EFFECTS OF HIGH PRESSURE PROCESSING ON THE EXTRATION AND PHYSICOCHEMICAL CHARACTERISTICS OF COLD BREW COFFEE

By

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ABSTRACT:

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Cold brew coffee is prepared by steeping ground coffee in water at ambient or refrigerated temperatures for 8 to 24 h. Cold brew coffees tend to be less bitter and less acidic than the conventional hot brewed counterparts. In this study, the effects of high pressure processing (HPP) on the extraction and physicochemical characteristics of cold brew coffee and property changes during 60-day storage were investigated. HPP facilitated the cold brew coffee extraction process, especially for whole beans. Moreover, whole bean brew with HPP had smooth and persistent foam and pleasant flavor, which has potential for preparing Nitro coffee. During 60-day storage, pH of cold brew coffee decreased while titratable acidity, caffeine, chlorogenic acid and total polyphenols contents increased, which can be accelerated by HPP. Findings from this project showed that HPP potentially could be used as an innovative method to prepare and preserve cold brew coffees.
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LIST OF ABBREVIATIONS

SCAA: Specialty Coffee Association of America
ICO: International Coffee Organization
HPP: High pressure processing
HHP: High hydrostatic pressure processing
UHP: Ultra-high pressure processing
HTST: High-temperature-short-time
LTLT: Low-temperature-long-time
TDS: Total dissolved solids
TPP: Total polyphenol
CGA: Chlorogenic acid
SEM: Scanning electron microscopy
RMSE: Root Mean Square Error
R²: Coefficient of determination
EY: Extraction yield
TA: Titratable acidity
Abs: Absorbance
HPLC: High performance liquid chromatography
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Chapter 1 Literature Review

1.1 Coffee

Coffee is one of the world’s most consumed beverages, along with water and tea. It is also one of the world’s most traded commodity, with about half a trillion cups consumed per year (Folmer, 2017). Besides brewing into beverages, coffee beans are natural sources of caffeine being extracted for other products, such as cola drinks, pharmaceuticals, and cosmetics through decaffeination processes. Coffee production has been increasing steadily from 6.31 to 9.51 million tons from 2003 to 2018. In 2017/2018, around 9.70 million tons of coffee were consumed worldwide (Access on May 2020; www.statista.com/statistics/263311/worldwide-production-of-coffee/).

Coffee has a long evolution history. The first wild coffee plant (Arabica) was discovered in Ethiopia. The dissemination of Arabica coffee started in the 8th century when their seeds were being transported from Ethiopia to Yemen where they were cultivated until the end of the 14th century. Coffee continued its expansion to India, Ceylon (now Sri Lanka), Java, and Indonesia, where commercial plantations began. In the early 17th century, coffee arrived in Europe, brought by a Dutch trader in 1616. They finally reached the American continent around 1912. Nowadays, coffee is one of the most widely consumed beverages globally (Folmer, 2017).

There are six main stages in the coffee life cycle from cherry to cup: growth, harvest, processing, roasting, grinding and extraction. Coffee plants typically grow in regions at 600 -
1800 m above the sea level and take about 210 d from blossom to fruit. They produce red cherry-like fruits that contain one to two seeds. After being separated from the fruit’s pulp, the seeds are known as “green coffee beans”. The green beans are lacking flavour. However, upon roasting, coffee’s characteristic sensory properties are developed (Buffo & Cardelli-Freire, 2004). In addition to the coffee varieties and their origins, environmental factors, such as rainfall, sunlight, temperature, and altitude, can also affect the growth of coffee cherries. The overall terroir and origin of coffee are the most critical factors determining the final coffee brew’s flavour and quality (Avelino et al., 2005).

Coffee cherries are harvested after they are ripe when they turn into bright red colour. Unripe coffee cherries would undermine the final quality of the coffee brew. Consequently, only ripe coffee cherries can be harvested. Selective hand picking and mechanical harvesting are employed during the harvest process. Hand-picking is more selective in choosing the ripen cherries but is also more expensive and time-consumming. Mechanical harvesting is less selective but is more efficient. Following harvest, the cherries will be sorted to ensure the final quality (Illy, 2002).

Coffee cherries must be processed immediately after harvest to prevent spoilage. Sun-drying and washing methods are usually adopted to reduce water content of coffee cherry from 65 % to 10 - 12 %. The sun-drying method, also known as natural drying, is carried out by spreading the cherries out on an open space under direct sunlight. Frequent turning/stirring of the desiccating fruits is essential to ensure uniform heating. This process
tends to result in coffee beverage with a strong body, sweetness, and complex attributes (Folmer, 2017). Dried cherries are then crushed to remove both the hulls and the parchment membrane layers surrounding the seeds before sorting and bagging. Alternatively, the coffee cherries are processed using the washing method, wherein they are mechanically pulped, and then fermented for 12 to 24 h to remove the mucilage, washed, and finally dried and liberated from the parchment covering (Illy, 2002). The washing method tends to result in brews with emphasized acidity and aroma, while dismissing some of the astringency (Folmer, 2017).

The green coffee beans are lacking the characteristics of coffee flavour and aroma. Roasting is an essential step to endow flavour and aroma to coffee beans. When the coffee beans are roasted to 170 - 230°C, many physicochemical changes occur, including water evaporation, development of brown color due to Mallard reactions, generation of a large volume of CO₂ due to Strecker degradation, expansion of bean volume with concomitant increase in porosity, weight loss, and so on. Volatile (e.g., aldehydes, alkyl pyrazines, phenols, dienes, furanones, thiols) and non-volatile compounds (e.g., melanoidins, peptides, oligosaccharides) generated during roasting are responsible for the final flavour of coffee brew (Schenker, Handschin, Frey, Perren, & Escher, 2000; Wang & Lim, 2014, 2017). Depending on the roasting degree, the colour of coffee beans turns to brown, dark brown, and black from an initial green progressively. Melanoidins from Mallard reactions and caramels from thermal degradation of carbohydrates and sugars are responsible for brown colour of roasted coffee beans. The roasted coffee beans are usually divided into light, medium and dark roast degree. During roasting process, the moisture content of coffee beans drops from
10 - 12 % to 1 - 5 %. Due to the formation of large amount of CO₂ (2 - 5 mL CO₂ per gram of coffee beans, up to 10 mL), the coffee bean volume is expanded greatly and its porous structure forms concomitantly. Normally, there are two roasting methods adopted: high-temperature-short-time (HTST) and low-temperature-long-time (LTLT). The former method can generate higher bean volume, a larger cumulated pore volume and larger cell wall micropores than the latter. For example, Schenker found that relative bean volumes of 1.74 and 1.42 for a medium roasted coffee using HTST and LTLT methods, respectively (Schenker, 2000; Wang & Lim, 2014). From the perspective of sensory attributes, HTST can produce stronger roasted and burnt notes, aroma intensity and bitterness while LTLT generates stronger green and floral notes and higher acidity (Schenker, 2000). For the chemical composition changes during the roasting process, large amounts of melanoidins are produced while the contents of sucrose, protein, amino acids, and chlorogenic acid decrease greatly, even being deplete (Wang & Lim, 2015). However, caffeine, another important composition in coffee beans, is less heat-sensitive and keeps stable during roasting (Hečimović, Belščak-Cvitanović, Horžić, & Komes, 2011). For the aroma evolution during the roasting process, light roasted coffee beans are characterized by sweet, floral, bread, and nutty flavor while more complex aroma profiles and a medium acidity and body are found in the medium roasted coffee beans. The dark roasted coffee beans are featured with cocoa, spicy, phenolic ashy, pungent, and dark roasted flavors. With the increase of roasting degree, the bitter taste of obtained coffee brew increases while the acidity decreases.
Grinding transforms the roasted coffee bean into grounds by applying mechanical forces to fracture the beans into particulates, with the aim of increasing their surface area to facilitate the extraction of soluble solutes. The grinding process is affected by the variability, moisture content, and roasting degree of the coffee beans. In general, high roasting degree (especially short time roasting) and low moisture content can lead to smaller particle size whereas low roasting degree and high moisture content can lead to larger particle size. Roasted coffee beans are ground to different particle sizes optimized for a specific brewing method. By and large, coffee grounds are categorized as fine, medium, and coarse grind sizes, which are intended for Turkish/espresso, drip filter, and French press brew methods, respectively (Folmer, 2017).

Finally, coffee brewing is a solid-liquid extraction to dissolve soluble compounds from the coffee matrix into a brew. Generally, coffee brewing involves percolating the coffee grounds with hot water (92 ± 2°C) for several seconds (e.g., espresso, single-serve capsule) up to a few minutes (e.g., Fresh press, filter drip). The brew is then separated from the spent coffee grounds by passing it through a cellulosic, thermoplastic, or metallic filter by gravity or hydraulic pressure. During the coffee extraction process, the mass transport phenomena can be summarized as follows: (1) penetration of water into the coffee bed which causes the displacement of air/gases as well as wetting and whirling-up of ground particles; (2) washing of soluble solutes and fines from the surfaces of particles that are ruptured during the grinding process; (3) penetration of water into the pores of the coffee particles; (4) swelling of the particles; (5) solubilization of soluble components; (6) diffusion of dissolved solutes to
the particle surfaces, which is the rate determining step of the extraction process; (7) convective mass transfer of solutes into the brew (Moroney, Lee, Brien, Suijver, & Marra, 2015). The intragranular and intergranular extraction processes are shown in Figure 1.1. Although coffee brewing methods vary considerably between countries, cultures, and brewing equipment, all extraction methods generally involve these phenomena.
Figure 1.1 Mass transport processes of coffee solute in the coffee bed during brew extraction. Adapted from Moroney, Lee, Brien, Suijver, & Marra (2015).
Extraction time is the interaction time between the brewing water and roasted coffee. It is an important factor influencing the coffee flavor and quality. There are nearly 2000 compounds identified in roasted coffee beans (Lee, Kempthorne, & Hardy, 1992). They are extracted in different extraction times due to their different solubility in the brewing water and different polarity. More than 90% of soluble components such as sugars, organic acids, caffeine, and other low molecular weight compounds (e.g., amino acids) were extracted from a few seconds (e.g., espresso coffee) to a few minutes (e.g., filter coffee). On the contrary, the less soluble components such as polysaccharide and some polyphenols are extracted after contacting with large amount of water for long time (Cordoba, Fernandez-Alduenda, Moreno, & Ruiz, 2020; Severini, Ricci, Marone, Derossi, & De Pilli, 2015). Similarly, high-polar compounds such as 2,3-butanedione are extracted at the beginning of extraction and less polar compounds such as damascenone are extracted at the end of extraction (Mestdagh, Davidek, Chaumonteuil, Folmer, & Blank, 2014).

The extraction efficiency is the quantity of soluble and less soluble components extracted from the coffee matrix into the coffee brew in a given time and is mainly affected by water temperature, pressure, coffee/water ratio, particle size, water quality, and brewing methods (Andueza et al., 2002; Andueza, et al., 2003; Wang, William, Fu, & Lim, 2016).

Water temperature is an important parameter of the coffee extraction process. From the point view of kinetic energy, high temperature can increase the kinetic energy of water molecules leading to the release of coffee components. Besides, the solubility of coffee
compounds also increases with the temperature in general. Consequently, the total dissolved solids of coffee brew are improved at high temperature. Furthermore, the high temperature also favors the release of volatile compounds, such as guaiacol and pyrazines. Cold brew coffee is made at room or refrigerated temperature. High-polarity compounds are easily extracted, while other compounds need to longer time, which is usually between 6 and 24 h (Rao & Fuller, 2018).

Pressure is usually required in the espresso (7 - 9 bars) and Moka pot (1 - 2 bars) methods. Pressure applied in espresso machines can push the very fine coffee grounds and oil droplets into the cup, which can affect the character and sensory profiles of espresso coffee. Pressure is also essential for the crema formation. CO₂ present in ground coffee is forced into the water phase when pressure is applied to the espresso machine. When dissolved CO₂ is slowly released after the pressure drops, some solids follow and form a dense and stable crema on the top of coffee brew. The pressure can prevent the evaporation of aromatic compounds compared to non-pressurized or low pressure extraction methods, such as drip and French press coffee (López, Wellinger, Gloess, Zimmermann, & Yeretzian, 2016).

The coffee/water ratio is described as the mass of ground coffee to the mass of water used in coffee brewing process. It is usually described as coffee mass per water volume. A high coffee/water ratio will result in the coffee brew with underdeveloped flavour while a low coffee/water ratio will result in over-extracted beverages with bitter or weak flavour (Andueza et al., 2007).
The particle size of ground coffee determines the extraction efficiency and further affects the quality of the final coffee beverage. Grinding can help to increase the interface between water and coffee by increasing the surface area of ground coffee and can also help to release the CO₂ and volatile compounds by breaking the coffee bean cells. During the coffee brewing process, the volume of coffee particles can increase up to 20 - 23 % in 10 - 15 min after water enters the cavities of coffee grounds. Consequently, particle size is regarded as variable with brewing time changes (Maria-L., Jean-C., & Remy, 2007). For espresso coffee, large particles can lead to the low extraction yield due to the induced channels and low tamping. In contrast, too small particles lead to over-extraction as a result of clog and subsequent increased extraction time and pressure (Baggenstoss, Perren, & Escher, 2008).

Coffee brew with typical drinking concentration is made up more than 95 % water. Second to the roasted coffee, water is the most important ingredient for coffee brew. Water parameters including hardness, acidity, and cations have been shown to affect the sensory properties of coffee brews (Gardner, 1957; Lockhart et al., 1955; Pangborn et al., 1971). The aromatic compounds of roasted coffee beans are in the form of aprotic, charge-neutral species, and as a collection of acids and conjugate salts (Hendon, Colonna-Dashwood, & Colonna-Dashwood, 2014). Therefore, the dissolution and extraction of these organic compositions are affected by the ions in the brewing water, such as Na⁺, Mg²⁺, and Ca²⁺. By using computational chemistry, it was found that brewing water rich in Mg²⁺ is the most suitable to extract the most coffee constituents while Ca²⁺ and Mg²⁺-rich water can brew the best coffee with balanced flavor (Hendon et al., 2014). For the anions, carbonates can
contribute to a bitter and flat coffee, whereas distilled water can produce excessively sour coffee brews. Besides, carbonates and bicarbonates can retard the coffee brewing time correlating to their concentrations in water. According to Equation 1, carbonates and bicarbonates also affect the formation of CO₂, which can impact the sensory and foaming properties of coffee brew (Folmer, 2017).

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+ \quad (\text{Equation 1})
\]

Hardness is defined as the sum of amounts or equivalent concentrations of calcium and magnesium ions in water. Specialty Coffee Association of America (SCAA) recommends an optimum brewing water of hardness of 17 - 85 mg/L CaCO₃. Total alkalinity is the measurement of the negative ion concentrations in the brewing water and is determined by measuring the amount of acid needed to bring the sample to a pH of 4.2 where alkaline compounds are regarded as used up. The result of total alkalinity in brewing water is represented as milligrams per liter of calcium carbonate (mg/L CaCO₃). Alkaline compounds such as bicarbonates and carbonates remove hydrogen ions (H⁺) and lower the acidity of the water. SCAA recommends the total alkalinity concentration at 40 mg/L CaCO₃ and pH 6.5 - 7.5 of coffee brewing water. Too much alkalinity can affect extraction, pH, and flavor of final coffee brew. Changes in hardness and alkalinity significantly affect the sensory attributes of a coffee. Filter coffee prepared with hard water (157.50 mg/L CaCO₃) has a bitter taste and
coffee brew prepared with medium hard water (71.67 mg/L CaCO₃) gives a sweet taste and is more aromatic while sourness is perceived in soft water brewed coffee (9.33 mg/L CaCO₃).

Coffee brews are characterized by extraction yield and brew strength. The extraction yield reflects the ratio of solids dissolved in the coffee brew compared to the initial amount of coffee used. An ideal extraction yield is between 18 - 22 %. Brews with extraction yield below 18 % are regarded as under-extracted or underdeveloped, resulting in a flat or acidic coffee brew. Brews with extraction yield above 22 % are thought to be over-extracted, leading to bitter and astringent coffee brew (Folmer, 2017). The strength of a coffee brew, which is measured as total dissolved solids (TDS), should exhibit 11.5 - 13.5 g/L, in other words, 1.15 - 1.35 % to achieve the Golden Cup Standard, according to SCAA Brewing Control Chart shown below (Figure 1.2). To meet the recommended coffee brew strength, coffee/water ratio (55 g/L ± 10 %), coffee-water contacting time (1 - 4 min for fine ground, 4 - 6 min for medium ground, 6 - 8 min for coarse ground), brewing water temperature (93.0 ± 3°C) are required (http://www.scaa.org/PDF/resources/golden-cup-standard.pdf).
Figure 1.2 The Specialty Coffee Association of America (SCAA) brewing control chart. Adapted from sca.coffee/sca-news/25/issue-13/towards-a-new-brewing-chart
After brewing, coffee beverages continue to undergo physicochemical changes, which can substantially affect their sensory properties. During storage after the coffee brew cooled down, substantial physicochemical changes in coffee brew occurred, affecting their appearance and taste that can decrease consumer acceptance. One of the most prominent changes during storage is the increase of perceived sourness, accompanied by the decrease of product pH and increase of titratable acidity (Manzocco & Lagazio, 2009). The increased sourness can be attributed to the hydrolysis of low molecular weight esters, and the thermal degradation of chlorogenic acids into their corresponding hydroxycinnamic acids, such as such as caffeic or ferulic acids (Pérez-Martínez, Sopelana, De Peña, & Cid, 2008b). Furthermore, the released of phenolic compounds, such as caffeic or ferulic acids, can contribute to the bitterness of coffee beverages. Moreover, the ferulic acid can act as the precursor for some flavour compounds, such as 4-vinylguaiacol, which further affect the coffee flavour. On the other hand, the caffeine content remains stable under typical storage conditions.

The changes in coffee beverages during storage are dependent on temperature and oxygen. Coffee beverages stored at 25°C with oxygen (with air headspace in the bottle) lost more aroma intensity and freshness, had stronger sourness and rancid taste than that at 4°C or without oxygen (without air headspace in the bottle) (Pérez-Martínez, Sopelana, De Peña, & Cid, 2008a, 2008b; Rosa, Barbanti, & Lerici, 1990). In general, both the high temperature and oxygen can accelerate the aging process of coffee beverage.
1.2 Overview of extraction methods and their parameters

At the consumer level, various coffee extraction methods have been developed based on equipments with different levels of complexity, such as boiling (Turkish), pour over (drip), French press, espresso, Moka pot, single-serve capsule, cold brew, and so on. The typical brew parameters for these methods are summarized in Table 1.1. Brief descriptions for these methods are presented in the following section.

Table 1.1 Typical parameters for selected coffee brewing methods (Martin and Christian. 2017).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Turkish</th>
<th>Pour over</th>
<th>French press</th>
<th>Espresso</th>
<th>Moka pot</th>
<th>Cold brew</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/coffee ratio (mL/g)</td>
<td>~ 20</td>
<td>~ 13 - 20</td>
<td>~ 15 - 20</td>
<td>3.5 - 6</td>
<td>~ 9 - 15</td>
<td>~ 4 - 15</td>
</tr>
<tr>
<td>Particle size (μm)</td>
<td>Fine (&lt; 150)</td>
<td>Medium (500 - 700)</td>
<td>Coarse (800 - 1000)</td>
<td>Fine (&lt; 200)</td>
<td>Fine (200 - 500)</td>
<td>Coarse (&gt; 800)</td>
</tr>
<tr>
<td>Compaction</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>7 - 9</td>
<td>1 - 2</td>
<td>0 - 0.1</td>
</tr>
<tr>
<td>Brewing time</td>
<td>3 - 4 min</td>
<td>3 - 10 min</td>
<td>2 - 5 min</td>
<td>25 - 30 s</td>
<td>3 - 5 min</td>
<td>8 - 24 h</td>
</tr>
</tbody>
</table>

Boiling is the simplest method to prepare the coffee brew. Turkish coffee is brewed in this manner. Here, fine (< 150 μm) coffee grounds are placed in a pot where water is added
and heated up to boiling. The resulting brew is then filtered by a strainer to remove the grounds. Boiling results in an intense, dark, and full-bodied coffee brew. Due to increased water contact time and elevated extraction temperature, boiling coffee is usually over-extracted with suspected fines in the brew and a bed of sediment at the bottom of the cup.

Pour over, also known as filter coffee or drip coffee, is one of the most common methods for preparing coffee beverages. The preparation of drip coffee is similar to that of the percolator coffee, except that the ground coffee is extracted only with fresh hot water without recirculating the brew through the ground coffee. For the drip brewing method, the ground coffee is introduced onto a disposable filter paper supported in a conical shaped holder. Alternatively, in paperless brewing, the reusable holder is equipped with a metallic or plastic mesh that holds the ground coffee. Hot water is then poured over the ground coffee gradually to moisten the coffee particles and allow the water to seep through the bed. As more water is introduced to the coffee bed, coffee brew exits the filter by gravity and is collected below in a cup or carafe. The obtained coffee brew tends to be transparent when a paper filter is used (Folmer, 2017). Studies have shown that cellulosic filter can retain diterpenes (e.g., cafestol and kahweol) that are known to raise low-density lipoprotein cholesterol levels. Hence, drip coffee prepared using a paper filter may confer better health benefits than unfiltered coffees (e.g., boiled, espresso, French-press) (Taylor & Demmig-Adams, 2007).
French press method involves steeping the ground coffee with hot water in a round glass beaker for 2 - 5 min followed by pushing a filter plunger (equipped with a fine wire or nylon mesh filter attached at the end of a plunger) that fits snugly to the beaker downward to separate the spent from the brew. The spent ground coffee is being packed and confined to the bottom of the beaker by the filter, while the coffee brew that passes through the filter is being collected in the top of the beaker. Due to the fine suspended particle and oil droplets, the French press coffee tends to have a full body and turbid characteristic.

Espresso is prepared on request from finely ground coffee (7 ± 0.5 g) under specific brewing conditions of 88 ± 2°C, 9 ± 1 bar hydraulic pressure, and 25 ± 5 s brewing time, to obtain a small cup (25 - 40 mL) of a concentrated coffee brew. Due to the high pressure applied on the compacted coffee bed, that process produces coffee brew with a characteristic foam head, commonly known as crema, made up of microscopic, emulsified oil droplets, ultrafine particles, and small gas bubbles. Espresso coffee is typically described as having a strong body, full aroma, balanced bitter and acid taste, and pleasant lingering aftertaste. Contributed by the oil droplet, espresso's flavour and aroma can linger for as long as 20 min after consumption (Illy, 2002).

The Moka pot has two chambers (lower and upper) that are screwed together and sealed with a rubber gasket. Before assembling the pot, the bottom chamber is filled with water, followed by inserting a funnel-shaped basket, such that the stem of the basket is submerged in water within the bottom chamber. The basket is fitted with a perforated disc filter that holds
the ground coffee. On the other hand, the top chamber has a built-in spout pointing upward at the chamber cavity center. Another perforated disc filter is fitted to the spout base, which fits over the top of the basket. During brewing, the assembled pot is heated on a stovetop. As the brewing water is heated up, the pressure buildup within the lower chamber forces the hot water upward through the coffee bed in the basket, exits the spout, and collects in the top chamber as a coffee brew. Due to the elevated pressure, the brewing water could reach a brewing temperature up to 110°C. Moka pot tends to produce strong coffee brew with a high extraction yield (Folmer, 2017; Gloess et al., 2013).

There is another coffee brewing method called percolator coffee, which is made by recirculating brewing water through the coffee ground bed. The percolator consists of a bottom vessel fitted with a vertical tube that leads to the upper part of the brewer where the coffee bed is located. The brewing water is introduced into the lower chamber. As the water is heated, the increased pressure in the bottom chamber forces the water through the tube into the upper chamber and distributes it over the top of the ground coffee. After passing through the ground coffee bed, the brew flows back to the lower chamber and then is recirculated. Due to the recirculating process, extensive extraction of soluble components in the coffee ground occurs, resulting in an astringent and strong coffee brew. Moreover, extended heating time and prolonged recirculation of brew can lead to the loss of volatile compounds.

Main physicochemical characteristics of the filter, French press, Moka, and espresso coffees are summarized in Table 1.2
Table 1.2 Main physicochemical characteristics of filter coffee, French press coffee, Moka coffee and espresso coffee (Folmer, 2017)

<table>
<thead>
<tr>
<th></th>
<th>Filter</th>
<th>French press</th>
<th>Moka</th>
<th>Espresso</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.4 - 5.5</td>
<td>5.1 - 5.3</td>
<td>5.0 - 5.2</td>
<td>5.1 - 5.8</td>
</tr>
<tr>
<td>TDS (g/L)</td>
<td>16.2 - 17.7</td>
<td>16.9 - 20.0</td>
<td>22.9 - 37.3</td>
<td>27.1 - 43.3</td>
</tr>
<tr>
<td>EY (%)</td>
<td>21.7 - 23.6</td>
<td>21.7 - 24.3</td>
<td>27.6 - 30.7</td>
<td>15.5 - 25.0</td>
</tr>
<tr>
<td>Abs 420 nm</td>
<td>0.29 - 0.47</td>
<td>0.30 - 0.60</td>
<td>0.65 - 0.92</td>
<td>0.78 - 1.67</td>
</tr>
<tr>
<td>L*</td>
<td>20.75 - 21.22</td>
<td>21.50 - 23.16</td>
<td>22.05 - 23.34</td>
<td>20.76 - 22.34</td>
</tr>
<tr>
<td>a*</td>
<td>0.29 - 1.06</td>
<td>0.86 - 1.07</td>
<td>1.02 - 2.54</td>
<td>0.74 - 2.13</td>
</tr>
<tr>
<td>b*</td>
<td>0.43 - 0.82</td>
<td>0.80 - 1.47</td>
<td>1.10 - 3.22</td>
<td>0.6 - 2.24</td>
</tr>
</tbody>
</table>

TDS: total dissolved solids; EY: extraction yield; Abs 420 nm: absorbance at 420 nm.
1.3 Arabica and Robusta coffee

There are two commercially important species of coffee plants, namely *Coffea arabica* (often called Arabica coffee) and *C. canephora* (also known as Robusta coffee). Around two thirds of the global coffee production are derived from the Arabica species while the Robusta and other species take up the remaining fraction. Robusta is a high-yielding and disease-resistant tree with a height of up to 12 m that grows best in warm, humid climates (Illy, 2002). It tends to produce brews with substantial body with relatively harsh and earthy aromas. Hence typically, Robusta coffees are not being used for brewing high-quality coffee beverages. They are often being processed into other products, such as instant coffee. On the other hand, Arabica coffee trees grown in highlands are medium-low yielding with a height of 5 - 6 m that are relatively more delicate to cultivate. They grow well in the temperate climate but are susceptible to infection by plant diseases. Brews made from Arabica beans have intense and intricate aromas often described as floral, fruity, honey, chocolaty, caramelly or toasted bread. The caffeine content of Arabica coffee is typically less than 1.5 % (w/w), which is lower than that in Robusta coffee (2.4 to 2.8 % w/w). Due to its more pronounced and finer flavour qualities, Arabica is considered of better quality and command for higher prices (Illy, 2002). Unfortunately, Arabica and Robusta coffee cannot be crossed to produce a hybrid plant with both of their advantages. Robusta coffee plants and all wild coffee species have 22 chromosomes, whereas the Arabica has 44. The main compositional differences of Arabica and Robusta coffees are summarized in Table 1.3.
Table 1.3 Chemical compound comparisons of Arabica and Robusta green coffee beans (Folmer, 2017).

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/100g)</th>
<th>Arabica</th>
<th>Robusta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbohydrates/fibre</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sucrose</td>
<td>6.0 - 9.0</td>
<td>0.9 - 4.0</td>
<td></td>
</tr>
<tr>
<td>Reducing sugars</td>
<td>0.1</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>34 - 44</td>
<td>48 - 55</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td>3.0</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Pectin</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Nitrogenous compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Protein/peptides</td>
<td>10.0 - 11.0</td>
<td>11.0 - 15.0</td>
<td></td>
</tr>
<tr>
<td>Free amino acids</td>
<td>0.5</td>
<td>0.8 - 1.0</td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>0.9 - 1.3</td>
<td>1.5 - 2.5</td>
<td></td>
</tr>
<tr>
<td>Trigonelline</td>
<td>0.6 - 2.0</td>
<td>0.6 - 0.7</td>
<td></td>
</tr>
<tr>
<td>Lipids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coffee oils</td>
<td>15.0 - 17.0</td>
<td>7.0 - 10.0</td>
<td></td>
</tr>
<tr>
<td>Diterpenes</td>
<td>0.5 - 1.2</td>
<td>0.2 - 0.8</td>
<td></td>
</tr>
<tr>
<td>Acids and esters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorogenic acids</td>
<td>4.1 - 7.9</td>
<td>6.1 - 11.3</td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.5 - 1.5</td>
<td>0.3 - 1.0</td>
<td></td>
</tr>
<tr>
<td>Quinic acid</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Malic acid</td>
<td>0.3 - 0.7</td>
<td>0.2 - 0.7</td>
<td></td>
</tr>
<tr>
<td>Succinic acid</td>
<td>tr - 0.15</td>
<td>0.05 - 0.35</td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
<td>tr - 0.14</td>
<td>tr - 0.39</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>tr</td>
<td>tr - 0.2</td>
<td></td>
</tr>
<tr>
<td>Minerals</td>
<td>3.0 - 4.2</td>
<td>4.4 - 4.5</td>
<td></td>
</tr>
</tbody>
</table>

tr = trace amounts
1.4 Coffee components and their health benefits

Coffee brews have significant amounts of health-promoting bioactive compounds such as caffeine, chlorogenic acid, and polyphenols, as shown in Table 1.4. Caffeine is a psychoactive compound that has been shown to enhance alertness, attention, memory, and mood (Borota et al., 2014; Nehlig, 2010; Smith, Sutherland, & Christopher, 2005), as well as physical endurance and exercise capacity (Goldstein et al., 2010). Other coffee components, such as chlorogenic acid, have also been shown to improve mood and cognition in healthy elderly (Cropley et al., 2012). Polyphenols in coffee beverages are the main source of antioxidant polyphenols in the diet of many consumers. Furthermore, chlorogenic acid, caffeine and polyphenols have been implicated in reducing the risk of Alzheimer’s and Parkinson’s diseases, type 2 diabetes, cancer, and cardiovascular diseases (Taylor & Demmig-Adams, 2007). Besides, coffee can also reduce the risk of mouth, pharynx, larynx, and basal cell skin cancer in human due to that the biologically active compounds, such as caffeine, flavonoids, lignans, and polyphenols, can help to increase energy expenditure, inhibit cellular damage, regulate DNA repair genes, possess anti-inflammatory properties, as well as inhibit metastasis (Rock et al., 2020). Coffee can also help to lower the risk of some digestive cancers due to its ability to influence intestinal transit time and liver metabolism of carcinogens (Rock et al., 2020; Taylor & Demmig-Adams, 2007).
Table 1.4 Typical chemical composition per 100 mL of coffee brew from medium roasted coffee (Folmer, 2017).

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Content (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine</td>
<td>50 - 380</td>
</tr>
<tr>
<td>Chlorogenic acids</td>
<td>35 - 500</td>
</tr>
<tr>
<td>Trigonelline</td>
<td>40 - 50</td>
</tr>
<tr>
<td>Soluble fibre</td>
<td>200 - 800</td>
</tr>
<tr>
<td>Protein</td>
<td>100</td>
</tr>
<tr>
<td>Lipids</td>
<td>0.8</td>
</tr>
<tr>
<td>Minerals</td>
<td>250 - 700</td>
</tr>
<tr>
<td>Niacin</td>
<td>10</td>
</tr>
<tr>
<td>Melanoidins</td>
<td>500 - 1500</td>
</tr>
<tr>
<td>Volatiles</td>
<td>tr</td>
</tr>
</tbody>
</table>

tr = trace amounts
1.5 Cold brew coffee

Unlike conventional coffee beverages brewed in hot water (> 90°C), as described above, cold brew coffee is prepared by steeping coffee ground in water at refrigerated or room temperature for 12 to 24 h (Angeloni, Guerrini, Masella, Innocenti, et al., 2019; Rao & Fuller, 2018). The solubility of coffee constituents in water is temperature-dependent. For example, caffeine’s solubility values in the water at 0, 15, 19.3, 80, and 100 °C are 6, 10, 16.1, 200, 666 mg/mL, respectively. Hence, the low extraction temperature involved during cold brewing process results in beverages with different sensory profiles as compared to the hot brew beverages. In general, cold brew coffees are perceived by consumers to be less bitter and less acidic than the conventional hot brewed counterparts (Lane, Palmer, Christie, Ehlting, & Le, 2017; McCain-Keefer 2020;). Due to its milder flavour, cold brew coffee has gained increasing consumer acceptance. It has been estimated that the global market for cold brew coffee was valued at US$321 million in 2017 and is expected to reach a staggering US$1.4 billion by 2023 (accessed on Nov. 26, 2020. www.statista.com/statistics/865389/cold-brew-coffee-market-value/).

Cold brew coffee should not be confused with the iced coffee, which is chilled hot-brewed coffee typically sweetened or flavored, and usually served over ice. Examples of cold brew coffee products include refrigerated/shelf-stable ready-to-drink, refrigerated/shelf-stable concentrates, and home brewed (McCain-Keefer, Meals, & Drake, 2020). Nitrogen-infused cold brew, also known as “nitro” coffee, is prepared by infusing cold
brew coffee with nitrogen gas in kegs. When the product is dispensed through a valve that results in a pressure drop, the nitrogen gas is supersaturated and released as small bubbles, creating a golden-colour and dense foam head (as shown in Figure 1.3). Nitro coffee exhibits distinctive flavour attributes, described as caramel/molasses, nutty, beany, ashy, sour, and silky mouthfeel. Compared with the traditional cold brew coffee, nitro coffee tends to be sweeter and less bitter while having a creamy taste and a velvety mouthfeel.

Figure 1.3 (a) “Nitro” cold coffee keg and (b) its head of microfoam. Photos are adapted from www.kickstarter.com/projects/growlerwerks/the-ukeg-nitro-cold-brew-coffee-maker (accessed on Sep. 9, 2020) and www.starbucks.com/menu/product/2121912/iced?parent=%2Fdrinks%2Fcold-coffees%2Fcold-brews (accessed on Sep. 9, 2020)

1.6 Recent development of cold brew coffee

Cold coffee brewing technology is relatively new; to date, systematic studies are limited. As in hot brew methods, cold brew coffee extraction is influenced by many factors, including
coffee variety, roast profile/degree, ground particle size, brew ratio, hardness of water, brewing method (drip, immersion, circulation etc.), brew time/temperature, and so on.

Cordoba et al. (2019) studied the effect of ground coffee size (medium-coarse, average 501 - 700 μm for medium and 701 - 900 μm for coarse) and extraction time (14 - 22 h) on the physicochemical properties of cold brew coffee. They found that brews from coarse ground at 22 h extraction resulted in the highest total dissolved solids, extraction yield (TDS), pH, titratable acidity (TA), and total phenolic content values compared with medium ground at 14 and 22 h extraction and coarse ground at 14 h extraction. It is easy to understand that the TDS of coffee brew would increase with the prolonged extraction time. However, TDS of coarse ground coffee brew was higher than medium ground coffee brew. It could be due to the caking effect of medium ground induced by the filter bag. It is important to have the coffee grounds well distributed in the brewing water when preparing cold brew coffee. Han et al. (2020) studied the effects of extraction conditions on the acrylamide/furan content and total phenol content of cold brew coffee by steeping and dripping methods at the temperature of 5 (refrigeration temperature), 10, and 20°C (room temperature) for 3, 6, 12, and 24 h. They found that acrylamide and total phenol content increased with the prolonged time. In contrast, furan contents decreased with the increasing extraction time by both steeping and dripping methods at three temperatures. Considering the potential health impacts of these compounds, the 24-h steeping method is recommended to make cold brew coffee with lowest furan contents, highest total phenol content and free radical anion scavenging activity. A recent study also found that crude polysaccharides and sugars extracted from cold brew coffee, such
as galactose, mannose, arabinose, and uronic acid, may enhance macrophage functions and
the intestinal immune system (Shin, 2017).

Due to the low temperature involved, cold brewed coffee exhibited different
physicochemical properties and sensory attributes as compared with the traditional hot brew
counterparts. Fuller and Rao compared the chlorogenic acids (CGA), caffeine concentrations
and pH of hot brew and cold brew coffee brewed for 6 and 1440 min, respectively, using
coarse dark roasted ground coffee. They found hot brew and cold brew coffee had
comparable CGA concentrations and pH. However, the cold brew coffee had higher caffeine
concentrations than the hot brew. There are two different extraction mechanisms for coffee
extraction: the fast extraction from the surface and near-surface matrix and the slow diffusion
of compounds through the intragranular pore network to the surface of coffee particles.
Because the CGA and acidic compounds (e.g., acetic, malic, formic, citric acids) are soluble
at room temperature, both hot and cold extraction experienced nearly complete extraction
during their respective steeping times, leading to comparable CGA concentrations and pH.
Caffeine is less soluble compared with CGA and acidic compounds. The diffusion of caffeine
through the intragranular pore structure is the rate limiting step in the coffee extraction
process. Due to the short extraction time (6 min), the diffusion process of hot water extraction
was limited, and did not allow the full extraction of caffeine across the larger radius particles.
However, the longer brewing times for the cold brew coffee contributed to the complete
caffeine extraction. That is why the cold brew coffee had higher caffeine concentration
compared with the hot brew (Fuller & Rao, 2017). Rao et al. (2018) also investigated the
acidity, antioxidant activity and chlorogenic acid contents of cold and hot brew coffees, using light roast coffees. They reported comparable pH values of both the cold and hot brew samples ranging from 4.85 to 5.13. However, the hot brew coffees had higher concentrations of total titratable acidity and antioxidant activity than the cold brew samples. They deduced that the hot brewed samples contained more non-deprotonated acids than the cold brewed coffees, and that these acids might have contributed to higher antioxidant activities in the hot brew coffee. In another study, Rao et al. (2020) reported that cold brew coffee has decreased acidity, lower concentration of brown-colored compounds (melanoidins and caramel, etc.) and TDS than hot water brewing methods. Moreover, these compounds with temperature-dependent solubility, such as melanoidins, are likely more responsible for the differences in pH, total titratable acidity, and total antioxidant capacity between the cold brew coffee and their hot counterpart.

The cold brewing process is time-consuming. Researchers have explored different methods to address this long cold brew extraction time. Angeloni et al. (2019) characterized and compared the physicochemical and sensory properties of coffees from cold steep and cold drip extraction methods. They found that the cold drip coffees had higher contents of bitter compounds (e.g., caffeine and chlorogenic acids) than the cold steep brews. Ahmed et al. (2019) investigated the effects of ultrasonication, agitation, stirring and their combined treatments on the physicochemical properties of cold brew coffee. They found that all the extraction techniques can enhance colour values, total soluble solids, antioxidant activities,
and organic acids compared with conventional cold brew coffee. They concluded that the combination of ultrasonication and agitation was the most efficient.

1.7 High Pressure Processing

High pressure processing (HPP), a non-thermal food processing technique, exerts 100 - 900 MPa of hydraulic pressure on packaged food products at cold (4 - 10°C) or ambient temperature for a few seconds to several minutes (Fernández-Jalao, Sánchez-Moreno, & De Ancos, 2019; Grauwet, Plancken, Vervoort, Hendrickx, & Loey, 2016). It is also known as high hydrostatic pressure processing (HHP) or ultra-high pressure processing (UHP).

Schematic diagram of a typical HPP unit is shown in Figure 1.4. Due to the lower temperature involved, the process does not produce thermolytic products (e.g., acrylamide, Maillard reaction products) and better preserves freshness, nutritional and organoleptic properties of food products than the conventional thermal processes, in addition to inactivating vegetative microorganisms and enzymes to minimize microbial spoilage and quality deterioration (Barba, Esteve, & Frigola, 2013; Toyofuku et al., 2017; Wolbang, Fitos, & Treeby, 2008). Consequently, HPP is widely used in the pasteurization and sterilization in food and pharmaceutical industries (Tao, Hogan, & Kelly, 2014).
Figure 1.4 Schematic diagram of an HPP unit. Unprocessed materials, such as the fresh, dried, and powdered products, are mixed with the selected solvent and then hermetically sealed in the high-density-polyethylene bags. These samples are treated in the chamber under pressure from 100 to 1000 MPa for a few seconds to several minutes (Scepankova, Martins, Estevinho, Delgadillo, & Saraiva, 2018).
During the HPP process with over 400 MPa pressure, cellular walls, membranes, and organelles of plants tend to be disrupted, resulting in the increased mass transfer rates (Corrales, Toepfl, Butz, Knorr, & Tauscher, 2008; Margarita Corrales, García, Butz, & Tauscher, 2009; Xi, 2017). Hence, another application of HPP is to extract the active ingredients from biomaterials to enhance extraction yield and shorten extraction time (Bermejo, Mendiola, Ibáñez, Reglero, & Fornari, 2015; Briones-Labarca, Muñoz, & Maureira, 2011; Jun, Deji, Ye, & Rui, 2011). For example, Jun applied the HPP technique to extract caffeine from green tea leaves and found that HPP can increase the extraction yield and found that caffeine extraction yield increased from 1.51 ± 0.30 to 4 ± 0.22 % when the pressure increased from 100 to 600 MPa (Jun 2009).

There are three main stages during a typical HPP extraction process. The first stage is the pressure boosting, during which the pressure is ramping up at a rate of 3 - 4 MPa/s for several minutes. During the compression process, the cell wall of food matrix is deformed. Concomitantly, the extraction solvent rapidly permeates through the cell wall, displaces the entrapped air/gases, and saturates the matrix. The solutes in the cells come in contact with the solvent, leading to an increase in extraction rate and yield. In the next stage, the final pressure (100 to 600 MPa) is established and held for a few seconds to several minutes. At this stage, diffusion of solutes against the concentration gradient continues to take place. Finally, at the end pressure holding stage, the pressure is relieved quickly in a few seconds to atmospheric pressure (Huang, Hsu, Yang, & Wang, 2013; Rastogi, Raghavarao, Balasubramaniam,
Therefore, the mechanisms of HPP-assisted extraction are increasing the penetration of solvent into cellular structures, improving mass transfer rate due to the destruction of cell structures, and facilitating the release of solutes. Moreover, since the ultrahigh pressure condition can disrupt noncovalent bonds (e.g., ionic, hydrophobic, and hydrogen bonds), HPP can induce changes in the secondary, tertiary, and quaternary structures of proteins, while the structures of low molecular compounds (e.g., peptides, vitamins, flavor and color compounds) tend to remain intact (Sílvia et al, 2020). Compared with other extraction methods, such as Soxhlet extraction, heat reflux extraction, and liquid-solid extraction, HPP-assisted extraction is a non-thermal process, which is favorable for the extraction of thermolabile compounds.
Chapter 2 Hypotheses and objectives

Cold brew coffee has gained increasing acceptance over the past decade due to its unique sensory profiles, often perceived by consumers to be less acidic and less bitter than the traditional hot-brewed counterparts. Generally, cold brew coffee is prepared by steeping coarse ground coffee (> 800 μm) in water at refrigerated or room temperature for 12 to 24 h.

From a processing standpoint, the preparation of cold brew coffee by water-steeping the roasted whole beans, instead of the conventional coffee ground, can greatly streamlined the production process. By eliminating the grinding step, which substantially breaks down the cellular structure of beans and generates considerable frictional heat that accelerates volatile losses, the roasted beans aroma is better preserved in whole beans. Also, unlike the typical brewing with coffee ground wherein the brew filtration is needed to remove the spent and fine particulates generated from the grinding process, whole bean steeping does not require a filtration medium, thereby greatly simplified the brewing procedure. In terms of storage stability, because their cellular structures remain intact, the whole beans have a considerable smaller surface area and hence less susceptible to staling (due to aroma loss and oxidative degradation) than the ground counterparts. However, these benefits are nullified by the reduced mass transfers of solutes during the extraction process; cold brewing of coffee using whole beans will be slower than the coffee ground due to the smaller surface area for solute diffusion in the former.
To accelerate the diffusion of solutes, an intervention is needed to induce force flow of water in/out the cellular matrices of coffee beans. To this end, it is hypothesized that high pressure processing (HPP) treatment above 400 MPa can facilitate the coffee extraction process by displacing the air/gas entrapped within the cellular structures of the beans by brewing water.

Ready-to-drink cold brew coffee beverage products are typically packaged in aluminum cans or plastic bottles. During storage, physicochemical property changes in cold brew coffee will occur, including a decrease in pH, increase in titratable acidity, the rates of which accelerate with increasing temperature. Acetic, malic, formic, and citric acids are the majority of perceived acidity in the coffee brew and play a crucial role in the acceptability of coffee brew. On the other hand, the polyphenols, caffeine, and chlorogenic acids are health-promoting bioactives that also contribute to coffee flavors. In ready-to-drink products, if the whole coffee beans were allowed to steep within the packaging after HPP treatment, it is hypothesized that the continual extraction will maximize the bioactives in the brew.

To test these hypotheses, the objectives of this thesis are: (1) To study the physicochemical properties of cold brews prepared from whole beans and ground coffee through a HPP treatment; and (2) To evaluate the changes in whole bean cold brew coffee after HPP treatment stored at room (22°C) and refrigerated temperature (4°C) for 60 d.
Chapter 3 Effect of high pressure processing on the extraction and physicochemical characteristics of cold brew coffee

3.1 Introduction

Coffee is one of the world's most consumed beverages, with about half a trillion cups consumed per year. In 2017/2018, around 9921.0 million kilograms of coffee were consumed worldwide (accessed on Feb. 4, 2021; www.statista.com/statistics/292595/global-coffee-consumption/). It is rich in chlorogenic acid, caffeine, and polyphenols, which have been implicated in reducing the risk of Alzheimer’s and Parkinson’s diseases, type 2 diabetes, cancers, and cardiovascular diseases (Taylor & Demmig-Adams, 2007). Unlike conventional coffee beverages brewed in hot water (> 90°C), cold brewed coffee is prepared by steeping roasted coffee ground in the water at refrigerated up to room temperature for 12 to 24 h. This condition results in cold brew coffees are less bitter, lower in acidity, and have milder flavour than the conventional hot brewed counterparts (Rao & Fuller, 2018; Rao et al., 2020). Due to these unique sensory profiles, cold brew coffee has gained considerable consumer acceptance over the past few years. In 2017, the global market for cold brew coffee was valued at US $321 million and is projected to reach a staggering US $1.37 billion in market value by 2023 (Feb. 4, 2021; https://www.statista.com/statistics/865389/cold-brew-coffee-market-value/).
Cold brew coffee is attracting coffee drinkers' preference rapidly. However, cold coffee brewing technology is relatively new; to date, systematic studies are limited. One challenge of cold brewing process is time-consuming and low extraction yield. Researchers are exploring different methods to address these issues. Ahmed et al. (2019) investigated the effects of ultrasonication, agitation, stirring and their combined treatments on the physicochemical properties of cold brew coffee. They found that all the extraction techniques can enhance colour values, total soluble solids, antioxidant activities, and organic acids compared with conventional cold brew coffee. They concluded that the combination of ultrasonication and agitation was the most efficient (Ahmed et al., 2019).

High pressure processing (HPP) exposes packaged products to elevated hydraulic pressure, in the range of 100 - 900 MPa, at a temperature ranging from 4 to 25°C for a few seconds to several minutes (Fernández-Jalao et al., 2019; Grauwet et al., 2016). Due to the low temperature involved, the non-thermal process does not produce thermolytic products (e.g., acrylamide, Maillard reaction products), thus better preserving freshness, nutritional, and organoleptic properties of food products than the conventional thermal processes. Moreover, since the elevated pressure treatment can inactivate vegetative microorganisms and denature some of the enzymes, HPP has been applied in food and pharmaceutical industries for pasteurization and sterilization of products to delay deterioration (Barba et al., 2013; Grauwet et al., 2016; Teixeira et al., 2013; Toyofuku et al., 2017; Wolbang et al., 2008; Yuan et al., 2018).
During the HPP process, the cellular wall, membrane, and organelles of plants are being disrupted, resulting in an increase in the mass transfer rates of solutes within the food matrix, such as tea leaves (Xi, 2017). Hence, HPP has been exploited to facilitate the extraction of bioactive compounds from biomaterials to enhance the extraction yield and shorten the extraction time (Bermejo et al., 2015; Briones-Labarca et al., 2011; Jun 2009; Jun et al., 2011; Pinela et al., 2018;). For example, Jun applied the HPP technique to extract caffeine from green tea leaves and found that HPP can increase the extraction yield from 1.51 ± 0.3 to 4 ± 0.22 % when the pressure increased from 100 to 600 MPa (Jun 2009). Corrales applied high hydrostatic pressure (600 MPa for 1 h) to extract anthocyanins from grape skins and anthocyanin content increased to 11.21 mg/g compared with the control sample at 7.93 mg/g (Corrales et al., 2008). Joo used ultra-high pressure to extract the phenolic compounds and amino acids from *Camellia sinensis* leaf and found a significant improvement of extraction yield from 2.1 (control sample) to 20.9 (50 MPa for 1 h) and 23.7 % (100 MPa for 1 h) (Joo et al., 2012).

In a typical brewing process, coffee beans must be ground into particles to enhance the extraction of water-soluble solutes into the brew. While this process greatly facilitated the extraction process, a step is needed to separate the spent coffee ground from the brew, by passing the latter through a filtration medium. The pore size of the filter must be carefully optimized to prevent the elution of fines, while preventing the development of excessive pressure drops during filtration and blockage. Moreover, the reduction in roasted coffee beans to ground not only adds an addition step to the brewing process, but also result in
considerable loss of aroma volatiles and increase the susceptibility of oxidation due to
enlarged surface area (Kallio, Leino, Koullias, Kallio, & Kaitaranta, 1990; Ross, Pecka, &
Weller, 2006). On the other hand, brewing with the whole beans would not require a filtration
medium nor bean grinding steps, thereby streamlining the production process. Also, brewing
with whole beans does not produce fine particulates resulting from the grinding, thereby
producing very transparent brews. However, whole bean steeping suffers from a reduced
mass transfer rate, resulting in prolonged extraction time and reduced yield. On the basis that
the food products are subjected to substantial internal-external pressure differences during the
pressurization and decompression steps in HPP, we hypothesized that the extraction time
using whole beans can be substantially shortened and extraction yield improved by applying
HPP during the coffee brewing process.

To test this hypothesis, roasted coffee of different sizes (fine, medium, coarse grounds,
and whole beans) was subjected to the HPP treatment at 400 MPa for 10 min in the presence
of brewing water at room temperature. The physicochemical properties of the resulting brews,
including total dissolved solids (TDS), caffeine, chlorogenic acid, and colour were evaluated.
To better understand the effect of HPP treatment, the microstructures of the HPP processed
beans were examined using scanning electron microscopy. Finally, the HPP-treated cold
brew coffees were evaluated by certified professional cuppers.
3.2 Materials and methods

3.2.1 Materials

According to Specialty Coffee Association of America (SCAA) recommendation for coffee brewing water, tap water (Guelph, ON, Canada) and reverse osmosis water (Milli-Q® Integral Water Purification System for Ultrapure Water, Darmstadt, Germany) were mixed at a ratio of 1:3 (v/v) to give brewing water of 207 μs/cm electrical conductivity. Dark roast coffee beans were supplied by Mother Parkers Tea & Coffee Inc. (Mississauga, ON, Canada) blended specifically for cold brew. PET bottles (8 oz) were purchased from Uline (Milton, ON, Canada). The filter paper was purchased from the local coffee store (Melitta Basket Coffee Filters). Methanol (HPLC grade), sodium hydroxide, Folin-Ciocalteu reagent, caffeine (99 % purity) and chlorogenic acid (99 % purity) were all purchased from Fisher Scientific International Inc. (Ottawa, ON, Canada).

3.2.2 Preparation of ground coffee

Before brewing, coffee beans were ground and sieved through Canadian standard sieves (W. S. Tyler Inc., ON, Canada). Fine (< 500 μm), medium (500 to 800 μm), and coarse coffee (> 800 μm) grounds were collected, respectively. The fine ground coffee was obtained from the fraction that passed through sieve No. 20, while the coarse ground coffee was the fraction retained by sieve No. 12. The medium ground was the fraction that passed through sieve No. 12 but retained by sieve No. 20. Whole beans were used as received without grinding.
3.2.3 Preparation of cold brew coffee using water with different hardness

The mixture of tap water and reverse osmosis water (RO) at different ratios 0:10, 1:3, 3:1, and 10:0 were used to make cold brew coffee. The conductivity of brewing water, which reflected the water hardness, was measured using a conductivity meter (Fisherbrand™ Benchtop Conductivity Meter). The conductivity and hardness of water are summarized in Appendix 1. Coarse ground coffee (20 g) was steeped in 100 mL at room temperature (about 22°C) for 18 h. The brews were collected by filtering the suspension through a filter paper. The pH and titratable acidity values were determined as described below.

3.2.4 Cold brew extraction process and procedure of HPP treatment

Before the HPP treatment, 20.7 g ground coffee or whole coffee beans were mixed with 207 mL water leaving no air headspace in the 20 oz PET bottles and capped. The bottles were then loaded into a 2 L HPP vessel (Avure Technologies, Inc., Middletown, OH, USA) and treated by HPP immediately at 400 MPa for 10 min. The ramping pressure rate was about 4 - 5 MPa/s, while the decompression from 400 MPa to atmospheric pressure was about 2 - 3 s.

After the treatment, ground coffee and whole coffee bean samples were taken out from the HPP vessel and left for steeping at room temperature for a period of 18 or 44 h. The brews were decanted and then subjected to physiochemical and sensory analyses.
3.2.5 Coffee extraction modeling

The coffee extraction plots of the coffee beans and ground coffee were fitted with Weibull distribution model. This is an empirical model that often used to describe food drying and hydration kinetics (MacHmudah, Martin, Sasaki, & Goto, 2012; Menges & Ertekin, 2006; Wang & Lim, 2014).

\[ TDS(t) = TDS_\infty \times [1 - \exp \left( -\frac{t}{\alpha} \beta \right)] \quad \text{(Equation 2)} \]

where \( t \) is extraction time (min); \( TDS(t) \) (%) is TDS of coffee brew at time \( t \); \( TDS_\infty \) (%) is TDS of coffee brew at infinity time; \( \alpha \) is scale parameter (min) and \( \beta \) is shape parameter (dimensionless). The \( \alpha \) parameter determines the rate and is related to the reciprocal of the process of rate constant, representing the time needed to accomplish approximately 63% of the process. The goodness of fit was evaluated on the basis of coefficient of determination \( (R^2) \) and root-mean-square error (RMSE). The \( R^2 \) is a measurement used to explain how much variability of one factor can be caused by its relationship to another related factor. This correlation is represented as a value between 0.0 and 1.0. A value of 1.0 indicates a perfect fit and is thus a highly reliable model for the prediction, while a value of 0.0 would indicate that the calculation fails to accurately model the data at all. The RMSE is frequently used to
measure the differences between sample values predicted by a model or an estimator and the values observed. RMSD is always non-negative, and a value of 0 (almost never achieved in practice) would indicate a perfect fit to the data. In general, a lower RMSD is better than a higher one.

### 3.2.6 TDS, brew volume, and extraction yield of ground and whole bean brews

Coarse ground and whole bean brews were selected for studying their physicochemical properties after steeping in water for 18 or 44 h, respectively. Total dissolved solids (TDS), which reflects the “body” of coffee brew (Gloess et al., 2013), was measured using the Coffee TDS Refractometer (Voice Systems Technology Inc. (Harvard, US) and expressed in percentage. Brew volume was determined in the graduated cylinder after gravity filtration by paper filter. Extraction yield is defined as the ratio of the mass of ground coffee that is being extracted into the brew to the total amount of ground coffee used (Angeloni, Guerrini, Masella, Bellumori, et al., 2019; Clarke, 2001):

\[
\text{Extraction Yield} = \frac{TDS \times W_{\text{brew}}}{W_{\text{ground coffee}}} \times 100\% \quad \text{(Equation 3)}
\]

where \( W_{\text{brew}} \) is the weight of coffee brew and \( W_{\text{ground coffee}} \) is the weight of coffee ground used for making the coffee (Wang et al., 2016).
3.2.7 Effects of HPP on the chemical properties of ground and whole bean brews

(1) pH and titratable acidity (TA)

pH and TA are important indicators of perceived acidity in the coffee brew. The pH of coffee brew was determined using a pH meter (Accumet Excel XL 20, Fisher Scientific, Ottawa, Canada). TA was determined by titrating 20 mL of coffee brew sample to pH 7.0 using 0.01 mol/L of NaOH solution. Results were expressed in grams of acetic acid per litre of coffee brew.

(2) Colour values

A chroma meter equipped with 20 mL rectangular cell made of optical glass (CR-400, Minolta, Osaka, Japan) was used to evaluate the colour of the brew, which was expressed by L*(lightness, black [0] to white [100]), a*(green [-] to red [+]), and b* (blue [-] to yellow [+]) values. Before determination, the chroma meter was calibrated by using a standard whiteboard.

(3) Total polyphenol (TPP) content

Total polyphenols (TPP) content is an indicator of the coffee brew’s antioxidant property (Gloess et al., 2013; Rao & Fuller, 2018; Xi et al., 2011). Folin-Ciocalteau assay was used to determine the TPP content, according to Singleton et al. (1965), with modifications. The Folin reagent was diluted ten times before use, and coffee brews were diluted four times using deionized water. An aliquot of 200 μL of the diluted coffee brew was pipetted into a
disposable cuvette, to which 0.5 mL of the diluted Folin-Ciocalteau reagent was added. The mixture in the cuvette was agitated for 5 s before adding 1.5 mL of 7.5 % (w/w) Na₂CO₃ solution. After agitation, the cuvettes were placed in a dark environment for 2 h at 22°C. The absorbance of the resulting solution at 765 nm wavelength was measured using a 60S UV-Visible Spectrophotometer (Thermo Fisher Scientific, USA). The TPP contents were expressed in grams of gallic acid per liter.

(4) Caffeine and chlorogenic acids (CGA)

The caffeine and chlorogenic acid (CGA) concentrations of the coffee brews were determined by high performance liquid chromatography (HPLC) (Farah, De Paulis, Trugo, & Martin, 2005; Fuller & Rao, 2017; Wang et al., 2016). The coffee brews were diluted 20 times using deionized water and passed through a 0.22 μm filter (Fisherbrand, Fisher Scientific International Inc., Ottawa, Canada) before the analysis. The HPLC (Model 2690, Waters, Milford, MA) was equipped with a photodiode array detector (Model 996, Waters, Milford, MA) and an Ultrasphere C₁₈ ODS (15 cm × 4.6 mm, 5 μm, Beckman Coulter, Inc. USA) column. The mobile phase used was 75 % (v/v) 10 mM citric acid solution (adjusted to pH 2.5 using 6 N HCl) and 25 % (w/w) HPLC grade methanol. Other HPLC conditions were as follows: flow rate: 0.4 mL/min; inject volume: 10 μL; running time: 40 min; detector wavelength: 273 nm for caffeine and 325 nm for CGA.
3.2.8 Foamability and foam stability

Foamability of the brew was evaluated by determining the foam head volume of coffee brew after bubbling with N₂ using VitraPOR Gas Distribution tube (Type B, Por.2, ROBU® Glasfilter-Geraete GmbH, Germany) for 10 s with a flow rate of 50 mL/min in a 100 mL graduated cylinder at room temperature. Foam stability was determined as the time (min) that the liquid phase beneath the foam layer appeared (Kamath, Wulandewi, & Deeth, 2008; Nunes & Coimbra, 1998; Nunes, Coimbra, Duarte, & Delgadillo, 1997). The maximum foam monitoring time was set as 30 min, which means that fading time longer than that was recorded as 30 min (Wang, Lim, Tan, & Fu, 2019; Wang et al., 2016). Each treatment was duplicated three times.

3.2.9 Scanning Electron Microscopy (SEM) of grounds and whole beans

The microstructural morphologies of ground coffee and whole coffee beans were examined to elucidate the effect of the HPP treatment on the porous structure of coffee. The coffee particles were dried at room temperature before SEM analysis (Quanta FEG 250, FEI Company, Hillsboro, OR USA). Ground coffee and whole coffee beans were mounted on metal stubs using double-sided adhesive carbon tape and then covered with a film of palladium gold on its surface using a sputter coater (Desk V TSC, Denton Vacuum, Moorestown, NJ, USA) and then were observed and photographed by an SEM with an accelerating voltage of 10 kV.
3.2.10 Sensory evaluation

Sensory evaluation was performed by two certified cuppers. The coffee brews were evaluated from the aspect of brightness, body, mouthfeel, sweetness, smooth and overall intensity. Cold brew coffee samples were prepared and stored at 4°C refrigeration before presenting to the cuppers. Water was used to rinse the mouth before cupping the samples. Scales with 15 cm line were used to mark the evaluation.

3.2.11 Data analysis

Each test in this study was repeated for at least three times, and results were expressed as mean ± standard deviation. Error bars in plots were standard deviations of the means. Figures were plotted in Microsoft Excel spreadsheet software. Statistical analysis was conducted using the SPSS and all the results are reported at 95% confidence interval or p > 0.05 (SPSS 22.0, SPSS Inc., Chicago, IL, USA).
3.3 Results and discussion

3.3.1 Effect of water hardness on cold brew coffee

Water hardness is defined as the sum of amounts or equivalent concentrations of calcium and magnesium ions in water. It can affect the pH, total acidity, taste, and flavor of coffee brew. In this research, water hardness was expressed as electrical conductivity. As shown in Table 3.1, the tap water: RO water blended at 0:10, 1:3, 3:1, 10:0 (w/w) had conductivity values at 1.8, 181.2, 482.7, and 662.7 μs/cm, respectively, which should be considered as very soft, soft, slightly hard, and hard (appendix 1).

As shown in Table 3.1, the cold brew coffee prepared with pure reverse osmosis water had the lowest pH (5.12) but had the highest titratable acidity (0.70 g/L). In general, with the increasing ratio of tap water, the pH of cold brew coffee increased, while the titratable acidity decreased. The cold brew coffee prepared with pure tap water had the highest pH (5.36) and lowest titratable acidity (0.65 g/L).
Table 3.1 Effect of water hardness on the pH and titratable acidity of cold brew coffee

<table>
<thead>
<tr>
<th>Tap water: RO (w/w)</th>
<th>0:10</th>
<th>1:3</th>
<th>3:1</th>
<th>10:0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (μs/cm)</td>
<td>1.8</td>
<td>181.2</td>
<td>482.7</td>
<td>662.7</td>
</tr>
<tr>
<td>pH</td>
<td>5.12 ± 0.03 d</td>
<td>5.19 ± 0.01 c</td>
<td>5.27 ± 0.01 b</td>
<td>5.36 ± 0.01 a</td>
</tr>
<tr>
<td>Titratable acidity (g/L)</td>
<td>0.70 ± 0.00 a</td>
<td>0.70 ± 0.00 a</td>
<td>0.67 ± 0.01 b</td>
<td>0.65 ± 0.01 c</td>
</tr>
</tbody>
</table>

RO means reverse osmosis water. Data were shown as mean values ± standard deviations. Different lowercase letters indicated a statistically significant difference (p < 0.05) while the same letter means no significant differences (P ≥ 0.05) in each row using a Tukey test.

Alkaline compounds in the brewing water, such as bicarbonates and carbonates, would be responsible for the decreased titratable acidity and increased pH of final coffee brew. They can remove hydrogen ions (H⁺) and neutralize the acids in coffee brew (Navarini & Rivetti, 2010; Sheibani & Mohammadi, 2018). Consequently, with the increasing portion of tap water in the brewing water, the pH of the cold brew coffee increased.

3.3.2 Effects of different HPP treatment parameters

Many studies have shown that HPP treatment of biomaterials can result in various degrees of disruption on the cell wall, membrane, and organelles (Bermejo et al., 2015; Hu et al., 2020; Sun, Kang, Chen, Liao, & Hu, 2019). When applied for the extraction, HPP can shorten processing time, increase extraction yields, and result in fewer impurities left in the extraction liquid than other traditional extraction methods (Khan, Aslam, & Makroo, 2019).
In the present study, it is hypothesized that the microstructural alterations and pressure perturbation during the HPP treatment can facilitate the mass transports of soluble from roasted coffee beans. To test this hypothesis, HPP parameters, including pressure, time, and pre-soaking time, were evaluated. Figure 3.1 summarizes the effects of pre-HPP soaking time, pressure, and time on the TDS values of whole bean brews that had been steeped for 44 h after the HPP treatment. As shown in Figure 3.1 (a), increasing pre-HPP soaking time up to 160 min resulted in the decrease of brew TDS from 1.56 to 1.21 %, beyond which the TDS values stabilized at around 1.20 % level, which is comparable to that of the untreated control samples (1.20 %). It is indicating that when the presoaking time was not long enough for water entering and filling the porous structure of coffee beans where CO₂ exists, the porous structure of coffee would be disrupted after applying HPP. That disruption would facilitate the mass transfer of components in coffee beans. Consequently, the TDS of HPP-treated coffee bean brew increased. However, with the increasing soaking time before HPP treatment, brewing water gradually filled the porous structure of coffee beans where the existing CO₂ was replaced. When HPP treatment was applied, hydraulic pressure in and outside of coffee bean cells kept equilibrium leading to no structural disruption of the coffee beans and no current or turbulence formed in the coffee bean matrix. Consequently, no TDS improvement was seen. It is suggesting that HPP treatment should be applied immediately after the coffee and brewing water were mixed to maximize the extraction efficiency.

HPP pressure in the range of 100 - 600 MPa and time from 30 to 1200 s had minimal effect on the extraction (Figure 3.1 (b), (c)) compared with control sample at 1.20 %.
Pressure above 100 MPa is sufficient to destroy the cell structure of biomaterials (Butz, Koller, Tauscher, & Wolf, 1994). Similar results were also found in the HPP-treated longan fruit pericarp at various time (2.5 - 30 min). Extraction yield remained stable with increasing treating time (Prasad et al., 2009). In our study, HPP pressure from 100 to 600 MPa for 30 to 1200 s would not further improve the TDS of cold brew coffee.
Figure 3.1 Total dissolved solids (TDS) of cold brew samples prepared from whole beans as affected by: (a) different pre-HPP soaking times with HPP treatment at 400 MPa for 10 min; (b) different HPP treating pressures for 10 min and treated immediately after coffee beans were soaked into water; and (c) HPP treating time at 400 MPa and treated immediately after coffee beans were soaked into water. TDS values of the brews were determined 44 h after the high-pressure processing (HPP) treatment.
3.3.3 Effect of HPP on coffee extraction of different particle sizes

In the present study, the TDS values of fine (< 500 μm), medium (500 to 800 μm), and coarse (> 800 μm) ground and whole bean brews with and without HPP treatment were monitored up to 60 h as presented in Figure 3.2. To further understand the coffee extraction kinetics of fine, medium, and coarse ground and whole coffee beans with and without HPP treatment, the Weibull Distribution model was fitted to the TDS data. The estimated parameter values of the Weibull Distribution model are summarized in Table 3.2. As shown in Figure 3.2 (a), the TDS value of fine ground brew after HPP treatment was even little lower than the control sample. It could be due to the participation (such as denaturation and aggregation of protein and polypeptides) in coffee brew induced by HPP treatment (Cullen & Tiwari, 2018; Zhu & Li, 2019). As the ground size increased to medium and coarse levels (Figures 1 a and b), higher TDS values were observed immediately after the HPP treatment as compared to the untreated controls. In comparison with the ground coffee, for the whole bean, substantially different trends were observed (Figure 1 b). Here, the TDS values of HPP-treated whole bean brew were much higher than the control. Besides, the TDS improvement after 9 HPP cycles was not as significant as that after 1 HPP cycle.

The solid lines of the plots are the best fit curves based on Weibull Distribution model (Equation 1). Since that the coefficients of determination ($R^2$) are higher than 0.97, it can be concluded that the Weibull distribution model fits the coffee extraction kinetics well. The $\alpha$ parameter determines the extraction rate and is related to the reciprocal of the process of rate
constant. Coffee brews with HPP treatment had a smaller $\alpha$ value than the control sample, which means HPP treatment can facilitate the coffee extraction process. $\alpha$ values increased with the increasing particle size, which indicates that extraction process became slower as the particle size of coffee rose from fine, medium, coarse ground to whole beans, implying that the extraction of solutes was limited by the reduced surface area. However, the effects of HPP on TDS improvement became more obvious with increasing particle size. The $TDS_\infty$ means TDS value of coffee brew at time infinity. It can be concluded that HPP treatment can increase the $TDS_\infty$ compared with the control samples and the $TDS_\infty$ decreased with the increasing particle size.
Figure 3.2 Total dissolved solids (TDS) of cold brew coffees as affected by the different grinding size and brewing time: (a) fine and medium ground; (b) coarse ground and whole beans. Coffee samples were treated at 400 MPa for 10 min at room temperature immediately after beans were soaked into water. TDS: total dissolved solids.
Table 3.2 Derived Weibull distribution model parameters ($\alpha$, $\beta$, TDS$_\infty$), RMSE (root mean square error), and coefficient of determination ($R^2$).

<table>
<thead>
<tr>
<th>Coffee samples</th>
<th>$\alpha$ (min)</th>
<th>$\beta$</th>
<th>TDS$_\infty$ (%)</th>
<th>RMSE</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine ground control</td>
<td>0.61</td>
<td>0.08</td>
<td>2.42</td>
<td>0.0169</td>
<td>0.9722</td>
</tr>
<tr>
<td>Fine ground with HPP</td>
<td>0.25</td>
<td>0.10</td>
<td>2.19</td>
<td>0.0078</td>
<td>0.9927</td>
</tr>
<tr>
<td>Medium ground control</td>
<td>24.24</td>
<td>0.31</td>
<td>1.97</td>
<td>0.0275</td>
<td>0.9849</td>
</tr>
<tr>
<td>Medium ground with HPP</td>
<td>13.91</td>
<td>0.24</td>
<td>2.06</td>
<td>0.0131</td>
<td>0.9957</td>
</tr>
<tr>
<td>Coarse ground control</td>
<td>65.46</td>
<td>0.42</td>
<td>1.87</td>
<td>0.0243</td>
<td>0.9902</td>
</tr>
<tr>
<td>Coarse ground with HPP</td>
<td>31.57</td>
<td>0.35</td>
<td>1.93</td>
<td>0.0317</td>
<td>0.9838</td>
</tr>
<tr>
<td>Whole beans control</td>
<td>2052.51</td>
<td>0.94</td>
<td>1.57</td>
<td>0.0273</td>
<td>0.9950</td>
</tr>
<tr>
<td>Whole beans with 1-cycle HPP</td>
<td>1194.82</td>
<td>0.52</td>
<td>2.05</td>
<td>0.0549</td>
<td>0.9865</td>
</tr>
<tr>
<td>Whole beans with 9-cycle HPP</td>
<td>797.21</td>
<td>0.48</td>
<td>2.11</td>
<td>0.0404</td>
<td>0.9905</td>
</tr>
</tbody>
</table>
For coffee extraction, there are two different extraction mechanisms brought by Moroney et al. (Fuller & Rao, 2017; Moroney, Lee, O’Brien, Suijver, & Marra, 2016); the first one is the extraction from the surface and near-surface matrix, and another is the diffusion of compounds through the intragranular pore network to the coffee bean surface. The extraction in the former is much faster than the latter. Hence, for brews made from the ground particles, because of their larger surface area, the extraction took place mainly through direct solubilizing of solutes from the particles surface. On the other hand, intragranular diffusion tended to be predominant during the brew extraction with the whole beans. The significant increase in TDS after the HPP treatment, as compared with the untreated control, can be attributed to the microstructural disruption of cellular structure in the bean matrices, thereby greatly increased the ingress of water and egress of brews. These processes are expected to facilitate by the substantial pressure perturbation during the pressurization and decompression stages of the process that result in viscous flow of fluids in/out the beans, making the solutes more accessible to the brewing water than the extraction at one atmospheric pressure. Although the coffee brew made by ground coffee possessed higher TDS, undesirable compositions, such as caramelized sugar, also may be extracted, which could add cold brew coffee with unpleasant, astringent and bitter taste (Susana Andueza, Paz De Peña, & Cid, 2003).
3.3.4 Effects of HPP on TDS, brew volume, and extraction yield of ground and whole bean brews

Physicochemical properties of coffee brews prepared from the course ground and whole beans, as discussed in Section 3.3.3, were further analyzed. The coarse ground coffee brew was made as traditional cold brew coffee and the brewing times of coarse ground coffee and whole coffee beans were 18 and 44 h, respectively. TDS, brew volume and extraction yield of course ground and whole bean brews are shown in Table 3.3.

The brew volumes obtained from whole beans were significantly higher than those from the ground coffee, 179 and 150 mL, respectively (p < 0.05). For ground coffee, over 2.5 g water per gram ground coffee will remain in the basket after brewing and the gravity filtration. However, for whole beans, about 1.5 g water per gram coffee beans will remain. The reduced brew volume obtained for the ground samples could be caused by the retention of residual brew within the free volume between the ground particulates.

An increase in TDS as observed after HPP treatment for both whole bean and ground coffee samples and then brewing for 44 and 18 h, respectively. The TDS was increased from 1.15 to 1.56 % (36 % increase) and 1.71 to 1.79 % (5 % increase) for whole bean and ground coffee, respectively. This phenomenon could be explained by that with large surface area in grounds and the effect of structural damages inflicted by the pressure treatment is less on the extraction rate as compared to the bean, which has relatively smaller surface area. The lower
increment of ground coffee compared with whole coffee beans would be due to the less severe structural damage than that happened in the whole beans.

Extraction yield is related to both the TDS and brew volume (Equation 3). According to different grinding size and extraction time, the extraction yield of cold brew coffee varies from 7.06 to 20.39 % (Cordoba et al., 2019). Extraction yield of coffee brew prepared by whole coffee beans with HPP treatment reached 13.50 %, which was the highest among these four samples, attributed to the lower brew retention of beans and HPP treatment. The extraction yield of coffee brew prepared by whole coffee beans without HPP treatment was the lowest, with a value of 9.90 %, which was limited by low mass transfer rate induced by the small surface area. The HPP treatment also improved the extraction yield of coarse ground coffee from 12.40 to 13.36 %.
Table 3.3 Brew volume, total dissolved solids (TDS), and extraction yield (EY) of cold brew coffees prepared from ground or whole bean, with or without high pressure processing (HPP) treatment. These values were determined after ground coffee and whole bean were brewed for 18 and 44 h, respectively.

<table>
<thead>
<tr>
<th>Physicochemical properties</th>
<th>Coarse ground</th>
<th>Coarse ground with HPP</th>
<th>Whole bean</th>
<th>Whole bean with HPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (mL)</td>
<td>149.8 ± 0.99 c</td>
<td>154.7 ± 3.00 b</td>
<td>178.8 ± 0.80 a</td>
<td>178.8 ± 0.68 a</td>
</tr>
<tr>
<td>TDS (%)</td>
<td>1.71 ± 0.01 b</td>
<td>1.79 ± 0.01 a</td>
<td>1.15 ± 0.02 d</td>
<td>1.56 ± 0.01 c</td>
</tr>
<tr>
<td>EY (%)</td>
<td>12.40 ± 0.19 c</td>
<td>13.36 ± 0.35 b</td>
<td>9.90 ± 0.11 d</td>
<td>13.51 ± 0.00 a</td>
</tr>
</tbody>
</table>

Data were shown as mean values ± standard deviations. Different lowercase letters indicated a statistically significant difference (p < 0.05), while the same letter means no significant differences (P ≥ 0.05) using a Tukey test in each row.
3.3.5 Effects of HPP on the chemical properties of ground and whole bean brews

(1) pH, and TA

pH and TA are responsible for the perceived acidity in the coffee brew. The pH measures the concentration of hydronium ions in coffee brew, while titratable acidity is the measurement of the total acid concentrations (also known as total acidity) (Batali, Cotter, Frost, Ristenpart, & Guinard, 2021; George & Patricia, 2010). As shown in Table 3.4, there is no significant difference in pH between these four samples while the whole bean control sample had lower titratable acidity values compared with other 3 samples. However, when normalizing the TA with TDS (i.e., TA/TDS), the whole bean extraction without HPP treatment showed the highest ratio, implying that the acidic components (e.g., acetic, malic, formic, citric acids) were extracted in the earlier stage of the process because they are more water-soluble than other compounds, such as polyphenols and melanoidins (Cordoba, Fernandez-Alduenda, Moreno, & Ruiz, 2020b; Gloess et al., 2013).

The acids (e.g., acetic, malic, formic, citric acids) present in the coffee brew are weak acids, which partially dissociates into their ions in water. The resulting salts formed (e.g., acetate) can act as the buffer for the pH change in the coffee brew. Besides, the presence of other dissolved ions in coffee brews, such as carbonates and bicarbonates from the brewing water, can also act as a buffer against pH change (Batali et al., 2021; Navarini & Rivetti, 2010).
(2) Color values

In terms of colour, the L* value of brew from whole bean without HPP treatment was the highest, implying that it had the lightest color among the brews. On the other hand, brews prepared from the coffee ground, with and without HPP treatment, had lower and comparable L* values. These findings corroborated well with the trend of the TDS values. For the a* and b*, similar trends as L* were found.

(3) Total polyphenol (TPP) contents

Polyphenols in coffee beverages are the main source of antioxidant polyphenols in the diet of many coffee drinkers. The TPP of coffee brew after HPP treatment were shown in Table 3.4. In general, the coarse ground coffee brews exhibited significantly (p < 0.05) higher TPP contents than the coffee bean brews. Moreover, the brew prepared from the whole bean treated with HPP had a higher TPP content (2.17 ± 0.06 g/L) than the untreated counterpart (1.41 ± 0.22 g/L), but the HPP treatment was not significant (p > 0.05) on effecting the TPP contents of coarse ground coffee brews.

(4) Caffeine and CGA contents

The effect of HPP treatment on caffeine and CGA followed similar trends as the TPP, although the magnitudes of changes differed due to the different solubility of these compounds in water. HPP treatments of tea leaves in water also showed similar enhanced caffeine and TPP extractions (Bermejo et al., 2015; Jun 2009; Xi et al., 2011).
Table 3.4: Total polyphenols (TPP), caffeine and chlorogenic acid (CGA) cold brew coffees prepared from ground or whole bean, with or without high pressure processing (HPP) treatment. These values were determined after ground coffee and whole bean were brewed for 18 and 44 h, respectively.

<table>
<thead>
<tr>
<th>Physicochemical properties</th>
<th>Coarse ground with HPP</th>
<th>Coarse ground with HPP</th>
<th>Whole bean with HPP</th>
<th>Whole bean with HPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.10 ± 0.00&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.08 ± 0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.10 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.09 ± 0.00&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>TA (g/L)</td>
<td>0.59 ± 0.02&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.59 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.52 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.60 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>TA/TDS</td>
<td>0.34 ± 0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.33 ± 0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.46 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.39 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>L*</td>
<td>10.94 ± 0.21&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10.93 ± 0.45&lt;sup&gt;c&lt;/sup&gt;</td>
<td>23.66 ± 0.16&lt;sup&gt;a&lt;/sup&gt;</td>
<td>12.13 ± 0.19&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>a*</td>
<td>6.89 ± 0.55&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.18 ± 0.33&lt;sup&gt;c&lt;/sup&gt;</td>
<td>23.61 ± 0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10.11 ± 0.37&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>b*</td>
<td>2.89 ± 0.22&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.34 ± 0.10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>23.51 ± 0.08&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.20 ± 0.14&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>TPP (g/L)</td>
<td>2.58 ± 0.26&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.69 ± 0.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.41 ± 0.22&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.17 ± 0.06&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Caffeine (g/L)</td>
<td>0.48 ± 0.00&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.49 ± 0.00&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.33 ± 0.02&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.36 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>CGA (g/L)</td>
<td>0.96 ± 0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.01 ± 0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.48 ± 0.04&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.71 ± 0.03&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Data were shown as mean values ± standard deviations. In each row, different lowercase letters indicated a statistically significant difference (p < 0.05), while the same letter means no significant differences (P ≥ 0.05). The TPP content were expressed in grams of gallic acid per liter.
3.3.6 Effect of HPP on foamability and foam stability

Foamability and foam stability properties affect the visual attributes of coffee foam head that determines consumer acceptance. Foamability is defined as the capacity of the surfactants to form foam and foam stability is described as the variations of foam height or volume with time, immediately after foam generation. Foamability and foam stability are interrelated, and the higher foam stability is associated with the greater foamability of solution (Malysa & Lunkenheimer, 2008; Nunes et al., 1997). These properties are crucial for the nitro cold brew coffee, which is prepared by infusing cold brew coffee with nitrogen gas in kegs. When serving, there is a golden colour and dense foam head over the coffee brew.

In coffee brew, the foamability is mainly affected by the concentrations of surface-active components, such as amino acids, peptides and low molecular weight melanoidins, while the foam stability is mainly dominated by the macromolecular components, such as polysaccharides, melanoidins, and polypeptides (Nunes & Coimbra, 1998; Nunes et al., 1997). The results of foamability and foam stability of coarse ground and whole bean brews with and without HPP treatment were shown in Figure 3.3. Difference in foamability among the four samples were not statistically significant ($p > 0.05$). It means that surface active components (e.g., amino acids, peptides) are easily be extracted into the coffee brew. However, the brew prepared from the whole bean without HPP treatment had significantly lower foam stability (Figures 3.3 and 3.4), which indicates that the macromolecular
components, such as polysaccharides, polypeptides, and melanoidins, are hard to be extracted without grinding and HPP treatment.

**Figure 3.3** Foamability and foam stability of four cold brew coffees. Data were shown as mean values ± standard deviations. In each figure, different letters mean significant differences (p < 0.05), while the same letters indicate no significant differences (P ≥ 0.05) using a Tukey test.
Another noteworthy phenomenon was that brews prepared from the whole coffee bean brews had smoother foam than those prepared from ground coffee brews. A possible explanation could be that the ground coffee brews had extracted more components (e.g., fatty acids, lipids) that are detrimental to foam smoothness (Masella et al., 2015).

**Figure 3.4** Foam changes in four cold brew coffees from 1 to 60 min. The scale bar is 2 cm. a: coarse ground; b: coarse ground with HPP; c: whole bean; d: whole bean with HPP. The foams were made by bubbling coffee brew with N\textsubscript{2} for 10 s with a flow rate of 50 mL/min and observed at room temperature.
3.3.7 Effects of HPP on microstructures of ground coffee and beans

From Figure 3.2, after HPP treatment, the TDS of ground coffee brew increased from 1.71 to 1.79 % while the TDS of whole bean brew increased from 1.15 to 1.56 %. In order to elucidate the mechanism of improved TDS values of HPP-treated ground coffee and whole bean brews, the microstructures of ground coffee and whole bean with and without HPP treatment were examined by scanning electron microscope (SEM).

From the SEM micrographs (Figure 3.5 a, b, c, d), the ground samples showed minimal changes in microstructures with and without HPP treatment, while great destruction was observed in the HPP-treated whole beans compared untreated counterparts. That phenomenon can explain why the TDS values of brews prepared from ground coffee and whole beans were improved by the HPP process and why the improvement between whole beans was higher than ground coffees. The similar destruction was also observed in the HPP-treated green tea leaf samples (Jun et al., 2011).
Figure 3.5 SEM micrographs of coarse ground coffee and coffee beans with and without HPP treatment at different magnifications: (a) coarse ground; (b) coarse ground with HPP; (c) whole bean; (d) whole bean with HPP. The scale bars are 500 and 200 μm, respectively. The microstructures were observed and photographed by an SEM with an accelerating voltage of 10 kV.
3.3.8 Sensory evaluation

The flavor of cold brew coffee is essential for consumer acceptance. Sensory evaluations of HPP treated ground and whole bean coffee brew were performed by certified cuppers. As we can see from the sensory profile spider chart (Figure 3.7), cold brew coffee made by whole coffee beans showed a higher brightness and sweet value but had a weaker body, lower smoothness, and overall intensity value. By contrast, cold brew coffee prepared by coarse ground coffee showed an opposite result; it had lower brightness and sweet value but had a stronger body, higher smoothness, and overall intensity. The sensory evaluation results are consistent with the physicochemical analyses reported in Section 3.3.4 and 3.3.5. Brews from coarse grounds, with and without HPP treatment, tasted more bitter and less sweet than the whole bean brews with and without HPP treatment because coarse ground brews tend to have more caffeine and chlorogenic acid than whole bean brew counterparts. Due to the higher TDS values, coarse ground brews possessed higher body and overall intensity than whole bean brews. It was also noted that the HPP treatment had no obvious effect on sensory profile of coarse ground brews except little roasted flavour, which may come from the roasted cellulose extracted by HPP. Besides, HPP treatment could improve the body, mouthfeel, smooth and overall intensity of whole bean coffee brew. According to the cuppers' evaluation, whole coffee bean brews showed more complex fruit flavors. Due to the lower TDS, whole bean brew without HPP treatment showed a flat taste. However, whole bean brews prepared with the HPP treatment had strengthened body, overall intensity, and a mellow taste. The cuppers commented that some consumers might be interested in that coffee brew, which may
have some market potential as an emerging cold brew coffee. Further research is needed to systematically characterize the sensory properties of the whole bean brews.

Figure 3.6 Sensory profiles of the respective four cold brew coffees. This sensory evaluation was completed by certified cuppers.
3.4 Conclusions

With the increasing hardness of brewing water, the obtaining cold brew coffee had significantly higher pH while the titratable acidity of these cold brew coffees decreased slightly. Consequently, a tap water to reverse osmosis water ratio of 1:3, with a conductivity of 181.2 μs/cm, was used as brewing water for following cold brew coffee.

The HPP treatment showed minimal effect on TDS values of fine, medium, and coarse ground coffee brews as compared to the untreated controls. However, TDS of whole bean brew increased to 1.56 % compared with the control sample (1.14 %). Different HPP treating pressure from 100 to 550 MPa and time from 10 to 1200 s have no significant effect (p < 0.05) on the TDS of cold bean coffee. However, with the increase of presoaking time from 0 to 360 min, the TDS of HPP-treated cold brew coffee decreased from 1.56 to 1.20 %. After 240 min presoaking time, the HPP treatment could not improve the TDS of cold bean coffee. For the coarse ground and whole bean coffee brew with and without HPP treatment, pH was not significantly different (p > 0.05). However, extraction yield, as well as caffeine, chlorogenic acid contents increased significantly (p < 0.05) after HPP treatment. These observations correlated well with the TDS values, which might be related to the destruction of coffee porous structure induced by HPP treatment as shown by the SEM. The brew volume of coffee beans was much higher than that of ground coffee brew. The foamability of these four samples showed no significant difference (p > 0.05). Except for the whole bean control
sample, the foamability of other three cold brew coffees lasted longer than 30 min and the
coffee brew made by whole beans showed finer foam than ground coffee brew. For SEM,
HPP treatment did not destroy the porous structure of coffee ground obviously, while the
coffee bean cells were destroyed greatly. Finally, the sensory evaluation showed that
HPP-treated coffee bean brews had a desirable taste and aroma profiles, based on the
feedback from the certified cuppers. In general, HPP treatment could be used as an innovative
method to make cold brew coffee with improved strength and desirable flavour profiles.
Chapter 4 Changes in physicochemical properties of HPP-treated cold brew coffee during storage

4.1 Introduction

After brewing, coffee beverages continue to undergo physicochemical changes, which can substantially affect their sensory properties. The most important change that affects coffee brews acceptability is the increasing perceived sourness during storage (Pérez-Martínez et al., 2008b; Rosa et al., 1990). The increase in titratable acidity and decrease in pH have been attributed to several reasons, including the hydrolysis of the quinic/chlorogenic acid lactones formed during the roasting process, the hydrolysis of low molecular weight esters, and the degradation of chlorogenic acids into their corresponding hydroxycinnamic acids (e.g., caffeic acid, quinic acid) (Pérez-Martínez et al., 2008b; Schrader, Kiehne, Engelhardt, & Maier, 1996). Besides these changes, aroma intensity and freshness of coffee brew tend to decrease with aging, in concomitant with the development of undesirable notes such as rancid stale flavours that ultimately lead to consumer rejection. These deterioration processes accelerate with increasing temperature (Pérez-Martínez et al., 2008b; Rosa et al., 1990). Moreover, the exposure of the coffee brew to oxygen can accelerate its oxidative deterioration (Pérez-Martínez et al., 2008b), implying that the use of barrier packaging is essential for product shelf-life extension.
From a preliminary study on cold brew extraction using roasted whole beans, it was observed that by continuously allowing the beans to steep in the brew after the HPP treatment, the total dissolved solids (TDS) of brew during aging continued to increase implying that soluble solutes were continually being extracted. This chapter investigates the changes in the key physicochemical properties of brews prepared from HPP-treated whole bean cold brew coffee for a duration of 60 d at room (22°C) and refrigerated (4°C) temperatures. The chemical parameters studied were TDS, pH, titratable acidity (TA), total polyphenols (TPP), caffeine, and chlorogenic acid (CGA) concentrations, which are related to the strength, sourness, acidity, bitterness, and astringency, respectively, of the coffee brew.
4.2 Materials and methods

4.2.1 Materials

According to the Specialty Coffee Association of America (SCAA) recommendation for coffee brewing water, tap water (Guelph, ON, Canada) and reverse osmosis water (Milli-Q® Integral Water Purification System for Ultrapure Water, Darmstadt, Germany) were mixed at a ratio of 1:3 (v/v) to give brewing water of 207 μs/cm electrical conductivity. The coffee beans were supplied by Mother Parkers Tea & Coffee Inc. (Mississauga, ON, Canada). The 237 mL (8 oz) polyethylene terephthalate (PET) bottles were purchased from Uline (Milton, ON, Canada). The coffee filter paper was purchased from the local coffee store (Melitta Basket Coffee Filters). Methanol (HPLC grade), sodium hydroxide, Folin-Ciocalteu reagent, caffeine (99 % purity) and chlorogenic acid (99 % purity) were all purchased from Fisher Scientific International Inc. (Ottawa, ON, Canada). The pH of the brew samples was measured by a pH meter (Accumet Excel XL 20, Fisher Scientific, Ottawa, Canada), which was calibrated every time before use.

4.2.2 Cold brew extraction process and procedure of HPP treatment

Before HPP treatment, 20.7 g coffee beans were mixed with 207 mL water leaving no air headspace in the PET bottles. The bottles were then loaded into a 2 L HPP vessel (Avure Technologies, Inc., Middletown, OH, USA) and treated by HPP immediately at 400 MPa for
10 min. The ramping pressure rate was about 4 to 5 MPa/s, while the decompression from 400 MPa to atmospheric pressure took about 2 to 3 s.

After the HPP treatment, the bottles were removed from the HPP vessel and allowed to steep at room (22°C) and refrigerated (4°C) temperature, respectively, for 1, 2, 5, 10, 30, 60 d. At these time points, the coffee brews were decanted from the PET bottles, filtered and then subjected to the physiochemical analyses.

### 4.2.3 Physicochemical analyses

The titratable acidity (TA) and pH are essential indicators of perceived acidity in the coffee brew. The pH of coffee brew was determined using a pH meter (Accumet Excel XL 20, Fisher Scientific, Ottawa, Canada). Titratable acidity was determined by titrating 20 mL of coffee sample to pH 7.0 using 0.01 mol/L of NaOH solution. Results were expressed in grams of acetic acid per litre of coffee brew.

Total dissolved solids (TDS), which reflects the “body” of coffee brew (Gloess et al., 2013), was measured using the Coffee TDS Refractometer (Voice Systems Technology Inc.) and expressed in percentage. On the other hand, the extraction yield, defined as the ratio of the mass of ground coffee extracted into the brew to the total amount of ground coffee used (Angeloni, Guerrini, Masella, Bellumori, et al., 2019; Clarke, 2001), was calculated according to following equation:
Extraction Yield = \[ \frac{TDS \times W_{\text{brew}}}{W_{\text{ground coffee}}} \times 100\% \]  \hspace{1cm} (Equation 3)

where \( W_{\text{brew}} \) is the weight of coffee brew and \( W_{\text{ground coffee}} \) the weight of coffee ground used for brewing the coffee (Wang et al., 2016).

Total polyphenol (TPP) content is an indicator of the antioxidant properties of the brew (Gloess et al., 2013; Rao & Fuller, 2018). Folin-Ciocalteau was used to measure the TPP, according to Singleton et al. (1965), with some modifications. The Folin reagent was diluted ten times before use, and coffee brews were diluted four times using deionized water. An aliquot of 200 μL of the diluted coffee brew was pipetted into a disposable cuvette, to which 0.5 mL of the diluted Folin-Ciocalteau reagent was added. The mixture in cuvette was agitated for 5 s before adding 1.5 mL of 7.5 % (w/w) \( \text{Na}_2\text{CO}_3 \) solution. After further agitation, the cuvettes were placed in a dark environment for 2 h at ambient temperature (about 22°C). The absorbance of the resulting solution at 765 nm wavelength was measured using a 60S UV-Visible Spectrophotometer (Thermo Fisher Scientific, USA). The TPP contents were expressed in grams of gallic acid per liter.

The caffeine and chlorogenic acid (CGA) concentration of coffee brew were determined by high performance liquid chromatography (HPLC) (Farah et al., 2005; Fuller & Rao, 2017; Wang et al., 2016). The coffee brews were diluted 20 times using deionized water and passed through a 0.22 μm filter (Fisherbrand, Fisher Scientific International Inc., Ottawa, Canada) before the analysis. The HPLC (Model 2690, Waters, Milford, MA) was equipped with a photodiode array detector (Model 996, Waters, Milford, MA) and an Ultrasphere C\textsubscript{18} ODS
(15 cm × 4.6 mm, 5 μm, Beckman Coulter, Inc. USA) column. The mobile phase used was 75 % (v/v) 10 mM citric acid solution (adjusted to pH 2.5 using 6 N hydrochloric acid) and 25 % (w/w) HPLC grade methanol. Other HPLC conditions were as follows: flow rate: 0.4 mL/min; inject volume: 10 μL; running time: 40 min; detector wavelength: 273 nm for caffeine and 325 nm for CGA.

4.2.4 Data analysis

Each test in this study was repeated for at least three times, and results were expressed as mean ± standard deviation. Error bars in plots were standard deviations of the means. Figures were plotted in Microsoft Excel spreadsheet software. Statistical analysis was conducted using the SPSS and all the results are reported at 95% confidence interval or p > 0.05 (SPSS 22.0, SPSS Inc., Chicago, IL, USA).

Weibull distribution model was fitted to the kinetic data of TDS, caffeine, and chlorogenic acids contents. This is an empirical model that often used to describe kinetics of food phenomena, such as drying, degassing, hydration (MacHamdah et al., 2012; Menges & Ertekin, 2006; Wang & Lim, 2014):

\[ C(t) = C_\infty \times [1 - \exp \left(-\left(t/\alpha\right)^\beta\right)] \]  

(Equation 4)
where t is extraction time (min); C(t) (%) represents TDS, caffeine, and chlorogenic acid concentrations at time t; C∞ (%) is TDS, caffeine, and chlorogenic acid concentrations at infinity time; α is scale parameter (min); and β is a shape parameter (dimensionless). The α parameter determines the rate and is related to the reciprocal of the process of rate constant, representing the time needed to accomplish approximately 63% of the process. The parameters of Equation 4 were estimated by using the Solver function in Microsoft Excel Spreadsheet by minimizing the residual sum of squares. The goodness of fit was evaluated on the basis of coefficient of determination (R²) and root-mean-square error (RMSE). The R² is a measurement used to explain how much variability of one factor can be caused by its relationship to another related factor. This correlation is represented as a value between 0.0 and 1.0. A value of 1.0 indicates a perfect fit and is thus a highly reliable model for the prediction, while a value of 0.0 would indicate that the calculation fails to accurately model the data at all. The RMSE is frequently used to measure the differences between sample values predicted by a model or an estimator and the values observed. RMSD is always non-negative, and a value of 0 (almost never achieved in practice) would indicate a perfect fit to the data. In general, a lower RMSE is better than a higher one.

4.3 Results and discussion

4.3.1 Changes in TDS during 60-d storage

The TDS values of brews, with and without HPP treatment stored at 4°C and 22°C are shown in Figure 4.1. The solid lines of the plots are the best fit curves based on Weibull
Distribution function (Equation 4). During the 60-day storage, the HPP-treated sample at 22°C always had the highest TDS, while the untreated sample at 4°C had the lowest TDS values. Comparing the HPP-treated sample at 4°C and untreated sample at 22°C during the initial 7 d of storage, the latter had lower TDS values than the former. However, as storage progressed beyond 7 d, the brews from both conditions had comparable TDS values. These observations corroborated well with the estimated parameters of the Weibull Distribution model (Table 4.1); the HPP-treated coffee brew at 22°C had the highest infinite TDS value at 2.08 % while the untreated coffee brew at 4°C had the lowest infinite TDS value at 1.61 %.

On the other hand, the HPP-treated coffee brew at 4°C and untreated coffee brew at 22°C had comparable infinite TDS values at 1.84 and 1.85 %, respectively. The rate of the coffee extraction can be represented by the reciprocal α value, i.e., the larger the α value, the slower the rate of coffee extraction. HPP-treated coffee brews at 4°C and 22°C have similar α values at 0.73 and 0.67 d, respectively, which means that the times taken for coffee to extract about 63 % of final TDS were 0.73 and 0.67 d, respectively. No HPP-treated coffee brews at 4°C and 22°C have comparable α values at 2.00 and 2.02 d, respectively. These results showed that the HPP treatment had enhanced the extraction rate during the whole bean extraction process while the room temperature cannot obviously improve the extraction rate compared with the refrigerated temperature. Since that all the coefficient of determination (R²) are higher than 0.96, it means the Weibull Distribution model fit the coffee bean extraction kinetics well.
Figure 4.1 Changes in TDS values of whole bean coffee brews with and without HPP treatments at 4°C and 22°C for 60 d. The solid lines are best fit regression equations based on the Weibull distribution model (Equation 4). Whole bean coffee brew was treated with HPP at 400 MPa for 10 min immediately after mixing water with coffee beans. Brews were steeped with roasted coffee beans in sealed PET bottles until analysis.
Table 4.1 Estimated parameters ($\alpha$, $\beta$, $C_\infty$), root mean square error (RMSE), and coefficient of determination ($R^2$) of Weibull distribution model for brews prepared with or without HPP treatment at 4 and 22°C.

<table>
<thead>
<tr>
<th>Coffee samples</th>
<th>$\alpha$ (d)</th>
<th>$\beta$</th>
<th>$C_\infty$ (%)</th>
<th>RMSE</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP at 22°C</td>
<td>0.73</td>
<td>0.38</td>
<td>2.08</td>
<td>0.0477</td>
<td>0.9620</td>
</tr>
<tr>
<td>HPP at 4°C</td>
<td>0.67</td>
<td>0.38</td>
<td>1.85</td>
<td>0.0267</td>
<td>0.9835</td>
</tr>
<tr>
<td>No HPP at 22°C</td>
<td>2.00</td>
<td>0.71</td>
<td>1.84</td>
<td>0.0388</td>
<td>0.9875</td>
</tr>
<tr>
<td>No HPP at 4°C</td>
<td>2.02</td>
<td>0.83</td>
<td>1.61</td>
<td>0.0351</td>
<td>0.9902</td>
</tr>
</tbody>
</table>
4.3.2 pH and titratable acidity content changes

The pH and titratable acidity (TA) are important sensory attributes of coffee brews. Acids account for approximately 16 - 21% of dissolved solids in coffee brew (Verardo, Cecconi, Geatti, & Giumanini, 2002). From Figure 4.2, it can be seen that the pH value of whole bean coffee brews decreased with increasing storage time. After 60-day storage, the pH of HPP-treated coffee brew at 22°C dropped to 4.95, while the HPP-treated cold brew coffee at 4°C had the smallest decrease to 5.19. The pH value of the untreated sample at 22°C and HPP-treated coffee brew at 4°C reached comparable pH at 5.19 and 5.17, respectively.

Overall, the TA contents followed an opposite trend to that of the pH value; all samples showed increases of TA values with increasing storage time. At 60-day storage, HPP-treated coffee brew at 22°C had the highest increase to 1.18 g/L, while the untreated coffee brew at 4°C had the slowest increase to 0.79 g/L. During the first 5 d, the HPP-treated sample at 4°C had higher titratable acidity than untreated sample at 22°C. However, beyond 5 d, the untreated sample at 22°C had higher titratable acidity values than the HPP-treated sample at 4°C. This observation implies that during the initial stage of extraction (5 d), the HPP treatment had a more prominent effect on the TA of whole bean coffee brew than the temperature effect, which may be attributed the enhanced mass transfer induced by the HPP treatment. However, as time progressed, the effect of temperature on TA became dominant, which could be related to the hydrolysis of chlorogenic acid, esters, quinic acid lactone and following aldehydic oxidation (Manzocco & Nicoli, 2007; Rosa et al., 1990).
Figure 4.2 Changes in pH (a) and titratable acidity (TA) (b) values of whole bean coffee brews with and without HPP treatment stored at 22°C and 4°C for 60 d. Whole bean coffee brew was treated with HPP at 400 MPa for 10 min immediately after mixing water with coffee beans. Brews were steeped with roasted coffee beans in sealed PET bottles until analysis. Results of TA were expressed in grams of acetic acid per litre of coffee brew.
4.3.3 Changes in total polyphenols (TPP) content during 60-day storage

The changes in TPP contents during storage are presented in Figure 4.3. For HPP-treated coffee brew at 22°C, the TPP content remained stable all the time at 2.39 - 2.42 g/L. For the HPP-treated coffee brew at 4°C and 22°C, the TPP values remained relatively stable throughout the 60-day storage, implying rapid extraction of TPP components. However, the untreated samples had relatively lower initial TPP values than the HPP treated counterparts. Samples stored at 22°C had a noticeable increase in TPP value during the first 5 d of steeping, and then stabilized at a TPP level of around 2.35 g/L, which was comparable with the HPP-treated cold brew coffee at 4°C. The TPP value of the untreated sample at 4°C increased progressively during the first 30 d of steeping and then stabilized at a TPP level of 2.36 g/L. Finally, at 60-day storage, all these four samples had a similar TPP content at 2.35 - 2.42 g/L.
Figure 4.3 Changes in total polyphenol (TPP) content of whole bean coffee brews with and without HPP treatments at 4°C and 22°C for 60 d. The solid lines are best fit regression equations based on the Weibull distribution model (Equation 4). Whole bean coffee brew was treated with HPP at 400 MPa for 10 min immediately after mixing water with coffee beans. Brews were steeped with roasted coffee beans in sealed PET bottles until analysis. The TPP contents were expressed in grams of gallic acid per liter.
4.3.4 Changes in caffeine and chlorogenic acid contents during 60-day storage

Changes in caffeine and CGA contents during the storage followed similar trends, as shown in Figures 4.5 and 4.6. The solid lines of the plots are the best fit curves based on Weibull Distribution function (Equation 4). The caffeine and CGA contents of all these 4 cold brew coffee samples increased during the 60-day storage. The HPP-treated coffee brew at 22°C had the highest caffeine and CGA contents, reaching the final levels of 0.49 and 1.01 g/L, respectively. During the first 2 d, the HPP-treated cold brew coffee at 4°C had higher caffeine content than the untreated sample at 22°C; however, after 2 d, the untreated sample at 22°C had higher CGA content than HPP-treated cold brew coffee at 4°C, reaching final caffeine and CGA contents of 0.42 and 0.95 g/L, respectively. Among the four samples, the untreated sample at 4°C had a lowest caffeine and CGA contents with final levels of 0.39 and 0.85 g/L, respectively. These observations imply that the extractions of caffeine and CGA were relatively slower as compared to TPP (Figure 4.4). Elevated temperature would facilitate the extraction process, although this could result in an increase in hydrolysis rate of chlorogenic acid (Pérez-Martínez et al., 2008b). For the caffeine, it is relatively stable at the room temperature, but polyphenol-protein sediments could form during storage, thereby lowering the caffeine content (Lekha & Lonsane, 1997; Yin, Xu, Yuan, Luo, & Qian, 2009).
Changes in caffeine content of whole bean coffee brews with and without HPP treatments at 4°C and 22°C for 60 d. The solid lines are best fit regression equations based on the Weibull distribution model (Equation 4). Whole bean coffee brew was treated with HPP at 400 MPa for 10 min immediately after mixing water with coffee beans. Brews were steeped with roasted coffee beans in sealed PET bottles until analysis.
Table 4.2 Derived Weibull distribution model parameters ($\alpha, \beta, C_\infty$), RMSE (root mean square error), and coefficient of determination ($R^2$).

<table>
<thead>
<tr>
<th>Coffee samples</th>
<th>$\alpha$ (d)</th>
<th>$\beta$</th>
<th>$C_\infty$ (g/L)</th>
<th>RMSE</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP at 22°C</td>
<td>3.27</td>
<td>0.39</td>
<td>0.52</td>
<td>0.0204</td>
<td>0.9518</td>
</tr>
<tr>
<td>HPP at 4°C</td>
<td>3.24</td>
<td>0.46</td>
<td>0.41</td>
<td>0.0251</td>
<td>0.9132</td>
</tr>
<tr>
<td>No HPP at 22°C</td>
<td>3.88</td>
<td>0.59</td>
<td>0.43</td>
<td>0.0293</td>
<td>0.9045</td>
</tr>
<tr>
<td>No HPP at 4°C</td>
<td>4.11</td>
<td>0.65</td>
<td>0.40</td>
<td>0.0264</td>
<td>0.9361</td>
</tr>
</tbody>
</table>
Figure 4.5 Changes in chlorogenic acid (CGA) content of whole bean coffee brews with and without HPP treatments at 4°C and 22°C for 60 d. The solid lines are best fit regression equations based on the Weibull distribution model (Equation 4). Whole bean coffee brew was treated with HPP at 400 MPa for 10 min immediately after mixing water with coffee beans. Brews were steeped with roasted coffee beans in sealed PET bottles until analysis.
Table 4.3 Derived Weibull distribution model parameters (α, β, $C_\infty$), RMSE (root mean square error), and coefficient of determination ($R^2$).

<table>
<thead>
<tr>
<th>Coffee samples</th>
<th>α (d)</th>
<th>β</th>
<th>$C_\infty$ (g/L)</th>
<th>RMSE</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPP at 22°C</td>
<td>2.30</td>
<td>1.02</td>
<td>0.99</td>
<td>0.0633</td>
<td>0.9356</td>
</tr>
<tr>
<td>HPP at 4°C</td>
<td>8.74</td>
<td>0.48</td>
<td>1.03</td>
<td>0.0275</td>
<td>0.9860</td>
</tr>
<tr>
<td>No HPP at 22°C</td>
<td>6.18</td>
<td>0.49</td>
<td>0.95</td>
<td>0.0516</td>
<td>0.9371</td>
</tr>
<tr>
<td>No HPP at 4°C</td>
<td>4.64</td>
<td>0.56</td>
<td>0.69</td>
<td>0.0601</td>
<td>0.8846</td>
</tr>
</tbody>
</table>
To further understand the caffeine and chlorogenic acid extraction kinetics with and without HPP treatment at room and refrigerated temperature, the Weibull distribution model was fitted to the caffeine and chlorogenic acid content data. The estimated parameter values of the Weibull Distribution function are summarized in Tables 4.2 and 4.3.

For caffeine concentrations, HPP at 22°C and 4°C have similar lowest α values at 3.27 and 3.24 d, respectively, which means that the times taken for coffee to extract about 63 % of final caffeine were 3.27 and 3.24 d, respectively. The control treatments (no HPP) at 4°C and 22°C had the higher α values at 4.11 and 3.88 d, respectively. These results indicate that both HPP treatment and higher temperature condition enhanced the caffeine extraction process. In terms of the \( C_\infty \) values, brew subjected to HPP treatment at 22°C had the highest value at 0.52 % while other 3 samples had comparable values ranging from 0.40 to 0.43 %. This observation implies that the combined HPP treatment and room temperature treatment can enhance the final caffeine content of whole bean coffee brew. For the chlorogenic acid content, the HPP treatment at 22°C had a lower final value than that of HPP at 4°C, indicating that the hydrolysis of chlorogenic acids might have occurred at elevated temperature.

4.4 Conclusion

This study monitored the changes in physicochemical properties of HPP-treated cold brew coffee during storage at 4 and 22°C. Overall, pH decreased during the 60-day storage
time, with the pH of HPP-treated cold brew coffees at 22°C dropped most significantly to 4.95, while the HPP-treated cold brew coffees at 4°C had the slowest decrease to 5.19. As expected, the pH of untreated samples at 22°C decreased faster than that at 4°C. TA values of all these samples increased with time, with the TA of HPP-treated coffee brew at 22°C increased most significantly to 1.18 g/L, while the HPP-treated coffee brew at 4°C had the slowest increase to 0.79 g/L. For the HPP-treated cold brew coffee at 4 and 22°C, TPP contents remained stable throughout the 60-day storage at 2.36 - 2.42 g/L. In comparison, the untreated samples at 22°C had a significant increase in TPP content during the first 5 d of steeping and then levelled off at 2.35 g/L. The TPP content of the HPP-untreated samples at 4°C increased significantly during the initial 30 d and then stabilized at around 2.36 g/L level. All these four samples had a similar TPP content at 2.35 - 2.42 g/L at 60 d. The caffeine and CGA contents of all these four cold brew coffee samples increased during the 60-day storage. The HPP-treated cold brew coffee at 22°C always had the highest caffeine and CGA content, and the caffeine and CGA contents reached 0.49 and 1.01 g/L, respectively. In the first 2 d, the HPP-treated cold brew coffees at 4°C had a higher caffeine content than untreated samples at room temperature, however, after 2 d, the untreated samples at room temperature had higher chlorogenic acid content than HPP-treated cold brew coffees at refrigerated temperature. Finally, the caffeine and CGA contents reached a similar level at 0.42 and 0.95 g/L, respectively. The control sample at 4°C had a little lower caffeine and CGA content during most of the storage time, and its final contents were also the lowest during these four samples at 0.39 and 0.85 g/L, respectively. In general, during the 60-day storage, pH of these
four samples decreased while TA, TPP, caffeine and CGA contents increased. Both the HPP treatment and 22°C can facilitate the coffee bean extraction process and they can cooperate to improve final TDS value and caffeine content. However, storage at elevated temperature can also accelerate the hydrolysis of chlorogenic acids. Conclusively, continual extraction after the HPP treatment can be utilized to maximize the bioactives in the brew and further improve coffee quality.
Chapter 5 Conclusions and future work

The first part of this study investigated the effects of water hardness on the pH and titratable acidity of cold brew coffees. In the second part of this research, the effects of high pressure processing (HPP) on the extraction and physicochemical characteristics of cold brew coffee were investigated. Moreover, the changes of physicochemical properties of the HPP-treated coffee brews during the subsequent 60-day storage were monitored. On the basis of the experimental findings and data analyses, the following conclusions can be drawn:

(1) Increasing hardness of brewing water increased the pH while it lowered the titratable acidity of the cold brews. In accordance with the recommendation from Specialty Coffee Association of America (SCAA) and the acidity findings of the coffee brew, the brewing water was standardized by blending tap water from the City of Guelph with a reverse osmosis water, at 1:3 (w/w) ratio, with an electrical conductivity of 181.2 μs/cm. The brewing water was adopted as brewing water for subsequent cold brew experiments.

(2) Through this study, it was found that HPP treatment can facilitate the coffee extraction process and increase the extraction efficiency. In general, HPP treatment showed minimal effect on TDS values of fine (< 500 μm), medium (500 to 800 μm), and coarse (> 800 μm) ground coffee brews as compared to the untreated controls. However, the TDS of whole bean brew increased significantly as compared with the
control bean sample. For coarse ground and whole bean brews subjected to HPP treatment at 400 MPa for 10 min, although the pH values for HPP-treated and control samples were not significantly different (p > 0.05), the extraction yield, caffeine content, chlorogenic acid content increased significantly (p < 0.05). These observations can be attributed to the destruction of porous structures of the coffee bean matrices caused by HPP treatment, as revealed by SEM analysis. The sensory evaluation provided the certified cuppers showed that the HPP-treated coffee bean brews had a desirable taste and aroma profiles. This study demonstrated that the use of whole roasted beans (instead of grounds), in conjunction with a HPP treatment, is promising for brewing cold brew coffees for the development of new products with unique sensory profiles.

(3) During the 60-day storage, pH values of whole bean brew with and without HPP treatment at 22 and 4°C decreased, while the TA, TPP, caffeine content, and CGA content increased. Both the HPP treatment and elevated temperature facilitated the subsequent post-HPP treatment soluble extraction. However, storage at elevated temperature (22°C) also accelerated the hydrolysis of chlorogenic acids compared with the refrigerated temperature (4°C), which may impact the acidity profile of the aged brews.

(4) The TDS, caffeine, and CGA extraction kinetic profiles during post-HPP storage fitted well with the Weibull Distribution model, with coefficient of determination (R²) values greater than 0.88. The α parameter of the model determines the
extraction rate and is related to the reciprocal of the process of rate constant, representing the time needed to accomplish approximately 63% of the process.

Whole bean brews with HPP treatment had lower $\alpha$ values compared with untreated samples, which means the HPP treatment can accelerate the extraction process. However, temperature had little effects on the extraction rates. HPP treatment and room temperature had synergetic effects on increasing the final TDS and caffeine content, as determined from the $C_\infty$ (%) parameter of the Weibull Distribution model, which is the concentration of the extract species at infinity time. However, HPP treatment at room temperature (22°C) had lower final CGA contents than HPP at refrigerated temperature (4°C), which may be attributed to the hydrolysis of CGA that accelerated at elevated temperature (22°C). Furthermore, HPP played an important role during the initial phase of extraction but had minimal effect during post-HPP bean steeping as compared to temperature effect.

In general, this research investigated some exploration about the application of HPP to make the cold brew coffee. Overall, results from this research showed that HPP treatment could be used for enhancing the cold brew extraction of whole coffee beans, which is promising for the development of new cold brew coffee products. During the 60-day storage, the contents of bioactive compounds, such as total polyphenols caffeine, and chlorogenic acids increased. The hypothesis that HPP treatment above 400 MPa can facilitate the coffee extraction process and increase the extraction efficiency and the hypothesis that the continual
extraction will maximize the bioactive compounds in the coffee brew were accepted.

However, there are still some areas that need further investigations:

(1) Since the proposed HPP-assisted whole bean brew in bottle is a new product concept, it is important to conduct marketing and consumer acceptance studies before commercialization. Moreover, since the beans are left in the brew after the HPP treatment, the implementation of a mechanism, such as a disposal filter insert on the bottle, is needed to prevent consumer from accidental ingestion of the beans. The filter should be removable to assist the consumer in emptying the beans from the plastic (e.g., PET) bottle and facilitate its recycling.

(2) HPP treatment at 340 - 680 MPa can denature the protein and reduce the rate of melanoidin formation and polymerization (Rastogi, Raghavarao, Balasubramaniam, Niranjan, & Knorr, 2007). As observed during the storage, the color of whole bean coffee brews became darker with increasing time. Moreover, the darkening of the brew did not correlate with the TDS values of the brews, implying that the colored components might be related to the continual formation of melanoidins during storage, which may have implication on the coffee brew’s antioxidant activity. The reason for the brew darkening during storage is unknown. Further research is needed in this area.

(3) Cold brew coffee is regarded as less bitter and acidic than its traditional hot counterparts. However, their caffeine contents are comparable. There must be other
bitter components, such as chlorogenic acid lactones and phenylindanes, are less extracted at room or refrigerated temperature during cold brew process. Besides, chlorogenic acid lactones and phenylindanes can contribute to coffee flavor and also may be of potential biopharmacological importance in humans (Frank, Zehentbauer, & Hofmann, 2006; Mancini, Wang, & Weaver, 2018). Temperature will influence the solubility of various compounds and hence chemical compositions of the brews prepared at different temperatures, which can affect the sensory quality of the coffee beverages (Arya & Rao, 2007). In the future studies, chlorogenic acid lactones, phenylindanes, carbohydrates, and so on should be investigated and compared at different brew temperatures.
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APPENDICES:

1. Relationship among TDS, conductivity, and hardness of water

<table>
<thead>
<tr>
<th>TDS (ppm)</th>
<th>Conductivity (us/cm)</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 70</td>
<td>0 - 140</td>
<td>Very Soft</td>
</tr>
<tr>
<td>70 - 150</td>
<td>140 - 300</td>
<td>Soft</td>
</tr>
<tr>
<td>150 - 250</td>
<td>300 - 500</td>
<td>Slightly Hard</td>
</tr>
<tr>
<td>250 - 320</td>
<td>500 - 640</td>
<td>Moderately Hard</td>
</tr>
<tr>
<td>320 - 420</td>
<td>640 - 840</td>
<td>Hard</td>
</tr>
<tr>
<td>Above 420</td>
<td>Above 840</td>
<td>Very Hard</td>
</tr>
</tbody>
</table>
2. Specialty Coffee Association of America (SCAA) Standard | Water for Brewing

Specialty Coffee

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Target</th>
<th>Acceptable Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odor</td>
<td></td>
<td>Clean/fresh, odor free</td>
</tr>
<tr>
<td>Color</td>
<td></td>
<td>Clear color</td>
</tr>
<tr>
<td>Total chlorine</td>
<td></td>
<td>0 mg/L</td>
</tr>
<tr>
<td>TDS</td>
<td>150 mg/L</td>
<td>75 – 250 mg/L</td>
</tr>
<tr>
<td>Calcium hardness</td>
<td>4 grains or 68 mg/L</td>
<td>1 – 5 grains or 17 – 85 mg/L</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>40 mg/L</td>
<td>At or near 40 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
<td>6.5 – 7.5</td>
</tr>
<tr>
<td>Sodium</td>
<td>10 mg/L</td>
<td>At or near 10 mg/L</td>
</tr>
<tr>
<td>Characteristic</td>
<td>150 mg/L</td>
<td>75 – 250 mg/L</td>
</tr>
</tbody>
</table>

Odor is based on sensory olfactory determination
Color is based on sensory visual determination
TDS measured based on a 4-4-2 conversion