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Thermostability of bioactive compounds during roasting process of coffee beans

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ABSTRACT

The effect of roasting conditions on some physicochemical characteristics of coffee beans as color, browning index, hydroxymethylfurfural (HMF), caffeine, phenolic acids, and antioxidant capacity were investigated. The thermostability of chlorogenic acid and caffeine was investigated using Arrhenius equation. Furthermore, principal component analysis (PCA) was applied to reveal the relationship between the phenolic profiles, browning index, and the antioxidant capacity of coffee. Chlorogenic acid was the main phenolic compounds in coffee beans. It gradually decreased from 34.181 to 2.584 mg/g of sample during roasting at 220 °C for 40 min. Gallic acid, caffeic acid and HMF increased at the beginning of roasting time and decreased afterward. The antioxidant capacity of green coffee showed the highest antioxidant capacity. Two principal components, (PC1 and PC2) with eigenvalues 5.89 and 2.5 respectively, which demonstrated 93.35% of the total variance in the data set. Therefore, the paramount way to reserve a good level of phenolic compounds in parallel with a good taste is the roasting of coffee at 180 °C for 20 min or 220 °C at 10 min.

1. Introduction

Coffee is a common beverage worldwide and its consumption is continuously increasing. *Coffea Arabica* and *Coffea Canephora* are the popular coffee species, which represent 40–60% of the global production of coffee beans (Jeszka-Skowron et al., 2015). Green coffee beans contain various phenolic compounds that exhibit antioxidant capacity, such as chlorogenic, caffeic, ferulic, and coumaric acids (Liang and Kitts, 2016). Chlorogenic acid is the most abundant phenolic acid in green coffee beans. The major form of chlorogenic acid is 5-O-caffeoylquinic acid, which consists of caffeic acid esterified with quinic acid (Moon et al., 2009; Moreira et al., 2015). The presence of covalently-linked chlorogenic acid derivatives in coffee results in high molecular weight phenol-nitrogen condensation reactions, generated by Maillard reaction products during the roasting process (Liang and Kitts, 2016).

Coffee roasting is a thermal process that changes the chemical and physical characteristics of green coffee beans. The most important factors of the roasting process are time and temperature (Baggenstoss et al., 2008; Fisk et al., 2012; Gloess et al., 2014). Variations in these two conditions during roasting will directly affect the moisture, carbohydrate, protein and phenolic acid contents. Consequently, affect the caramelization, Maillard reactions, oxidation, pyrolysis and formation of color and aroma, which are important to suite the consumers needs (Sunarharum et al., 2014; Liu et al., 2016).

Different approaches have been used to evaluate the optimum degree of roasting. These include color development, thermal degradation of chlorogenic acid, and generation of melanoidins via Millard reactions (Baggenstoss et al., 2008). The present study aims at optimizing the roasting process conditions (such as time and temperature) by studying their effect on the phenolic profiles, caffeine, hydroxymethylfurfural (HMF), browning index (BI), and antioxidant capacity of roasted coffee. Besides, the thermal stability of predominant compounds in coffee beans; caffeine, and chlorogenic acid, was investigated using the Arrhenius equation to calculate the activation energy (Ea), constant rate (K) as well as D values. The principal component analysis (PCA) was applied to reveal the relationship between the phenolic profiles, browning index, and the antioxidant capacity of coffee.

2. Material and methods

2.1. Material and chemicals

Green coffee beans, Coffea Arabica, cultivated in Ethiopia, were obtained from El-Orouba Coffee Company, Cairo, Egypt. The

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geographical origin of the sample and its type was confirmed by the supplier. Gallic acid, chlorogenic acid, caffeic acid, cinnamic acid, ferulic acid, p-coumaric caffeine, HMF, and Folin–Ciocalteu, DPPH (2,2-Diphenyl-1-picryl-hydrazyl), ABTS (2,2-azino-bis(3-ethil-benothiazoline-6-sulfonic acid), TPTZ (2, 4, 6- tripyridyl-s-triazine) and sodium carbonate were purchased from Sigma-Aldrich Chemical Co. Inc. (Louis, USA). HPLC-grade acetonitrile and methanol were purchased from Tedia Company, Inc., Fairfield, OH 45014, USA. Ultrapure water from a Milli-Q system (Millipore, Bedford, MA, USA) was used in all experiments.

2.2. Roasting

Three batches of coffee beans (400g) were weighted and each batch was divided into four sub-group, 100 g each. The roasting process of green coffee beans was carried out using a drying oven (Thermo scientific, type Heratherm OMS60, Germany) as a single layer at different temperatures (160 °C, 180 °C and 220 °C) for 10, 20, 30, and 40 min hold at each temperature to cover the three basic levels of roasting being light, medium and dark (Somporn et al., 2011; Pokorná et al., 2015). The green coffee beans were used as a control sample. All roasted coffee bean samples were ground using an electrical mill (Thomas Wiley Laboratory Mill Model 4) and kept at -20 °C until analysis.

2.3. Color attributes

The color attributes of coffee samples were measured using a spectrocolorimeter with the CIE color scale (Hunter, Lab scan XE) according to Commission Internationale de l'Eclairage (CIE) (1976). The instrument was standardized against the white tile of Hunter Lab color standard (LX No.16379): X = 77.26, Y = 81.94, and Z = 88.14. The L*, a*, and b* values were reported. Total color difference (ΔE) was calculated as the following equation:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (1)$$

2.4. Preparation of coffee extracts

The extracts were prepared according to the method described by Budryn et al. (2009). Briefly, green and roasted ground coffee samples were extracted with hot water (75 °C), with an extraction ratio of 1:20, and homogenization for 5 min using an ultrasonic bath (WiseClean, Korea). The samples were then centrifuged at 7000 rpm for 15 min. The samples were filtered with Whatman No. 2 filter paper. The extraction was repeated twice for each sample as in the previous steps.

2.5. Chromatographic analysis of phenolic compounds, HMF and caffeine

Chromatographic analysis of phenolic compounds, HMF, and caffeine were carried out using HPLC model 1100 (Agilent Technologies, CA, USA) system equipped with a quaternary pump, an autosampler injector, and a diode array detector (DAD) according to Kim et al. (2006) with some modification. Ten microliters of samples were injected into an Agilent Eclipse XDB C18 (150 × 4.6 μm; 5 μm) column maintained at 35 °C. The gradient elution consisted of acetonitrile (solvent A) and 2 % acetic acid in water (solvent B) at a flow rate of 0.8 mL/min. Elution was initiated at 0% solvent A; the percentage of solvent A was increased to 15% in 30 min, then to 50% in 20 min, and finally to 100% for 5 min. There was 10 min of post-run for reconditioning. DAD was adjusted at 254 nm for caffeine, 280 nm for HMF, and 280, 320, and 360 nm for benzoic and cinnamic acid derivatives, respectively. Identification and quantification of target compounds were performed by matching the retention times and peak areas with those of the standards.

2.6. Browning index

The absorbance of the five-fold diluted solution of the coffee brews was measured at 420 nm using a UV-VIS spectrophotometer (Labomed Inc., USA) as described by Chung et al. (2013).

2.7. Determination of total phenolic content

The total phenolic content (TPC) was determined according to the Folin-Ciocalteu procedure (Zilic et al., 2012). Briefly, aliquot 50 μL of the extract was pipetted into a test tube and adjusted to 3.5 mL with distilled water. Then, 250 μL of Folin- Ciocalteu reagent was added. After 5 min, the mixture was neutralized with 1.25 mL of 20% sodium carbonate (Na2CO3) solution. The absorbance was measured at 725 nm against the solvent blank after 40 min of incubation in dark at ambient temperature. The total phenolic content was determined through a calibration curve prepared with chlorogenic acid and expressed as milligrams of chlorogenic acid equivalent (mg CAE) per gram of coffee bean sample.

2.8. Determination of antioxidant capacity of extracts

2.8.1. Determination of radical DPPH scavenging capacity

The free radical scavenging capacity of extracts was determined using the stable DPPH* according to Hwang and Do Thi (2014). Aliquot 50 μl of extracts were mixed with 2.95 ml of 200 μM of DPPH*. The absorbance was measured at 517 nm against pure methanol after 1 h of incubation in the dark. The standard curve was prepared using Trolox. Results were expressed as milligrams of Trolox equivalent (mg TE) per gram of coffee bean sample.

2.8.2. Determination of radical ABTS scavenging capacity

The stock solutions of ABTS* reagent was prepared according to Hwang and Do Thi (2014) by reacting equal quantities of a 7 mM aqueous solution of ABTS* with 2.45 mM potassium persulfate for 16 h at ambient temperature in the dark. The working solution was then prepared by diluting 1 mL ABTS* solution with 60 mL of ethanol: water (50:50, v/v) to obtain an absorbance of 1.0 ± 0.02 units at 734 nm using the spectrophotometer. Extracts (50 μL) were reacted with 4.95 ml of the ABTS* solution for 1 h in a dark condition. Then the absorbance was taken at 734 nm. The standard curve was prepared using Trolox. Results were expressed milligrams of Trolox equivalent (mg TE) per g gram of coffee bean sample.

2.8.3. Ferric reducing capacity power (FRAP) assay

The FRAP assay was determined according to Hwang and Do Thi (2014). The stock solutions included 300 mM acetate buffer (3.1 g sodium acetate trihydrate and 16 mL glacial acetic acid, pH 3.6), 10 mM TPTZ solution in 40 mM HCl, and 20 mM ferric chloride (FeCl3.6H2O) solution. The fresh working solution was prepared by mixing 25 mL acetate buffer, 2.5 mL TPTZ solution, 2.5 mL FeCl3.6H2O solution; then the FRAP solution was warmed at 37 °C before using. Extracts (50 μL) were allowed to react with 3.95 ml of the FRAP solution for 30 min in the dark condition. the absorbance of the colored product was recorded at 593 nm. The standard curve was drawn from measuring the absorbance of Trolox standard solutions at the same wavelength. The results were expressed milligrams of Trolox equivalent (mg TE) per gram of coffee bean sample.

2.9. Thermostability parameters

The thermostability parameters were performed by first-order kinetics as described by Nisha et al. (2005) using linear regression between Ln (Ct/C0) versus 't', to calculate the rate of constant (K), where C0 and Ct are the quantitative value of the component under consideration at time zero and time t (min), respectively. Furthermore, the activation energy was calculated by the Arrhenius equation as indicated below:

$$k = A0 \exp(-Ea/RT) \quad (2)$$

Where, k (rate constant), A0 is a frequency constant (1/min), R is a constant equal to 8.314 J/mol-K and Ea is activation energy (KJ/mol) and T is the absolute temperature.

2.10. Statistical analysis

The ANOVA and Duncan's multiple range tests were performed for statistical analysis using Assistat computer programs (Silva and Azevedo, 2006). Values of ($p < 0.05$) was considered to be statistically significant. The PCA model was carried out using the XLStat (2007).

3. Results

3.1. Effect of roasting on physico-chemical attributes of coffee beans

3.1.1. Color, browning index, and HMF

Color is the main physical characteristics of food products as it influences consumer acceptability (Merken et al., 2001). Color of coffee is an important indicator for controlling and ascertaining the quality of the coffee roasting process (Saklar et al., 2001). The effects of roasting time and temperature on L*, a*, b*, and ΔE Hunter parameters as well as browning index and HMF are shown in Table 1. The L* parameter of coffee beans decreased as the time and temperature of the roasting process increased (Table 1). The L* value of coffee beans decreased from 64.30 for green coffee beans to 36.68 and 30.30 after 40 min of roasting at 160 and 180 °C, respectively. Moreover, coffee beans roasted at 220 °C showed drastically reduced L* values (21.48). On the other hand, the parameters a* and b* which indicate redness and yellowness, respectively, increased at the beginning of roasting time and decreased afterward. The highest a* value (14.29) at 160 °C was observed after 30 min, while it was 14.31 and 13.76 after 20 min at 180 and 220 °C, respectively (Table 1). A similar extent of the parameter b* was observed, but the maximum value (32.24) at 160 °C was recorded after 20 min, while it was 32.70 and 30.22 after 10 min at 180 and 220 °C, respectively. In general, the ΔE value (Eq. 1) of roasted coffee significantly increased with increasing roasting time and temperature. The highest ΔE value (44.79) of the coffee samples was observed during roasting at 220 °C for 40 min. The obtained results are very close to the chromatic parameters previously reported by Bicho et al. (2012) for both Arabica and Robusta coffee powder roasted at 200–240 °C for 5–12 min.

The significant decreases in L* values and increases in a*, b*, and ΔE values with increasing roasting time and temperature could be due to the formation of brown pigments through the non-enzymatic browning (Maillard reaction) and phospholipids degradation as well as thermal oxidation of polyphenols (Budryn et al., 2009; Patras, Brunton, O'Donnell and Tiwari, 2010). The obtained results of L*, a*, b* and ΔE were similar to those previously reported by Budryn et al. (2009) and Chung et al. (2014).

Table 1 also shows that the browning index (Abs420) of the roasted coffee beans. It significantly increased ($p < 0.05$) with increasing roasting time and temperature. The browning index increased from 0.068 for the unroasted beans to 0.455, 0.464, and 0.615 for coffee beans roasted for 40 min at 160, 180, and 220 °C, respectively. The increase of browning index (Abs420) could be attributed to increasing roasting time and temperature, which results in more formation of brown pigment via Maillard reactions and thermal oxidation (Patras, Brunton, O'Donnell and Tiwari, 2010).

Hydroxymethylfurfural is the most intermediate furanic compound during Millard's reaction. HMF is formed as a result of the thermal decomposition of hexoses sugars under acidic conditions and can cause an increase in the brown color to the thermally processed food product (Shapla et al., 2018). The formation of HMF during roasting of coffee is presented in Table 1. At 160 °C, HMF gradually increased during roasting up to 0.32 mg/g after 40 min, while at 180 °C the maximum concentration of HMF (0.34 mg/g) formed after 20 min then decreased. At 220 °C, HMF increased to 0.30 mg/g after 20 min with a fast degradation of up to 40 min where most of the HMF decomposed further (0.04 mg/g). The degradation of HMF may be due to the reaction between furanic compound and amino acid degradation products or condensed with aldols and nitrogen-free polymer to generate flavor compounds and melanoidins with different molecular weight (Hofmann, 1998).

3.1.2. Phenolic profile of green and roasted coffee

Phenolic profiles of coffee bean extracts including gallic acid, pyrocatechol, chlorogenic acid, caffeic acid, *p*-coumaric acid, quercetin and kaempferol are presented in Table 2. Chlorogenic acid dominated the phenolic compounds in the coffee bean samples (34.181 mg/g fresh sample). The concentration of this acid drastically reduced (2.584 mg/g sample) during roasting at 220 °C for 40 min. Gallic and caffeic acids seemed to increase at the beginning of roasting time and decreased afterwards. Gallic acid reached the maximum at 160 °C after 30 min (0.384 mg/g), while caffeic acid reached the maximum at the same temperature

Table 1. Color attributes of green and roasted coffee.

Roasting temperature (°C)	Roasting Time (min)	L*	a*	b*	ΔE	BI (Abs_{420})	HMF (mg/g)
Green coffee		64.30^{A}	2.71^{J}	20.78^{F}	0.00^{K}	0.068^{J}	ND
160	10	63.10^{B}	7.33^{I}	28.43^{D}	9.02^{J}	0.075^{J}	ND
	20	50.62^{E}	12.77^{D}	32.24^{A}	20.50^{G}	0.177^{G}	0.10
	30	41.95^{F}	14.29^{A}	29.48^{C}	26.65^{F}	0.341^{F}	0.29
	40	36.68^{G}	13.83^{B}	25.72^{E}	30.20^{E}	0.455^{D}	0.32
180	10	53.89^{D}	11.76^{F}	32.70^{A}	18.24^{H}	0.108^{I}	0.05
	20	35.86^{H}	14.31^{A}	26.02^{E}	31.18^{D}	0.376^{E}	0.34
	30	30.86^{I}	13.63^{BC}	20.78^{F}	35.20^{C}	0.454^{D}	0.28
	40	30.30^{I}	13.49^{C}	20.50^{F}	35.69^{C}	0.464^{C}	0.23
220	10	57.79^{C}	9.44^{G}	30.22^{B}	13.31^{I}	0.148^{H}	0.02
	20	36.48^{GH}	13.76^{B}	25.70^{E}	30.35^{E}	0.498^{B}	0.30
	30	25.08^{J}	12.09^{E}	14.89^{G}	40.78^{B}	0.608^{A}	0.12
	40	21.48^{K}	9.19^{H}	9.45^{H}	44.79^{A}	0.615^{A}	0.04
MSD		0.816	0.219	0.464	0.527	0.0073	

BI = browning index, HMF = 5-hydroxymethyl furfural.
Means with the same letter in the same column are not significantly different.
MSD = Minimum significant difference.

Table 2. Phenolic acid profile of green and roasted coffee (mg/g).

Roasting temperature (°C)	Compound	Roasting Time (min)				
		0	10	20	30	40
160	Gallic	ND	0.096	0.306	0.384	0.249
	Chlorogenic	34.181	25.843	19.485	16.238	12.721
	Caffeic	2.172	2.415	3.528	2.770	2.344
	p-coumaric	0.056	0.055	0.049	0.049	0.038
	Cinnamic	0.034	0.031	0.037	0.033	0.028
	Quercetin	0.154	ND	ND	ND	ND
	Kaempferol	0.093	ND	ND	ND	ND
	Caffeine	9.880	10.074	11.129	10.841	11.475
	Pyrocatechol	ND	ND	ND	0.082	0.112
180	Gallic	ND	0.228	0.337	0.080	0.050
	Chlorogenic	34.181	21.637	12.917	9.737	9.325
	Caffeic	2.172	2.870	2.432	1.899	1.803
	p-coumaric	0.056	0.052	0.041	0.024	0.022
	Cinnamic	0.034	0.026	0.028	0.026	0.025
	Quercetin	0.154	ND	ND	ND	ND
	Kaempferol	0.093	ND	ND	ND	ND
	Caffeine	9.880	10.289	11.084	11.241	11.514
	Pyrocatechol	ND	ND	0.093	0.153	0.161
220	Gallic	ND	0.136	0.346	0.064	ND
	Chlorogenic	34.181	20.807	11.930	5.827	2.584
	Caffeic	2.172	2.697	2.282	1.222	0.585
	p-coumaric	0.056	0.051	0.045	0.014	ND
	Cinnamic	0.034	0.034	0.032	0.021	0.008
	Quercetin	0.154	ND	ND	ND	ND
	Kaempferol	0.093	ND	ND	ND	ND
	Caffeine	9.880	10.234	11.203	11.610	11.868
	Pyrocatechol	ND	ND	0.134	0.176	0.186

ND = not detected.

after 20 min. The same trend was observed at 180 and 220 °C, but the maximum values were obtained after 20 and 10 min for gallic and caffeic acids, respectively. This could be due to the fact that, during roasting, chlorogenic acid slowly degraded to increase caffeic and quinic acids. Also, the increase of gallic acid may be due to the breakdown of hydrolysable tannins (glucose esters of gallic acid) into their constituent gallic acid and carbohydrates.

Similar results were reported by Somporn et al. (2011), Pérez-Hernández et al. (2012) and Galvez Ranilla, Genovese and Lajolo (2009). They reported that the roasting process can cause the release and degradation of some phenolic compounds in seeds. Moreover, Rakic et al. (2007) found that an increase of phenolic acids as gallic acid, ferulic and *p*-coumaric acids may have occurred during heat treatments of some common beans.

Changes in other phenolic compounds such as *p*-coumaric acid and cinnamic acid showed gradual decrease during roasting, but its thermal stability was higher if compared to other phenolic compounds. Quercetin and kaempferol were only detected in green coffee bean and completely destroyed in all roasted coffee samples. On the contrary, pyrocatichol, which was not found in green coffee, was detected in roasted coffee samples as a degradation product derived from chlorogenic acid. From the results in Table 2, it is clear that pyrocatechol formation occurred under drastic roasting conditions. The highest content of pyrocatechol (0.186 mg/g) was found in coffee beans during roasting at 220 °C for 40 min. Previously, Kamiyama et al. (2015) reported the formation of pyrocatechol in coffee roasted at 250 °C. Furthermore, Funakoshi-Tago et al. (2020) reported that pyrocatechol was detected as chlorogenic acid decomposition upon roasting of coffee beans.

Caffeine contents of green and roasted coffee samples varied in a narrow range from 9.880 mg/g in green coffee beans to 11.87 mg/g roasted coffee at 220°C/for 40min (Table 2). The apparent increment of caffeine could be mainly due to its thermostability and the mass losing of thermolabile compounds during the roasting process. Moreover, caffeine thermal resistance was higher than chlorogenic and caffeic acids during roasting conditions (Crozier et al., 2012; Liu and Kitts, 2011). The thermostability of caffeine may be due to its higher melting point (238 °C) than chlorogenic (207 °C) and caffeic acid (223 °C). These results are in agreement with previous findings by Hecimovic et al. (2011). They confirmed the caffeine content of all roasted coffee samples was thermostable under different temperatures and times of roasting conditions.

3.1.3. Total phenolic content and antioxidant capacity of green and roasted coffee

3.1.3.1. Total phenolic content (TPC). Phenolic compounds have received considerable attention because of their potential antioxidant capacities and free radical scavenging abilities, which are beneficial to human health (Lopez-Velez et al., 2003; Li et al., 2006; Govindarajan et al., 2007). In general, the TPC gradually decreased with increasing temperature and time of roasting conditions. Green coffee beans contained 52.79 mg CAE/g, which significantly decreased to 43.72 and 42.98 mg CAE/g coffee roasted at 160 and 180 for 40 min, respectively. In the case of coffee roasted at 220 °C, this trend was even more pronounced, TPC decreased to 30.93mg CAE/g (Table 3). These results could be due to the greater degradation of chlorogenic acid at higher temperatures (Table 2). These results are in agreement with those previously reported by Somporn et al. (2011) and Pokorna et al. (2015), who found that TPC of coffee beans gradually decreases during roasting.

Table 3. Total phenolic contents and antioxidant capacity of green and roasted coffee.

Roasting temperature (°C)	Roasting Time (min)	Total phenols (mg CAE/g)	DPPH (mg TE/g)	ABTS (mg TE/g)	FRAP (mg TE/g)
Green coffee	0	52.79^{A}	63.37^{A}	63.80^{A}	63.68^{A}
160	10	46.14^{B}	54.59^{G}	55.32^{H}	55.13^{G}
	20	45.43 ^{BC}	57.12 ^{EF}	57.54 ^{EFG}	57.60^{F}
	30	44.65 ^{BCDE}	57.64 ^{DE}	58.75 ^{DEF}	58.67 ^{EF}
	40	43.72 ^{CDE}	58.16 ^{CDE}	59.21 ^{CDE}	59.13 ^{DE}
180	10	45.71^{B}	54.49^{G}	55.76 ^{GH}	55.54^{G}
	20	45.02 ^{BCD}	59.98 ^{BCD}	62.09 ^{AB}	61.66 ^{BC}
	30	43.36 ^{DE}	61.81 ^{AB}	63.14^{A}	62.59 ^{AB}
	40	42.98^{E}	54.71 ^{FG}	56.78 ^{FGH}	54.78^{G}
220	10	45.10 ^{BCD}	60.17 ^{BC}	60.95 ^{BC}	60.66 ^{CD}
	20	43.59 ^{DE}	59.48 ^{BCDE}	59.73 ^{CD}	59.82 ^{CDE}
	30	38.53^{F}	48.32^{H}	50.85^{I}	49.90^{H}
	40	30.39^{G}	35.37^{I}	37.51^{J}	37.00^{I}
MSD		1.82	2.50	2.04	1.86

CAE - chlorogenic acid equivalent, TE - trolox equivalent.
Means with the same letter in the same column are not significantly different.
MSD – Minimum significant difference.

3.1.3.2. Antioxidant capacity of green and roasted coffee beans. The antioxidant capacity of coffee samples roasted at different temperature and times, measured by DPPH, ABTS, and FRAP assay, are presented in Table 3. Green coffee beans showed higher antioxidant activity ($p < 0.05$) than roasted samples under all roasting conditions. The antioxidant capacity of coffee beans significantly decreased at the beginning of the roasting process. For instance, ABTS values were 55.32, 55.76, and 60.95 mg TE/g of coffee beans roasted for 10 min at 160, 180, and 220 °C, respectively, compared to 63.80 mg TE/g of green coffee beans. At 160 °C, ABTS values gradually increased during roasting to 59.21 mg TE/g of coffee beans roasted for 40 min. At 180 °C, ABTS values increased up to 63.14 mg TE/g coffee beans roasted for 30 min, then decreased afterword. A different trend was observed at 220 °C as the ABTS values gradually decreased during roasting. DPPH and FRAP values showed the same trend (Table 3). Similar results were observed by Del Castillo, Ames and Gordon (2002). They found that ABTS values of *Coffea arabica* increased during light and medium roasting levels. Also, several investigations demonstrated that the antioxidant capacity of coffee increased with roasting to a certain extent (Cämmerer and Kroh, 2006; Sacchetti et al., 2009). Changes in the antioxidant capacity of coffee beans upon roasting are associated with the degradation of chlorogenic acid and the formation of Maillard reaction products which exhibit antioxidant capacity. The occurrence of Maillard reactions during the roasting process of coffee was attributed to non-covalent interactions between phenolic compounds and melanoidins to produce complexes that has varying degrees of antioxidant capacity (Wolfe and Liu, 2007). The present study found similar antioxidant capacity for roasted coffee at 160 and 180 °C for 40 min and green coffee, while higher antioxidant capacity ($p < 0.05$) was found in coffee roasted at 220 for 30 or 40 min.

3.2. Degradation kinetics of chlorogenic and caffeine during roasting

Understanding thermal degradation and thermostability parameters of bioactive compounds in coffee beans are important to optimize its nutritional and sensory quality (Chung et al., 2013). In this concern, the degradation kinetics of chlorogenic and caffeine were evaluated during the roasting process of coffee. First-order Arrhenius kinetics (Eq. 2) with the linear regression was plotted to calculate the reaction rate constant and activation energy as well as decimal reduction time of chlorogenic acid and caffeine during roasting of coffee at different temperatures and times. The results of the kinetic parameters are presented in Table 4. The activation energy of chlorogenic acid and caffeine were 26.023 and 10.032 kJ mol^{-1}, respectively. Also, the D values of chlorogenic acid were 94.340, 54.945, and 38.023 min compared to 666.667, 526.316 and 454.545 min for caffeine at 160, 180, and 220 °C, respectively.

The activation energy is the minimum amount of energy required to promote a chemical reaction. A chemical reaction starts when the molecules are exposed to energy equal to or greater than the activation energy. Therefore, the activation energy demonstrates the effect of temperature on the rate of the chemical reaction. Several investigations applied the Arrhenius equation (Eq. 2) for calculation of activation energy. Among them, Vargas-Elías (2016) reported that the activation energy was 52.27 kJ mol^{-1} to start the mass loss during coffee roasting. Moreover, the activation energy for the degradation of chlorogenic acid during coffee roasting was 44.4 kJ mol^{-1} (Perrone et al., 2010).

Chlorogenic acid fitted first-order kinetics at different temperatures (160, 180, and 220 °C) showed a good correlation coefficient (R^2) which ranged from 0.991 to 0.999, depending on temperature. Furthermore, the roasted coffee showed a linear degradation of chlorogenic acid with time and temperatures. Generally, the roasting of coffee at 220 °C

Table 4. Thermo kinetic degradation parameters of chlorogenic acid and caffeine during roasting of coffee beans.

Compound name	Temp (°C)	k (min^{-1})	Ea (KJ. mol^{-1})	D-value (min)	semi log eq.	R^2
Chlorogenic acid	160	0.0242	26.023	94.340	y = -0.0106x + 1.522	0.994
	180	0.0418		54.945	y = -0.0182x + 1.527	0.999
	220	0.0606		38.023	y = -0.0263x + 1.575	0.991
Caffeine	160	0.0036	10.032	666.667	y = 0.0015x + 0.985	0.994
	180	0.0043		526.316	y = 0.0019x + 0.992	0.889
	220	0.0051		454.545	y = 0.0022x + 0.995	0.921

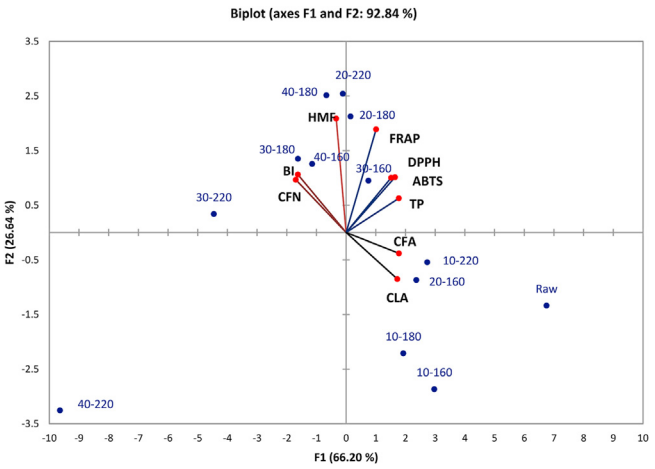

Figure 1. Principal Component Analysis of physico-chemical parameters during roasting conditions. CFA-caffeic acid, CLA – chlorogenic acid, CFN- caffeine, TP – total phenols and BI - browning index.

showed a greater chlorogenic degradation rate than samples roasted at 180 and 160 °C. A similar finding was observed by Diviš et al. (2019) and Kamiyama et al. (2015). They reported that the increase of roasting time at high temperatures provides more degradation of chlorogenic and caffeic acids.

The principal component analysis is used to interpret the relationships between chlorogenic acid, caffeic acid, total phenols, antioxidant capacities, HMF, browning index, and caffeine of green and roasted coffee. Two principal components, PC1 and PC2 with eigenvalues 5.89 and 2.5 respectively, explained 92.84 % of the total variance in the data set.

As shown in Figure 1 caffeic and chlorogenic acids exhibited similar behavior. They showed significant positive correlation ($r = 0.973$) and significant negative correlation with caffeine and browning index ($r = -0.9$). Considering PC1, the parameters include CLA, CFA, TP, DPPH, ABTS, and FRAP), which presented on the positive side of Figure 1, had higher concentration and correlated to mild and moderate roasting conditions. While caffeine index (CFN) and browning index (BI) (located in the negative side of Figure 1) are correlated to the aggressive roasting conditions. In this concern, Souza & Benassi (2012) applied the PCA to investigate the effect of the roasting process on the chemical constituents of coffee. Then reported that the main parameters of PC1 were chlorogenic acid (positive correlation) and caffeine (negative correlation), and PC2 correlated to the degradation of chlorogenic acid and development of browning compounds. Also, the PCA biplot indicated that the highest content of HMF was in coffee samples roasted at moderate conditions (180 °C at 20 min). Similar results were reported by Diviš et al. (2019).

4. Conclusions

The present study investigated Physico-chemical changes during the roasting process of coffee (particularly phenolic acids and caffeine). In general, the TPC gradually decreased with increasing temperature and time of roasting conditions. Green coffee beans showed higher antioxidant capacity ($p < 0.05$) than roasted samples at all roasting conditions. Caffeine thermal resistance was higher than in chlorogenic and caffeic acids. Coffee samples roasted at 220 °C showed a greater chlorogenic degradation rate than those roasted at 180 and 160 °C. Caffeic and chlorogenic acids were positively correlated ($r = 0.973$), but negatively correlated with caffeine and browning index with $r = -0.9$. Therefore, it is paramount to roast coffee in a way that reserves a good level of phenolic acid in parallel with a good taste. Optimum conditions for roasting coffee in the current work were at 180 °C for 20 min or 220 °C at 10 min.

Declarations

Author contribution statement

Fathy M. Mehaya: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Ayman A. Mohammad: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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