

## The diffusion kinetics of carbon dioxide in fresh roasted and ground coffee

Brent A. Anderson <sup>a</sup>, Eyal Shimoni <sup>b</sup>, Rémy Liardon <sup>c</sup>, Theodore P. Labuza <sup>d,\*</sup>

<sup>a</sup> Department of Biosystems and Agricultural Engineering, University of Minnesota, 1334 Eckles Avenue, St. Paul, MN 55108-6099, USA

<sup>b</sup> Department of Food Engineering and Biotechnology, Technion—IIT, Haifa, Israel

<sup>c</sup> Nestlé Product Technology Centre Orbe, NESTEC Ltd., CH-1350 Orbe, Switzerland

<sup>d</sup> Department of Food Science and Nutrition, University of Minnesota, 1334 Eckles Avenue, St. Paul, MN 55108-6099, USA

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### Abstract

Carbon dioxide is produced as a result of many reactions that take place during roasting of coffee. Although some carbon dioxide is released during roasting and upon grinding, some is trapped and slowly released creating a packaging problem. Either vacuum packaging to prevent a billowing of the package or special film to release CO<sub>2</sub> from inside the package are required. In addition, the coffee is usually tempered in order to maximize release of CO<sub>2</sub> before packaging. In this research, the diffusion kinetics of carbon dioxide release from fresh roasted and ground coffee during tempering were determined. The CO<sub>2</sub> degassing results fit a series expansion of Fick's law for unsteady state diffusion using either one or two effective diffusivities based on an analysis of transport mechanisms. The calculated effective diffusivity was between 0.5 and  $10 \times 10^{-13}$  m<sup>2</sup>/s. It appears that pressure flow and Knudsen diffusion take place and are important during tempering.

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### 1. Introduction

Coffee beans are roasted using hot combustion gases or air at temperatures above 200 °C to develop the characteristic flavors, colors, and aromas (Clarke & Macrae, 1987). Carbon dioxide is the major gas produced during roasting. According to Clarke and Macrae (1985), 87% of gases released from roasted coffee are carbon dioxide. In comparison, the content of carbon dioxide in air is only approximately 0.027–0.037%. Up to 10 ml of carbon dioxide (at STP) can be produced per gram of roasted coffee (Barbera, 1967), although values of 2–5 ml per gram are often reported (Clarke & Macrae, 1985). The amount of carbon dioxide produced during roasting depends upon the type of coffee and the roast conditions. The carbon dioxide is formed as a result of the many reactions that occur including Strecker degradation, pyrolysis of sugars, and the Maillard reaction. The carbon dioxide formed is trapped in the

coffee and slowly diffuses out after roasting and grinding, thus a tempering period is required before packaging. Illy and Viani (1995) reported that tempering to get rid of carbon dioxide requires up to 360 h for roasted and ground coffee and up to 2400 h for roasted whole coffee beans, during which time, the coffee can lose quality. Cardelli and Labuza (2001) indicated there was a loss of 10% of the shelf life for every 24 h coffee was held at room temperature in air. If coffee is packaged prior to proper tempering, the eventual evolution of CO<sub>2</sub> may cause the package to burst. This is of concern, especially with the increased use of flexible films for packaging rather than rigid cans. Thus a balance between time to temper and loss of shelf life must be made, requiring the need for an analysis of CO<sub>2</sub> diffusion kinetics.

Several physical changes take place in the coffee bean during roasting. Moisture is lost and the color is darkened. Beans expand in size due to the internal build-up of gases, which along with the high temperatures allow for the formation of internal pores and pockets. At the typical roasting temperatures, the coffee bean is raised above its glass transition temperature and becomes rubbery. This along with the increase in pressure causes

\* Corresponding author. Tel.: +1-612-624-9701; fax: +1-612-625-5272.

E-mail address: [tplabuza@tc.umn.edu](mailto:tplabuza@tc.umn.edu) (T.P. Labuza).

### Nomenclature

$c_A$	concentration of A	$R$	ideal gas constant
$D_{\text{eff}}$	effective diffusivity	$r$	radius of pore
$D_{KA}$	Knudsen diffusion coefficient	$T$	absolute temperature
$d$	diameter of a pore	$t$	time
$g_c$	gravitational velocity constant	$z$	distance
$M_A$	molecular weight of A	$\varepsilon$	porosity
$N_A$	molecular flux of A	$\lambda$	mean free path length for a gas
$P$	pressure	$\mu$	viscosity
$Q$	volumetric flow rate	$\rho_{\text{bulk}}$	bulk density

the structure to expand. When the beans are then cooled back down to room temperature, the coffee structure is below the glass transition temperature making the bean brittle and easy to grind but also forming pockets and a porous structure with large surface areas where  $\text{CO}_2$  may be trapped or absorbed.

The weight of dry mass also decreases due to the pyrolysis reactions, which results in a decreased bean solids density. Massini, Nicoli, Cassara, and Lerici (1990) reported that the structural changes of the coffee bean during roasting such as the increase in number and size of internal cavities, the dilation in size, and the decrease in weight and density, are closely related to the amount of  $\text{CO}_2$  released.

The pore structure formed during roasting has an effect on the mass transfer phenomena during storage and the gas adsorption capacity of the roasted coffee bean (Radtke & Heiss, 1975; Saleeb, 1975). The pore networks in roasted coffee bean consist of both macropores (evacuated cells) and micropores. Different researchers have studied the macropores using light microscopy and scanning electron microscopy, showing they range from 20 to 40  $\mu\text{m}$  in diameter (Schenker, Handschin, Frey, Perren, & Escher, 2000). Measuring the size of the micropores is more difficult. Saleeb (1975) measured the uptake of  $\text{CO}_2$  at dry ice temperatures and used the Kelvin equation to determine pore size distributions. He found that the average pore size that held the majority of the  $\text{CO}_2$  was between 17 and 33 Å and theorized that they took an ink-bottle shape. Hinman (1993) also concluded that high-energy interactions observed from the isotherm measurements could only result from the presence of pores with dimensions a small multiple of the  $\text{CO}_2$  molecule's diameter. Schenker et al. (2000) measured pore sizes of roasted coffee using a mercury porosimeter and found the majority of the pores ranged in diameter from 10 to 50 nm. The researchers also found that the pore diameters were larger for high temperature roasts than for low temperature roasts.

Carbon dioxide diffuses out of ground coffee faster than from whole beans. This is due to the disruption of

structure mentioned above, as well as the increased surface-to-volume ratio and decreased distance that the molecules have to diffuse. Heiss and Radke (1977) reported that 45% of the  $\text{CO}_2$  held after roasting was released within the first 5 min after grinding. Barbera (1967) found that the amount of carbon dioxide released doubled when the particle size was reduced from 1000 to 500  $\mu\text{m}$ . However, the reduction in particle size also allows ground coffee to be more susceptible to staling caused by oxidation as compared to whole beans because of the larger surface-to-volume ratio and smaller diameter through which oxygen can diffuse.

There has been very little published on the mechanism and kinetics of carbon dioxide release from coffee. Most studies (Heiss & Radke, 1977; Radtke & Heiss, 1975, etc.) have measured the release of carbon dioxide in closed packages, so the gas phase  $\text{CO}_2$  concentration increases over time reducing the driving force for release. Clarke and Macrae (1987) discussed the likelihood of two mechanisms being involved: the diffusion flow due to a carbon dioxide concentration differential and hydrodynamic flow due to pressure differentials. They also raise doubts that Fickian diffusion can be used to model the release since a pressure differential is present.

In order to understand the release of carbon dioxide, the parameters of carbon dioxide diffusion kinetics need to be determined. The goal of this research was to determine the diffusion kinetics of carbon dioxide from freshly roasted and ground coffee and to discuss the specific transport mechanisms that are important in this process.

## 2. Materials and methods

### 2.1. Varieties of coffee

Two different varieties of coffee were used for these experiments. Green Arabica beans grown in Kenya and green Robusta beans grown in Togo were used and stored at room temperature in plastic-lined paper bags.

Table 1  
Roast conditions used in the experiments

Coffee variety	Roast time (min)	Roast degree	Roast temp. (°C)	Air flow setting	Hunterlab values			Experiment
					<i>L</i>	<i>a</i>	<i>b</i>	
Togo Robusta	5	Medium	246	2	20.9	8.2	8.9	A
	5	Dark	262	2	16.4	5.5	5.4	B
	15	Medium	225	2	20.4	7.6	8.3	C
	15	Dark	235	1	16.2	5.4	5.2	D
Kenya Arabica	5	Medium	235	1	18.9	8.4	8.5	E
	5	Dark	250	1	16.1	6.4	5.5	F
	15	Medium	202	1	21.0	8.1	8.6	G
	15	Dark	225	1	17.0	6.4	5.4	H

## 2.2. Roasting of coffee beans

Green coffee beans were roasted in 50 g batches using a bench-top Neuhaus fluidized bed sample roaster RFB-L (Neuhaus-Neotec, Germany), equipped with air flow, temperature and time control. Two roast times were used in these experiments: a short roast of 5 min and a long roast of 15 min. The airflow rate and temperature were adjusted to obtain two different roast degrees at these roast times for both varieties of coffee. Roast degree was measured using a Color/Difference Meter D25-2 (Hunterlab, Virginia) on the ground coffee samples. A medium roast (Hunterlab *b*-value of 8.5) and a dark roast (Hunterlab *b*-value of 5.4) were selected for these experiments. Table 1 shows the conditions used to achieve the desired degree of roast.

## 2.3. Grinding roasted coffee samples

Roasted coffee beans were equilibrated at the degassing temperature overnight. During the equilibration period, the beans were flushed with N<sub>2</sub> at approximately 100 ml/min. The following morning, the coffee beans were ground using a small scale Super Jolly coffee grinder (Mazzer Luigi s.r.l., Venezia, Italy). Two different grind settings are used, and the particle size distributions were measured using a Malvern Particle and Droplet Laser Beam Sizer (Malvern, Worcheser, England). Setting 7.5, a fine grind, resulted in an average particle size ( $D_{43}$ ) of approximately 350  $\mu\text{m}$  (range 316–366  $\mu\text{m}$ ), and setting 8.5, a medium to coarse grind, resulted in an average particle size of approximately 570  $\mu\text{m}$  (range 486–589  $\mu\text{m}$ ). Ground coffee samples from every experiment were collected. A graph of a typical grind size distribution is shown in Fig. 1 for a Kenya Arabica sample that has a  $D_{43}$  value of 542  $\mu\text{m}$ .

## 2.4. Measurement of carbon dioxide content

Carbon dioxide content was determined by the method of Hinman (1993) in an apparatus shown in

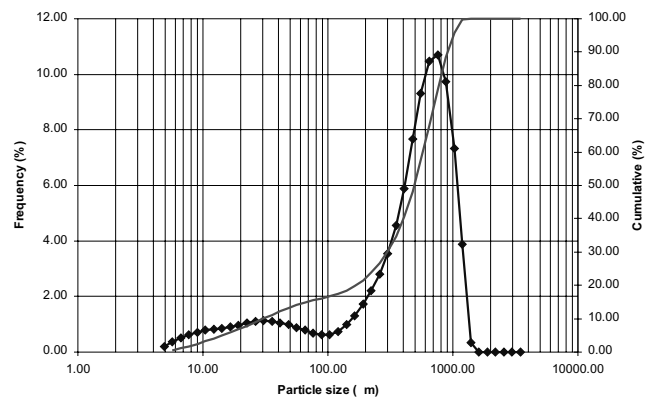


Fig. 1. Typical grind size distribution (Kenya Arabica,  $D_{43} = 542$ ).

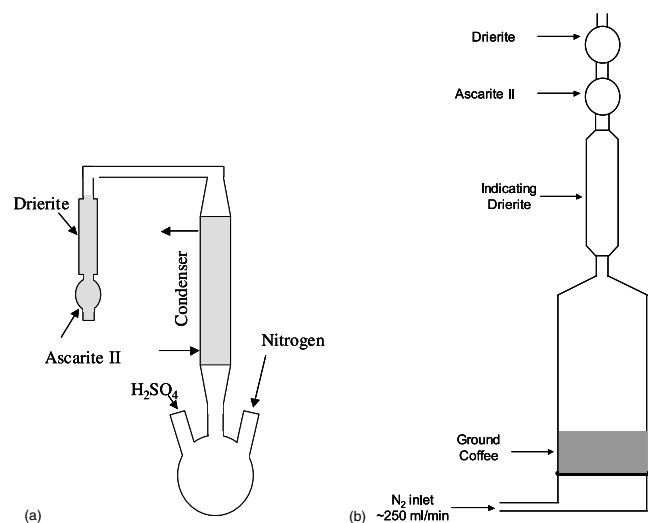
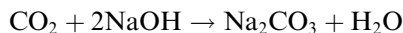
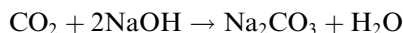


Fig. 2. (a) Apparatus for measuring initial and final CO<sub>2</sub> content and (b) apparatus for measuring CO<sub>2</sub> degassing from roast and ground coffee.

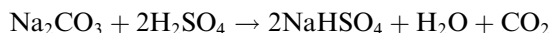
Fig. 2(a). The carbon dioxide in the coffee was trapped by mixing the ground coffee with 100 ml of an alkali tri-sodium citrate solution (50 g/l tri-sodium citrate in 0.25 M NaOH):



This solution is weighed and added to a three-entries distillation flask connected to a condenser supplied with cold water. A column of Drierite (anhydrous calcium sulfate from W.A. Hammond Drierite Company Ltd., Xenia, OH) was used to remove any moisture from the carbon dioxide vapors released. A carbon dioxide trapping column containing Ascarite II (Thomas Scientific, Swedesboro, NJ) was weighed to the tenth of a milligram and connected to the end of the Drierite column. Ascarite II is a NaOH coated silica gel that traps the carbon dioxide as follows:



50 ml of 2.5 M  $\text{H}_2\text{SO}_4$  was added by syringe to the flask, and nitrogen, at approximately 90 ml/min, was bubbled into the solution. The  $\text{H}_2\text{SO}_4$  reacts with the carbonate and releases the carbon dioxide, as described in the following:



The flask was heated to 50–70 °C and extracted for one hour, while stirring with a magnetic stir bar. After one hour, the column containing Ascarite II was weighed, and the  $\text{CO}_2$  concentration was calculated. This procedure was carried out on a sample immediately after grinding and on the three replicate samples after the end of degassing. Initial  $\text{CO}_2$  levels (immediately after roasting) and final levels (from the end of the degassing experiments) are shown in Table 2.

#### 2.4.1. Carbon dioxide degassing measurements

A special apparatus was built for the degassing experiments as shown in Fig. 2(b). Three glass columns were used and all experiments were done simultaneously in triplicate (different columns). The columns are approximately 9 cm in diameter and 28 cm tall in two sections for adding and removing coffee. The columns contain a 9 cm diameter glass filter to support the coffee. The columns were prepared by covering the inlet with Parafilm (American National Can, Greenwich, CT) and closing the outlet using a rubber stopper. Coffee was

ground at the proper setting and then immediately added to the column, which was then assembled into the closed system described previously. Time zero was measured when the second column was filled. Once all of the columns were filled (usually within 2–3 min), they were placed in an incubator set to the degassing temperature. The stoppers in the outlet were removed and replaced with carbon dioxide trapping columns. The Parafilm over the inlet was removed and an  $\text{N}_2$  hose was attached. Nitrogen was brought in from the bottom of the column at a flow rate of approximately 250 ml/min. The nitrogen flow rate should be high enough to sweep the carbon dioxide gas away from the ground coffee so that the surrounding environment contained virtually no carbon dioxide gas. Higher flow rates of nitrogen were also tested, but there was no difference in the rate of carbon dioxide evolution; therefore a flow rate of 250 ml/min was chosen. The nitrogen flowed up through the bed of ground coffee and through a 12 cm column of Drierite to remove any moisture from the gas. The carbon dioxide was then trapped using a column containing Ascarite II. A second trap containing Drierite was placed on top of the Ascarite II column. This was added to collect any moisture that was produced from the reaction of  $\text{CO}_2$  with Ascarite II, but might not have been held for the long periods of time required for the  $\text{CO}_2$  degassing experiments. The carbon dioxide trapping columns (Ascarite II column and the second Drierite column) were weighed to the tenth of a milligram on an analytical balance at intervals over a period of 48 h or until the  $\text{CO}_2$  trapping columns began losing weight. The increase in weight as a function of time was attributed to the gain of  $\text{CO}_2$  that reacted to and was absorbed by the chemical. Measurements were taken every 10 min for the first half-hour, then hourly and less frequently as the rate of gain decreased.

The degassing data collected was fitted using Eq. (1), the series expansion of Fick's law for unsteady state diffusion for a spherical geometry (Crank, 1975).

$$\frac{C_t}{C_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[ \frac{-D_{\text{eff}} n^2 \pi^2 t^2}{r^2} \right] \quad (1)$$

Table 2  
Carbon dioxide content results

Experiment	Coffee type	Roast time (min)	Roast degree	Grind size ( $\mu\text{m}$ )	Degassing temperature (°C)	Initial $\text{CO}_2$ content (mg/g)	Final $\text{CO}_2$ content (mg/g)
A	Togo Robusta	5	Medium	570	40	6.23	1.94 ± 0.09
B	Togo Robusta	5	Dark	350	40	7.03	0.90 ± 0.11
C	Togo Robusta	15	Medium	350	20	5.61	2.10 ± 0.60
D	Togo Robusta	15	Dark	570	20	8.55	3.22 ± 0.24
E	Kenya Arabica	5	Medium	570	40	4.44	0.45 ± 0.04
F	Kenya Arabica	5	Dark	350	20	4.97	0.61 ± 0.18
G	Kenya Arabica	15	Medium	570	20	3.98	1.10 ± 0.16
H	Kenya Arabica	15	Dark	570	40	5.11	0.31 ± 0.03

where  $C_t$  is the concentration at time =  $t$ ,  $C_0$ , concentration at time = 0,  $D_{\text{eff}}$ , effective diffusivity,  $r$ , average radius of particle from distribution.

The first 200 terms in the series expansion were used. The value for final  $\text{CO}_2$  concentration in this model was set at zero since the  $\text{CO}_2$  remaining after degassing (Table 2) acts as though it is trapped and does not actively take part in the kinetic and equilibrium processes. The radius used in the model was from the average particle diameter,  $D_{43}$  measured for the sample. For each set, the data from three replicates was individually fitted using an effective diffusivity value. The data was fit using the Microsoft® Excel Solver function and solving for a minimum sum of squared errors. The resulting effective diffusivity values were then averaged for the three replicates. As noted in Table 2, and because of limitations on time, not every combination of conditions was performed for each coffee.

### 3. Results and discussion

#### 3.1. Initial and final carbon dioxide content

Measurements of initial carbon dioxide content were taken immediately after grinding of the beans. Initial carbon dioxide contents ranged from 4.0 to 8.6 mg  $\text{CO}_2$  per gram of coffee, with an overall average of 5.7 mg/g (2.9 ml/g at STP) as shown in Table 2. As seen, the Togo Robusta samples had higher initial carbon dioxide contents (average of 6.9 mg/g) than did the Kenya Arabica samples (average of 4.6 mg/g). This confirms the statement that Clarke and Macrae (1985) made regarding roasted Robusta beans containing more carbon dioxide than do roasted Arabica beans most likely due to a higher carbohydrate content. According to Illy and Viani (1995), green Robusta coffee beans contain 54.4% carbohydrates and 8% sucrose, while green Arabica coffee beans contain 49.8% carbohydrates and 4% sucrose.

The degree of roast was also important. A darker roast contains more  $\text{CO}_2$  initially than does a lighter roast. In these experiments, the darker roasts have an average initial  $\text{CO}_2$  content of 6.4 mg/g, while the lighter roasts have an average content of 5.1 mg/g. This is to be expected, because more chemical reactions take place in a dark roast, thus there should be more  $\text{CO}_2$  produced.

Table 2 also shows the final carbon dioxide content results. The average final  $\text{CO}_2$  content was 1.3 mg/g of coffee (0.7 ml/g at STP) and ranged from 0.3 to 3.2 mg/g. The overall average final  $\text{CO}_2$  content for Togo Robusta samples was 2.0 mg/g, while the average final  $\text{CO}_2$  content for Kenya Arabica samples was 0.6 mg/g. This suggests that Togo Robusta coffee traps or holds more  $\text{CO}_2$  at equilibrium than does Kenya Arabica coffee. Togo Robusta coffee also had more  $\text{CO}_2$  initially, corroborating the idea of more trapped  $\text{CO}_2$ .

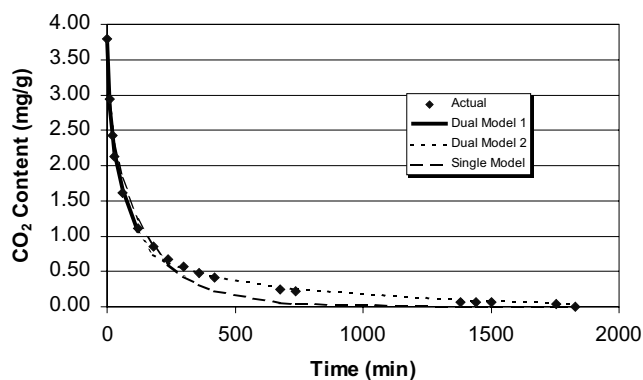


Fig. 3.  $\text{CO}_2$  degassing data modeled using single model and dual model in linear coordinates for Experiment E (Kenya Arabica, 5 min, medium roast, 570  $\mu\text{m}$ , 40 °C).

#### 3.2. Degassing kinetics

Fig. 3 shows an example of the diffusion loss of  $\text{CO}_2$  for Experiment E (Kenya Arabica coffee, 5 min, medium roast, 570  $\mu\text{m}$  and 40 °C). Table 3 summarizes the results of the calculated effective diffusivities using several different models for the data. Each of the individual fits had a correlation coefficient ( $r^2$ ) of at least 0.97, with an average over 0.98 as noted in Table 3. Using a single  $D_{\text{eff}}$  model, the overall average effective diffusivity calculated was  $5.30 \times 10^{-13} \text{ m}^2/\text{s}$  (range of  $3.05\text{--}10.37 \times 10^{-13} \text{ m}^2/\text{s}$ ). The values calculated for effective diffusivity are about two orders of magnitude lower than the  $2\text{--}20 \times 10^{-11} \text{ m}^2/\text{s}$  that was determined by Bichsel (1979) and Spiro and Chong (1997) for the diffusion of caffeine in coffee during decaffeination. The diffusivities are about one order of magnitude lower than the  $15\text{--}27 \times 10^{-12} \text{ m}^2/\text{s}$  that was found by Xiong, Narsimhan, and Okos (1991) for diffusion of moisture from pasta. They are on the same order in magnitude as the  $4\text{--}45 \times 10^{-13} \text{ m}^2/\text{s}$  reported by Doulia, Tzia, and Gekas (2000) for diffusion of moisture in oilseeds at 25 °C. Thus, the range of effective diffusivities calculated in these experiments appears to be reasonable for a porous solid.

The degassing curves seem to indicate that there were two different mechanisms occurring. Initially there should be some pressure driven flow of carbon dioxide out of the coffee particles since the pressure of  $\text{CO}_2$  is greater than one atmosphere, as was noted by Clarke and Macrae (1985). In addition, there will be diffusional flow present, which, depending on the size of the pores may take place as molecular diffusion or Knudsen diffusion. The time at which the changeover in mechanism occurs appears to be consistent across the majority of experiments with a range between about 60 and 120 min. Therefore, the data were also fitted using a dual model in which the data was broken up into segments of short times (data collected for times up to the changeover) and

Table 3

Carbon dioxide degassing results

Experiment	Degassing temperature (°C)	Measured avg. diameter (μm)	Calculated $D_{\text{eff}}$ (m <sup>2</sup> /s × 10 <sup>-13</sup> )					
			Overall	$r^2$	Short time	$r^2$	Long time	$r^2$
A	40	587	10.4 ± 2.0	0.997	9.7 ± 1.8	0.991	9.7 ± 4.8	0.980
B	40	367	3.2 ± 0.4	0.991	3.7 ± 0.3	0.994	1.1 ± 0.1	0.984
C	20	388	5.1 ± 1.0	0.984	6.7 ± 1.4	0.998	1.1 ± 0.2	0.994
D	20	589	3.6 ± 0.7	0.986	5.7 ± 1.0	0.994	1.4 ± 0.2	0.987
E	40	486	5.6 ± 0.5	0.990	6.7 ± 0.9	0.988	1.6 ± 0.2	0.990
F	20	316	3.5 ± 1.2	0.975	4.4 ± 1.3	0.983	0.5 ± 0.1	0.994
G	20	542	3.0 ± 0.6	0.992	3.8 ± 0.9	0.994	1.0 ± 0.1	0.995
H	40	549	7.9 ± 0.8	0.992	8.7 ± 0.9	0.987	2.5 ± 0.4	0.985

long times (data collected at times after the changeover). For each of these segments, the data was fit using the series expansion model of Fick's law (Eq. (1)) as was done for the single model.

In the example, using linear coordinates of CO<sub>2</sub> concentration versus time, both the single model and dual model appear to fit the actual data well and both have  $r^2$  values of greater than 0.99 as noted in Fig. 3 and Table 3. However, when plotted using semi-log coordinates as shown in Fig. 4, it is apparent that the slope changes and the single diffusion coefficient model does not predict as well at times greater than about 120 min. A second example can be seen in Figs. 5 and 6, for the degassing data of Experiment D (Togo Robusta coffee, 15 min, dark roast, 570 μm, and 20 °C).

When the carbon dioxide diffusion data was modeled for each coffee using the dual model with two effective diffusivities, the overall average effective diffusivity was  $6.18 \times 10^{-13}$  m<sup>2</sup>/s at short times and  $2.38 \times 10^{-13}$  m<sup>2</sup>/s at long times. This indicates that after the first 60–120 min after grinding, the effective diffusivity on average decreases by over 50%.

Temperature had a strong influence on the diffusivity. When the single model effective diffusivities at 40 °C are averaged and compared to the average of those at 20 °C,

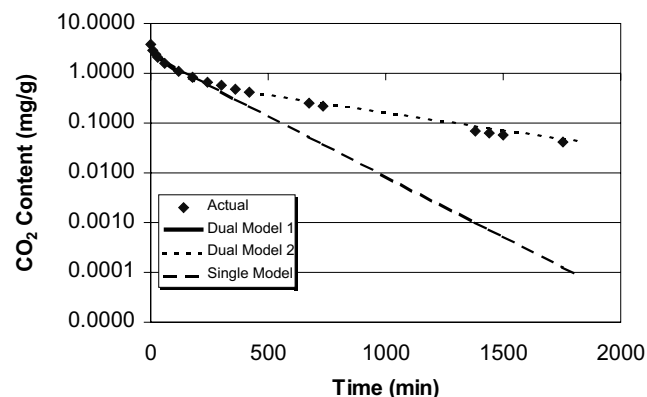


Fig. 4. CO<sub>2</sub> degassing data modeled using single model and dual model in semi-log coordinates for Experiment E (Kenya Arabica, 5 min, medium roast, 570 μm, 40 °C).

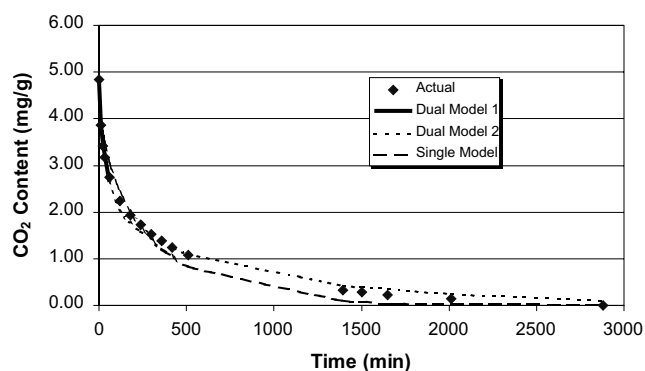


Fig. 5. CO<sub>2</sub> degassing data modeled using single model and dual model in linear coordinates for Experiment D (Togo Robusta, 15 min, dark roast, 570 μm, 20 °C).

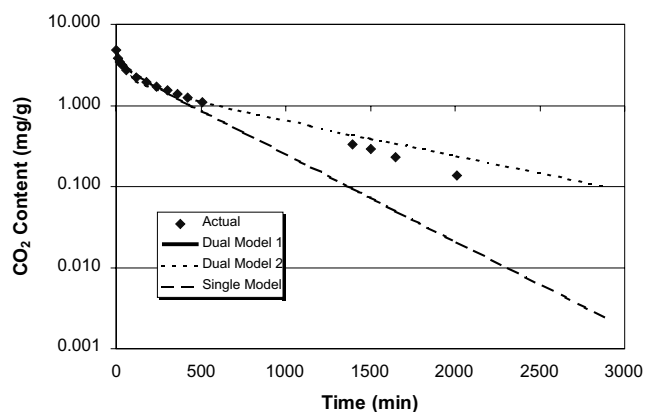


Fig. 6. CO<sub>2</sub> degassing data modeled using single model and dual model in semi-log coordinates for Experiment D (Togo Robusta, 15 min, dark roast, 570 μm, 20 °C).

it can be seen that a 20 °C increase in temperature raised the effective diffusivity by 70%. Similarly for the dual model, the 20 °C increase caused the diffusivity on average to increase by 30% at short times and over three times at long times. This dependence on temperature is higher than would be expected based on molecular diffusion, Knudsen diffusion, or viscous flow. Therefore surface

diffusion may play an important role in the diffusion mechanism, since it has been known to sometimes have a strong dependence on temperature (Cussler, 1997).

Based upon the size of the CO<sub>2</sub> molecule and the pore size distribution that other researchers have measured, calculations can be done to better understand the mass transfer phenomena that are occurring. Diffusion of gases in pores is usually characterized using the mean free path of the gas molecule and the pore size. The mean free path for carbon dioxide can be calculated based on Eq. (2) and depends on the temperature and the pressure of the gas:

$$\lambda = \frac{3.2\mu}{P} \sqrt{\frac{RT}{2\pi g_c M_W}} \quad (2)$$

In these experiments, the mean free path would be shortest at low temperatures (20 °C) and when the internal pressure in the coffee is the highest, which is the beginning of the experiment. The mean free path would be longest at high temperatures (40 °C) and when the internal pressures come to equilibrium at the end of the experiment. Based on the maximum initial value of CO<sub>2</sub> found (8.6 mg/g), a bulk density of 0.35 g/ml, and a porosity of 0.4 (Radtko & Heiss, 1975), the maximum internal pressure should be 4.40 atm:

$$\begin{aligned} P(\text{atm}) &= \frac{C_{\text{CO}_2} \rho_{\text{bulk}} RT}{M_W \varepsilon} \\ &= \frac{(8.6 \text{ mg/g})(0.35 \text{ g/ml}(\text{total})) (82.057 \text{ cm}^3 \text{ atm/mol K})(313 \text{ K})}{(44 \text{ g/mol})(1000 \text{ mg/g})(0.4 \text{ ml}(\text{pore})/\text{ml}(\text{total}))} \\ &= 4.40 \text{ atm} \end{aligned}$$

Therefore, the mean path length ranges from a minimum of  $0.95 \times 10^{-6}$  cm to a maximum of  $4.90 \times 10^{-6}$  cm:

$$\begin{aligned} \lambda_{\min} &= \frac{3.2\mu}{P} \sqrt{\frac{RT}{2\pi g_c M_W}} \\ &= \frac{3.2(0.00014 \text{ g}_m/\text{cm s})}{4.40 \text{ atm}(1033.2 \text{ g}_f \text{ cm}^2/\text{atm})} \\ &\quad \times \sqrt{\frac{(84,780 \text{ g}_f \text{ cm/mol K})(293 \text{ K})}{2\pi(980 \text{ g}_m \text{ cm/g}_f \text{ s}^2)(44 \text{ g}_m/\text{mol})}} \\ &= 0.95 \times 10^{-6} \text{ cm} \end{aligned}$$

$$\begin{aligned} \lambda_{\max} &= \frac{3.2\mu}{P} \sqrt{\frac{RT}{2\pi g_c M_W}} \\ &= \frac{3.2(0.00016 \text{ g}_m/\text{cm s})}{1 \text{ atm}(1033.2 \text{ g}_f \text{ cm}^2/\text{atm})} \\ &\quad \times \sqrt{\frac{(84,780 \text{ g}_f \text{ cm/mol K})(313 \text{ K})}{2\pi(980 \text{ g}_m \text{ cm/g}_f \text{ s}^2)(44 \text{ g}_m/\text{mol})}} \\ &= 4.90 \times 10^{-6} \text{ cm} \end{aligned}$$

Several researchers have attempted to measure the pore size distribution of roasted coffee and have reported differing results. However in general, the majority of pores are thought to be in the range of 2–50 nm in diameter (Barbera, 1967; Schenker et al., 2000). Based on these values of mean path length and pore size, the Knudsen number ( $N_{\text{Kn}} = \lambda/2r$ ) ranges from 0.19 to 24.5, which categorizes the mass transfer in either the transition or Knudsen regimes. This gradual change from the transition region to the Knudsen region as the internal pressure decreases could be a cause of the two different diffusivities described earlier.

However, there was also a pressure differential present, which caused viscous flow to occur. The release of internal pressure when coffee beans were ground and internal pockets were broken could allow viscous flow to occur. The viscous flow lessens and eventually comes to a stop as the total pressure differential with the surrounding atmosphere decreases. This may also have had influence in the two mechanisms observed.

Finally, there is a possibility that surface diffusion occurred and that there were constant interactions between the CO<sub>2</sub> molecules and the coffee matrix or lipids. Surface diffusion can occur when gas molecules absorb to solid surfaces. When this occurs, the gas molecules are thought to “hop” from one site on the solid to another. Values for surface diffusivity can vary greatly and are often highly dependent on temperature. Researchers have found that some amount of CO<sub>2</sub> adsorbed to the coffee, even at equilibrium. These interactions may affect and possibly slow the diffusion of CO<sub>2</sub> from roasted coffee. Based on Eq. (3), the expected Knudsen diffusivity coefficient is between  $5.0 \times 10^{-7}$  and  $1.3 \times 10^{-5}$  m<sup>2</sup>/s.

$$D_{\text{KA}} = \frac{2}{3} r \sqrt{\frac{8TR}{\pi M_A}} = 9700r \sqrt{\frac{T(\text{K})}{M_A}} \quad (3)$$

This is much higher than the effective diffusivities that were determined in these experiments, even if porosity and tortuosity factors were included in the calculated values. Adding molecular diffusivity and viscous flow terms should not decrease the diffusivity to the degree that was observed. Therefore, it is very likely that interactions between the CO<sub>2</sub> molecules and the coffee slow the diffusion resulting in the very low values (i.e.  $\sim 10^{-13}$  m<sup>2</sup>/s). The high dependence on temperature that was found also suggests that surface diffusion may be important (Cussler, 1997).

The actual diffusion mechanisms taking place in these experiments are very complicated. There are likely influences from Knudsen diffusion, transition-region diffusion, pressure-driven viscous flow, surface diffusion, and interactions between the CO<sub>2</sub> gas and the coffee itself. A more rigorous diffusional model, such as those discussed by Krishna (1993), may better fit the data with the addition of other fitting terms. However, due to the

variability in the data itself, it is unlikely that other models will make a significant improvement. In addition, the other models would be more difficult to apply to real world applications due to the additional fitting terms that would need to be determined for each specific case.

#### 4. Conclusions

In these experiments, the diffusion kinetics of carbon dioxide from freshly roasted and ground coffee were determined. The carbon dioxide degassing curves were successfully modeled using a series expansion of Fick's law for unsteady state diffusion from a sphere (Crank, 1975). The overall effective diffusivities determined were rather low, but reasonable, ranging from  $3.1$  to  $10.4 \times 10^{-13} \text{ m}^2/\text{s}$ .

The degassing data seemed to indicate that two major mechanisms could be occurring. Using one diffusivity value fits the data extremely well for about the first two hours of degassing, but then the rate appears to change. Using a second diffusivity value for times greater than about two hours appears to better fit much of the data. Using this dual diffusivity model resulted in short time effective diffusivities ranging from  $3.7$  to  $9.7 \times 10^{-12} \text{ m}^2/\text{s}$ , and values at long times ranged from  $0.5$  to  $9.7 \times 10^{-13} \text{ m}^2/\text{s}$ .

The actual diffusion mechanism is quite complicated. It is likely that a combination of mechanisms is occurring including Knudsen and transition-region diffusion, pressure-driven viscous flow, surface diffusion, and interactions between the  $\text{CO}_2$  molecules and the coffee matrix.

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