DOI:10.1021/jf102110u

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

Modeling Weight Loss and Chlorogenic Acids Content in Coffee during Roasting

Daniel Perrone,[†] Raul Donangelo,[‡] Carmen M. Donangelo,[†] and Adriana Farah*,[†]

[†]Laboratório de Bioquímica Nutricional e de Alimentos, Universidade Federal do Rio de Janeiro, Instituto de Química, Departamento de Bioquímica, Ilha do Fundão, CT bloco A, 21949-900 Rio de Janeiro, RJ, Brazil, and [‡]Instituto de Física, Universidade Federal do Rio de Janeiro, Ilha do Fundão, CT bloco A, C.P. 68.528, 21941-972 Rio de Janeiro, RJ, Brazil

Roasting is a key step in the production of a high-quality coffee. Roasting degree is directly related to coffee chemical composition and may be determined objectively by weight loss after roasting. Chlorogenic acids (CGA) are thermally labile phenolic compounds that play an important role in the final cup quality and health benefits of coffee. Considering the interest in finding a reliable method to predict weight loss and CGA content in coffee, models have been developed to estimate these parameters during roasting. Weight loss was successfully modeled ($r = 0.99$) independent of the instant temperature. CGA degradation followed first-order Arrhenius-compliant kinetic models with good predictability ($r = 0.98$), especially for light to moderately dark samples. In both cases distinct models for *Coffea arabica* and *Coffea canephora* were calculated, because of differences in chemical composition and cell wall structure between these species. The proposed models may become important predictive tools in the coffee industry.

KEYWORDS: Modeling; chlorogenic acids; weight loss; coffee roasting

INTRODUCTION

The coffee industry is one of the most economically important food industries in the world. Roasting is a key step for the production of high-quality roast and ground coffees, because it is during the roasting process that the desired color, aroma, and taste of the beans are produced (*1*, *2*). Roasting is a process depending on time and temperature, in which physical and chemical changes are induced by pyrolysis (*3*). The chemical composition of roasted coffee is directly related to the roasting degree and depends upon the characteristics of the coffee bean as well as the roasting conditions (*4*). The roasting degree may be determined by the color of the beans, weight loss, flavor and aroma development, or chemical changes of certain components (*5*). The use of sophisticated techniques, such as laser mass spectroscopy (*6*) and gas chromatography (*4*), has been proposed as possible, although expensive, alternative tools for the online control of the roasting process. In the industry, however, to deliver consistent quality one often trusts an experienced roaster who, on the basis of his expertise and senses, uses a subjective and empirical indicator such as visual color of the beans to control the process (*6*). Alternatively, measurement of the beans' weight loss during the roasting process could be a simple and low-cost nonsubjective way to assess roasting degree. However, because it cannot be performed online during roasting, it cannot be directly used as a process control parameter.

*Corresponding author (phone +552125627352; fax +552125628213; e-mail afarah@iq.ufrj.br).

On the other hand, modeling weight loss may be considered a useful tool to predict adequate process parameters to obtain, on a regular basis, coffee beans with the desired roasting degree. Moreover, such models would have implications in the assessment of the thermally induced changes in various natural coffee components and contaminants, which are degraded (chlorogenic acids, trigonelline, bioactive amines, mycotoxins) (*7*−*10*) or formed (chlorogenic acid lactones, niacin, melanoidins, polycyclic aromatic hydrocarbons) (*7*, *8*, *11*, *12*) during coffee roasting.

Chlorogenic acids (CGA) are a class of phenolic compounds formed by the esterification of certain *trans*-cinnamic acids with (−)-quinic acid. The main subgroups of chlorogenic acid isomers in coffee are the caffeoylquinic acids (CQA), feruloylquinic acids (FQA), and dicaffeoylquinic acids (diCQA) (*13*), which together account for 98% of total CGA composition (*14*). CGA represent 4−12% of green coffee constituents in mass and contribute to the final acidity, astringency, bitterness, and overall cup quality of the beverage (*1*, *15*, *16*). During roasting, CGA is lost as a consequence of the thermal breakage of carbon−carbon covalent bonds, resulting in isomerization in the initial roasting stages and epimerization, lactonization, and degradation in the later stages (*14*, *15*). Several beneficial health effects have been attributed to CGA and their lactones, such as antioxidant, antimicrobial, antidiabetes, hepatoprotective, and antimutagenic activities (*16*−*18*).

Despite the relevance of measuring CGA isomers in coffee, most studies investigating CGA content have focused exclusively on 5-CQA, the most abundant CGA isomer in coffee, for which commercial standards are available. Although the Folin−Ciocalteu

 Published on Web 11/04/2010

assay for total phenolics could be used for an alternative measurement of CGA content in coffee, it usually leads to an overestimation because other natural coffee reductant components are known to interfere in the assay (*19*). In addition, as CGA comprise a large class of compounds (*14*, *15*), it is usually difficult and time-consuming to obtain a satisfactory chromatographic separation of all CGA compounds. Therefore, the possibility of predicting coffee CGA content during roasting is of great interest.

In the past two decades, a series of independent studies dealing with the effect of roasting on weight loss and CGA content in coffee have been performed by our research group (*1*, *7*, *14*−*16*, *20*−*22*). During these studies, the existence of a relatively regular behavior pattern in relation to the kinetics of CGA degradation was noted. Considering the potential importance of finding a reliable method to estimate weight loss and CGA content in coffee, the objective of this study was to develop models to predict these parameters during roasting.

MATERIALS AND METHODS

Database. The considered database consisted of two coffee samples (*Coffea canephora* and *Coffea arabica*, both from Guaxupé, Minas Gerais, Brazil), which were roasted at four different temperatures during six different time periods, totaling 48 experiments. *C. arabica* and *C. canephora* samples were separated into two sets of experiments, and distinct model parameters were determined for each coffee species. To validate the models, experiments were further randomly divided into a learning database (total of 32 experiments) to compute model parameters and a validation database (total of 16 experiments) to test the prediction ability of the models. The database included CGA data on both green and roasted samples as well as weight loss data during the roasting process.

Roasting. All coffee samples (30 g) were roasted in a commercial spouted bed roaster (i-Roast2 model 40011, Hearthware Home Products, Gurnee, IL) operating at set temperatures of 170, 180, 190, or 200 °C for 4, 5, 6, 7, 8, or 9 min, followed by a fixed 4 min air-cooling period. A thermometer probe continuously monitored the air temperature inside the roasting chamber, which was recorded at 1 min intervals. The repeatability of the roasting process was evaluated in a six-replicate experiment, where the coffee sample was roasted at 170 °C for 6 min. The obtained coefficient of variation for percent weight loss was very low (0.6%). Therefore, we found it appropriate to roast coffee beans once in each condition. The color of coffee samples was determined by comparison with color disks from the "Roasting Color Classification System" (Agtron-SCAA, Reno, NV; 1995), following the standards used by the Brazilian Coffee Industries Association (ABIC).

Weight Loss. The percent weight loss (%WL) of coffee beans after each roasting condition was calculated using the equation

$$\%\mathrm{WL} = \frac{(W_{\mathrm{br}} - W_{\mathrm{ar}})}{W_{\mathrm{br}}} \times 100 \tag{1}$$

where W_{br} and W_{ar} are the weights before and after roasting, respectively.

Water Content. To express the amount of CGA on a dry basis (db), the water content of freshly ground green and roasted coffee beans was determined gravimetrically according to the AOAC method (*23*).

Chlorogenic Acids Analysis. Chlorogenic acids in the green and roasted coffee samples were analyzed in duplicate using liquid chromatography techniques according to the methods described by Farah et al. (*7*) and Perrone et al. (*14*). A total of nine CGA compounds were quantified in all samples: 3-, 4-, and 5-CQA, 3-, 4-, and 5-FQA, and 3,4-, 3,5-, and 4,5-diCQA. The sum of these compounds, hereafter referred as total CGA, was used for modeling CGA degradation.

Weight Loss Modeling. The weight loss models were developed using the roasting curves and weight loss measurements of the coffee samples, assuming that the weight loss rate was either independent or linearly dependent on roasting temperature.

Model 1: Weight Loss Rate Independent of Temperature. The first developed model hypothesizes that the weight loss rate is independent of the roasting temperature. In this simplest model one can assume

$$\frac{\mathrm{d}[\Delta m(T(t))]}{\mathrm{d}t} = a \tag{2}$$

where $\Delta m(T(t))$ is the weight loss (%) at a certain time t (min) when coffee is being roasted at a temperature of T (°C) and a is a constant.

After integration of eq 3 on the time interval between 0 and t_{f}, which corresponds to the final roasting time (t_{R}) plus the 4 min standard cooling period ($t_{\mathrm{f}} = t_{\mathrm{R}} + 4'$), we obtain

$$\Delta m = \int_0^{t_{\mathrm{f}}} a\,\mathrm{d}t = a[t_{\mathrm{f}}] \tag{3}$$

From the relationship above we may write the variance associated with the parameter value a as

$$f(a) = \sum_{i=1}^{i=n_{\mathrm{expt}}} [(t_f)a - \Delta m]^2 \tag{4}$$

where n_{expt} is the number of measurements performed. From minimization of this variance we obtain an estimate for the value of a:

$$a = \sum_{i=1}^{i=n_{\mathrm{expt}}} \Delta m_{(t_f)}(t_f) / \sum_{i=1}^{i=n_{\mathrm{expt}}} (t_f)^2 \tag{5}$$

Substituting this value of a into eq 3, the weight loss predicted by the model can be finally obtained.

Model 2: Linear Temperature Dependence. This version of the model hypothesizes that the weight loss rate is linearly dependent on the roasting temperature:

$$\frac{\mathrm{d}[\Delta m(T(t))]}{\mathrm{d}t} = a + bT(t) \tag{6}$$

where $\Delta m(T(t))$ is the weight loss (%) at a certain time t (min) when coffee is being roasted at a temperature of T (°C) and a and b are constants.

After integration, this equation becomes

$$\Delta m = \int_0^{t_{\mathrm{f}}} [a + bT(t)]\,\mathrm{d}t = a[t_{\mathrm{f}}] + b\int_0^{t_{\mathrm{f}}} T(t)\,\mathrm{d}t \tag{7}$$

where

$$\int_0^{t_{\mathrm{f}}} T(t)\,\mathrm{d}t$$

corresponds to the area under the roasting curve ($\mathrm{area}_{t_{\mathrm{f}}}$), which can be estimated using the trapezoidal rule for numerical integration. We have, then

$$\Delta m_{\mathrm{expt}} = a[t_{\mathrm{f}}] + b \times \mathrm{area}_{t_{\mathrm{f}}} \tag{8}$$

which leads to an expression for the objective function

$$f(a,b) = \sum_{i=1}^{i=n_{\mathrm{expt}}} \{[(t_{\mathrm{f}})a + \mathrm{area}_{t_{\mathrm{f}}} \times b] - \Delta m\}^2 \tag{9}$$

which, after minimization with respect to a and b, leads to a set of two equations

$$\left[\sum_{i=1}^{i=n_{\mathrm{expt}}} (t_{\mathrm{f}})^2\right] a + \left[\sum_{i=1}^{i=n_{\mathrm{expt}}} \mathrm{area}_{t_{\mathrm{f}}}(t_{\mathrm{f}})\right] b = \sum_{i=1}^{i=n_{\mathrm{expt}}} \Delta m_{(t_{\mathrm{f}})}(t_{\mathrm{f}}) \tag{10}$$

$$\left[\sum_{i=1}^{i=n_{\mathrm{expt}}} \mathrm{area}_{t_{\mathrm{f}}}(t_{\mathrm{f}})\right] a + \left[\sum_{i=1}^{i=n_{\mathrm{expt}}} (\mathrm{area}_{t_{\mathrm{f}}})^2\right] b = \sum_{i=1}^{i=n_{\mathrm{expt}}} \Delta m_{(t_{\mathrm{f}})} \times \mathrm{area}_{t_{\mathrm{f}}} \tag{11}$$

which can be numerically solved to obtain the values of a and b. Using eq 8, the theoretical weight loss can be finally obtained.

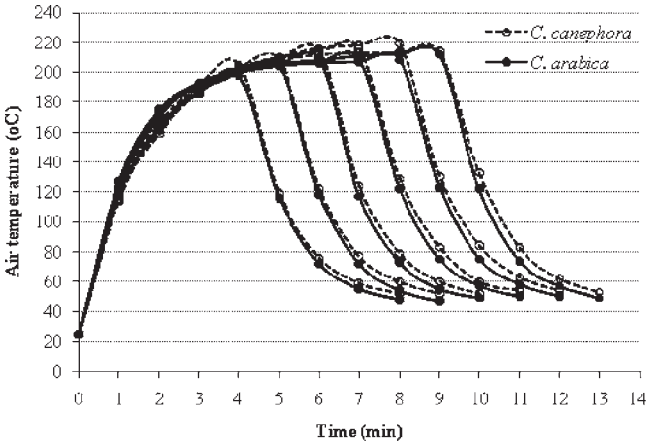

Figure 1. Typical time−temperature roasting curves, represented by those obtained when coffee samples were roasted at a set temperature of 180 °C for 4, 5, 6, 7, 8, or 9 min, followed by a fixed 4 min air-cooling period. *Y*-axis shows the air temperature inside the roasting chamber.

Table 1. Experimental and Calculated Weight Loss Values for the *C. canephora* Sample Using Models Assuming That the Weight Loss Rate Was Independent (Model 1) or Linearly Dependent (Model 2) on the Roasting Temperature[a]

		calculated wt loss (%)			
roasting time (min), t_R	experimental wt loss (%), $\Delta m(t_f)$	model 1	relative error (%)	model 2	relative error (%)
		170 °C			
4	11.99	11.51	−4.0	12.03	0.3
5	13.22	12.94	−2.1	13.25	0.2
6*	14.18	14.38	1.4	14.50	2.3
7	16.03	15.82	−1.3	15.59	−2.7
8	16.54	17.26	4.4	16.89	2.1
9*	17.78	18.70	5.2	18.01	1.3
		180 °C			
4*	13.00	12.30	−5.4	13.44	3.4
5	14.47	13.84	−4.4	14.74	1.8
6	16.14	15.37	−4.8	15.88	−1.6
7*	16.77	16.91	0.8	16.94	1.0
8	18.42	18.45	0.1	18.10	−1.7
9	18.98	19.98	5.3	19.29	1.7
		190 °C			
4*	12.85	12.94	0.7	14.03	9.1
5	14.90	14.56	−2.3	15.28	2.5
6	16.53	16.18	−2.1	16.59	0.3
7	18.57	17.80	−4.2	17.82	−4.0
8*	19.56	19.41	−0.7	19.02	−2.8
9	19.87	21.03	5.8	20.20	1.7
		200 °C			
4	20.42	19.50	−4.5	20.43	0.0
5*	21.76	21.94	0.8	22.37	2.8
6*	23.36	24.37	4.3	24.59	5.3
7	26.46	26.81	1.3	26.77	1.2
8	29.82	29.25	−1.9	29.04	−2.6
9	30.89	31.69	2.6	31.34	1.5

[a] Coffee samples marked with an asterisk comprised the validation database of the models.

In a similar spirit, more complicated models were tested, such as a quadratic temperature dependence model. However, the use of such models did not improve prediction of the weight loss during roasting.

Table 2. Experimental and Calculated Weight Loss Values for the *C. arabica* Sample Using Models Assuming That the Weight Loss Rate Was Independent (Model 1) or Linearly Dependent (Model 2) on the Roasting Temperature[a]

		calculated wt loss (%)			
roasting time (min), t_R	experimental wt loss (%), $\Delta m(t_f)$	model 1	relative error (%)	model 2	relative error (%)
		170 °C			
4	12.63	12.22	−3.2	12.80	1.3
5*	14.15	13.75	−2.8	14.12	−0.2
6*	15.72	15.28	−2.8	15.53	−1.2
7	17.25	16.81	−2.6	16.82	−2.5
8	18.43	18.33	−0.5	18.22	−1.1
9	19.15	19.86	3.7	19.60	2.4
		180 °C			
4	13.33	12.91	−3.1	13.76	3.3
5	15.41	14.53	−5.7	15.14	−1.8
6*	16.30	16.14	−1.0	16.35	0.3
7	18.10	17.76	−1.9	17.62	−2.7
8*	18.77	19.37	3.2	18.99	1.2
9	19.83	20.99	5.8	20.16	1.6
		190 °C			
4	13.73	13.21	−3.8	14.03	2.2
5*	16.30	14.87	−8.8	15.40	−5.5
6*	16.88	16.52	−2.1	16.78	−0.6
7	19.03	18.17	−4.5	18.33	−3.7
8	19.47	19.82	1.8	19.69	1.1
9	20.75	21.47	3.5	20.96	1.0
		200 °C			
4	16.98	17.25	1.6%	17.20	1.3%
5*	19.72	19.41	−1.6%	19.38	−1.7%
6	21.95	21.56	−1.8%	21.56	−1.8%
7	23.94	23.72	−0.9%	23.73	−0.9%
8	25.53	25.88	1.4%	25.90	1.5%
9*	27.32	28.03	2.6%	28.08	2.8%

[a] Coffee samples marked with an asterisk comprised the validation database of the models.

Kinetic Calculations for CGA Degradation. The kinetic model proposed in this study (eq 13) was chosen because of the balance between its simplicity and the good fitting of experimental data it provided. We assumed that the kinetic parameters followed the Arrhenius law.

A general reaction rate expression for the degradation kinetics can be written as (*24*−*26*)

$$-\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k[\mathrm{C}]^m \quad (12)$$

where [C] is the quantitative value of the component under consideration, k is the reaction rate constant, and m is the order of the reaction. Degradation of CGA has been reported to follow first-order kinetics (*27*), of which the integrated rate equation can be expressed as

$$\ln([\mathrm{C}]_t/[\mathrm{C}]_0) = -k_T t \quad (13)$$

where $[\mathrm{C}]_0$ and $[\mathrm{C}]_t$ are the concentrations of CGA at time zero and time t (min), respectively, and k_T is the temperature-dependent degradation rate constant, defined by the Arrhenius equation

$$k_T = A_0 \exp(-E_a/RT) \quad (14)$$

where E_a is the activation energy of the reaction (kJ mol^{-1}), R is the universal gas constant (8.3145 J mol^{-1} K^{-1}), T is the absolute temperature (K), and the pre-exponential factor constant A_0 is the frequency factor (min^{-1}).

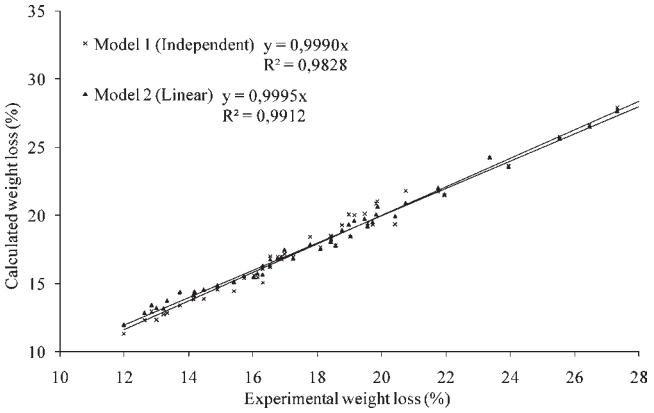

Figure 2. Comparison of experimental and calculated weight losses (%) in roasted coffee samples using models assuming that the weight loss rate was independent (model 1) or linearly dependent (model 2) on the roasting temperature.

RESULTS AND DISCUSSION

Weight Loss Modeling. Coffee samples were roasted at 170, 180, 190, or 200 °C for 4, 5, 6, 7, 8, or 9 min. Air temperature inside the roasting chamber was monitored at 1 min intervals, yielding time−temperature roasting curves. Typical roasting curves obtained for both samples with the set temperature of 180 °C are depicted in **Figure 1**. The experimental and calculated weight loss values for the *C. canephora* and *C. arabica* coffee samples using the two models proposed are presented in **Tables 1** and **2**, respectively. As a consequence of the differences in their chemical composition and cell wall structure (*28*), different model parameters were determined to predict weight loss for *C. arabica* and *C. canephora* beans. Satisfactory correlations ($r > 0.99$) between calculated and experimental weight losses were obtained using both models (**Figure 2**). Residual analysis showed that residues were normally distributed and homoscedastic. Considering both samples, the average relative error was 2.9% in the case of model 1 and 2.0% for model 2. The quadratic temperature dependence model of the weight loss rate, not presented here, led to an average relative error of 1.7% Although the tested models showed similar efficiency in terms of correlation between experimental and calculated values and of relative error, the results clearly suggest the adoption of the quadratic temperature dependence model, but because of simplicity, good prediction, and the fact that knowledge of instant temperature is not needed, model 1 may be preferred. This means that once a series of roasting curves are obtained at certain process parameters (set temperature for a specific roasting equipment, roasting batch mass, and species), the model parameters proposed here may be calculated. Then, future predictions of weight loss could be made solely on the basis of the roasting time, with no need to monitor the instantaneous temperature inside the roaster's chamber during the process.

Chlorogenic Acids Degradation Kinetic Models. Table 3 shows the concentrations of total CGA in green and roasted coffee samples used to compute the degradation kinetic models. Total CGA contents in green *C. canephora* and *C. arabica* were 10.16 and 8.28 g/100 g dwb, respectively, which are in agreement with various studies in the literature (*13*−*16*, *20*, *21*, *29*). From the CGA results, it was evident that samples roasted at higher roasting temperatures presented more pronounced CGA losses, as expected.

Using linear regression analysis, the degradation data were analyzed using the standard integrated rate equation to determine the overall order and rate constant for the degradation reaction. A correlation coefficient $r > 0.98$ in all samples confirmed that CGA degradation followed first-order reaction at all temperatures tested, as expected from previous papers in the literature (*27*).

Table 3. Total CGA Content in Green and Roasted Coffee Samples Used To Compute the Degradation Model[a]

		chlorogenic acid content (g/100 g dwb)	
temp (°C)	time (min)	*C. canephora*	*C. arabica*
green	0	10162.2 ± 76.4	8277.4 ± 121.5
170	4	4942.5 ± 50.5	3931.9 ± 242.7*
	5	3741.5 ± 1.3*	2566.1 ± 8.4
	6	2516.3 ± 54.9*	2285.9 ± 18.8
	7	1147.5 ± 18.9	1374.7 ± 46.2*
	8	1032.4 ± 2.9	1175.0 ± 29.6
	9	606.1 ± 19.2	944.1 ± 23.4
180	4	4595.3 ± 284.1	4036.2 ± 21.9
	5	2945.3 ± 3.0	3002.7 ± 39.2
	6	1780.8 ± 6.3*	1911.4 ± 85.4*
	7	1088.2 ± 15.1	1675.4 ± 0.7
	8	493.8 ± 7.2	1206.0 ± 12.5*
	9	507.8 ± 50.8*	840.0 ± 6.7
190	4	3703.0 ± 21.5*	3035.7 ± 20.8
	5	2559.0 ± 7.7	2088.1 ± 8.2
	6	1088.3 ± 3.3	1378.6 ± 10.1
	7	579.5 ± 29.6	1186.1 ± 17.6*
	8	371.3 ± 5.0*	771.7 ± 17.6*
	9	162.9 ± 2.6	460.8 ± 0.3
200	4	1524.7 ± 63.4	1483.7 ± 16.1*
	5	183.9 ± 0.4*	666.4 ± 1.2*
	6	123.9 ± 0.9	331.2 ± 0.3
	7	30.1 ± 0.3*	154.2 ± 0.5
	8	19.4 ± 1.7	84.9 ± 1.8
	9	13.0 ± 0.2	57.0 ± 0.8

[a] CGA values are presented as the mean ± SD of two replicates of analysis. Coffee samples marked with an asterisk comprised the validation database of the models.

Figure 3 shows the first-order plots of CGA degradation in *C. canephora* and *C. arabica* samples at 170, 180, 190, and 200 °C. The half-life time ($t_{1/2}$), required for CGA to degrade to 50% of its original value, was calculated from the rate constant k_T, as $t_{1/2} = \ln 2/k_T$. The average rate constants for CGA degradation in *C. arabica* and *C. canephora*, respectively, increased from 0.2665 and 0.4116 min^{-1} at 170 °C to 0.5875 and 0.9691 min^{-1} at 200 °C. A corresponding decrease in half-life, from 2.60 and 1.68 min at 170 °C to 1.18 and 0.72 min at 200 °C, was observed.

Figure 4 shows the Arrhenius plot for total CGA degradation in *C. canephora* and *C. arabica*. The linear nature of the obtained plots ($r > 0.96$) indicates that thermal degradation of total CGA conforms to the Arrhenius equation (eq 14). Apparent activation energy E_a (kJ mol^{-1}) was calculated as a product of the gas constant R (8.3145 J mol^{-1} K^{-1}) and the slope of the graph obtained by plotting ln$k$ versus $1/T$. The apparent activation energies for CGA thermal degradation in *C. arabica* and *C. canephora* were found to be 44.4 and 48.4 kJ mol^{-1}, respectively. Using a tubular reactor operated under approximately isothermal conditions, Sharma et al. (*27*) reported an apparent activation energy of 79 kJ mol^{-1} for 5-CQA pyrolysis, which is of the same magnitude as the value calculated in this study. The slightly higher activation energy for CGA degradation in *C. canephora* compared to *C. arabica* could be explained by intrinsic differences

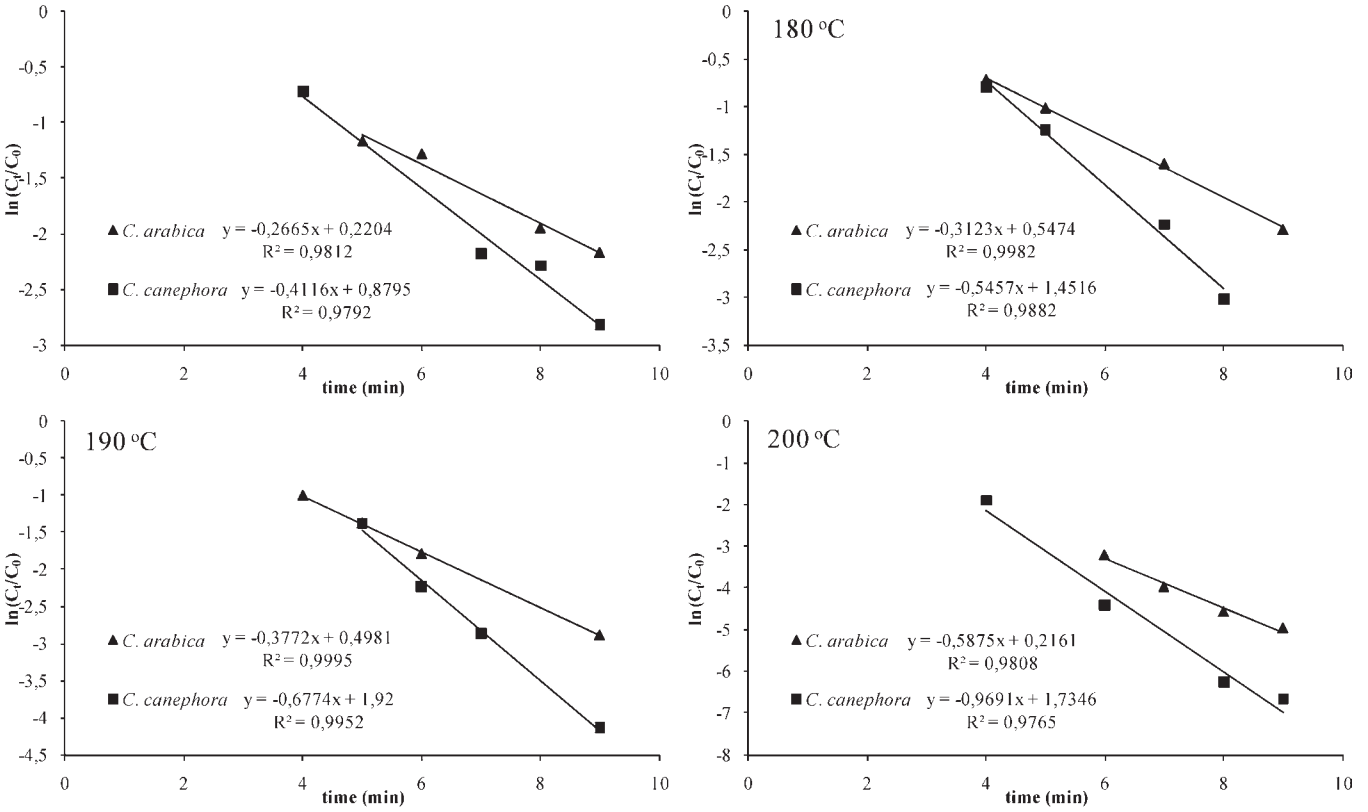

Figure 3. First-order plots of total CGA degradation in coffee samples at 170, 180, 190, and 200 °C.

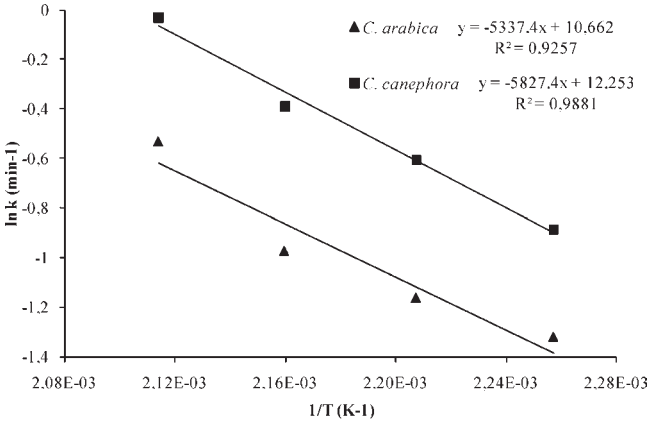

Figure 4. Arrhenius plot for total CGA degradation in *C. arabica* and *C. robusta*.

in the cell wall structures of both species (*15*, *16*, *28*). The frequency factors A_0 (min^{-1}) were calculated as the exponential of the intercept of the Arrhenius plot at $1/T = 0$ and found to be 4.27×10^4 and 2.10×10^5 min^{-1} for *C. arabica* and *C. canephora*, respectively. Taken together, E_a and A_0 indicate the number of successful collisions that have enough kinetic energy to lead the reaction of CGA degradation.

To predict the degradation of total CGA during coffee roasting, eq 14 was used together with the determined rate constants for CGA degradation, k_T. A strong correlation ($r = 0.98$) between experimental and calculated values was obtained (**Figure 5**). Residual analysis showed that residues were normally distributed and homoscedastic. Even though an average relative error of 16.5% was found between experimental and calculated values, this was mostly attributed to the dark-roasted samples. In these samples, very low amounts of total CGA were found (from 0.184 to 0.013 g/100 g dwb), causing higher deviations for calculated values. However, when these deviations are translated into absolute values, their significance is irrelevant. When only mild roasting conditions were considered, the proposed model predictions were shown to be good. Prediction of CGA content for samples with contents of >0.2 g/100 g dwb, for example, showed an acceptable relative error, on average, 10.6%. Considering coffee samples that presented weight losses of up to 18% (moderately light to moderately dark, depending on species), which are the most relevant roasting degrees for the coffee industry, an average relative error of 12.9% was found. This relative error is in line with values reported by other modeling studies found in the literature (*25*, *26*). When modeling the degradation of *β-N*-oxalyl-L-2,3-diaminopropionic acid, a nonprotein neurotoxic amino acid in grass pea flour, Tarade et al. (*26*) reported an average relative error of 18.4% using first-order Arrhenius-compliant kinetic models. In this way, the proposed model in the present study is suitable for the prediction of total CGA degradation during coffee roasting. Although only one sample of each coffee species was used to generate the present CGA degradation models, on the basis of our previous experience with CGA loss during roasting, it is possible to say that, most probably, model predictions will be valid for different coffee cultivars of the same species, given that the same roasting conditions are maintained. Actually, the proposed model approach was applied to data from previous independent studies (*1*, *7*, *14*−*16*, *20*−*22*), which comprised seven *C. arabica* and three *C. canephora* cultivars, and we observed that weight loss and CGA degradation of all cultivars of a single species could be predicted by its respective model.

In conclusion, coffee weight loss during roasting was successfully modeled independently of the instant temperature during the process. CGA degradation during coffee roasting followed first-order reaction kinetics. A mathematical model was developed,

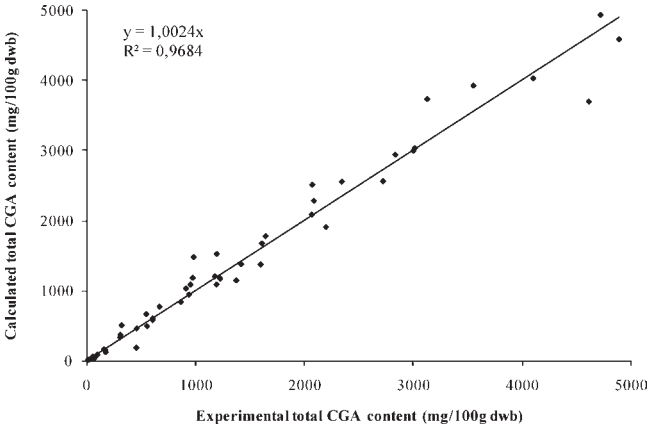

Figure 5. Comparison of experimental and calculated total CGA content (g/100 g dwb) in roasted coffee samples using a kinetic model based on a first-order reaction rate and the Arrhenius law.

using the apparent activation energy of CGA degradation and the temperature-dependent reaction rate, which complied with the Arrhenius equation. This model was capable of predicting the thermally induced degradation of CGA, especially for light to moderately dark-roasted coffee samples. Altogether, the proposed models may become important predictive tools in the coffee industry.

ACKNOWLEDGMENT

We thank José Mauro Costa Monteiro for supplying coffee samples and Izaura Nascimento for assistance with coffee roasting experiments and CGA analysis.

LITERATURE CITED

(1) Farah, A.; Monteiro, M. C.; Calado, V.; Franca, A.; Trugo, L. C. Correlation between cup quality and chemical attributes of Brazilian coffee. *Food Chem.* **2006**, *98*, 373−380.

(2) Mwithiga, G.; Jindal, V. K. Physical changes during coffee roasting in rotary conduction-type heating units. *J. Food Process. Eng.* **2003**, *26*, 543−558.

(3) Clarke, R. J. Coffee: roast and ground. In *Encyclopedia of Food Sciences and Nutrition*, 1st ed.; Caballero, B., Trugo, L. C., Finglas, P. M., Eds.; Academic Press: Oxford, U.K., 2003; Vol. 7, 1487 pp.

(4) Dutra, E. R.; Oliveira, L. S.; Franca, A. S.; Ferraz, V. P.; Afonso, R. J. C. F. A preliminary study on the feasibility of using the composition of coffee roasting exhaust gas for the determination of the degree of roast. *J. Food Eng.* **2001**, *47*, 241−246.

(5) Hernández, J. A.; Heyd, B.; Irles, C.; Valdovinos, B.; Trystram, G. Analysis of the heat and mass transfer during coffee batch roasting. *J. Food Eng.* **2007**, *78*, 1141−1148.

(6) Dorfner, R.; Ferge, T.; Yeretzian, C.; Kettrup, A.; Zimmermann, R. Laser mass spectroscopy as on-line sensor for industrial process analysis: process control of coffee roasting. *Anal. Chem.* **2004**, *76*, 1386−1402.

(7) Farah, A.; de Paulis, T.; Trugo, L. C.; Martin, P. R. Effect of roasting on the formation of chlorogenic acid lactones in coffee. *J. Agric. Food Chem.* **2005**, *53*, 1505−1513.

(8) Stennert, A.; Maier, H. G. Trigonelline in coffee. III. Calculation of the degree of roast by the trigonelline/nicotinic acid ratio. New gas-chromatographic method for nicotinic acid. *Z. Lebensm.Unters. Forsch. A* **1996**, *202*, 45−47.

(9) Oliveira, S. D.; Franca, A. S.; Glória, M. B. A.; Borges, M. L. A. The effect of roasting on the presence of bioactive amines in coffees of different qualities. *Food Chem.* **2005**, *90*, 287−291.

(10) Suárez-Quiroz, M.; de Louise, B.; Gonzalez-Rios, O.; Barel, M.; Guyot, B.; Schorr-Galindo, S.; Guiraud, J. The impact of roasting on the ochratoxin A content of coffee. *Int. J. Food Sci. Technol.* **2005**, *40*, 605−611.

(11) Borrelli, R. C.; Visconti, A.; Mennella, C.; Anese, M.; Fogliano, V. Chemical characterization and antioxidant properties of coffee melanoidins. *J. Agric. Food Chem.* **2002**, *50*, 6527−6533.

(12) Houessou, J. K.; Maloug, S.; Leveque, A.; Delteil, C.; Heyd, B.; Camel, V. Effect of roasting conditions on the polycyclic aromatic hydrocarbon content in ground *Arabica* coffee and coffee brew. *J. Agric. Food Chem.* **2007**, *55*, 9719−9726.

(13) Clifford, M. N. Chlorogenic acids and other cinnamates − nature, occurrence and dietary burden. *J. Sci. Food Agric.* **1999**, *79*, 362−372.

(14) Perrone, D.; Farah, A.; Donangelo, C. M.; de Paulis, T.; Martin, P. R. Comprehensive analysis of major and minor chlorogenic acids and lactones in economically relevant Brazilian coffee cultivars. *Food Chem.* **2008**, *106*, 859−867.

(15) Farah, A.; de Paulis, T.; Moreira, D. P.; Trugo, L. C.; Martin, P. R. Chlorogenic acids and lactones in regular and water-decaffeinated arabica coffees. *J. Agric. Food Chem.* **2006**, *54*, 374−381.

(16) Farah, A.; Donangelo, C. M. Phenolic compounds in coffee. *Braz. J. Plant Physiol.* **2006**, *18*, 23−36.

(17) Moreira, D. P.; Monteiro, M. C.; Ribeiro-Alves, M.; Donangelo, C. M.; Trugo, L. C. Contribution of chlorogenic acids to the iron-reducing activity of coffee beverages. *J. Agric. Food Chem.* **2005**, *53*, 1399−1402.

(18) Natella, F.; Nardini, M.; Gianetti, I.; Dattilo, C.; Scaccini, C. Coffee drinking influences plasma antioxidant capacity in humans. *J. Agric. Food Chem.* **2002**, *50*, 6211−6216.

(19) Naczk, M.; Shahidi, F. Extraction and analysis of phenolics in food. *J. Chromatogr., A* **2004**, *1054*, 95−111.

(20) Trugo, L. C.; Macrae, R. A study of the composition of roasting on the chlorogenic acid composition of coffee using HPLC. *Food Chem.* **1984**, *15*, 219−227.

(21) Farah, A.; Neves, D. F.; Trugo, L. C.; Rosenthal, A.; Modela, R. R. C. Compostos fenólicos em café torrado. In *Annals of the 2nd Simpósio de Pesquisa dos Cafés do Brasil*, Vitória, Brazil; Embrapa: Brasilia, Brazil, 2001; 1485 pp.

(22) Moreira, D. P.; Farah, A.; Donangelo, C. M. Kinetic behavior of chlorogenic acids and lactones during roasting of Brazillian *Coffea arabica* and *Coffea canephora* cultivars. In *Proceedings of the XXI International Conference on Coffee Science*, Paris, France; Prospero: Italy, 2006; pp 244.

(23) AOAC. *Official Methods of Analysis of the Association of Official Analytical Chemists*, 17th ed.; Association of Official Analytical Chemists:Gaithersburg, MD, 2000.

(24) Özdemir, M.; Devres, O. Kinetics of color changes of hazelnuts during roasting. *J. Food Eng.* **2000**, *44*, 31−38.

(25) Nisha, P.; Singhal, R. S.; Pandit, A. B. A study on degradation kinetics of riboflavin in green gram whole (*Vigna radiate* L.). *Food Chem.* **2005**, *89*, 577−582.

(26) Tarade, K. M.; Singhal, R. S.; Jayram, R. V.; Pandit, A. B. Kinetics of degradation of ODAP in *Lathyrus sativus* L. flour during food processing. *Food Chem.* **2007**, *104*, 643−649.

(27) Sharma, R. K.; Fisher, T. S.; Hajaligol, M. R. Effect of reaction conditions on pyrolysis of chlorogenic acid. *J. Anal. Appl. Pyrol.* **2002**, *62*, 281−296.

(28) Fischer, M.; Reimann, S.; Trovato, V.; Redgwell, R. J. Polysaccharides of green Arabica and Robusta coffee beans. *Carbohydr. Res.* **2001**, *330*, 93−101.

(29) Leloup, V.; Louvrier, A.; Liardon, R. Degradation mechanisms of chlorogenic acids during roasting. In *Proceedings of the XVI International Conference on Coffee Science*, Paris, France; Prospero: Italy, 1995; 192 pp.

Received for review June 2, 2010. Revised manuscript received September 29, 2010. Accepted October 13, 2010. We acknowledge financial support from Consórcio Brasileiro de Pesquisa e Desenvolvimento do Café − EMBRAPA, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) (Brazil).