacting plasma species bombardment can lead to C-C bond scissions that abstract CH_2 from terminal bonds generating metastable C-radicals. This carbon radical can further on react with furfural forming 2-furylmethyl ketone [32]. Part of the reactions observed in the powdered coffee subjected to cold plasma was also observed in the treatment of ready-to-drink coffee subjected to plasma processing [33]. The main difference was on the reaction selectivity due to the much greater presence of water, thus plasma-induced water radicals.

Only slight changes were observed in coffee powder pyrroles. The main difference was in forming 1-(2-furanylmethyl)-1H-pyrrole, which was not present in the untreated sample. The production of 1-(2-furanylmethyl)-1H-pyrrole might have occurred by the reaction of 2-methyl-1H-pyrrole and 2-methylfuran following a similar pathway as described by Baltes and Knoch [34].

The content of pyrazines increased in the first 15 min of treatment and then reduced after 30 min. This trend indicates that pyrazines are probably intermediate compounds. Among the cyclic nitrogenated compounds, there was a percentual increase in pyridine and 4-methyl pyrimidine and net consumption of 2,6-dimethylpyrazine, 2,3-dimethylpyrazine, 2-ethylpyrazine, and 3-ethyl-2,5-dimethylpyrazine. The highest decrease was observed for 3-ethyl-2,5-dimethylpyrazine (91%), 2-ethylpyrazine, and 2,3-dimethylpyrazine (30%).

Figure 3 presents a proposed chemical pathway for the transformation observed in cyclic nitrogenated compounds. The reactions observed with pyrazines were mainly C-C bond scissions with CH_2 abstraction. Compounds with more and longer branches tended to scission toward blends with fewer or shorter components. As such, 3-ethyl-2,5-dimethyl-pyrazine was transformed into either ethylpyrazine, 2,6-dimethylpyrazine, or 2,3-dimethylpyrazine, and the latter compounds were converted to 4-methylpyrimidine. The reaction is followed by NH abstraction forming pyridine, which under some operating conditions, is oxidized to 3-methylpyridine.

The reaction pathways presented in this work have been described previously in biochemistry and chemistry research. The reactions between furfural, 2-methylfuran, and furfuryl methyl ether were described by Velea et al. [35]. The formation of 5-methyl-2-furaldehyde and furfural from methyl and dimethylfurans has been described by Traynelis et al. [36]. Several reactions derived from furfural have been discussed by Zeitsch [37]. The degradation pathway of alkylpyrazines have been proposed and described by Zhang et al. [38].

3.2. Modifications in the Aroma Profile. Figure 4 shows the changes in the coffee powder's five main odor descriptors. The plasma-induced reactions on coffee powder volatiles directly influenced its aroma profile, with considerable
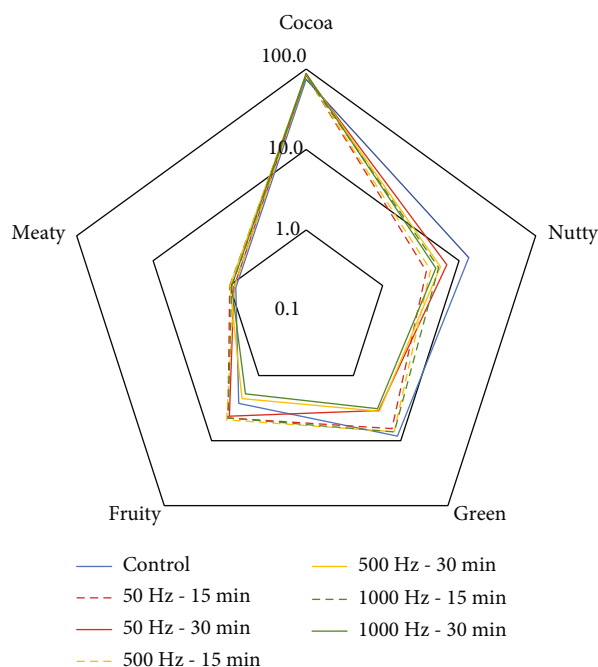
FIGURE 4: Radar plot of coffee aroma profile.

modifications in the strength of the cocoa, nutty, and green descriptors.

The untreated powdered coffee beans aroma was characterized by 75.4% cocoa, 12.3% nutty, 8.7% green, 2.7% fruity, and 0.8% meaty descriptors. Plasma-induced reactions enhanced the importance of the cocoa descriptor and considerably decreased the importance of the green and nutty descriptors. A disadvantage of plasma processing was in the decrease on the aroma intensity observed due to a reduction in the total OAV by 20 to 51%. This reduction indicated a significant loss of intensity.

The reduction in cocoa, nutty, and green descriptors' OAV was the main responsible for the decrease in total OAV. This reduction was caused by the decrease in the concentration of 2-methylbutanal, 3-methylbutanal, 3-ethyl-2,5-dimethylpyrazine, and hexanal compounds that have low odor threshold and greatly contribute toward coffee powder aroma.

The importance of the cocoa descriptor increased from 75% to between 84 and 90%, despite the decrease in the concentrations of 3-methylbutanal and 2-methylbutanal. The increased relevance occurred due to a higher loss of the total OAV of the nutty and green descriptors. The importance of the nutty descriptor greatly decreased from 12.3% to between 1.9 and 4.3% and occurred due to the decrease in 3-ethyl-2,5-dimethylpyrazine concentration.

The green descriptor lost its relevance from 8.7% to between 3.3 and 7.5% of the total OAV, caused by the reduction in the hexanal content. Hexanal is usually associated with light roasted coffees, which customers do not accept well [13]. Although its loss of intensity, the green descriptor became the second most relevant descriptor in the coffee powder after plasma treatment.

The fruity descriptor enhanced its importance because of the increase in the concentrations of 2-furan methanol acetate and 2-pentyl furan. These two latter compounds are usually associated with overdeveloped roasts and are considered a defect in coffee [12].

The coffee powder used herein presented six components with low odor threshold (< 0.01 mg/L): one pyrrole, two furans, and three aldehydes. The few aromatic chemical compounds with low odor thresholds make the aroma modulation in coffee powder a more difficult challenge. Plasma processing increased the cocoa descriptor importance under all operating conditions, not allowing reasonable control of the changes in the coffee powder.

The modulation of the coffee aroma can be done only for the fruity, nutty, meaty, and green descriptors, since changes in operating conditions can increase or decrease the relevance of these descriptors. Given the low relevance of these four descriptors (< 16%), cold plasma treatment can only change the notes of coffee powder aroma. This situation is very different from the modifications that could be done in camu-camu juice [39], where modulation of three main notes (citrus, woody, and herbal) was feasible. In camu-camu juice, cold plasma induced far more chemical changes than in coffee powder because more compounds of only two main classes of chemical compounds were present (terpenoids and sesquiterpenoids), allowing a more significant modulation of aroma.

Although only four more minor relevant descriptors can be modulated by applying cold plasma, this modulation can be important for developing gourmet or specialty coffees, where consumers appreciate different notes. The increase in importance of the cocoa descriptor from 75% to between 84 and 90% is positive since this is a very desirable note in

coffees. The reduction that can be achieved in the green and fruity descriptors is a positive aspect of plasma processing because these attributes are undesired in coffee.

4. Conclusions

Several chemical reactions were induced in coffee volatiles by DBD plasma processing. Extensive chemical modifications occurred with the coffee's aldehydes, furans, and pyrazines. Little chemical modifications occurred with the coffee's pyrroles compounds. The excitation frequency showed high significance in modulating the changes toward oxidation and C-C bond scissions. The extension of processing time increases the effects of plasma reactive species in the chemical compounds that characterize the powder aroma. The overall reduction of volatile compounds with low odor thresholds was the main disadvantage of plasma processing because it leads to a less pronounced aroma. The increase in desirable cocoa notes and decrease of undesired green and fruity notes were the main advantage of plasma processing. The plasma-induced chemical reaction can be helpful to process coffees with aroma defects, characterized by high amounts of compounds with green and fruity notes.

Data Availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare no conflict of interest.

Authors' Contributions

S. Rodrigues was assigned in the formal analysis, resources, writing, reviewing, and editing. F. A. N. Fernandes was responsible in the conceptualization, investigation, formal analysis, writing, reviewing, and editing.

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