NON-THERMAL COLD-BREW COFFEE CONCENTRATION

A Project Paper

Presented to the Faculty of the Graduate School

of Cornell University

in Partial Fulfillment of the Requirements for the Degree of

Master of Professional Studies in Agriculture and Life Sciences

Field of Food Science and Technology

by

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August 2021

ABSTRACT

The rapid growth of the ready-to-drink and cold brew coffee markets point to the need for concentration methods that can maintain a high quality of these beverages. Cold brew coffee differentiates itself from hot extraction methods primarily through its heat labile aroma and flavor components. Thus, a nonthermal concentration process is crucial for product quality retention, especially since existing concentration methods (thermal concentration and reverse osmosis) fail to satisfy all three criteria: high degrees of concentration, low energy costs, and no quality loss. In this review paper with a small experimental component, forward osmosis (FO) was evaluated as means to produce cold brew coffee concentrate. Although preliminary tests found trace amounts of high melting point lipids which prove problematic for membrane regeneration and attainable flux, FO still shows promise as a nonthermal concentration method for cold brew coffee with no quality loss and low energy expenditure.

BIOGRAPHICAL SKETCH

Kirsten Wei was born and raised in Palo Alto, California. She attended University of California Davis and graduated in 2018 with a Bachelor of Science in Food Science and Technology. She then spent two years at a food and biotech start-up formulating products with plant-derived protein sweeteners before pursuing an MFS at Cornell University.

During her time at Cornell University, she joined the IFTSA & Mars Product Development team to develop Tofumisu, a sustainable plant-based alternative to tiramisu.

After graduation, Kirsten will be working in consumer research and insights at Curion in Chicago, IL.

This work is dedicated to my parents, Grace and Francisco.

ACKNOWLEDGMENTS

A huge thank you to my advisor, Dr. Carmen Moraru, who has shown me nothing but support and encouragement since the first day we met. Writing has always been challenging for me, this project paper was no different! I couldn't have done it without her invaluable expertise and continuous guidance.

I would also like to thank my lab mates for being so welcoming and taking time out of their busy schedules to help me on my project: Joseph Dumpler, Andreea Beldie, Alexandra Hall, Hanyu Chen, Bailey Gong, and Matthew Sheehan.

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1. Cold Brew Coffee: A Growing Product Category

Coffee is among the most consumed beverages in the world. According to International Coffee Organization, consumers drink 1.4 billion cups of coffee a day globally. In the United States alone, 450 million cups of coffee are consumed every day and as much as 63% of American adults drink coffee daily (NCA, 2019). According to Jill Failla, Foodservice Analyst at Mintel, "The $15.1 billion coffee category is projected to grow a respectable 22% through 2024 largely thanks to the trendsetting RTD coffee segment, which is on pace to outgrow the long-time coffee leader, roasted coffee, within five years." (Mintel, 2019). Younger consumers enjoy a wide variety of coffee drinks, with a preference for ready to drink (RTD) coffee, instant coffee, and espresso beverages. The cold-brew market alone is poised to grow at a CAGR of 28% during the 2020-2024 forecast period (MarketWatch, 2021). The COVID-19 pandemic almost completely removed retail coffee's foodservice competition, and shelter-in-place orders forced many to work from home, reducing their need for away from home coffee. This change will likely become permanent even once the pandemic subsides. Some consider that the recession will motivate consumers to trade expensive coffee shop drinks for more affordable retail options, indicating an opportunity for brands to promote high quality retail coffee drinks as affordable luxuries (Caleb Bryant, Mintel, 2020).

According to surveys conducted by Mintel in 2017 and in 2019, coffee was the most purchased beverage for personal consumption at home **(Figure 1)**. The rapid growth in the RTD and innovative category segments such as cold brew coffee, leads to the need for accessible high-quality concentrates which reduce transportation costs, extend shelf-life, and increase consumer convenience.

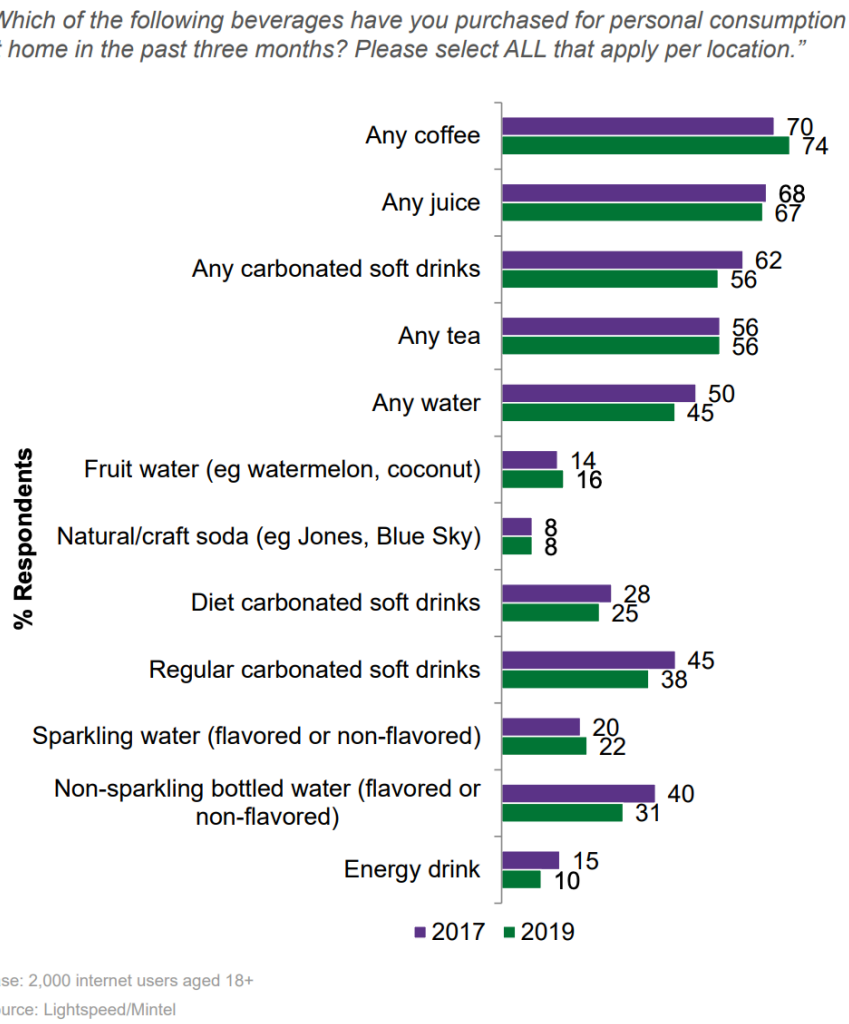

FIGURE 1. BEVERAGE PURCHASE FOR AT-HOME CONSUMPTION, APRIL 2017 AND 2019 (MINTEL)

COLD BREW COFFEE: PROCESSING AND CHARACTERISTICS

Coffee extraction is the final step in coffee making before consumption and determines the characteristics of the brew. Extraction parameters like brew time, temperature, water quality, pressure, and particle size determine the final flavor. The cold brew coffee method is often described as infusion with room temperature water (20-25°C) or lower for a longer steeping time of 8 to 24 hours. In a study on cold brew extraction at water temperatures of 5°C and 15°C, the bulk of the extraction occurred in the first 3-5 hours of infusion (Portela, Almeida, Mori,

Yamashita, Benassi, 2021). Moreover, Fuller & Rao (2017) found that caffeine and 3-CGA concentrations reached equilibrium after 6-7 hours.

Brewing methods include infusion (direct) and stepping (indirect). In stepping, water is slowly dripped into a coffee panel supported by a filter and the beverage is collected underneath. In immersion or infusion, the grounds are in direct contact with the water, then separated to obtain the final beverage. Due to the time and temperature of the extraction, cold brew coffee has a unique flavor profile that can be characterized as buttery, sweet, with chocolate notes (Angeloni, Guerrini, Masella, Bellumori, et al., 2019; Cordoba et al., 2021). Its flavor is attributed to the retention of volatile aroma compounds that are lost during hot extraction. Thus, a nonthermal concentration process would be necessary to achieve a high-quality concentrate with no loss to sensorial properties.

Cold brew coffee is often touted to be less acidic, less bitter, and sweeter than its hot brew counterparts (Mestdagh et al., 2017). Literature does not show cold brew to have less perceived acidity than hot brewed counterparts. Total acidity and pH are often used to characterize the perceived acidity of coffee beverages but studies have shown no reliable correlation (Andueza, Vila, de Pena, Cid, 2007, Gloess et al., 2013). Hot brew coffee was shown to have higher concentrations of total titratable acids than cold brew (Rao & Fuller, 2018). Other studies report that brewing method does not make a difference in pH, acidity, caffeine, chlorogenic acids, and CQA (Angeloni et al., 2019, Fuller & Rao, 2017). Angeloni et al. (2018), found stepping or dripping to have higher caffeine content than immersion methods for cold brew.

Findings on the difference in aromatic compounds and sweetness intensity between cold and hot brew coffee are less contested. Sensory tests conducted by trained panelists characterized cold brew coffee having a higher intensity of sugar caramelization and sweet taste when compared

to cold drip and French press coffee. Odorants such as aldehydes like 2-methylbutanol found in roasted coffee beverages are related to buttery, malty, and caramel flavor (Toci, Boldrin, 2018; Caporaso et al., 2018).

Thus, the key differentiator between cold and hot brewed coffee is its aromatic profile. In a study comparing the differences between specialty and regular quality coffee using hot and cold brew methods, Cordoba et al. (2021) found brew method to have more impact on final brew flavor and quality. Sensory panel data reflected hot brewed coffee to have more undesirable sensory attributes like paper, green/vegetative, spices, roasted, acrid, astringency, and bitterness, regardless of the bean quality. Likewise, cold brew coffees had the highest floral aromas.

PHYSICOCHEMICAL CHARACTERISTICS OF BREWED COFFEE

There are more than 70 species of coffee bean producing plants. The two main commercially available species are *Coffea arabica* (Arabica) and *Coffea canephora* (Robusta), providing 75% and 25% of the world's production, respectively (Mussato, Machado, Martins, Teixeira, 2011). The beans from each species display different morphology and chemical composition **(Table 1).**

Extraction parameters determine the brew characteristics. A coffee beverage is comprised of water soluble and insoluble components. The water-soluble components include chlorogenic acids, caffeine, nicotinic acid, and volatile hydrophilic compounds (Farah, 2012). The coffee bean also includes other components like cellulose, minerals, sugars, lipids, tannins, and polyphenols (Mussato, Machado, Martins, and Teixeira, 2011). Although the lipid fraction is not water soluble, some of it reaches the beverage especially with the use of high temperatures and pressure. The concentration of components, non-volatile and volatile, determine the final sensory attributes and characteristics.

TABLE 1. CHEMICAL COMPOSITION OF GREEN COFFEE (BELITZ ET AL., 2009)

Component	Arabica[a]	Robusta[a]	Constituents
Soluble carbohydrates	9–12.5	6–11.5	
Monosaccharides	0.2–0.5		Fructose, glucose, galactose, arabinose (traces)
Oligosaccharides	6–9	3–7	Sucrose (>90%), raffinose (0–0.9%), stachyose (0–0.13%)
Polysaccharides	3–4		Polymers of galactose (55–65%), mannose (10–20%), arabinose (20–35%), glucose (0–2%)
Insoluble polysaccharides	46–53	34–44	
Hemicelluloses	5–10	3–4	Polymers of galactose (65–75%), arabinose (25–30%), mannose (0–10%)
Cellulose, β(1–4)mannan	41–43	32–40	
Acids and phenols			
Volatile acids	0.1		
Nonvolatile aliphatic acids	2–2.9	1.3–2.2	Citric acid, malic acid, quinic acid
Chlorogenic acid	6.7–9.2	7.1–12.1	Mono-, dicaffeoyl-, and feruloylquinic acid
Lignin	1–3		
Lipids	15–18	8–12	
Wax	0.2–0.3		
Oil	7.7–17.7		Main fatty acids: 16:0 and 18:2 (9,12)
N compounds	11–15		
Free amino acids	0.2–0.8		Main amino acids: Glu, Asp, Asp-NH_2
Proteins	8.5–12		
Caffeine	0.8–1.4	1.7–4.0	Traces of theobromine and theophylline
Trigonelline	0.6–1.2	0.3–0.9	
Minerals	3–5.4		

PERCENT VALUES IN DRY-WEIGHT BASIS

TOTAL SOLIDS AND EXTRACTION YIELD

Total dissolved solids (TDS) is the ratio of solubilized solids in the beverage to the total mass. Extraction yield (EY) is the ratio between the mass of extracted coffee soluble components and the mass of coffee grounds used. TDS associated with mouthfeel, strength of coffee. The extraction parameters determine the compounds that make it into the brewed coffee and determine the flavor of the brew.

PH AND TOTAL ACIDITY

Total acidity and pH have been used to characterize acidity of coffee. pH quantifies the aqueous hydrogen ion concentration and measures the deprotonated acid molecule levels in a

sample (Cordoba et al., 2020). Total titratable acidity (TA) is a measure of all acidic protons in a sample, including non-dissociated protons that can be neutralized by the addition of a strong base (Fuller & Rao, 2018). Studies are inconclusive in relating the either titratable acidity or pH to perceived acidity.

NON-VOLATILES

The non- volatile components of coffee include carbohydrates, chlorogenic acids, lipids, organic acids, melanoidins, minerals, and nitrogen compounds, like caffeine and trigonelline (Ludwig, Clifford, Lean, Ashihara, & Crozier, 2014). Lipid concentration is higher in coffee brewed without filter papers. In a study comparing the lipid content in coffee by different extraction methods, only 7/150 ml cup mg of lipids were retained in the paper filtered method compared to 60-160 mg lipids/150 ml in espresso, and 50 mg lipids/150 ml with a metal screener (W.M.N. Ratnayake, R. Hollywood, E. O'Grady, B. Stavric, 1993). Characterization of the lipid of the brew, filter paper, and spent coffee grounds showed no difference in the profile, demonstrating that the filter paper equally retained all lipids. Lipids are crucial in the brew characteristics as they form emulsions that retain certain aromatic compounds and contribute to the mouthfeel of the beverage. Caffeine and trigonelline are the most abundant nitrogen compounds and both contribute to the bitterness intensity of a coffee beverage.

THE LIPID FRACTION OF COFFEE

Dong et al. tested seven types of coffee (*Coffea robusta*) for FA, AA, volatile composition of green coffee beans, chlorogenic acids, trigonelline, caffeine, total lipid, total protein. Major fatty acids: linoleic acid, palmitic acid, oleic acid, arachic acid. (Dong et al., 2015).

The lipid fraction of coffee is similar to edible vegetable oils, with triacylglycerols, sterols and tocopherols. The lipid content of green Arabica and Robusta coffee beans ranges from 10-

15%, most of it is oil and a small amount is wax, which come from the outer layer of the bean. Coffee wax only makes up 0.2-0.3% of the total weight. Treatments such as polishing, dewaxing, steaming, or decaffeinating can be used to remove the waxy layer (Karl Speer, Isabelle Kolling-Speer, 2006).

VOLATILE ORGANIC COMPOUNDS

Roasted coffee has over 1000 volatile compounds, with 30-50 compounds mainly responsible for coffee aroma (Cantergiani et al., 2001). Pyrazines, furans, aldehydes, ketones, and pyrroles make up more than 70% of the volatile compounds in coffee (Cordoba, Fernandez-Alduenda, Moreno, Ruiz, 2020).

The predominant aromatic volatile compounds in both hot and cold brewed coffee are furans and pyrazines. In cold brew coffee, the highest number of volatile compounds are furans (Cordoba et al., 2019). Volatile furans are associated with sweet, nutty, caramelly, roasted, and earthy aromas and flavor. Pyrazines have been associated with nutty, earthy, roasted, and green aromas. Moreover, hot brewed coffee was found to have the highest content of volatile compounds linked to unpleasant notes like green, licorice-like, medicinal, sulfur, garlic, smoke, burnt, napthyl, phenolic, and spicy (Cordoba et al., 2019).

Hot water is efficient in extracting the less soluble and polar compounds related to bitter, acrid, and astringent flavors that are not extracted using the cold brewing method. Overall, cold brew coffees have more volatile compounds exhibiting sensory attributes like buttery, sweetness, and lower TA than hot brewed coffees.

2. METHODS FOR CONCENTRATION OF FLUID FOODS. NONTHERMAL CONCENTRATION USING MEMBRANES

Vast amounts of liquid food are industrially concentrated to reduce storage, packaging, handling, and transportation costs (Petrotos, Lazarides, 2001). As brewed coffee has a very high amount of water, long term storage and transportation of coffee can also benefit from concentration. Evaporative concentration is the most widely used liquid concentration process in the food industry, which removes water as vapor through heating. Although evaporation can achieve a high degree of concentration (45 – 60°Brix, depending on the product), the severe degradation of sensory and nutritive properties have a detrimental effect on consumer perception and acceptability of thermally concentrated products. Evaporation imparts "cooked" off-flavors, and significantly reduces the product quality through the loss of thermally sensitive components like aromatic volatiles, color, vitamins, phytochemicals. Use of high temperatures can result in 90% loss of volatile aroma compounds within the first five minutes of processing (Bardhan, Subbiah, Mohanty, 2020). Additionally, evaporation is an energy intensive process.

Reverse Osmosis (RO) is a non-thermal concentration process that uses hydraulic pressure to move water across a selective membrane against the concentration gradient.

Compared to evaporation, RO requires less energy, less investment cost, avoids thermal degradation of compounds and does not cause cooked off-flavors. However, the use of high levels of hydraulic pressure limits the achievable concentration, because it causes membrane fouling due to the accumulation and compaction of the cake layer on the membrane surface, an unavoidable effect of hydraulic pressure and concentration polarization. . For example, in tomato juice concentration, a popular concentrated liquid food, only 9°Brix can be achieved by RO (Petrotos and Lazarides, 2001). However, the use of hydraulic pressure limits the concentration capabilities and contributes to a higher fouling propensity especially when dealing with complex liquid streams including coffee.

Overall, both evaporation and reverse osmosis (RO) fail to satisfy three criteria: (1) high concentration rates, (2) low energy costs, and (3) concentrates without quality loss (Blandin et al., 2020).

Another nonthermal membrane concentration process, forward osmosis (FO) utilizes the osmotic concentration gradient as the driving force of water across a semi-permeable membrane. FO has high rejection rate, low fouling propensity, and can be operated without significant pressure or temperature gradient, and therefore can be considered as a potential candidate for a broad range of concentration applications where current technologies still suffer from critical limitations (Blandin et al. 2020). FO does not damage the nutritive nor sensorial properties of the final concentrate and can reach concentration rates comparable to evaporation.

Like RO, FO is a nonthermal concentration process that leads to little loss of sensorial and nutritional quality of the processed liquid food products. However, FO has several advantages over pressure-driven membrane processes such as RO that make it commercially attractive, including: (1) FO does not require external hydraulic pressure for operation and hence has potential for significant energy saving; (2) FO has lower membrane fouling propensity as the feed solids are not compacted against the membrane; and (3) unlike RO, FO can potentially be used to achieve the concentration factors typical of evaporation (Terefe et al., 2016).

Herron et al. (1994) demonstrated the applicability of FO technology to concentrate coffee from 5°Brix to 63°Brix using a high fructose corn syrup draw solute (DS). Various other studies demonstrated the possibility to concentrate the following: pineapple juice up to 60° Brix (Babu, Rastogi, Raghavarao, 2006), Kokum juice from 2 to 52° Brix (Nayak, Valuuri, Rastogi, 2011), beetroot, pineapple and grape juice from 2.3 to 52° Brix, 8.0 to 54.6° Brix and 4.4 to 54° Brix,

respectively (Nayak, Valluri, Rastogi). This review aims to evaluate the potential of FO processing for cold brew coffee concentration and discuss foreseeable challenges.

3. Forward Osmosis: Process and Parameters

3.1. How Does Forward Osmosis Work?

Osmosis is the movement of water across a semi-permeable membrane, from low to high solute concentration. FO employs a highly concentrated draw solution (DS) to create an osmotic pressure difference from the feed solution (FS). **Figure 2** depicts an FO system along with the regeneration of the draw solution. As water flows from the FS (low solute concentration) to the DS (high solute concentration), solutes and suspended solids are rejected. Thus, the FS is effectively concentrated as the DS is diluted. The FS and DS are circulated within the system until the FS reaches the desired level of concentration. The greater osmotic pressure generated by the DS, the greater rate of water diffusion or flux.

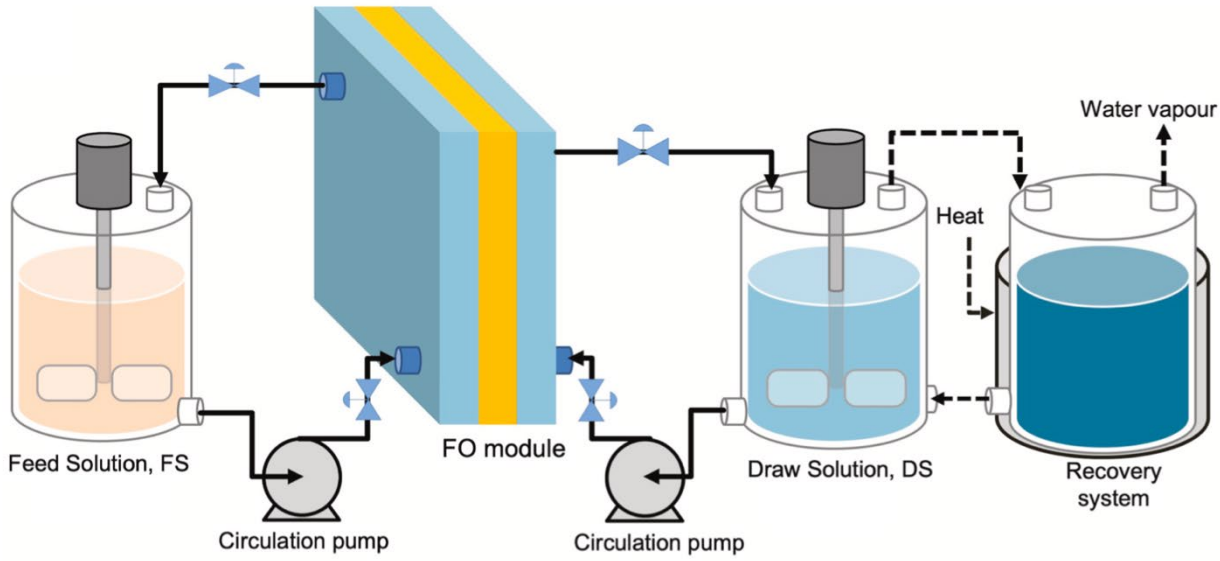

FIGURE 2. SCHEMATIC ILLUSTRATION OF FO OPERATION. ADAPTED FROM WENTEN, KHOIRUDDIN, REYNARD, LUGITO, JULIAN, 2021)

The semi-permeable membranes used in FO are typically asymmetric, with a dense active layer and a porous support layer. When the active layer is facing the FS, the configuration is known as FO mode, and when is facing the support layer the configuration is known as pressure retarded osmosis (PRO) mode. For liquid food concentration and other high fouling feeds, the FO mode is typically used, as less fouling occurs. Compared to other concentration processes, FO may offer significant cost savings as it does not require the use of high heat nor hydraulic pressure. However, an energy intensive step in FO is the regeneration of the draw solute. One study found that the specific energy consumption was 0.65kWh/kg for FO, half of which came from osmotic agent regeneration (Menchik, Moraru, 2015).

3.2. Forward Osmosis Membranes

The ideal FO membrane achieves high water flux, rejects dissolved solutes and ions, is compatible with the draw solution, and is mechanically robust (Shaffer et al. 2015). The active layer (~100 nm) should be dense for solute rejection and the support layer should be thin and highly porous to reduce ICP (~200 nm) (Terefe et al., 2016).

The most common commercially available membrane materials are cellulose triacetate (CTA), tricellulose acetate, and polyamide thin film composite (TFC). CTA membranes must operate in the range of pH 4.0-8.0 and are not safe from microbial growth. TFC membranes have a selective polyamide active layer formed by interfacial polymerization (IP; used for thin-film composites) on top of a polysulfone support layer fabricated by phase separation. TFC has a higher temperature and pH tolerance compared to CTA (Terefe et al., 2016). The highly hydrophilic nature of CTA membranes aids in reducing fouling. **Table 2** depicts FO membrane manufacturers and their commercial status as of 2016.

TABLE 2. FO MEMBRANE MANUFACTURERS (TEREFE ET AL., 2016)

Aquaporin A/S (Copenhagen, Denmark) *www.**aquaporin**.dk*	Aquaporin protein	Proprietary	Development
Fluid Technology Solutions Inc. (Albany, OR, USA), formerly Osmotek and HTI *www.**fts**h2o.com*	Cellulose triacetate Thin film composite Cellulose triacetate, Osmotek unit	Spiral wound Spiral wound Proprietary	Commercial Commercial Commercial
Oasys Water Inc. (Boston, MA, USA) ***www.oasyswater**.com*	Thin film composite	Spiral wound	Commercial
Porifera Inc. (Hayward, CA, USA) ***www.porifera**.com*	Thin film composite	Plate and frame	Commercial
Toyobo Co. Ltd. (Osaka, Japan) *www.**toyobo**-global.com*	Thin film composite	Hollow fiber	Precommercial

Aquaporins are a type of pore forming proteins which allow water passage in cell membranes, while blocking hydrophobic molecules and ions. Aquaporin inside hollow fiber FO membranes utilize the proteins' innate properties for water separation. In a case study that used Aquaporin inside, coffee was concentrated from 2 to 45°Brix with a draw solution of 1.5 M $MgCl_2$. The membrane was reportedly fully recovered by simple water flushing. In a study on the concentration of tea with Aquaporin inside, reverse solute flux was observed. A small concentration of NaCl (0.424 g L^{-1}) ended up in the tea concentrate, but that did not damage the original flavor (Bardhan et al. 2020).

Membrane modules may be configured in several ways, namely plate and frame, spiral wound, tubular, and hollow fiber **(Figure 3)**. Spiral wound FO membrane configurations are similar to commercial RO units, with adjustments to have increased flow. Spiral wound modules are commonly used for wastewater treatment due to their high packing density and small footprint, making this configuration an optimal choice for processing large volumes of feed. However,

membrane fouling poses a significant challenge and pre-treatments are required to first remove the bulk of fouling components. In plate and frame configurations, spacers separate the flat sheet membranes in cassette packages. These modules are advantageous to use for high fouling feeds, but typically have a large footprint and are not suitable for processing high volumes. Tubular and hollow fiber membranes are packed in large bundles to increase the surface to area ratio and density.

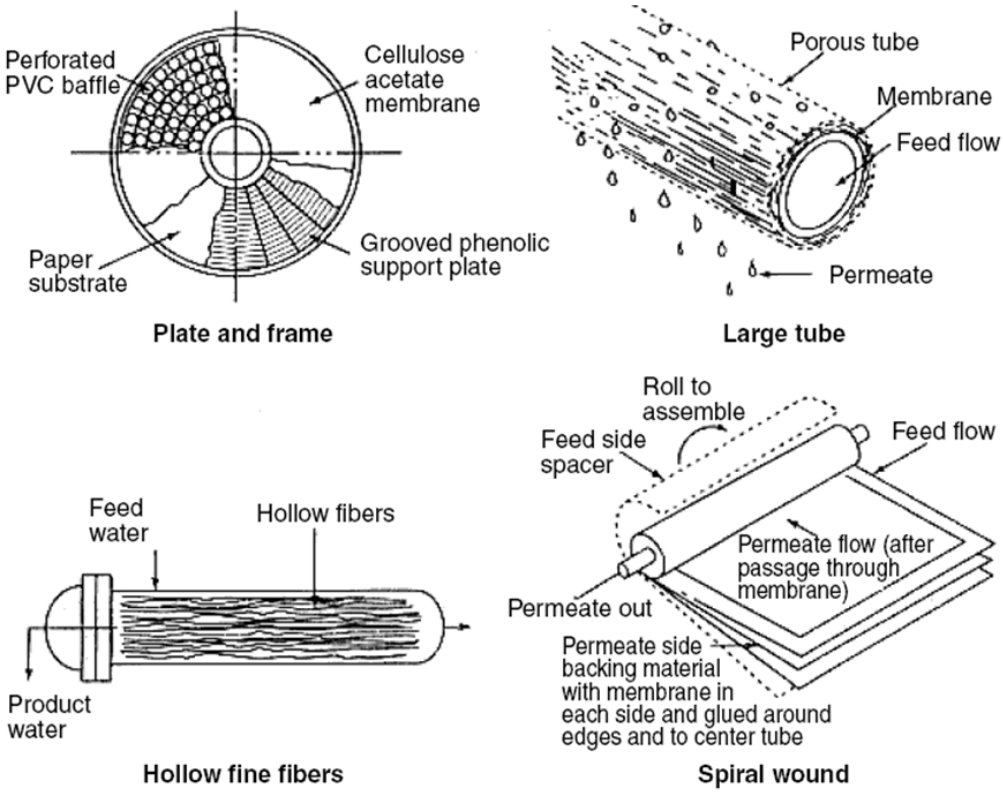

FIGURE 3. DESIGN VARIANTS OF FO MEMBRANE MODULES. FROM (SINCERO & SINCERO, 2003)

Herron et al. (1994) patented the use of an osmotic concentration cell in which the semipermeable membrane dividing the DS and FS is held by rod-shaped support members for a "corrugated" flow path **(Figure 4)**.

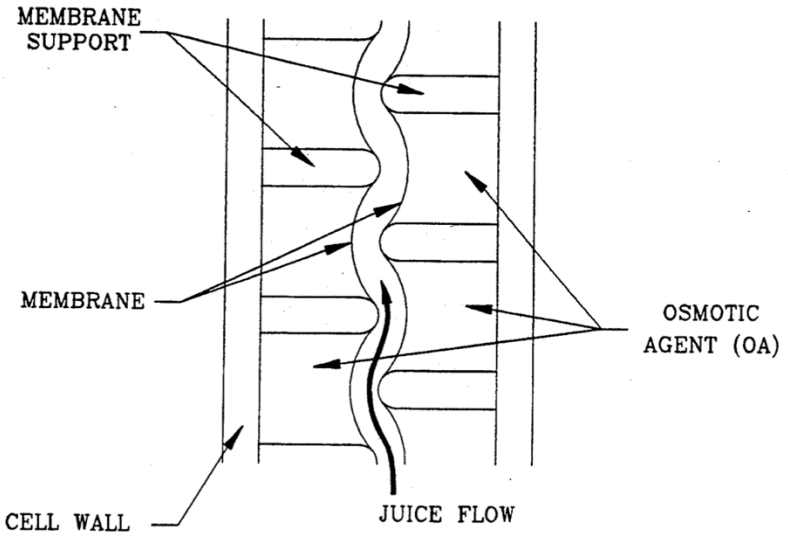

FIGURE 4. SIDE VIEW OF THE OSMOTIC CONCENTRATION CELL PATENTED BY HERRON ET AL. (1994)

3.3. DRAW SOLUTES FOR FORWARD OSMOSIS

The driving force of FO is the osmotic concentration gradient between the concentrated draw solution (DS) and the dilute feed. The DS should have high osmotic pressure, close to neutral pH, be non-toxic, inert, and be easily regenerated (Chun et al., 2017). In concentration of liquid foods, reverse solute diffusion from the DS side to the feed side becomes a concern due to contamination of the feed (product). Thus, the DS must be generally regarded as safe (GRAS) and not degrade the quality of the product if trace concentrations are passing through the membrane. Additional considerations in DS selection include cost, small reverse diffusion rates, chemical

stability, and compatibility with the FO membrane. **Table 3** summarizes the DS used in a few liquid food FO processes.

Inorganic salts meet the criteria of high osmotic pressure, inexpensive, and non-toxic. However, the regeneration of such DS is expensive, they have higher rates of reverse solute diffusion, and can create internal concentration polarization (ICP), which will be defined in the next section. NaCl is often used due to its affordability, low viscosity, and high performance. Having low viscosity reduces severity of ICP. Inorganic salts are sometimes used in conjunction to select for favorable characteristics. $MgCl_2$ has a higher osmotic pressure than NaCl, but is costly. Thus, a binary DS such as NaCl and $MgCl_2$ can be used for a higher osmotic pressure and lower cost than pure $MgCl_2$ (Long et al., 2016). CaCl2, KHCO3, MgCl2, MgSO4, NaHCO3, and CaCl2 have also been tested as DS (Rastogi, 2015).

The drawback to inorganic salt DS is the high rate of reverse solute diffusion. Thus, researchers turned to organic DS like amino acids, sucrose, gluconate salts, and starch (Wenten et al., 2021). Some organic DS have comparable water flux to that of inorganic DS but are less biostable. Generally, organic DS are prone to degradation, microbial spoilage, lower water fluxes, but less reverse solute diffusion compared to in organic DS. Sucrose is often tested as DS for its cheap cost and ease of recovery. However, its deficiencies include high viscosity and ICP, susceptibility to microbial growth and fouling, and caramelization during recovery.

Synthetic DS have been manufactured to address the limitations of organic DS. DS materials include poly-acrylic acid salts (PAA-Na), hydroacid complexes, carboxyethyl amine sodium salts (CASSs), functionalized magnetic nanoparticles (MNPs), thermosensitive and responsive hydrogels (PSA-MBA, PNIPAM-MBA) (Wenton et al., 2021). Synthetic DS produce

favorable water fluxes, but their disadvantage is that they are non-renewable and are costly to produce.

TABLE 3. SUMMARY OF FO FOR LIQUID FOOD CONCENTRATION APPLICATIONS. ADAPTED FROM BARDHAN ET AL. (2020)

Feed solution	Draw solution	Temperature (°C)	Average flux(kg m^{-2} h^{-1})
Grape	8 M NaCl	–	2.5
Coffee	74° Brix fructose/ glucose	–	4
Raspberry	69° Brix Corn syrup	25	1.4
Tomato juice	4 M NaCl	25	3.1
Red Raddish	60° Brix corn syrup	Room temperature	1.2
Pineapple	4 M NaCl	25	1.6
	2.75 M NaCl + 0.9 M sucrose	25	1.15
Sucrose	4 M NaCl	30	5.8
Tomato juice	22.23 w/w% NaCl	Room temperature	3.5
Kokum	6 M NaCl	30	15
Beetroot	6 M NaCl	25	7.5
Pineapple	6 M NaCl	25	6.5
Grape	6 M NaCl	25	4
Orange Press liquor	4 M NaCl	20	11.72
Apple juice	2 M Potassium sorbate	25	5 LMH

It is favorable to have an easily regenerated DS for lower energy consumption and costs. The DS may be recycled in multiple ways, such as thermal processing, membrane filtration, and membrane distillation. Thermal processes can regenerate the DS easily but at the cost of high energy consumption (30-50kWh/m^3). In the thermal recovery of sugar-based DS, organic acids can be added to prevent caramelization (Herron et al., 1994). Membrane processes that can be used to regenerate DS include nanofiltration and RO, which are driven by hydraulic pressure. Membrane distillation is thermally driven and separates vapor through hydrophobic membrane pores.

3.4. Performance of FO and Factors That Affect it

Flux in FO systems is determined by the osmotic concentration gradient represented by the equation below:

$$J_W = A(\Delta\pi - \Delta P)$$

A is the water permeability coefficient of the membrane, $\Delta\pi$ is the osmotic pressure differential across the membrane ($\pi_{draw\ solution} - \pi_{feed}$), and ΔP = the hydraulic pressure difference across the membrane, which is generally negligible in FO.

In FO, the support layer of the membrane and boundary layers created by concentration polarization can reduce the flux. Concentration polarization is the build-up of concentration gradients both inside and around the forward osmosis membrane during operation. These gradients reduce the osmotic pressure difference around the membrane active layer and limits the attainable water flux, thus slowing the concentration efficiency. There are four types of concentration polarization, with two main categories, external concentration polarization (ECP) and internal concentration polarization (ICP), and two subcategories, dilutive and concentrative. **Figure 5** shows the types of concentration polarization in both FO and PRO mode.

In dense, symmetric membranes that reject feed and draw solutes, ECP takes place at the membrane surface. Solutes are concentrated on the surface of the feed side as water permeates through the membrane (concentrative ECP). Solutes are diluted at the surface of the draw side as water enters from the feed side (dilutive ECP).

For asymmetric membranes that have a dense rejection layer (active layer) and an underlying porous support layer, ICP happens in the porous support layer and ECP on the inter-phase between the rejection layer and surrounding solutions. In FO mode (FS facing the active layer), the water permeating through the support layer dilutes the DS inside the support (dilutive ICP) and concentrative ECP takes place on the active layer. When the active layer faces the DS,

the solutes in the support are concentrated as water permeates through the membrane (concentrative ICP). Dilutive ECP takes place on the dense rejection layer.

ECP can be mitigated with cross flow velocity on the active layer side and increasing the temperature. High fluid velocity along with turbulent flow can reduce the effects of fouling and external concentration polarization, even with high solute content feeds (Petrotos et al., 2010, Herron et al., 1994).

While the effects of ECP can be reduced using high fluid velocity coupled with turbulent flow, ICP is dependent on the structure of the support layer and diffusivity of the solute. Thus, there has been research focusing on the improvement of support layer properties relating to porosity and selectivity.

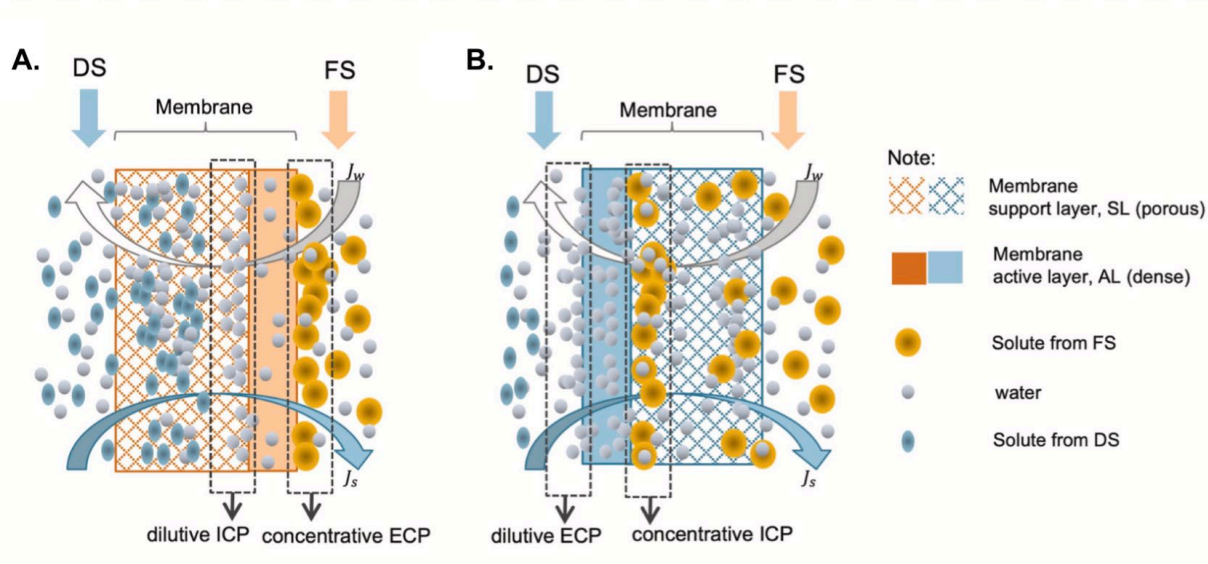

FIGURE 5. ILLUSTRATION OF ICP AND ECP IN FO MODE (A) AND PRO MODE (B). (WENTEN, KHOIRUDDIN, REYNARD, LUGITO, JULIAN, 2021)

MEMBRANE FOULING

Fouling occurs when the membrane becomes obstructed and thus reduces the flux (efficiency of the process). Fouling from FO is relatively easier to remove compared to RO because

the cake layer is not compacted by hydraulic pressure. There are four types of fouling: (1) organic, (2) inorganic, (3) colloidal, (4) biological. A combination can happen simultaneously especially for complex streams and in the presence of proteins that can form a gel layer on the membrane. Fouling is more easily removed in FO mode (AL-FS) than PRO mode (AL-DS) due to the density and porosity.

Most studies on organic fouling in FO processes agree that membrane fouling is nearly fully reversible with physical cleaning methods such as osmotic back flux, hydraulic flushing, and increasing cross-flow velocity. Both hydraulic flushing and osmotic backwashing were found to be more than 95% effective in removing organic fouling and scaling, but did not remove colloidal fouling (Kim, Li, Ghaffour, 2020). Inorganic fouling from the crystallization of soluble salts is almost fully reversible in FO mode, but not in PRO mode. Studies show that rinsing of FO membranes with high cross-flow velocity and low ionic strength solution show high success in reversing fouling as shown by scaling with gypsum, silica, and fouling proteins (Shaffer et al., 2015). In more extreme situations (biofouling or combined fouling), it may be necessary to use a combination of cleaning methods including chemical cleaning (Lan Li, Xing-peng Liu, Hui-qiang Li, 2016).

Organic and colloidal fouling are likely the predominant fouling mechanisms for FO of cold brew coffee. Herron et al. (1994) recovered the membrane between runs of coffee concentration with 5-10 minutes of water flushing. After flushing, no deposits of coffee were visibly left on the membrane. Then, an ULTRASIL cleaner was circulated for 5 minutes between batches then rinsed with water. The observed decline in flux of successive runs was minimal.

In a nanofiltration coffee concentration study, coffee was first centrifuged to remove insoluble particles to reduce membrane fouling (Bingjie Pan, Peng Yan, Lei Zhu, Xianfeng Li,

2013). Another case study on the concentration of coffee aroma using Aquaporin Inside, the membrane was fully recovered with water flushing. A study on the FO concentration of tea extract removed organic foulant deposits by rinsing with 0.1M NaOH for 30 minutes followed by rinsing with deionized water until the TDS of the outlet streams were equivalent to that of DI water (Bardhan et al., 2020).

4. Cold Brew Coffee Concentration: Preliminary Experimental Findings

Currently, there have not been many published studies on the research of FO coffee concentration and none on cold brew coffee concentration. The project objective was to identify potential roadblocks through a literature review, with a small experimental component.

Cold brew coffee sourced from the company Kru coffee was concentrated with a rotary evaporator (BUCHI Rotvapor) under partial vacuum, for about 40 minutes or until the concentrate became viscous, and physicochemical characteristics analyzed. Each batch size was approximately 340 g. The original sample and five concentrated samples **(Figure 6)** were analyzed for °Brix, water activity (a_W), and total solids (at 100°C) in triplicate. The concentrates were then centrifuged at 5,500 rpm for 10 minutes.

After centrifugation of the concentrate, a layer of sediment was observed at the bottom of the sample tubes. The material mainly consists of soluble and insoluble fibers leftover from the coffee extraction. No separation of lipids was found.

The physico-chemical characteristics of the concentrates are shown in the table below.

TABLE 4. PHYSICOCHEMICAL ANALYSIS OF COLD BREW COFFEE CONCENTRATES

Product	Physico-chemical analysis				Centrifugation results
	°Brix (average)	a_W (average± SD)	pH (average± SD)	Total solids (average± SD)	*Settings: 5,500 rpm / 4,000xg / 10 min / 8.85-8.87 g per sample*
Cold Brew	1.78	0.996±0.002	5.05±0.01	1.39±0.05	No visible change or separation
2_10/12/2020	21.0	0.971±0.007	5.32±0.03	18.05±0.15	Least sediment
3_10/9/2020	38.9	0.956±0.002	5.39±0.03	33.72±0.12	Lots of sediment (up to 6 ml line on tube)
1_10/9/2020	39.0	0.958±0.000	5.41±0.02	34.00±0.16	Medium sediment (5 mL line on tube)
2_10/9/2020	44.1	0.946±0.001	5.46±0.02	38.84±0.05	Medium sediment

In this preliminary test of cold brew coffee concentration using the Rotovap, a trace amount of high melting point lipids were found to accumulate on the flask. After three runs of Rotovap concentration, a white "waxy" residue was deposited on the inside of the round bottomed flask shown below in **Figure 7**.

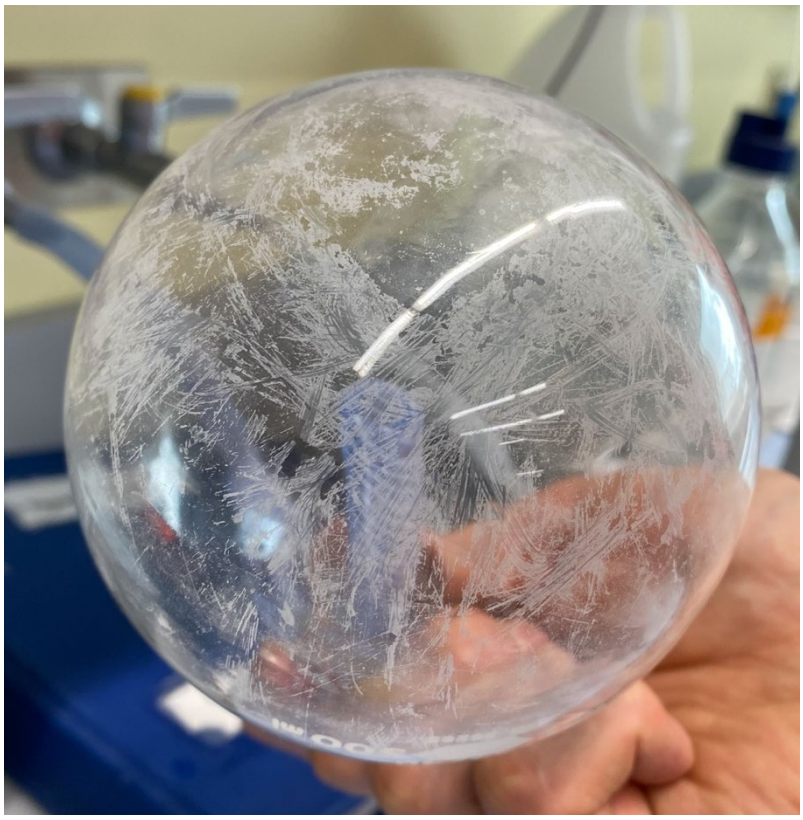

FIGURE 7. DEPOSITS OF HIGH MELTING POINT LIPIDS ON THE INNER SURFACE OF FLASK

This could not be easily removed by detergents or ethanol. Thus, a solution of hexane, acetone, and chloroform (1:1:1) was gently swirled within the flask to remove the residue. After the first extraction, some residue still remained and a second extraction with hexane was used. Both extraction solutions were collected and dehydrated for DSC analysis.

DSC analysis of the coffee concentrates and extracts were performed as follows: 15-110°C at 2°C/minute. DSC results indicate the presence of substances with melting points around 65-75°C and 95-105°C **(Figures 8-9)**.

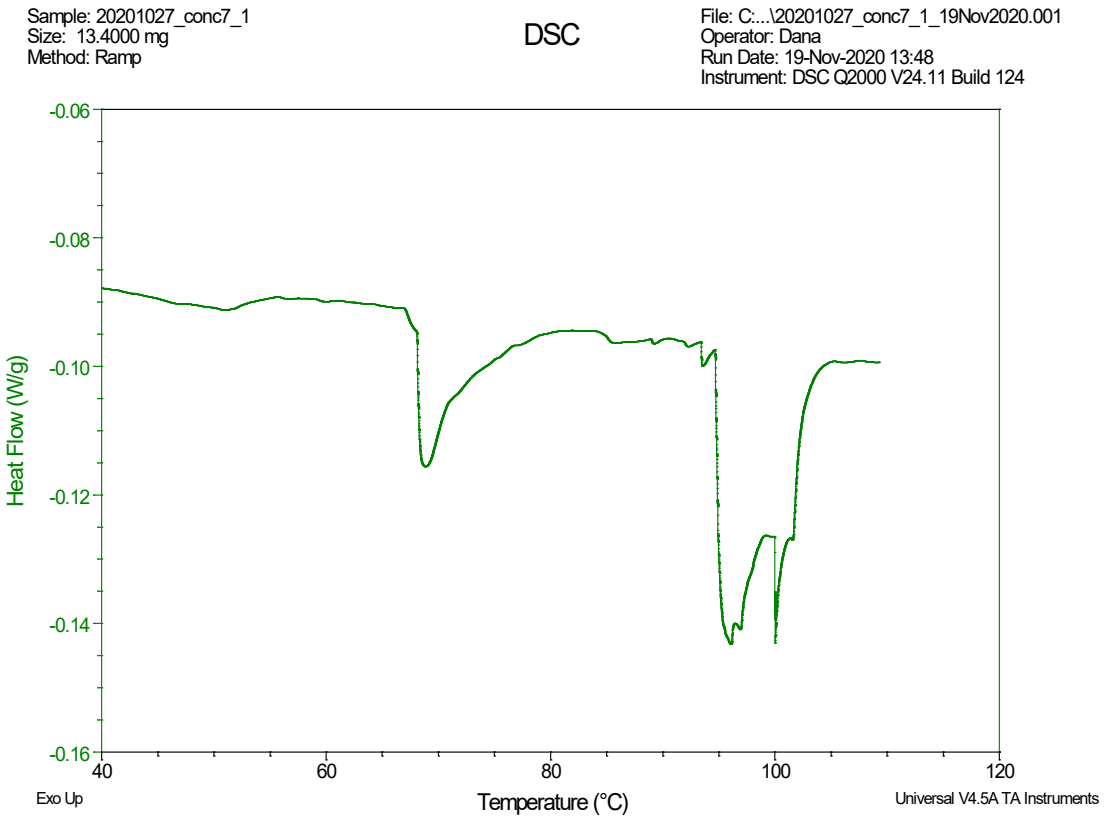

FIGURE 8. DSC THERMOGRAM OF WAX EXTRACT 1

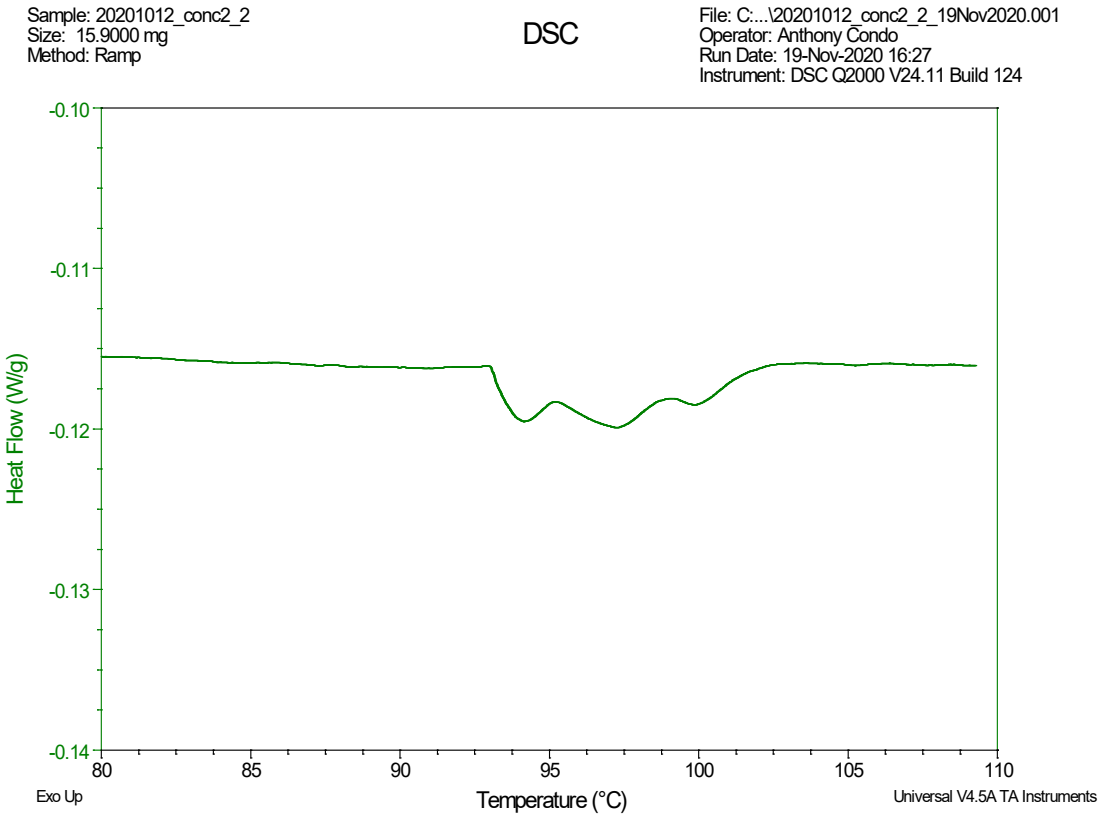

FIGURE 9. DSC THERMOGRAM OF WAX EXTRACT 2

Lastly, particle size analysis was performed on cold brew samples obtained from Kru coffee. The coffee was filtered through a 0.1-0.2 microfiltration filter. Particle fractions of 200 nm and 500 nm were found in the filtered samples. These fractions will require detailed chemical analysis and identification in the future.

OBSERVATIONS AND DISCUSSION

The initial coffee had 1.78 °Brix and 1.39 % total solids, which is very low, but expected from a cold brew in which lower extraction temperatures are used. To achieve a final concentrate of 35-45°Brix, a very long concentration process will be necessary.

Additionally, while FO can concentrate the cold brew coffee to high °Brix, it does not ensure food safety and prevent microbial growth, an the a_W and pH of the samples are within the range susceptible for microbial attack. The original samples and concentrated samples were stored at 4°C for more than a month. Within this time frame, no visible microbial spoilage was observed. However, a formal shelf-life test would be needed for confirm these observational findings. One study evaluated five stabilization techniques (HPP, microfiltration, UV irradiation, pasteurization, and blast chilling) for the shelf-life extension of cold brew coffee (Bellumori et al., 2021. It was found that samples treated with HPP and pasteurization were stable after four months of storage at room temperature. HPP is a potential lead as a method of shelf-life extension without the use of preservatives or heat.

DSC analysis of the waxy residue revealed it to have a high melting point. Although this wax was only found in trace amounts, this may be extremely difficult to remove from the porous membrane surface. This wax is likely a remnant of the outer layer of the coffee bean, which makes up only 0.2-0.3% its total weight. As mentioned before, polishing, dewaxing, steaming, or decaffeinating are methods which can be used to remove the waxy layer from the bean. Filtration steps can be applied to the liquid beverage for further removal of suspended solids and lipids. In a study on oily wastewater treatment (<1 um droplet sizes), an ultrafiltration step was used to remove emulsified oil, suspended solids, and microorganisms (Sui Zhang, Peng Wang, Xiuzhu Fu, Tai-Shung Chung, 2014).

PROPOSED NEXT STEPS

1. Identify the components in the wax residue through analysis of cold brew or roasted coffee beans and develop a treatment for its removal from the cold brew coffee before concentration. A pretreatment of filtration, or centrifugation can be used to remove the

lipid and other insoluble solids to minimize fouling during subsequent membrane concentration.

2. Selection of DS and membrane. Screen for compatible DS that are cost effective, deliver high osmotic pressure, are non-toxic and GRAS, can be easily regenerated, and have low reverse diffusion rates. The chosen membrane should achieve high water flux, reject dissolved solutes and ions, and be compatible with the draw solution. Several studies have shown promise with membranes embedded with aquaporin proteins.
3. Test the efficacy of physical and chemical membrane cleaning methods for membrane regeneration. Current literature on the FO concentration of liquid foods including juices, teas, wines, and coffees have shown simple washing of the membrane with water to reverse almost all fouling of the membrane. However, the presence of high melting point lipids poses a challenge for membrane recovery. More research must be completed to find a suitable cleaning process.
4. Shelf-life and sensory tests are recommended to validate the quality of the final product. Accelerated shelf-life tests can be used to quickly determine which shelf-life extension processes may work the best. Sensory testing is also important to determine if the product is acceptable to the consumer.

CONCLUSIONS

There are increasingly more studies on the physicochemical and sensorial differences on cold and hot brewed coffee. To date, there is sparse literature on non-thermal concentration methods of coffee beverages, much less for cold brew coffee. The combination of quality retention and low operating costs make FO a promising technology for the concentration of heat labile liquid foods, including cold brew coffee. However, there are still many challenges that

must be addressed such as membrane performance, ICP and ECP, and reverse solute diffusion. Further research will create the knowledge and optimize the process for high-quality and cost-effective beverages for consumers to enjoy.

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