EVALUATION OF FORWARD OSMOSIS AND THERMAL CONCENTRATION FOR QUALITY RETENTION OF CHERRY JUICE AND CONCENTRATE

A Thesis

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ABSTRACT

Concentration optimization of cherry juice to 60°Brix was evaluated with forward osmosis (FO) at 26-35°C, and thermal evaporation (TC) under high vacuum at 70°C. Sensory evaluation of juices was conducted by discrimination and descriptive tests. A 10°C increase in temperature in FO concentration increased water flux by 35% and decreased concentration time by 19%. FO yielded higher initial retention of anthocyanins and red color, and similar sensory properties compared to TC. A 12-week shelf life study at room temperature of control, FO and TC samples included analysis of brix, color, phenolics, total anthocyanin, viscosity and major anthocyanins. Stability of anthocyanins and red color in reconstituted (13^{o}Brix) cherry juice samples did not present significant differences due to the concentration process. Anthocyanins and red color losses over time were significantly higher when juices were stored as concentrate. Additional studies on the effect of ascorbic and added flavonoids on anthocyanin stability are recommended.

BIOGRAPHICAL SKETCH

Marcela Patino was raised in Cuenca, Ecuador, the middle daughter of an OB/GYN and farmer. Her initial interest in food science can be explained by the influence of both her parent's professions: the academically - inclined nature of her mom and the practical, down-to-earth perspective of her father. Yet, Marcela's eventual passion for the field stemmed from an innate curiosity in one of the most common activities humans delight in- eating- and from a desire to impact individual's lives on a day-to-day scale. Marcela attended the University of Azuay and obtained a bachelor's degree in Food Engineering in 2011, while interning as quality controller for dairy and sausage companies, and researching industrial safety, making nutritional supplements from dried fruit, and dairy biotechnology, respectively. After graduation, she moved to the United States, and she worked in Minneapolis in pursuit of a position in R&D at General Mills. For two years, Marcela took delight in her work there as a product developer, contributing to the family-oriented company's fruit snacks products. Soon, her drive to further service her team led her to join Cornell University as a graduate student in Dr. Olga Padilla-Zakour's lab. During her time at Cornell, Marcela was a teaching assistant, an undergraduate mentor, a graduate student representative for IFT, and a student representative on the Board of Faculty of Science and Technology. She participated in IFTSA & MARS competitions, in which Cornell placed nationally for their environmentally sustainable banana peel snack, and in 2016, was awarded the IFT Scholarship for Outstanding Achievement in Food Science. She worked for both Kraft-Heinz as a RDQ intern and at PepsiCo as a R&D intern, broadening her horizons with work in reformulating coffee recipes through sensory data analysis and ingredient science of extruded snacks. After completing her Master's in Food Science, with a minor in Applied Economics and Management, Marcela will return to General Mills as a food scientist.

To my beloved mother:

Marcia.

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LIST OF ABBREVIATIONS

FO: Forward Osmosis

TC: Thermal Concentration

C: Control /Fresh cherry juice

C-3R: Cyanidin-3-rutinoside

C-3G: Cyanidin-3-glucoside

C-3GR: Cyanidin-3-glucosyl-rutinoside

C-3S: Cyanidin-3-sophoroside

HPLC: High Performance Liquid Chromatography

CHAPTER 1

INTRODUCTION

Justification

Tart Cherry juice is extensively used in the food industry as a good source of natural antioxidants, which provide protection against harmful free radicals. These properties generated a consumer market with increasing demand. Nonetheless, it has been noticed that shelf-stable tart cherry juice offerings at retail, which declare cherry juice concentrate (from thermal concentration treatment) in their ingredients, generally have less measurable anthocyanins than shelf-stable juice that is not from concentrate. The concentration of cherry juice requires the partial removal of water ideally without any changes in the composition of solids, leaving all or most of the original components such as fruit sugars, phenolics, anthocyanins, minerals and vitamins in the concentrated solution, in order to achieve longer shelf life and reduce storage and transportation costs. Thermal evaporation (TC) is one of the most widely used methods to concentrate cherry juice. However, it leads to the loss of bioactive compounds and fresh juice flavor, color degradation and development of cooked taste. An alternative method is the application of membrane concentration through forward osmosis (FO). This concentration is performed at ambient temperature and pressure, where a draw solution is used to pull the water out of the product. Because no heat is applied to remove water, this innovative technology, based on the natural phenomenon of osmosis, operates under mild conditions, and it can preserve at a higher degree the nutritional and bioactive compounds, the product aroma, flavor and color. Furthermore, it also minimizes energy consumption, reducing costs and the environmental impact of the production processes. Thus, the aim of this study is to evaluate the quality of cherry juice concentrated via TC and FO.

Composition of cherry juice

Sour cherries are good raw material for the production of functional foods, such as juices and concentrates, mainly because they provide a significant content of polyphenols, especially anthocyanins. Additionally, sour cherries contain twice as much ascorbic acid as oranges, and they are high in sugars, tannins and organic acids (Seeram and others 2002).

Table 1. Major sugars, acids and minerals of sour cherry juice. Adapted from Bonerz and others (2006).

Sour Cherry Juice	
Glucose (g/L)	48.7-63.4
Fructose (g/L)	39.6-52.2
Ascorbic acid (mg/L)	43-177
Lactic acid (g/L)	<0.1
Malic acid (g/L)	19-27.4
Citric acid (g/L)	0.08-0.14
Phosphate (mg/L)	526-692
Potassium (mg/L)	2140-3686
Magnesium (mg/L)	148-172
Sodium (mg/L)	2-6
Calcium (mg/L)	267-368

Major components

Phenolic compounds in cherry juice

The total phenolic content of sour cherries ranges from 2704 to 4988 mg gallic acid equivalent (GAE) per kg (Bonerz and others 2006). In a study done by Bonerz and others (2006), in sour cherries from various cultivars the major non-colored phenolic compounds identified were neochlorogenic acid (67–278 mg/kg), chlorogenic acid (6–58 mg/kg), quercetin-3- rutinoside (10–44 mg/kg), p-coumaric acid derivatives (6–41 mg/ kg), quercetin-3-glucoside (2–4 mg/kg), kaempferol-3-rutinoside (0–13 mg/kg) and isorhamnetin-3-rutinoside (3–26 mg/kg). It is important to mention that, in sour cherries, the content of colored-phenolics, i.e., anthocyanins, is

much higher than the colorless phenolic compounds.

Table 2. Major colorless phenolic compounds in sour cherry juice as analyzed by HPLC/UV (mg/L mean for duplicates). Adapted from Bonerz and others (2006).

Colorless phenolic compound	(mg/L)
Neochlorogenic acid	212
Chlorogenic acid	119
Quercetin-3- rutinoside	23
3-coumaroylquimic acid	603
Quercetin-3-glucoside	3
Kaempferol-3-rutinoside	4
Isorhamnetin-3-rutinoside	20

Anthocyanins in cherry juice

Anthocyanidins are aglycones that consist of an aromatic ring [A] attached to a heterocyclic ring [C] that contains oxygen; this C ring is also connected by a carbon–carbon bond to a third aromatic ring [B] (Konczak and Zhang 2004). Anthocyanins are water soluble and unstable compounds derived from anthocyanidins by attaching sugars.

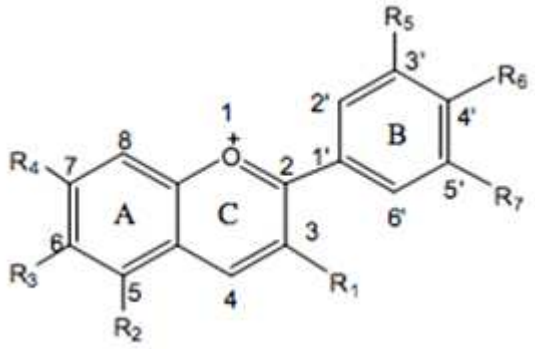

Fig 1. General anthocyanin structure. Adapted from:

https://commons.wikimedia.org/wiki/File:Anthocyanidine.svg

The color shown by an anthocyanin depends on the resonant structure of the flavylium ion (Wrolstad and others 2005). The structure of anthocyanins vary, based on the position and number of hydroxyl groups on the molecule, the degree of methylation of the hydroxyl groups, the type of sugar groups attached to the phenolic ring, and the nature of any aliphatic or aromatic acids attached to the sugar groups (Table 3).

Table 3. Cyanidin substitution pattern. Adapted from: Castañeda-Ovando and others (2008).

Name	Substitution pattern							Color
	R1	R2	R3	R4	R5	R6	R7	
Cyanidin	OH	OH	H	OH	OH	OH	H	Orange Red

A study done by Jakobek and others (2007) reported that sour cherry juice contained only cyanidin based pigments, with the HPLC chromatographs documenting cyanidin-3-glucosylrutinoside as the major anthocyanin, followed by cyanidin-3-rutinoside, cyanidin-3-sophoroside and cyanidin-3-glucoside.

Table 4. Mass fractions of major anthocyanins in sour cherry and its juice. Adapted from: Repajic and others (2015).

Cy-3-glu equivalents (mg/g)	Fresh Fruit			Juice		
cyanidin-3-glucosylrutinoside	1.32	±	0.08	2.62	±	0.08
cyanidin-3-rutinoside	0.72	±	0.04	1.18	±	0.04
cyanidin-3-sophoroside	0.13	±	0.01	0.25	±	0.01
cyaniding-3-glucoside	0.008	±	0.001	0.01	±	0.001

Anthocyanin from tart cherry juice and human health

Various studies promote the consumption of sour cherry juice, mainly because of several associated beneficial effects in human health. These benefits include a high antioxidant potential and novel antioxidant compounds present in cherry juice that help to fight free radicals (Chen

and others 1996; Rice-Evans and others 1996; Wang and others 1999). Additionally, research has shown that the ingestion of cherry juice helps to decrease inflammation and muscle soreness, provides greater strength following exercise (Connolly and others 2006; Saric and others 2009), decreases sugar, fat and insulin levels in the blood (Seymour 2009), improves sleep (Pigeon and others 2009) and might have beneficial effects against colon cancer (Kamei and others 1995; Kang and others 2003; Bobe and others 2006; Garrido and others 2010).

Factors affecting stability of anthocyanin in cherry juice

Anthocyanin's stability is influenced by temperature, light, pH, phenolic compounds, sugar and sugar degradation products, oxygen, ascorbic acid, structure and concentration of anthocyanins, presence of complexing compounds (flavonoids, salts, metals, proteins) and oxidative enzymes (Markakis 1982). The stability of anthocyanidin compounds is influenced by the B ring substituents and the presence of additional hydroxyl or methoxyl groups, which decrease the aglycone stability in neutral media (Fleschhut and others 2006). Previous studies had demonstrated that some acids lower anthocyanin color stability. For instance, a high concentration of ascorbic acid (AA) has negative impact on anthocyanin stability because AA and its degradation by-products accelerate degradation of purple sweet potato anthocyanin and anthocyanin extracts from acerola during storage (Rosso VVD 1999; Li J and others 2014).

Color stability of anthocyanins during storage

Studies have found that during storage the addition of sugars benefits the color stability of anthocyanins in rich black currant and elderberry concentrates presumably by reducing water activity. Nowicka and Wojdyło (2016) showed that the addition of some natural sweeteners additives (palm sugar, erythritol, steviol glycoside, xylitol and inulin) in sour cherry juice puree, can have a protective effect on polyphenol content, especially on anthocyanins and consequently

on color, and antioxidant activity, after 6 months of shelf life. However, when heat treatment was applied, fructose was shown to accelerate anthocyanin decay due to the formation of sugar degradation products, such as furfural and hydroxymethylfurfural (HMF) that proved to favor pigment decay (Hubberman and others 2006). Also, a study done by Navruz and others (2016), showed that the addition of phenolic compounds such as gallic acid (GA) to sour cherry juice concentrates, increased the stability by 37% for cyanidin-3-rutinoside and 53% for cyanidin-3-glucosylrutinoside.

Importance of anthocyanin in color retention for the food industry

Anthocyanins are responsible for the attractive red color of sour cherry products such as juice and juice concentrate, in addition to the positive effect on human health. Color may be one of the most important attributes that directly influences preference, selection and eating desires of the consumers (Delgado and Paredes 2003). The consumption of naturally-derived colorants has increased significantly, primarily related to their image of healthy, safe and good quality products, which constitutes a great challenge to food industries (Carocho and others 2014). Anthocyanins can be easily incorporated in aqueous media, hence their use as natural water-soluble colorants in juices (Pazmiño and others 2001). Nonetheless, they are unstable to heat, oxygen, and light and have reduced chemical stability, therefore the goal in the food industry is to make juices more attractive to consumers by minimizing losses of nutritional compounds and by preserving the visual appearance across processing, storage and transportation.

Thermal processing in juice concentration

Fruit juices are generally thermally evaporated using vacuum to improve shelf life, reduce storage and transportation costs. Thermal processing is one of the most widely used methods of evaporation. It applies high temperatures (50 to 150 °C) during processing to achieve a high concentration in a relatively short time. Previous studies have shown that evaporative concentration of fluid food results in heat induced deterioration of sensory and nutritional quality of finished product. This includes decrease in the stability of anthocyanins, degradation of color, loss of fresh juice flavors and development of cooked taste due to thermal treatment, and subsequent storage conditions may cause substantial changes in bioactive compounds. (Bhaskara and others 2006). Additionally, the use of vacuum evaporation for juice concentration is highly energy-intensive (Petrotos and Lazarides 2001).

Forward osmosis in juice concentration

Fruit juice concentrate prepared by forward osmosis (FO) was demonstrated to be of superior quality in comparison with juice concentrated by vacuum evaporator (Herron and others 1994). During FO concentration, water is transported from the lower osmotic pressure solution (feed) to the higher osmotic pressure solution (draw solution). This concentration is performed at ambient temperature and pressure, and the difference of the water chemical potential between the feed and draw solution, separated by a semi-permeable hydrophilic membrane, is the only driven force that pulls the water part of the product, and it is expressed in terms of osmotic pressure (Nayak and Rastogi 2010). Therefore, because no heat is applied to remove water, this novel technology operates under mild conditions, which ensures not only a higher preservation of the product quality properties (Popper and others 1966; Bolin and others 1971; Loeb and Bloch

1973; Rodriguez-Saona and others 2001; Babu and others 2006; Nayak and Rastogi 2010; Nayak and others 2011; Zhao and others 2012a, b), but also a low energy consumption (Kravath and Davis 1975), which leads to a reduction of the costs and the environmental impact of the production processes. (Cath and others 2006; Sant'Anna and others 2012; Zhao and others 2012a).

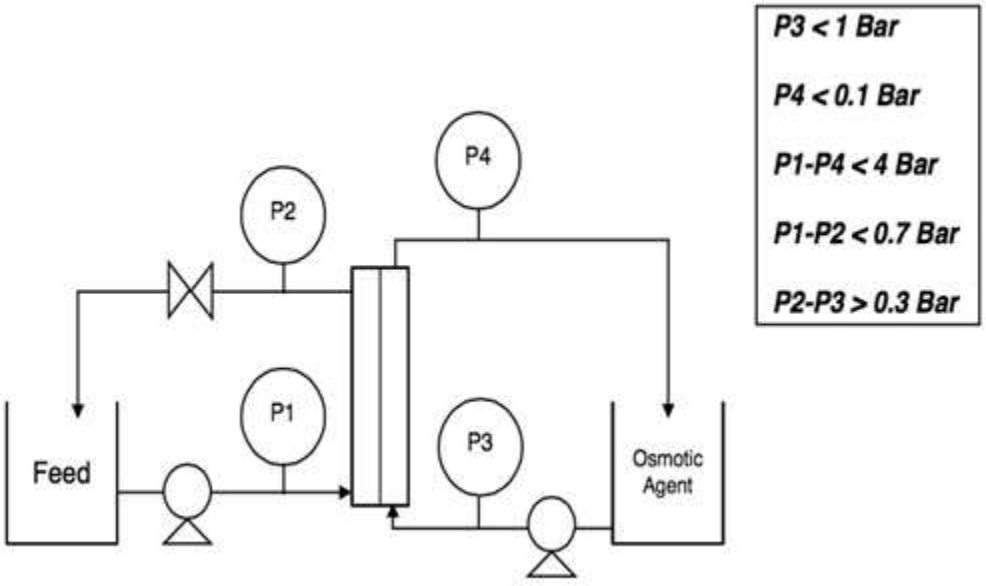

Fig 2. Design and pressure guidelines of forward osmosis Ederna equipment. E2.5x20 Module Datasheet (V1/07.2014). www.ederna.com

Asymmetric membrane in Forward Osmosis

FO membrane separates the feed solution and draw solution (osmotic agent, OA), where a balance of the partial pressure takes place between the two solutions. The build-up of concentration gradients both inside and around forward osmosis membranes during operation is known as concentration polarization. This can be internal or external and have two sub-

categories; dilutive and concentrative (Cath and others 2006). Asymmetric membranes used in FO consist of two layers: the active layer (a high-density layer for high solute rejection) and a loosely bound support layer (a thin membrane with minimum porosity for low internal concentration polarization); this creates a high external concentration polarization on the interphase between the active layer and surrounding solutions, thus higher water flux (McCutcheon and Elimelech 2006).

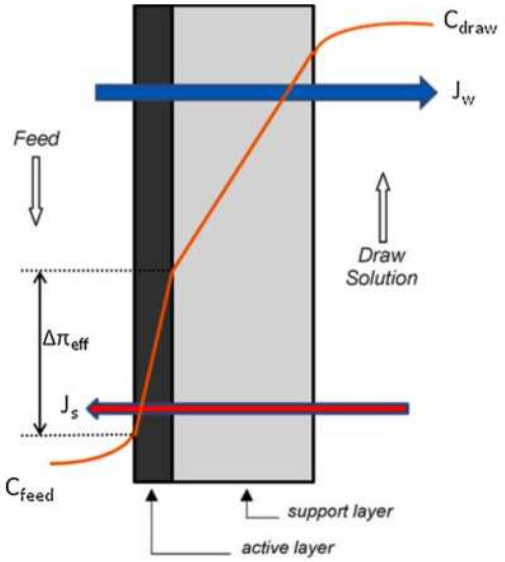

Fig 3. Dilutive internal concentration polarization across an asymmetric membrane in forward osmosis with active layer facing the feed solution. C_{feed}, C_{draw}, $\Delta\pi_{eff}$ and J_w symbolize the feed solution concentration, draw solution concentration, effective driving force and water flux, respectively. Adapted from Zhao (2012a).

The improvement of water flux in FO has been related to an increase in temperature. However, limitations have been found due to the severity of internal and external concentration polarization at higher fluxes. High internal concentration polarization in the support layer together with a high internal clogging of the FO support structure were related to loss of water

flux (Li and others 2011a). Zhao and Zou (2011a), demonstrated that internal concentration polarization in the support layer was strongly dependent on the physical-chemical properties of the solution facing the support layer.

Draw Solution in Forward Osmosis

An efficient concentration through FO would depend on the correct selection of the draw solution (OA). Important factors to consider are: OA should have higher osmotic pressure than the feed solution to produce high water flux, it should be water-soluble, solid at ambient temperature and pressure, should be safe to handle, and cost-effective to ensure economic applicability of the FO process.

Scale Up in Forward Osmosis

The retention of product quality and at the same time the economical feasibility of application have led to the development of unconventional concentration techniques such as FO. Research has shown that with the application of FO, the capital and operating costs at a commercial-scale water treatment concentration plant are lower in comparison with pressure-driven membrane processes, such as reverse osmosis. Forward osmosis uses significantly less electric energy if the osmotic agent solution can be easily recovered or discarded thus using less or lower input energy (Garcia-Castello and others 2009). The recovery or disposal of osmotic agent solution may incur high energy or capital costs, which are considered as necessary problems and require a proper evaluation before this technology can be used on a wider scale (McCutcheon and others 2005).

Objectives

From preliminary studies we have observed that shelf-stable tart cherry juice offerings at retail, which declare cherry juice concentrate in their ingredients, generally have less measurable anthocyanins than shelf-stable juice that is not from concentrate. Similarly, packaged cherry

juice concentrate available at retail exhibits less anthocyanins (on a single strength basis) than single strength packaged juices (both from concentrate and not from concentrate).

Therefore the purpose of this study is to:

1. Evaluate forward osmosis method vs thermal concentration as an alternative method to produce cherry juice with a higher concentration of anthocyanin, target brix, and better cost efficiency.

2. Perform a shelf life study to determine if anthocyanins are more stable over storage time in single strength juice prepared by forward osmosis or by thermal concentration.

3. Evaluate the stability of anthocyanins over storage time in single strength cherry juice and in concentrate.

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CHAPTER 2

EVALUATION OF FORWARD OSMOSIS AND THERMAL CONCENTRATON FOR QUALITY RETENTION OF CHERRY JUICE AND CONCENTRATE

Abstract

The aim of this study was to study tart cherry juice concentrated through forward osmosis and thermal concentration, in order to determine and analyze the effect of processing variables of temperature and pressure on juice composition, and the impact of storing juice and concentrate on quality parameters.

Optimization of concentration to 60°Brix was evaluated with an Ederna forward osmosis (FO) unit at 1.7-2.7 Bars and 26-35°C, and thermal concentration (TC) under vacuum at 70°C. A 12 week shelf life study at room temperature of juice and concentrate included analysis of brix, color (spectrophotometric method), total phenolic content (Folin-Ciocalteu reagent method), total anthocyanins (pH differential method), pH and viscosity. Stability of major anthocyanins in untreated (control), FO and TC samples was determined with HPLC. Sensory evaluation of juices was performed using discrimination and descriptive tests. A 10^{o}C increase in temperature in FO concentration, increased water flux by 35% and decreased concentration time by 19%. Concentration of cherry juice using FO has advantages over TC in terms of higher retention of anthocyanins, red color, and similar sensory properties. Stability of anthocyanins and red color at 520 nm in reconstituted (13^{o}Brix) cherry juice samples did not present significant differences due to the concentration process. Anthocyanins and red color at 520 nm losses over time were significantly higher when juices were stored as concentrate. The concentration of cherry juice by using FO represents a feasible option to process heat sensitive juices at low temperatures to maintain the nutritional and overall quality of the juice, as anthocyanin content and sensory attributes are fully preserved.

MATERIALS AND METHODS

Chemicals and reagents

Anthocyanin standards of cyanidin-3-sophoroside, cyanidin-3-glucosylrutinoside, cyanidin-3-glucoside, and cyanidin-3-rutinoside were obtained from Extrasynthese (Genay, France). Organic solvents used for high performance liquid chromatography (HPLC) were 99.8+% grade methanol, obtained from Alfa Aesar (Ward Hill, MA), 99.9% grade ethyl acetate from Fisher Scientific (FairLaw, NJ) and 99.98% grade acetonitrile purchased from OmniSolv EMD Chemicals Inc. (Gibbstown, NJ). All other chemicals were reagent grade, sodium acetate was purchased from VWR international (Solon OH), hydrochloric acid was purchased from VWR International (Radnor, PA), phosphoric acid was obtained from Mallinckrodt Baker Inc (Phillipsburg, NJ), potassium chloride was obtained from Fisher Scientific (FairLaw, NJ), folin-ciocalteau reagent, gallic acid and sodium carbonate were obtained from Sigma Chemical (St Louis, MO). McIlvaine's buffer was analytical grade and obtained from LabChem Inc (Pittsburgh, PA). Chemicals were used directly as received from the manufacturer.

Sour cherry juice

Sour cherry juice, *Prunus cerasus L* blend of varieties grown in the northeast of NY state, was supplied from a juice manufacturing facility in NY. Freshly prepared juice samples were collected in high-density polyethylene food grade buckets and stored at 1.6°C, for less than one day, before conducting experiments. Juice at 13.8±0.1°Brix was used to produce the concentrates with a total soluble solids content of 60±1°Brix.

Forward osmosis concentration of cherry juice

The forward osmosis (FO) treatments were performed on a bench scale Ederna Lab Unit consisting of stainless steel assembly, equipped with 30 L tank with a gear pump designed to contain the osmotic agent (OA), a gear pump for sample circulation, a stainless housing for Ederna membranes. The membrane used was proprietary Ederna type E+ (cellulose triacetate, FDA compliant) with a working area of 0.5 m^2.

Modifications were performed to allow the production of larger volumes at controlled temperature of 25-35°C, a 20 L tank was adapted to contain feed solution, and a plate heat exchanger (AGC engineering PR0013) was connected for sample temperature control. The OA was purchased from Ederna (H□Os™) as a concentrated potassium lactate solution and adjusted to 61°Brix before starting the concentration process.

Cherry juice and OA solution were run in a closed loop until achieving a juice Brix of 60±1. For the FO pressure and temperature optimization study, a volume of 8 L of fresh cherry juice was processed per batch to obtain a final concentrate volume of 1.0±0.1 L. For the shelf life study an initial volume of 20 L of fresh cherry juice was processed per lot to obtain a final concentrate volume of 2.7±0.2 L. The water flux was calculated by measuring the difference between the increasing weight of OA out from the system and decrease in weight of OA into the system, once every 10 min. The temperature of feed solution was measured using a calibrated thermometer from the Ederna Lab Unit operating system. The membrane was oriented with the cherry juice against the membrane selective layer and the osmotic agent solution against the membrane support layer. This minimizes internal concentration polarization and abrasive effects of food compounds in the support layer.

Table 5. Technical specifications of Ederna forward osmosis system. Adapted from: www.ederna.com

Dimensions (W x H x D)	50 x 90 x 30 cm Installed on a lab bench. Excluding osmotic agent tank.
Net weight	19 kg
Voltage	220/240 V
Frequency	50/60 Hz
Power consumption	200 W
Maximum pump rotation speed	2700 rpm
Acceptable temperature range	5-40 °C
Maximum pressure	4 Bars

Thermal concentrate of cherry juice and variable optimization sample preparation

The first stage consisted of optimizing the osmotic pressure difference between feed and osmotic agent, and feed temperature for cherry juice processing A total volume of 1.2 L of cherry juice was thermally concentrated (TC) using a vacuum rotary evaporator (BUCHI, R-114, 2 L capacity) at 70°C and 609.6 Torr of vacuum to achieve 61.0±2.9°Brix and a final volume of 0.85±0.02 L. Fresh cherry juice (C), FO concentrate samples were kept in glass bottles and covered with aluminum foil; whereas TC cherry juice concentrate samples were collected in amber bottles. Both, FO and TC, treatment samples were stored at 0-4°C. Quality analyses were carried out in triplicates, after 1 or 2 days of each concentration process.

Thermal concentration of cherry juice and shelf life sample preparation

The second part of this study consisted on the analysis of quality parameters during storage of fresh juice, concentrates and reconstituted juices. A volume of 15 L of cherry juice per batch was concentrated in a stainless steel steam jacketed kettle with vacuum and agitation (GROEN, DNTA 10SP, 38 L capacity), concentrations were done maintaining 70°C at 609.6 Torr of vacuum until 65.0±0.1°Brix was reached obtaining a final volume of 2.25 L. Fresh cherry juice (C), FO concentrate, TC concentrate and reconstituted single strength juices to 13°Brix from

FO and TC treatments were pasteurized in a heat exchanger (MicroThermics unit, 25HV UHT/HTSL) at 90°C for 15 seconds, hot packed in 8 oz PET bottles, capped and inverted for 3 min, cooled in a water bath at 40°C and stored at room temperature (21°C) protected against light. Samples were pulled for quality analysis every three weeks.

Sensory analysis of cherry juice

Consumers

Consumers were recruited from the Cornell Sensory testing database to participate in a cherry juice sensory evaluation test. Participants were scheduled using doodle poll with a maximum of 8 participants each 15 min section with no delay on the test time. Walk-ins were also allowed in this study as there was no particular requirement to participate except that participants must have no allergies or intolerances to cherry juice. Sensory evaluation was conducted at the Cornell Sensory testing facility with 60 participants, man and women, ages 18+.

Test design and evaluation

Sensory evaluation was conducted following the guidelines and policies of the Cornell Institutional Review Board for Human Participants. RedJade software (RedJade ®, Redwood Shores, CA, USA) was used to design the test, questionnaires and to collect data. At the beginning of the test, each participant had to accept the participant study agreement in order to continue with the study. In this agreement, participants had a description of the research, risk and benefits of performing the study, confidentiality protection and contact emails in case of any concern. Sensory evaluation of fresh cherry juice and reconstituted juices from FO and TC treatments was conducted after 1-week of storage. Juice was kept at 4°C and served at room temperature, in 5 oz white plastic cups labeled with 3-digit random codes. About 30 ml of the test sample, maintaining a headspace, was poured into the labeled cup. Standard light, filtered water and plain crackers were available during the test. Each participant rated sensory attributes of color, appearance, flavor/taste and overall perception by using discrimination test with 9-

point hedonic scale and descriptive test evaluation. Participants received a $5 reward for their participation.

Statistical analysis of sensory data

Data was collected with RedJade software (RedJade ®, Redwood Shores, CA, USA). Software JMP® version 12.0 (SAS Institute, Cary, USA) was used to statistically analyzed data with pair T-Test and categorical comparison.

QUALITY ANALYSIS

Measurement of anthocyanins by UV-visible spectroscopy

Method described by Giusti and Wrolstad (2001) was followed. Anthocyanin pigments undergo reversible structural transformations with a change in pH manifested by strikingly different absorbance spectra. The colored oxonium form predominated at pH 1.0 and the colorless hemiketal form at pH 4.5. The pH differential method is based on this reaction, and permits accurate and rapid measurement of the total anthocyanins, even in the presence of polymerized degraded pigments and other interfering compounds. Potassium chloride 0.025 M buffer, pH 1.0 and 0.4 M sodium acetate buffer, pH 4.5 were prepared. Cherry juice concentrate by FO and TC were used to prepare two dilutions per sample, one with potassium buffer, pH 1.0 and the other with sodium acetate buffer, pH 4.5, by taking 0.3 ml of each sample into 2.5ml of buffer. Solutions were set to equilibrate for 15 min. The absorbance of each dilution was measured in Ultra Scan VIS – HunterLab spectrophotometer, at the vis-max and at 700 nm, against a blank cell filled with distilled water. The absorbance of diluted sample (A) was calculated by using the following formula:

$$A = (A_{vis\text{-}max} - A_{700})_{pH1.0} - (A_{vis\text{-}max} - A_{700})_{pH4.5}$$

The monomeric anthocyanin pigment concentration in the original samples was calculated as

follows utilizing cyanidin-3-glucoside anthocyanin as the reference:

Monomeric pigment (mg/liter) = (A* MW * DF *1000 / ξ *1)

Molecular Weight = MW= 449.2 g/mol

Dilution Factor = DF = 2.5/0.3= 8.33

Molar absorptivity= ξ = 26900

Determination of total phenolic compounds

Total phenolics where measured following the procedure of Singleton and Rossi (1965), using the Folin-Ciocalteau reagent. Standard curve was obtained by preparing, in a 100 ml volumetric flask, a working solution of gallic acid by first dissolving 0.5 g of gallic acid in 10 ml of 100% ethanol and diluting to 100 ml using dH_2O. Five point-curve plus zero point was obtained by adding 0, 0.2, 0.4, 0.6, 0.8, 1.0 ml of the working solution individually to six separate 50 ml volumetric flasks. This made a standard curve consisting of 0, 20, 40, 60, 80, 100 ppm points. Measurements at 765 nm were taken using test tubes and 40 ul of standard sample or water (to serve as a blank), 520 ul of dH_2O, 40 ul of Folin-Ciocalteau reagent and vortexed, followed by incubation at room temperature for 6 min. Then 400 ul of sodium carbonate solution were added, vortexed, incubated for 90 min at room temperature, and measured at A_{765} against the 0 point of the standard curve as the blank. Lastly the curve was plot and the total phenol content in samples was calculated and reported as gallic acid equivalents (GAE) in ppm.

pH, viscosity and total soluble solids

The pH of the samples was measured using a pH meter (Thermo Scientific Ross Sure-Flow pH Meter). Viscosities of the samples were measured using Brookfield DV-III Plus Ultra

Viscometer using spindle V-72 and V-73. The total soluble solids (TSS) of the samples were measured as °Brix using a Leica Auto ABBE Benchtop Refractometer at 25 ± 2°C.

Color determination of cherry juice

For red juices, industry standard is to measure corrected absorbancy (CA) at 530 nm and 430 nm (Welch's Company, personal communication). Color values of FO and TC samples were measured using a spectrophotometer (Thermo Scientific- GENESYS 10S UV-VIS), were the optical density (OD) of a dilute solution of product was calculated. Dilute solutions were used in color measurement work in order that OD be measured within the linear range. Dilutions were made in buffer (pH 3.2) in order to minimize the effect of pH on color. Distilled water was used to zero the colorimeter. A volume of 1350 ul of each sample was diluted into 50 ml volumetric flask with 4.6 ml of McIlvaine's buffer 3.2; followed by 15min rest time. Readings were taken at A_{520nm} and $A_{430nm.}$ The aliquot of original samples was chosen so that upon dilution with the buffer solution, the resulting optical density reading felt within a range of 0.3 - 0.7 OD.

HPLC analysis of anthocyanins

High Performance Liquid Chromatography (HPLC) technique was followed according to a method originally modified by Manns and Mansfield (2012). Analysis of relevant anthocyanins in fresh cherry juice, juice concentrates and reconstituted juices from FO and TC treatments were evaluated every six weeks. After conditioning the cartridge with 100% MeOH and 0.1N HCl, three replicates of each sample of 2 ml each were loaded, rinsed with 1 ml of 0.01N HCl, then 40 ml of 95:5 acetonitrile:0.01N HCl. Each sample wash was drained under gravity and collected for evaporation. The residue was extracted three times with 3 ml of ethyl acetate, centrifuged, and the remainder acetonitrile extract was re-suspended in 1 ml of 0.01N HCl,

filter through 0.22 um polyethersulfone (PES) membrane into an HPLC vial. All juice concentrate samples were analyzed on the HPLC system the same day they were prepared. The analytical HPLC system employed was a Hewlett Packard 1100 Series with ChemStation software for LC 3D systems Rev. B.04.03[16]. Anthocyanin compounds separation was done in a Microsorb, C18, HPLC Column from Rainin Instrument Company. Elution was performed with a mobile phase A1 consisting of water:phosphoric acid (99.5:0.5) and mobile phase B2 consisting of acetonitrile:water:phosphoric acid (50:49.5:0.5). Operating conditions were as follows: flow rate of solvents 2 ml/min, 30°C column temperature, 20 ul injection volume of standards and samples. A 3 min re-equilibration period was used between individual runs. UV-VIS spectra were recorded at 520 nm. Quantification of mass fractions of individual anthocyanin in cherry juice, concentrate and reconstituted samples was based on comparison of their retention times and total area with those of authentic standards.

Table 6. High Performance Liquid Chromatography mobile phase gradient. Adapted from Manns and Mansfield (2012).

Time (min)	%B (ACN:H2O:H_3PO4) (50: 49.5: 0.5)	Flow (ml/min)	Max.Press (Bars)
0	5	2	300
0.01	5	2	300
13	30	2	300
16.5	65	2	300
17.5	100	2	300
19.5	100	2	300
20.5	5	2	300

DATA ANALYSIS

Variable optimization data analysis

For the study of the optimization of feed temperature and pressure difference between feed and osmotic agent, a factorial 2^2 design was carried out. Four different FO cherry juice concentration treatments were carried in triplicates (Table 6). Responses of water flux, cost, anthocyanins, phenolics, color, pH and viscosity were compared within each other and against TC using JMP® version 12.0 (SAS Institute, Cary, USA). Data were analyzed through one-way ANOVA and followed by multiple comparisons, using student T, and differences were statistically significant when $p<0.05$. Graphical plots were obtained using Microsoft Excel 14.7.1.

Shelf life data analysis

With statistical software JMP® version 12.0 (SAS Institute, Cary, USA), the study evaluated the stability of quality parameters (anthocyanins, phenolics, color) of fresh cherry juice against reconstituted juices from FO and TC treatments, as well as concentrates and reconstituted juices from FO and TC treatments. The 12-week storage results were evaluated with one-way ANOVA, with T student as a repeated measure by multiple comparisons with Bonferroni correction $p<0.001$ and $p<0.0007$. Similarly, the stability of relevant anthocyanin was analyzed by one-way ANOVA using student T, and differences were statistically significant when Bonferroni $p<0.002$ and $p<0.001$. Graphical plots were obtained using Microsoft Excel 14.7.1.

RESULTS AND DISCUSSION

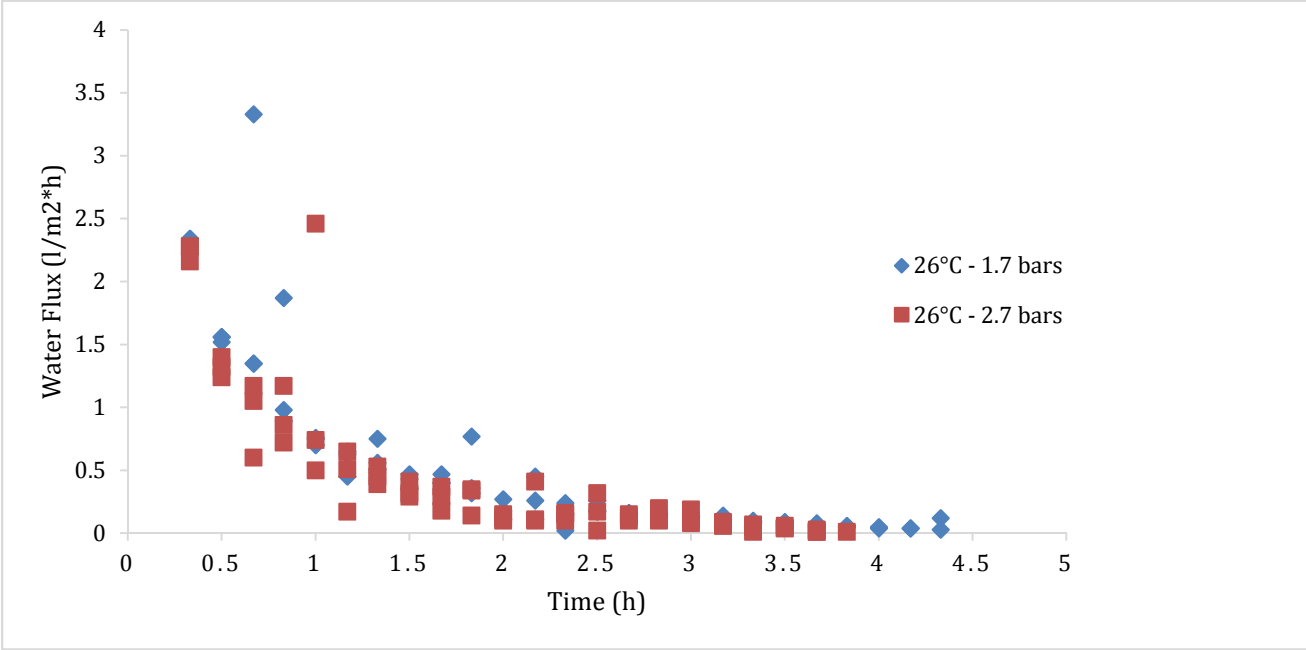
Variable optimization

An essential step for an effective utilization of FO in the food industry is the study of the optimum process parameters of feed temperature and osmotic pressure difference between feed and osmotic agent, on water flux (table 7) and quality effects in the juice concentrate (table 8). Initially, a full factorial statistical analysis was completed with all FO treatments showing that the two processing variables did not have a significant interaction with each other across quality parameters, and that only temperature had a significant effect on water flux (pressure difference did not, $p>0.05$). Figure 4 shows the water flux obtained during different FO concentrations of cherry juice. Initially, a high water flux was recorded but after one hour it decreased dramatically by an average of 74.0±4.6% for all FO treatments. This initial drop in water flux can be the result of a continuous deposit of high molecular weight compounds on the membrane's dense surface, building up an intense concentration of the feed, substantially increasing the osmotic pressure of the solution and negatively affecting the water transmembrane flux (Sant'Anna and others 2016). After this initial decrease, the water flux declines more steadily as the cherry juice becomes more concentrated increasing its osmotic pressure and reducing the FO driving force across the membrane (Sant'Anna and others 2016). Results from different studies (McCutcheon and Elimelech 2006; Gray and others 2006) confirmed that internal concentration polarization is the cause of the substantial flux decline. Statistical analysis showed that the effect of temperature on water flux is significantly different between treatments. Table 7 shows an increase in temperature from 26 to 35°C resulted in a significant ($p<0.05$) increase of 35% in the average water flux (2.68±0.14; 3.62±0.01 respectively). A similar trend was found in a study conducted by Babu and others (2006), where 74.0±4.6% increase in water flux was observed with an increase in temperature from 25

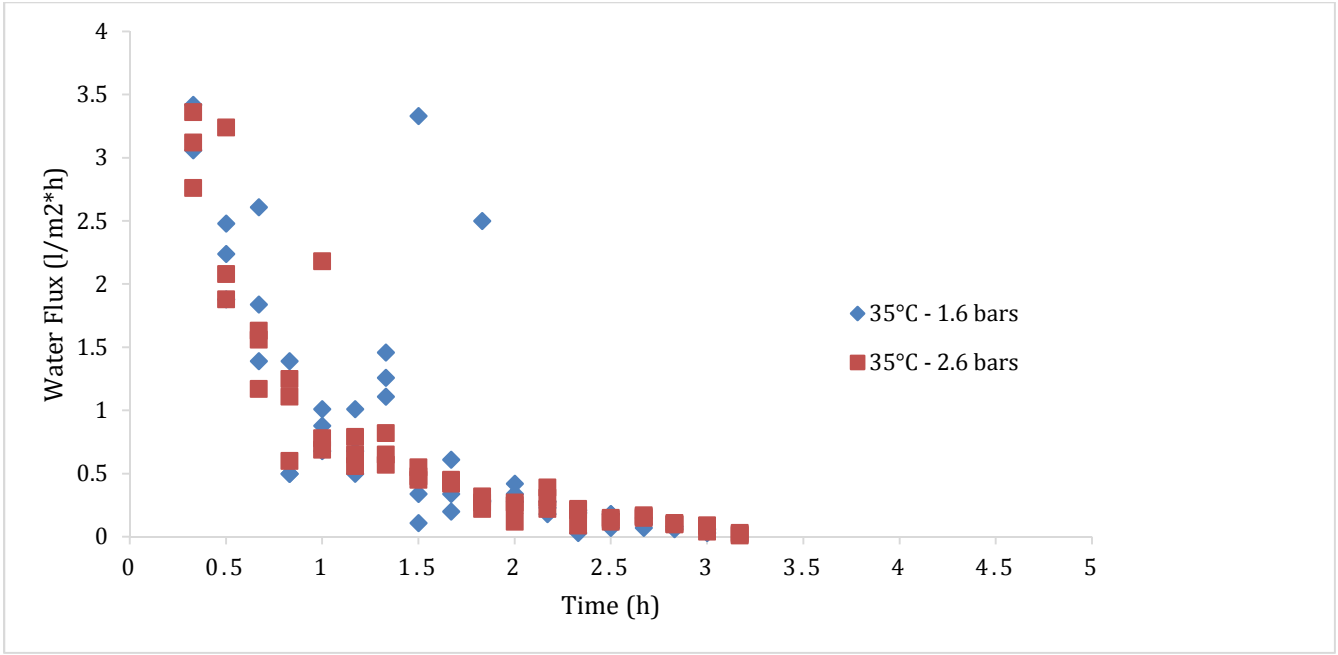
to 45°C in FO concentration of pineapple juice. The increase in temperature lowers the viscosity of solutions and increases the diffusion coefficients, which results in an increase in trans membrane flux (Petrotos and others 1998). Since temperature variation in the FO process did not have a significant effect ($p>0.05$) in quality parameters (anthocyanin, color, phenolics, viscosity), all FO treatments were grouped as one treatment and compared to the thermal concentration (TC) process. The results form physico-chemical properties are summarized in table 8. Statistical analysis indicated that there is a significant difference ($p<0.05$) between FO and TC on cherry juice quality, primarily on anthocyanin, red-color at 520 nm and viscosity. No significant changes were seen in phenolics or color at 430 nm. Figure 5 shows a significantly higher retention of anthocyanins in FO (93.4%) than in TC (83.3%). Likewise, red color at 520 nm showed an increase of 3.9% whereas in TC samples it a decrease of 9.3% was observed. These results are similar to findings from Petrotos and others (2010), as they observed a considerable better red color of tomato juice concentrate produced by FO than by vacuum evaporation. The decrease in color at 520 by TC can be due to the higher non-enzymatic browning index of thermally concentrated samples due to excessive exposure of sugars and anthocyanins to high temperatures during the thermal treatment process (Nayak and Rastogi 2010). Anthocyanin pigments quickly degrade during thermal processing because they are highly sensitive to heat, and as a consequence, a dramatic impact on color quality can happen and may also compromise nutritional properties (Patras and others 2010). Therefore, the concentration process of cherry juice using FO has advantages over thermal concentration in terms of higher retention of anthocyanins and color.

Table 7. Average water flux for concentration of cherry juice from different forward osmosis treatments. *Values are means ± SD (n=3).

Av Temperature (°C)	Av Pressure (Bars)	Av Water Flux (L/m^2*h)
26	1.7	*2.78±0.19
26	2.7	*2.57±0.12
35	1.6	*3.63±0.15
35	2.6	*3.61±0.18

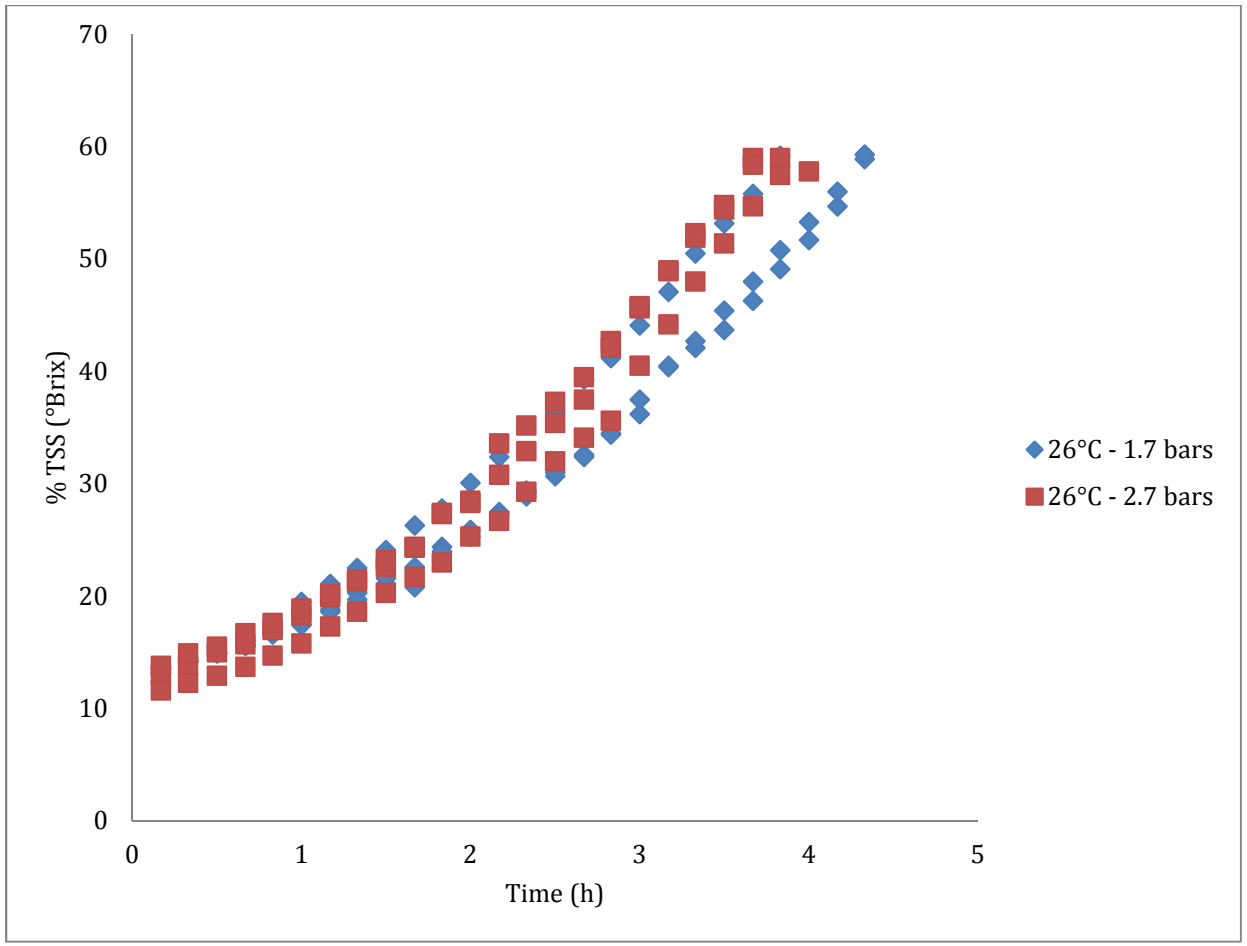


(a)

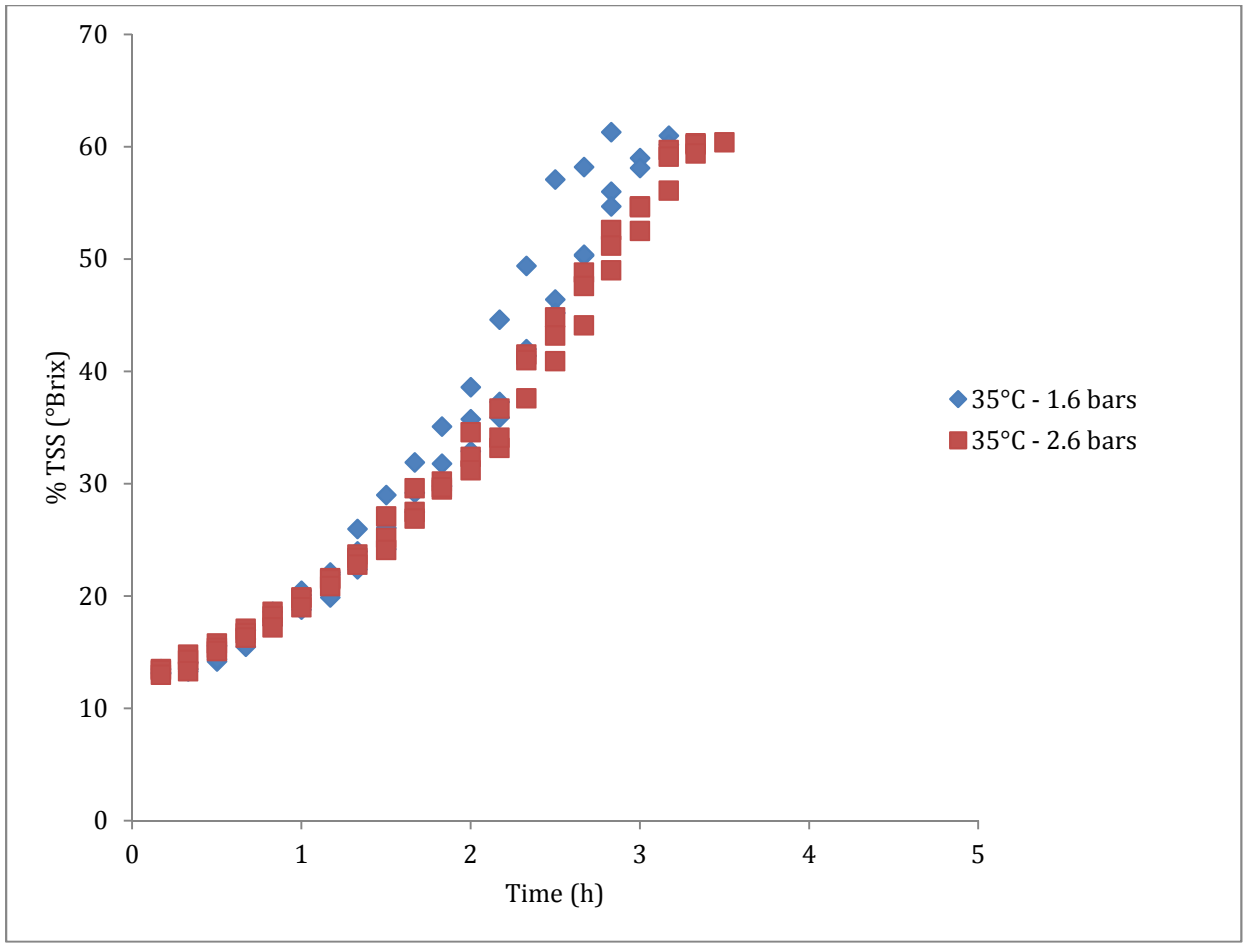


(b)

Figure 4. Forward osmosis concentration of cherry juice at (a) 26°C and (b) 35°C feed temperature and at 1.6-2.7 Bar pressure difference between osmotic agent and feed solution.


70
60
50
40
30
20
10
0
% TSS (°Brix)
0
1
2
3
4
5
Time (h)
26°C - 1.7 bars
26°C - 2.7 bars

(a)



(b)

Figure 5. Changes in total soluble solids concentration over time during forward osmosis concentration of cherry juice at (a) 26°C and (b) 35°C.

Table 8. Fresh cherry juice (J) and reconstituted juice from concentrate (R), physico-chemical properties from different forward osmosis (FO) and *thermal concentration processes. Values are means ± SD (n=3).

Treatment	Product	Anthocyanin (mg/l)	Phenolics (GAE ppm)	Color 430nm (CA/ml Juice)	Color 520nm (CA/ml Juice)	Viscosity (kg/(s.m))
	J	79.8 ± 0.2	1225 ± 47	1.5 ± 0.0	3.3 ± 0.0	43.0 ± 2.6
26°C - 1.7 bars	R	78.0 ± 2.5	1299 ± 44	1.7 ± 0.2	3.4 ± 0.2	43.3 ± 2.1
	J	60.8 ± 13.4	1195 ± 140	1.7 ± 0.0	2.8 ± 0.8	40.8 ± 0.8
26°C - 2.7 bars	R	57.4 ± 14.9	1298 ± 82	1.6 ± 0.1	3.0 ± 0.5	44.2 ± 1.5
	J	56.1 ± 0.8	1395 ± 26	1.4 ± 0.0	2.6 ± 0.1	43.0 ± 2.3
35°C - 1.6 bars	R	49.1 ± 1.4	1407 ± 20	1.7 ± 0.1	2.7 ± 0.1	43.2 ± 1.3
	J	69.4 ± 7.9	1231 ± 76	1.5 ± 0.0	3.3 ± 0.3	50.9 ± 0.7
35°C - 2.6 bars	R	65.8 ± 9.3	1338 ± 145	1.8 ± 0.0	3.3 ± 0.3	52.9 ± 0.1
	J	46.0 ± 1.2	1859 ± 160	1.5 ± 0.5	2.2 ± 0.0	42.7 ± 0.1
* 70°C - 609.6 Torr vacuum	R	38.3 ± 2.4	1913 ± 95	1.5 ± 0.4	2.0 ± 0.1	56.7 ± 0.4

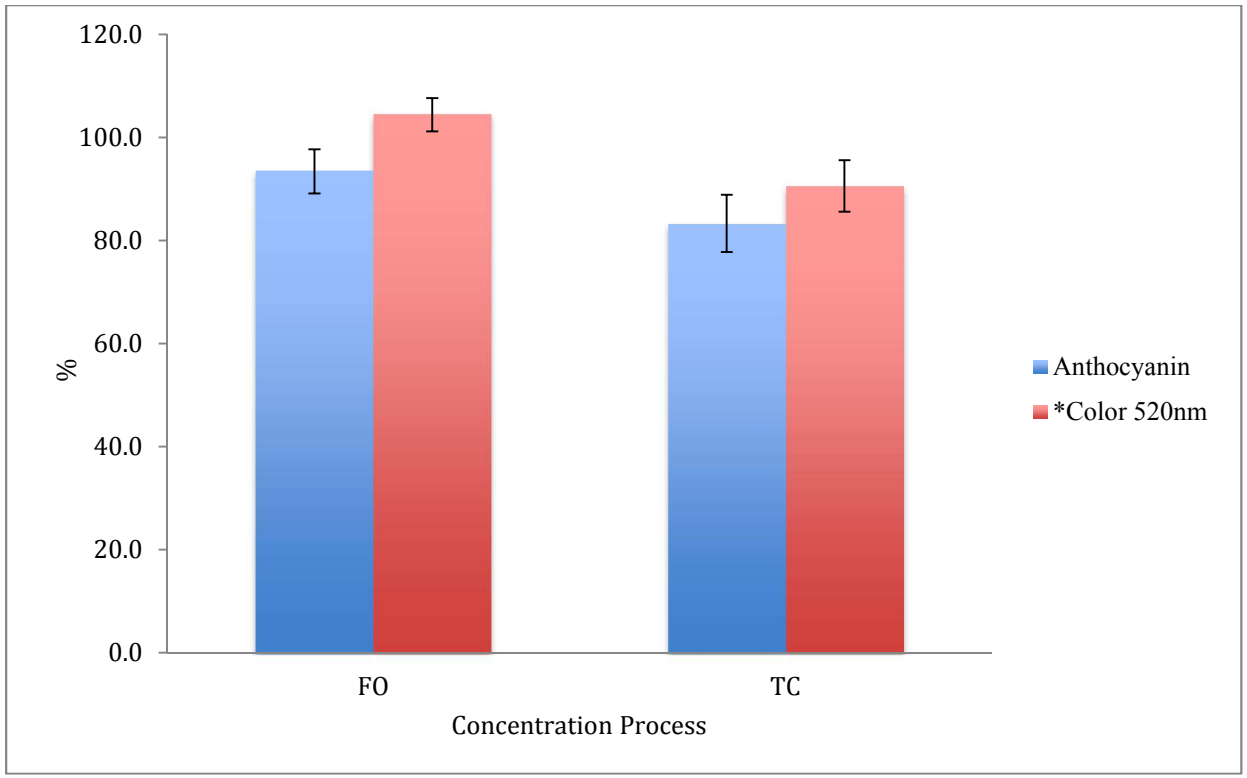


Figure 6. Percent retention of anthocyanins and color units at 520 nm in cherry juice concentration through forward osmosis (FO) and thermal concentration (TC).

Stability of anthocyanins, phenolics and color of fresh cherry juice, reconstituted cherry juice from forward osmosis and reconstituted cherry juice from thermal concentration during storage

The color stability of anthocyanins is influenced by pH, temperature, structure and concentration of anthocyanins, presence of complexing compounds such as other flavonoids, and phenolics acids (Markakis 1982). In the present study, TC and FO samples did not show changes in juice or concentrate pH during storage. The pH values ranged between 3.6 - 3.7. Therefore, differences in pH values were minor without practical implications. In all diluted treatments, a significant degradation of anthocyanins and color at 520 nm was seen across the 12-week storage period. Colorless polyphenol concentration of the juices was not significantly affected during storage. Monomeric anthocyanin retention at the end of 12-weeks at 21°C, from different treatments did not show a significant difference between them (fresh cherry juice 33.2%±3.2, reconstituted cherry juice from forward osmosis 30.3%±4.6 and reconstituted cherry juice from thermal concentration 32.0%±3.5). Changes in anthocyanin concentration of sour cherry juices was reported by Bonerz and others (2006), with only 25-30% retention after 24 weeks of storage at 20°C. This retention is higher than the one achieve with reconstituted juices from thermal and forward osmosis concentration, possibly due to higher hot pack temperature, 90°C, than the one applied by the cited study of 85°C and more heat resistant cultivars of cherries used on his study eg. *cv.Cigany 7* (Bonerz and others 2006). However, the color at 520 nm retention at the end of 12 weeks in fresh cherry juice, 64.1%±6.5, was similar to the reconstituted cherry juice from forward osmosis, 60.8%±7.7, and somewhat lower retention was seen with reconstituted cherry juice from thermal concentrate, 56.4%±3.6. However, the differences between treatments were no significant at each specific time. This is mainly due to chemical reactions that happen due to the instability of anthocyanins in process

and storage, where polymeric pigments are rapidly formed. Bonerz and others (2006), found that color hue in sour cherry juice is not strongly affected whereas saturation of color decreased during storage. During storage of all diluted cherry juices, a gradual decrease in the peak area of each major anthocyanin was quantified. Independently of the treatment conditions, cyanidin-3-sophoroside which represented 8.1±1.0% of the total area at zero time, showed significant ($p<0.002$) area losses for control and reconstituted cherry juice from thermal concentration (89.9%, 87.6% respectively), while lower loss was seen with reconstituted cherry juice from forward osmosis (51%). Intermolecular interactions in which colorless flavonoids or other phenolic compounds react with weak hydrophobic forces with anthocyanins occur mostly in fruits and berries (Andersen 2002). Cyanidin-3-rutinoside, initially with 24.0%±0.7 of the total area, showed significant ($p<0.002$) area losses under control and reconstituted cherry juice from forward osmosis concentration (68.5%, 65.5%) and 40.4% loss with reconstituted cherry juice from thermal concentrate after 12 weeks. From a previous study, done by Bonerz and others (2006), it was found that rutinoside contributed to the formation of the colorless phenolic compound quercetin-3-glucoside. Additionally, they pointed out that pyruvic acid, takes part in plant glycolysis and therefore it participates in the formation of new pigments such as pyrano-cyanidin-3-rutinoside resulting from possible reaction with aceltadehyde, a natural aroma component present in cherries, and the original anthocyanin cyanidin-3-rutinoside. On their study, this agent pigment, 5-carboxypyrano-cyanidin-3-rutinoside, was detected in sour cherry juice and its formation occurred after 8-12 weeks of storage time at 20°C. The major anthocyanin, cyanidin-3-glucosylrutinoside, was the most stable pigment across all sample treatments and no significant interaction was reported between anthocyanins quantification from different treatments and degradation time for cyanidin-3-glucoside and cyanidin-3-glucosylrutinoside. However, a higher percent degradation of cyanidin-3-glucosylrutinoside was seen in reconstituted juice from FO than in reconstituted juice from TC during the 12-week

storage. This can explain a higher red color retention in reconstituted juice from FO, since from previous studies in cherry juice done by Bonerz and others (2006), it was shown that the anthocyanin-pyruvic acid adduct (5-carboxypyrano-cyanidin-3-glucosylrutinoside) of cyanidin-3-glucosylrutinoside, may contribute to the development of the orange-red color during storage. The researchers also found that the formation of this new pigment, 5-carboxypyrano-cyanidin-3-glucosylrutinoside, occurred rapidly during storage time at 20°C. They also reported condensation products of flavan-3-ol monomers (catechin or epicatechin) and cyanidin-3-glucosylrutinoside, and an increase in the concentration of this new compound during storage. Thus, a slightly higher degradation of cyanidin-3-glucosylrutinoside in reconstituted juice from FO than in reconstituted juice from TC during shelf life can be indicative of pigment condensation and the consequent increase in formation of red color over storage.

Stability of anthocyanin, phenolics and color of cherry juice concentrates and reconstituted single strength cherry juices, from forward osmosis and thermal concentration during storage.

The stability of quality parameters (anthocyanins, phenolics, color at 430 nm, color at 520 nm) of pasteurized reconstituted juices from FO and TC were compared against its corresponding concentrates. A high correlation was found between the degradation of anthocyanin, color at 520 nm and phenolic content and storage time or different treatments (Table 9). In general, regardless of the treatment, the extend of anthocyanin degradation through time, increased with solids content. Monomeric anthocyanin percent retention at the end of 12 weeks, from sour cherry concentrates, 13.0%±0.3, was significant lower than reconstituted cherry juice treatments, 31.2%±1.2. Reacting molecules, such as oxygen, become closer in the concentrate form than in the diluted juice, which may cause the acceleration of chemical reactions (Wang and Xu 2007). Oxygen can either directly react with anthocyanins or oxidize other colorless or

brown products. Cemeroglu and others (1994), showed that anthocyanins in sour cherry juice concentrate at 71°Brix had a lower activation energy, E_a=19.14 kcal/mole, and therefore were more susceptible to thermal degradation than those of single strength juices at 15°Brix, E_a=16.37 kcal/mole. Additionally, major soluble solids of sour cherry juice such as glucose, fructose and malic acid, have been documented to effectively accelerate anthocyanin breakdown (Meschter 1953; Markakis and others 1957; Tinsley and Bockian 1960; Dravingas and Cain 1968). Furthermore, concentrates of FO and TC may have higher concentration of ascorbic acid (AA) than its reconstituted forms, producing free radicals by activating molecular oxygen and causing oxidative cleavage of the pyrilium ring in anthocyanin molecules (De Rosso and Mercadante 2006). As a result of the interaction between AA and anthocyanin, monomeric anthocyanin content may have decreased. A plausible reason why FO concentrate does not significantly retain the stability of anthocyanins when compared to concentrates with TC, might be because a lower degradation of AA due to the application of lower temperatures during the FO process than TC (where the increase in temperature is directly proportional to the decrease in vitamins such as AA). Navruz and others (2016) found that the addition of cherry steam extract with high AA content, 31.1mg/L, into thermally concentrated cherry concentrate can be the cause of a significant degrease in anthocyanins over time at 20°C. Thus, a higher retention of AA in FO concentrates can cause a higher degradation effect on monomeric anthocyanin during storage at 21°C. Additionally, the presence of a high concentration of AA has a negative impact on anthocyanin stability because AA and its degradation by-products accelerate degradation of anthocyanin during storage. The presence of AA has shown a negative impact on anthocyanins stability, leading to the mutual degradation of these compounds. The main mechanism for degradation of anthocyanis in the presence of AA consists of direct condensation of AA on the carbon 4 of the anthocyanin molecule, causing the loss of both, with a small contribution from the free radical reaction. On the other hand the loss

of color caused by AA, occurs due to oxidative cleavage of the pyrilium ring by a free radical mechanism in which the AA acts as a molecular oxygen activator, producing free radicals (Skrede and others 1992). Concentrate from TC showed a better retention, 56.4%±3.6, of color at 520 nm than in reconstituted cherry juice from TC, 38.2%±1.9. Phenolics analysis indicated a higher retention of these compounds in concentrate from TC, than in its diluted form. This was in accordance to previous research done by Cemeroglu and others (1994), where the half life color of sour cherry concentrate (71°Brix) was around 5 weeks at room temperature (20°C). They also reported that lower storage temperatures (5°C) showed a 10-fold increase (~52-weeks) in the life of color of concentrates. Therefore, it is important to cool the concentrates as soon as it is produced and to store it cold. It is important to realize that the increase in polymeric color values of the samples may be attributed to anthocyanin polymerization, copigmentation or anthocyanin degradation in concentrates (Kopjar and others 2011). Concentrate from FO showed a better retention, 92.6%±16.1, of color at 520 nm than reconstituted cherry juice from forward osmosis, 60.8%±7.7, and phenolics analysis indicated a higher retention of these compounds in concentrate from FO, 68.9%±3, than its diluted form 59.1±4.8. In case of cherry concentrate from FO and TC, an increase in stability of polymeric color formation during storage, might be attributed to anthocyanin degradation due to higher concentration of AA in cherry concentrates from FO and TC. Additionally, there are many factors influencing copigmentation, the most relevant ones are anthocyanin structure, copigment structure and concentration of anthocyanin relative to copigment (Eiro and Heinonen 2002). Thus, a plausible reason for a lower retention of color at 520 nm and phenolics in reconstituted cherry juice samples from FO and TC when compared to their corresponding concentrate forms, might be not enough copigmentation between anthocyanin and copigments in the cherry juices, caused by the ratio of copigments (individual phenolics) to anthocyanins (not sufficient for copigmentation). Hence, it is important to analyze the amount

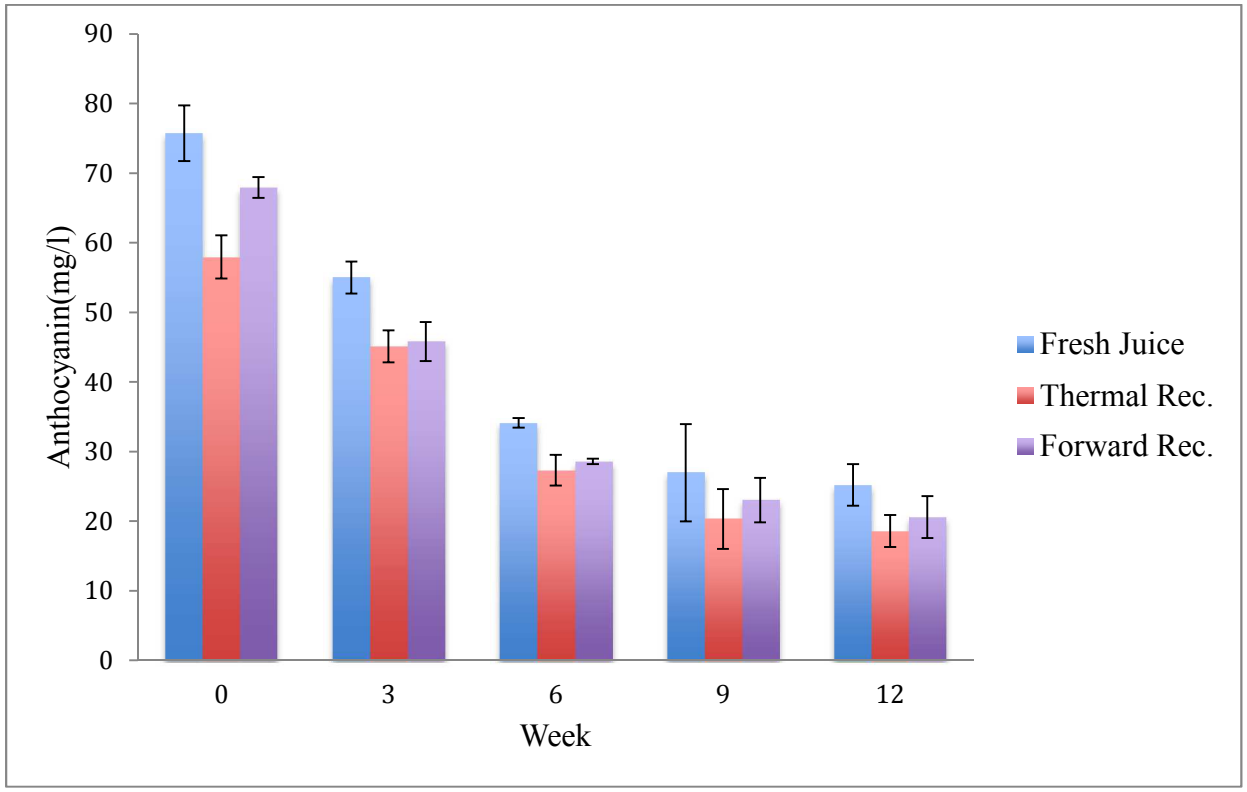
of individual phenolics in reconstituted and concentrate samples. Across all samples, before storage, cyanidin-3-glucosilrutinoside (60.3%±7.9) was the major anthocyanin, followed by cyanidin-3-rutinoside (23.6%±2.4), cyanidin-3-sophoroside (8.2%±1.0) and cyanidin-3-glucoside (7.9%±2.4). Similar to these results, the same anthocyanins were also identified by Navruz and others (2016) in cherry juice concentrate. Furthermore, in this study the stabilities of individual anthocyanins, were also determined. At the end of a 12 week storage the lowest contents of individual anthocyanins were found in FO concentrate samples. A full factorial analysis between reconstituted juices and concentrates, showed strong interaction between treatments and storage time, particularly for cyanidin-3-sophoroside, cyanidin-3-rutinoside and cyanidin-3-glucoside. Cyanindin-3-sophoroside in reconstituted cherry juices from FO and TC, at 7.76% and 7.2%, did not show significant variation of the total area at zero time against concentrate versions from FO and TC, 9.62% and 8.39%. However, at the end of the shelf life, reconstituted cherry juice from FO had a significant higher retention of 49% whereas concentrate from the same treatment only had 18.1% for this anthocyanin compound. The opposite retention occurred with samples from thermal treatment, where the concentrate form provided a significantly high retention of cyanindin-3-sophoroside, 33.7%, and the reconstituted form only show 12.4% retention. In the case of cyanidin-3-rutinoside, a significant decrease ($p<0.002$) was seen under the concentrate forms from FO and TC treatments, where only 5.7% and 18.2% was retained correspondingly; and better retention was seen with the reconstituted forms at 34.5% and 59.6% respectively. Previous studies done in cherry juice by Bonerz and others (2006) reveled that quercetin-3-glucoside was derived from rutinoside (it was found to be a rutinoside with 625 as the molecule ion, 479 after the loss of rhamnose and the aglycon 317 after the further loss of glucose). The difference between the stabilities of different anthocyanins results from the different sugar contents, and since the β-(1,6) linkage between glucose and rhamnose residues of cyanidin-3-rutinoside is weak, this

compound is more prompt to glycolysis with the formation of ageing phenolic compounds. From previous studies of stability of anthocyanins in sour cherry concentrates by Navruz and others (2016), the time needed for 50% degradation of cyanidin-3-rutinoside at 20°C was around 6-weeks, in agreement with our results. Furthermore, the reason for a slight variability on the retention of cyanidin-3-rutinoside in FO concentrate vs. TC concentrate, may be due to the slight differences in soluble solid contents of the concentrates that are more prompt to cleavage of the corresponding sugar moieties from their anthocyanins. Additionally, epicatechin, a colorless phenolic compound found in cherry juice at low concentrations in the range of 24-336 mg/L may play a role in anthocyanin stability. According to Navruz and others (2016) when epicatechin is at a high concentration level, such as in concentrates, it leads to the reduction content of cyanidin-3-rutinoside and corresponding copigmentation and color increase. In a study done by De Rosso and Mercadante (2006), the relative degradation of acai anthocyanins was dependent on the conditions of the system. For example, cyanidin-3-glucoside and cyanidin-3-rutinoside, which corresponded to, respectively, 13% and 87% of the total relative area, were degraded by 63% and 56% under light and oxygen. Therefore, a high exposure to oxygen in concentrated cherry samples could be the cause of a higher degradation of mainly cyanidin-3-glucoside and cyanidin-3-rutinoside. Cyanidin-3-glucosilrutinoside showed the highest stability in reconstituted samples compared to concentrated samples from both FO and TC treatments for 12 weeks at 21°C and its stability was higher than cyanidin-3-rutinoside for all reconstituted and concentrated samples. Similarly to the study from Navruz and others (2016), in sour cherry juice concentrate, cyanidin-3-glucosilrutinoside was more stable than than cyanidin-3-rutinoside during 15 weeks at 20°C. As previously mentioned, the difference between the stabilities of different anthocyanins results from the difference in sugar contents and thus the higher stability of cyanidin-3-glucosilrutinoside (Janeiro and Brett 2007). Cyanidin-3-glucoside in FO concentrate initially comprised 15.4% of the total anthocyanin

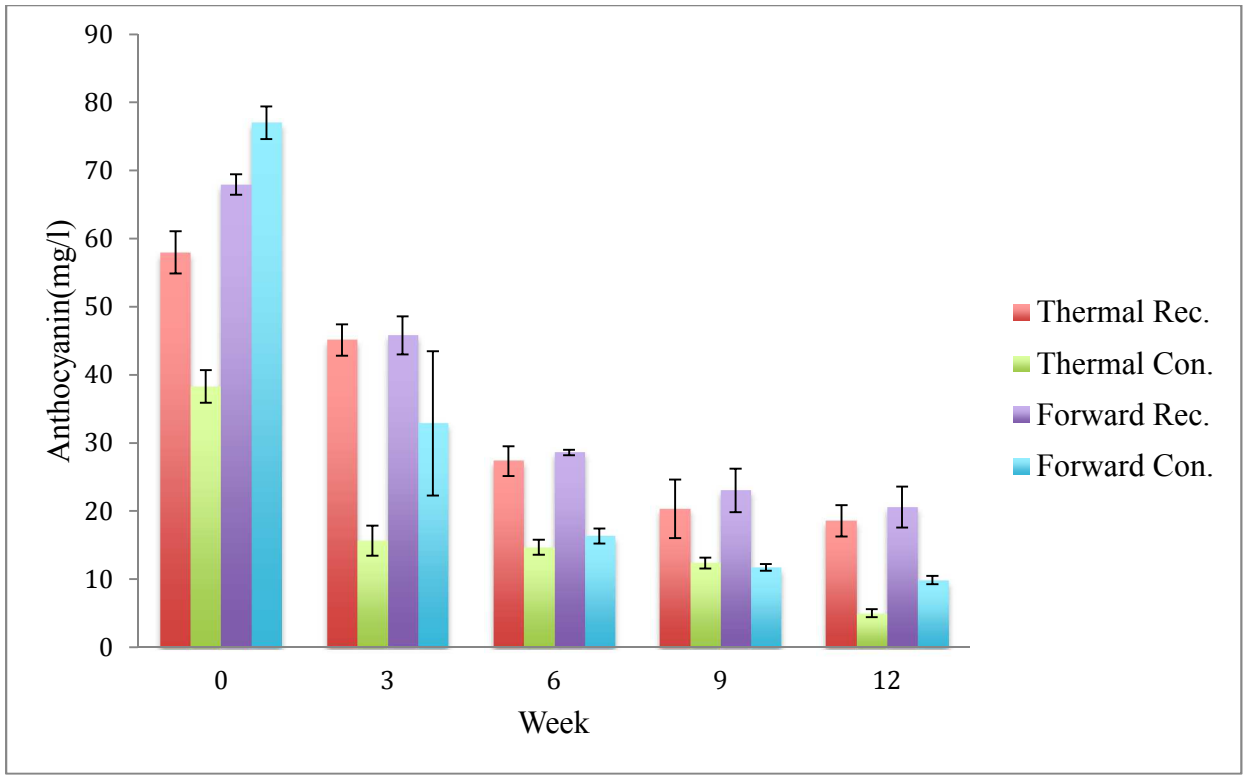
area, which was the highest initial quantification of this compound when compared to concentrate samples from TC and reconstituted versions of FO and TC, 3.6%, 6.91% and 5.5% respectively, possibly due to a lower degradation during the concentration process at low temperatures. At the end of the shelf life, it showed a significantly lower retention over time, 11.1%, when compared to concentrate samples from TC and reconstituted versions of FO and TC, 40.1%, 38% and 43%. From previous studies done be Navruz and others (2016), the highest degradation of monomeric anthocyanin was observed when thermally concentrated cherry juice was stored at 20°C. Additionally, Eiro and Heinonen (2002), noticed that intermolecular pigmentation in terms of hyperchromic effect (λ_{max} of the absorption spectrum increase), took place relatively strongly in cyanidin-3-glucoside. Thus, the increase in color intensity is more profound when cyanidin-3-glucoside intermolecular pigmentation takes place. This can plausibly explain the significant higher retention of color at 520 nm in concentrate from FO samples than in concentrate from TC and reconstituted samples from FO and TC. Bonerz and others (2006) showed that anthocyanin-pyruvic adducts have a higher stability than anthocyanin by itself and may contribute to the development of orange-red colors. It also showed that 5 carboxypyrano-cyanidin-3-(2glucosylrutinoside) resulted from the reaction of cyanidin-3-(2glucosylrutinoside) with pyruvic acid.

Table 9. Quantification of anthocyanins, phenolics, color at 430 nm and 520 nm from fresh cherry juice, reconstituted juice form thermal concentrate, thermal concentrate, reconstituted forward osmosis juice, forward osmosis concentrate, during 12-week storage at 21^{o}C. Values are means ± SD (n=3).

Anthocyanin (mg/l)												
Week	Fresh Juice			Thermal Rec.			Thermal Con.			Forward Rec.			Forward Con.		
0	75.7	±	4.0	58.0	±	3.1	38.3	±	2.4	68.0	±	1.5	77.0	±	2.4
3	55.0	±	2.3	45.1	±	2.3	15.7	±	2.2	45.8	±	2.8	32.9	±	10.6
6	34.1	±	0.7	27.3	±	2.2	14.7	±	1.1	28.6	±	0.4	16.3	±	1.1
9	26.9	±	7.0	20.3	±	4.3	12.4	±	0.8	23.0	±	3.2	11.7	±	0.5
12	25.2	±	3.0	18.6	±	2.3	5.0	±	0.6	20.6	±	3.0	9.9	±	0.6
Phenolics (ppm)															
Week	Fresh Juice			Thermal Rec.			Thermal Con.			Forward Rec.			Forward Con.		
0	1383	±	100.6	1394	±	50.8	1913	±	94.6	1510	±	195.4	1299	±	44.1
3	1299	±	64.6	1364	±	21.9	1599	±	20.5	1380	±	23.2	1674	±	53.7
6	1596	±	25.1	1663	±	54.6	1542	±	221.6	1429	±	207.4	1450	±	51.9
9	1378	±	139.7	1403	±	50.1	1213	±	227.0	1258	±	110.4	1356	±	44.7
12	1495	±	56.8	1567	±	71.4	1511	±	36.7	886	±	51.4	894	±	31.5
Color at 430 nm															
Week	Fresh Juice			Thermal Rec.			Thermal Con.			Forward Rec.			Forward Con.		
0	1.8	±	0.0	2.1	±	0.1	1.7	±	0.2	2.0	±	0.4	1.5	±	0.4
3	1.5	±	0.1	1.4	±	0.0	1.3	±	0.1	1.6	±	0.2	1.3	±	0.2
6	1.7	±	0.0	1.7	±	0.1	1.7	±	0.4	1.5	±	0.1	1.5	±	0.1
9	1.2	±	0.1	1.4	±	0.2	1.4	±	0.1	1.7	±	0.2	1.9	±	0.1
12	1.5	±	0.2	1.4	±	0.1	1.5	±	0.0	1.5	±	0.1	1.7	±	0.1
Color at 520 nm															
Week	Fresh Juice			Thermal Rec.			Thermal Con.			Forward Rec.			Forward Con.		
0	3.0	±	0.0	2.8	±	0.1	3.4	±	0.2	3.2	±	0.4	2.0	±	0.1
3	2.3	±	0.1	1.9	±	0.1	1.5	±	0.2	2.4	±	0.2	2.0	±	0.4
6	2.3	±	0.0	2.3	±	0.1	1.8	±	0.5	2.1	±	0.0	1.7	±	0.1
9	1.7	±	0.2	1.7	±	0.2	1.4	±	0.1	2.3	±	0.1	2.0	±	0.2
12	1.9	±	0.1	1.6	±	0.1	1.3	±	0.0	1.9	±	0.0	1.8	±	0.2

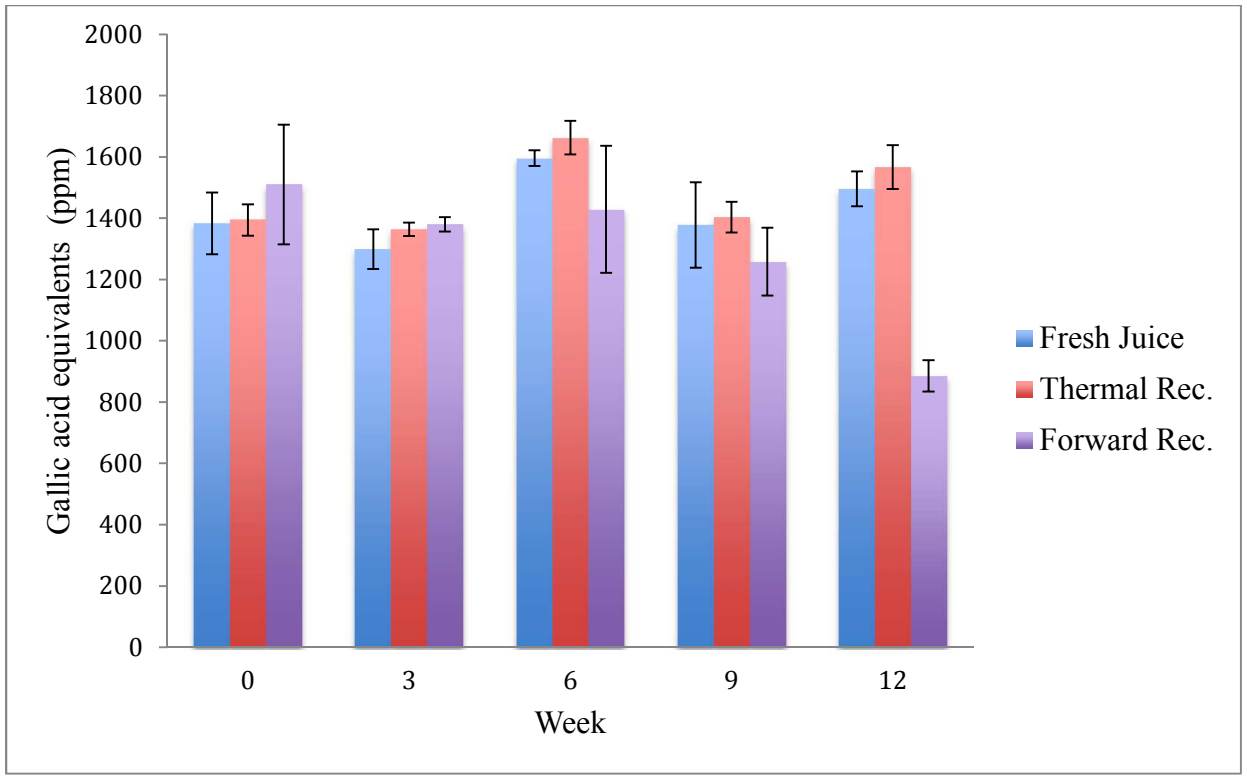

90
80
70
60
50
40
30
20
10
0
Anthocyanin(mg/l)
0
3
6
9
12
Week
Fresh Juice
Thermal Rec.
Forward Rec.

(a.1)

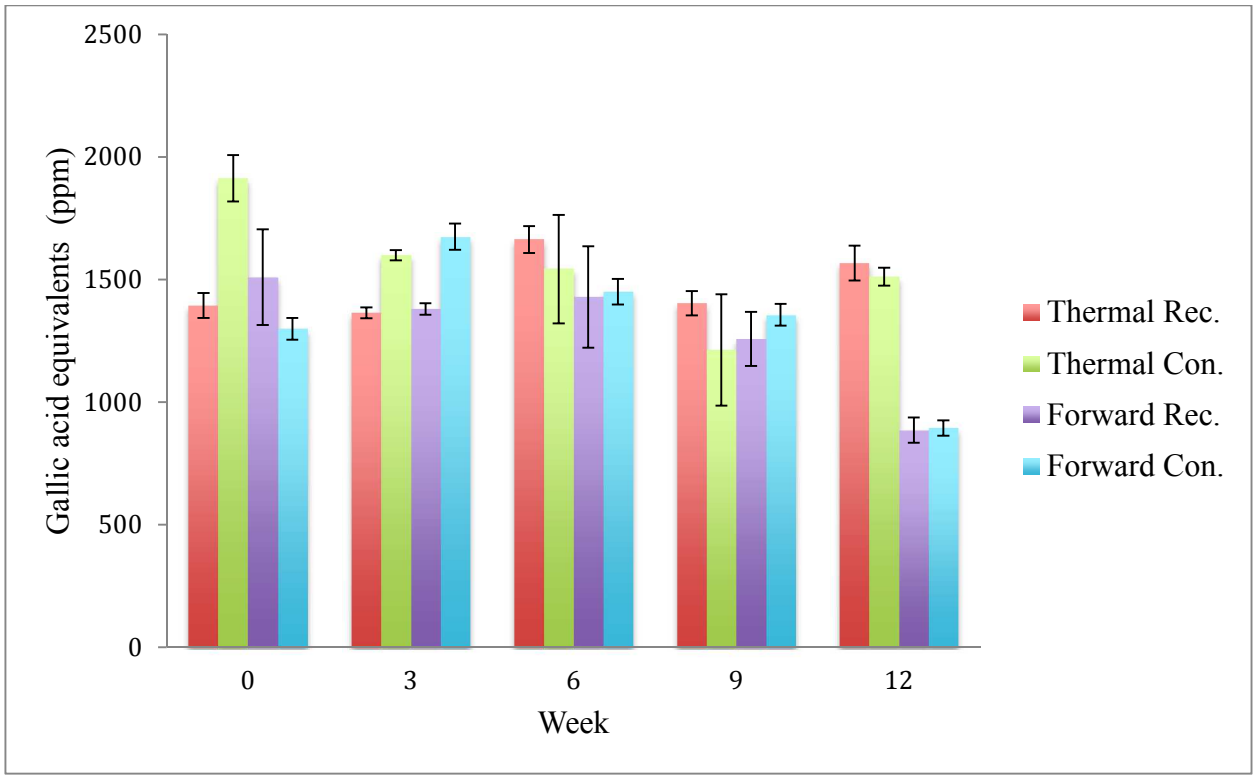


(a.2)

Figure 7. (a.1) Anthocyanin stability comparison between diluted cherry juice samples (fresh juice, thermal reconstituted from concentrate, forward osmosis reconstituted from concentrate). (a.2) Comparison of diluted samples vs. concentrated cherry juice samples (thermal concentrate, forward osmosis concentrate) during 12-week storage at 21^{o}C. Values are means ± SD (n=3).

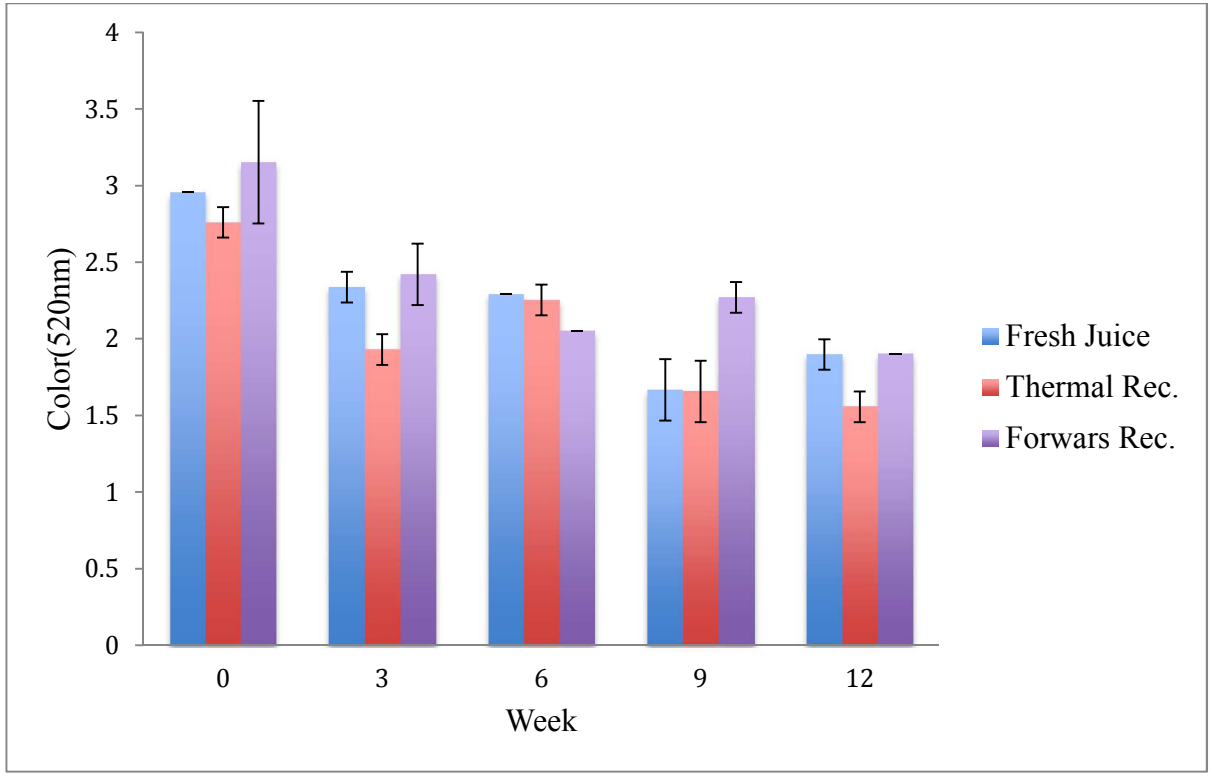

2000
1800
1600
1400
1200
1000
800
600
400
200
0
Gallic acid equivalents (ppm)
0
3
6
9
12
Week
Fresh Juice
Thermal Rec.
Forward Rec.

(b.1)

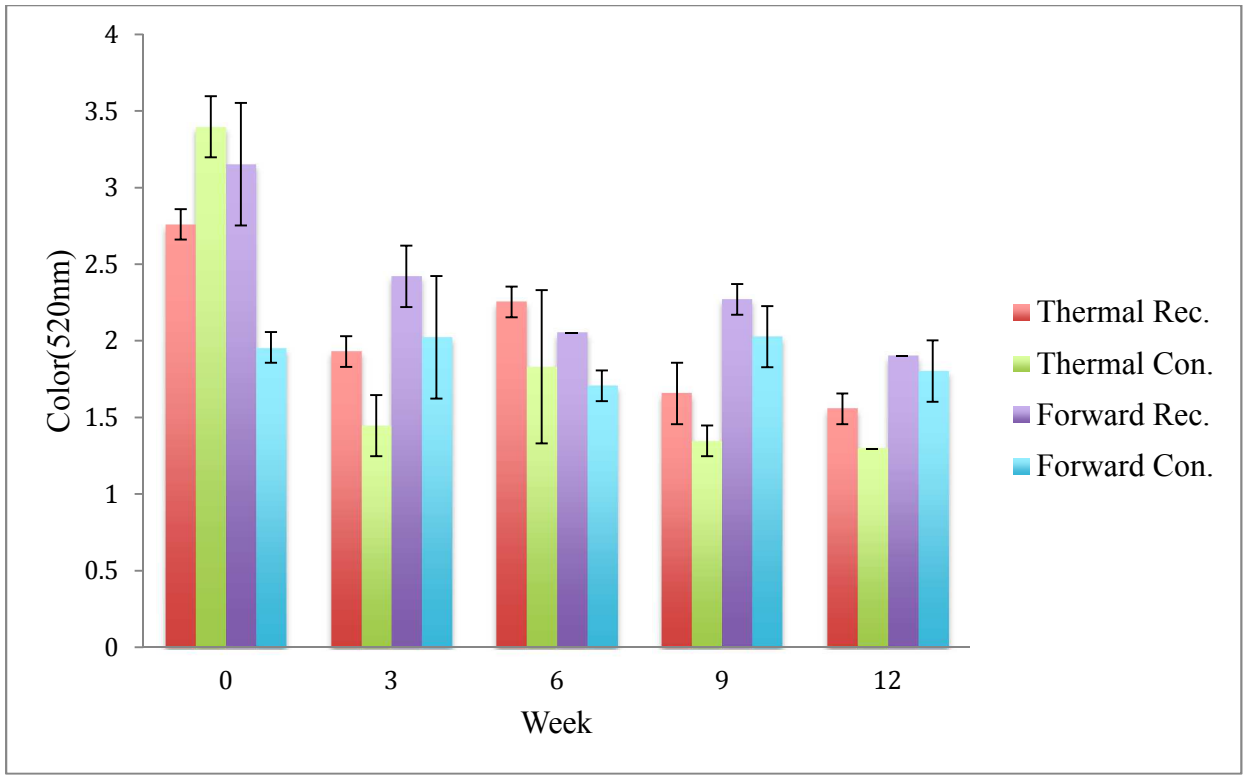


(b.2)

Figure 8. (b.1) Phenolics stability comparison between diluted cherry juice samples (fresh juice, thermal reconstituted from concentrate, forward osmosis reconstituted from concentrate). (b.2) Comparison of diluted samples vs. concentrated cherry juice samples (thermal concentrate, forward osmosis concentrate) during 12-week storage at 21^{o}C. Values are means ± SD (n=3).


4
3.5
3
2.5
2
1.5
1
0.5
0
Color(520nm)
0
3
6
9
12
Week
Fresh Juice
Thermal Rec.
Forwars Rec.

(c.1)



(c.2)

Figure 9. (c.1) Color at 520 nm stability comparison of diluted cherry juice samples (fresh juice, thermal reconstituted from concentrate, forward osmosis reconstituted from concentrate) (c.2) Comparison of diluted samples vs. concentrated cherry juice samples (thermal concentrate, forward osmosis concentrate) during 12-week storage at 21^{o}C. Values are means ± SD (n=3).

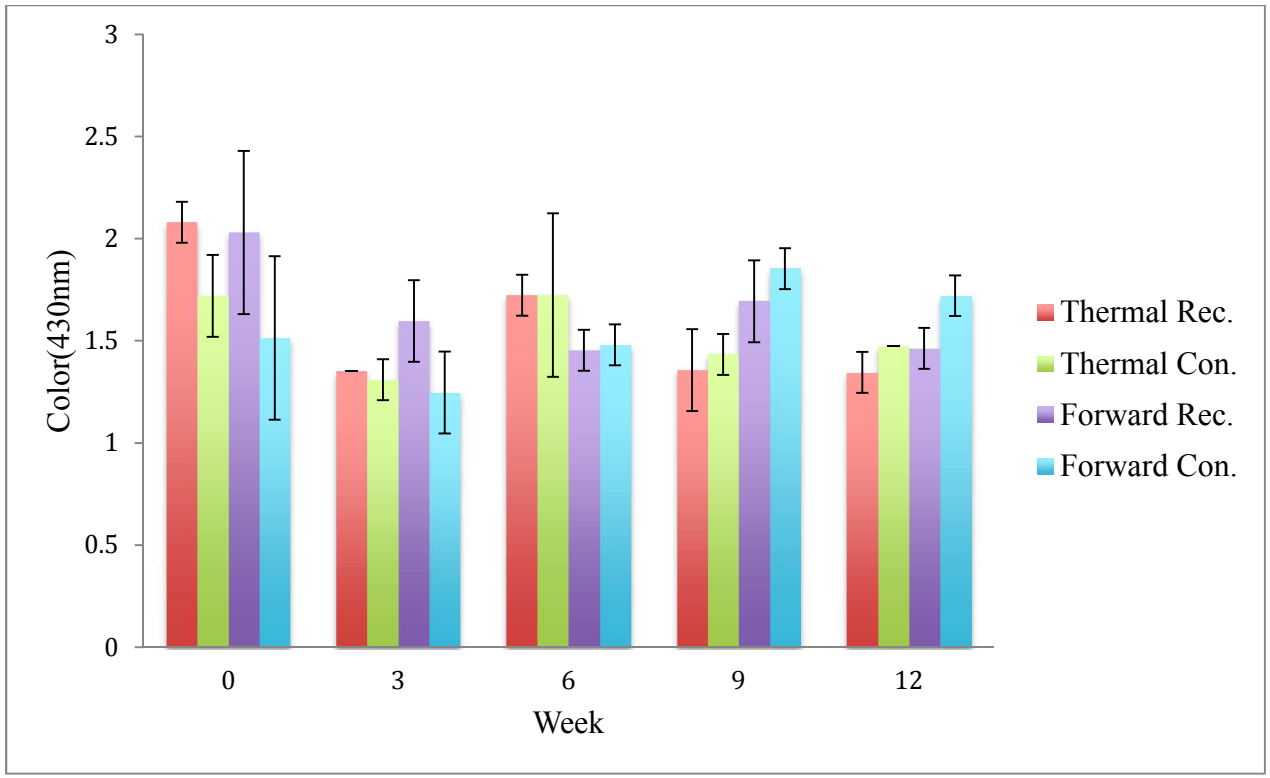


Figure 10. Color at 430 nm stability comparison of diluted cherry juice samples (fresh juice, thermal reconstituted from concentrate, forward osmosis reconstituted from concentrate) during 12-week storage at 21^{o}C. Values are means ± SD (n=3).

Table 10. Percent retention of total anthocyanins, cyanidin-3-sophoroside (3S), cyanidin-3-glucosylrutinoside (3GR), cyanidin-3-glucoside (3G), cyanidin-3-rutinoside (3R), over storage at 21°C. Values are means ± SD (n=3).

% Retention					
Description	Week	Fresh Juice	Thermal Rec.	Thermal Con.	Forward Rec.	Forward Con.
Tot. Antho.	6	95.4 ± 18.9	125.0 ± 52.1	66.0 ± 65.9	83.0 ± 14.7	18.3 ± 6.7
C-3S		44.2 ± 15.3	83.4 ± 29.3	47.0 ± 42.0	73.9 ± 27.2	20.3 ± 3.0
C-3GR		124.9 ± 36.5	152.3 ± 75.5	73.0 ± 74.6	93.8 ± 9.5	27.5 ± 14.9
C-3G		41.1 ± 31.3	70.1 ± 20.5	38.7 ± 15.4	40.7 ± 23.4	3.0 ± 0.7
C-3R		83.5 ± 19.1	99.1 ± 35.6	59.0 ± 60.7	70.6 ± 18.6	11.9 ± 4.4
Tot. Antho.	12	40.3 ± 11.7	79.8 ± 4.4	22.9 ± 3.6	48.6 ± 12.2	8.6 ± 0.3
C-3S		10.1 ± 9.7	12.4 ± 12.5	33.7 ± 0.1	49.0 ± 12.2	18.1 ± 3.1
C-3GR		54.3 ± 5.8	103.8 ± 18.8	22.1 ± 4.5	55.6 ± 14.7	8.3 ± 1.9
C-3G		16.5 ± 16.1	43.0 ± 41.0	40.1 ± 16.6	38.0 ± 28.8	11.1 ± 6.8
C-3R		31.5 ± 12.0	59.6 ± 8.1	18.2 ± 3.4	34.5 ± 10.0	5.7 ± 0.7

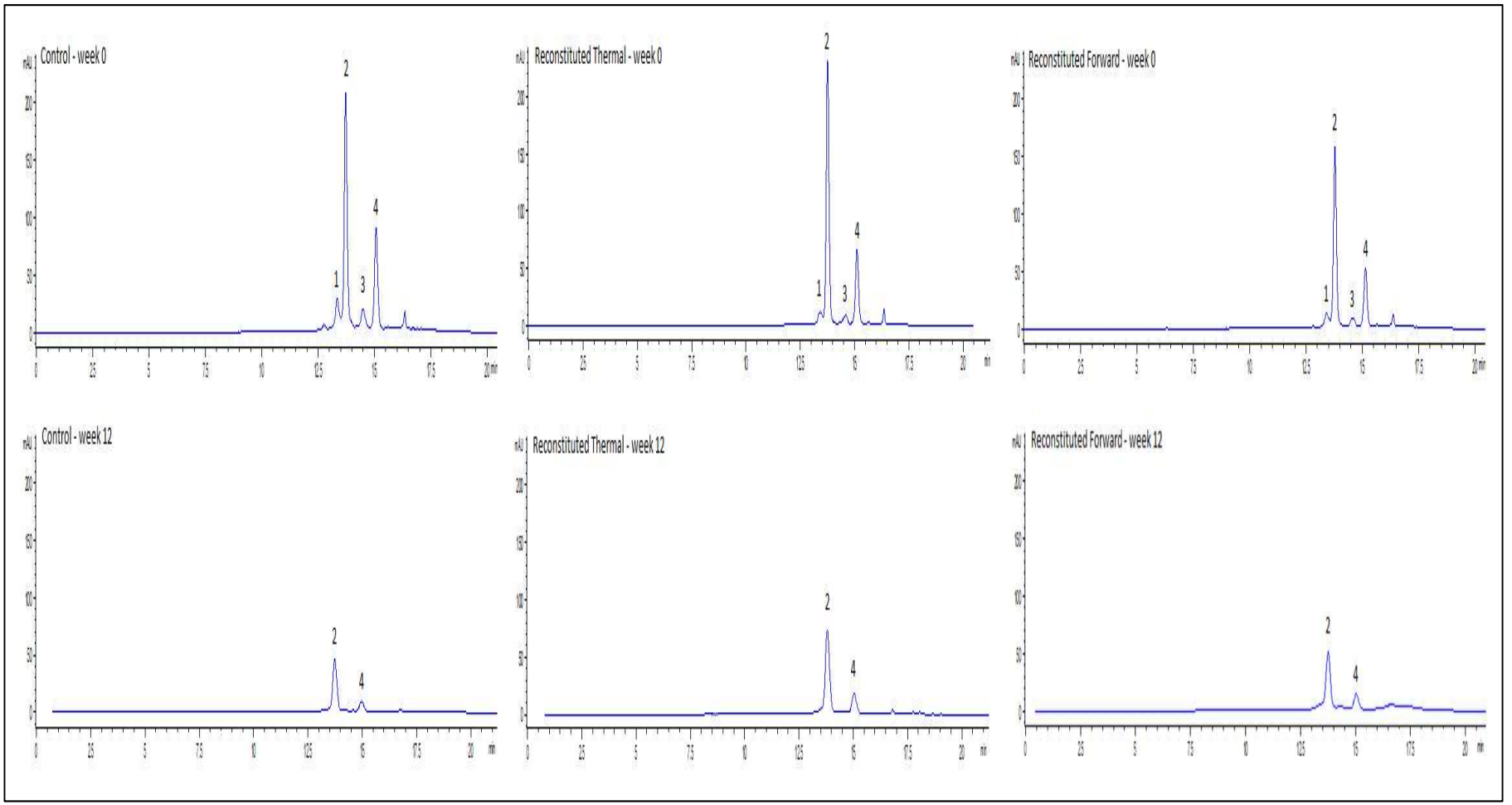


Figure 11. HPLC chromatograms of the anthocyanin compounds of reconstituted cherry juice at week 0 and week 12. Peak identification: 1) cyanidin-3-sophoroside, 2) cyanidin-3-glucosyl-rutinoside, 3) cyanidin-3-glucoside, 4) cyanidin-3-rutinoside.

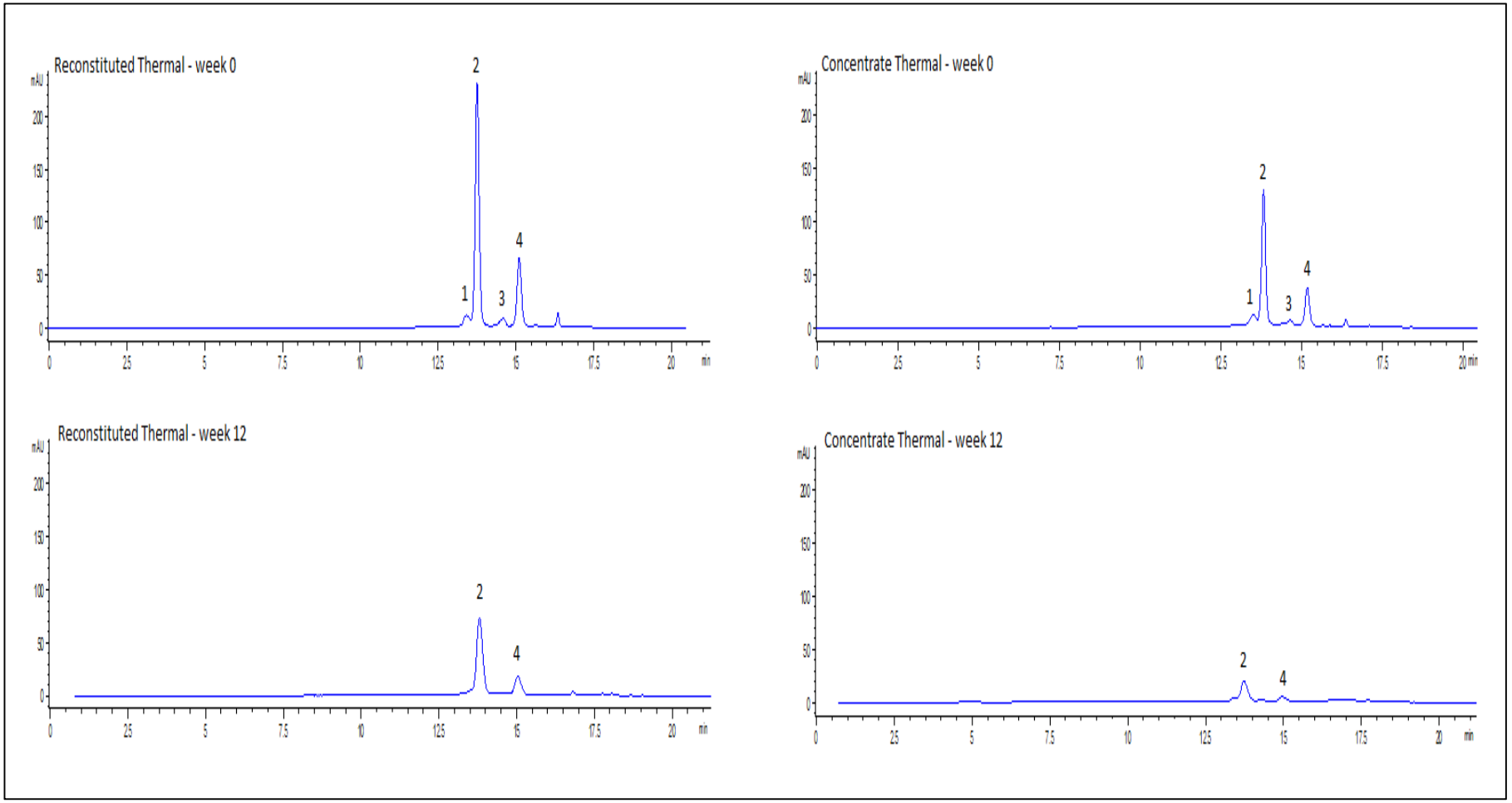


Figure 12. HPLC chromatograms of the anthocyanin compounds at week 0 and week 12 from reconstituted cherry juice vs. concentrate for thermal concentration. Peak identification: 1) cyanidin-3-sophoroside, 2) cyanidin-3-glucosyl-rutinoside, 3) cyanidin-3-glucoside, 4) cyanidin-3-rutinoside.

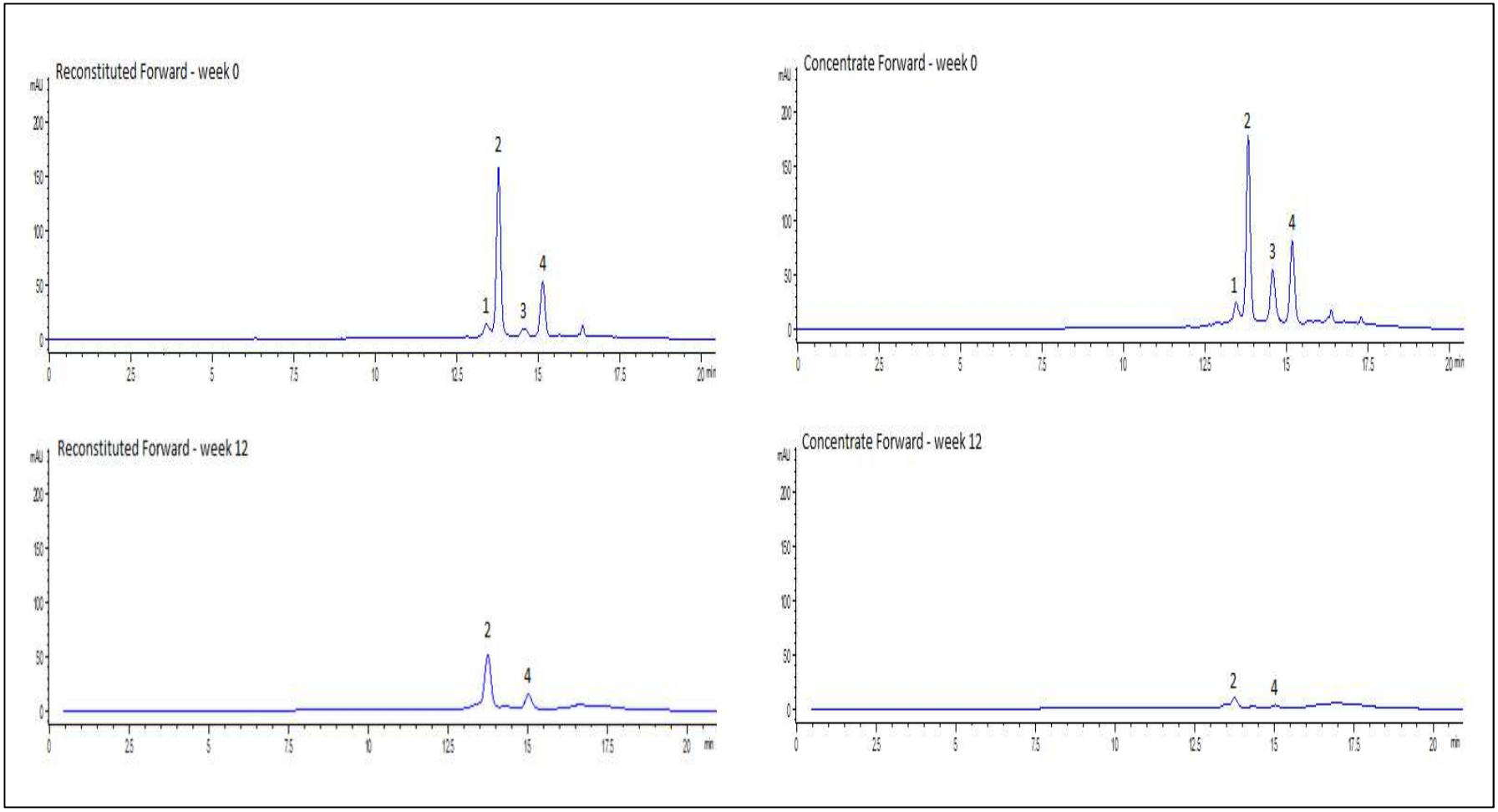


Figure 13. HPLC chromatograms of the anthocyanin compounds at week 0 and week 12 from reconstituted cherry juice vs. concentrate for forward osmosis. Peak identification: 1) cyanidin-3-sophoroside, 2) cyanidin-3-glucosyl-rutinoside, 3) cyanidin-3-glucoside, 4) cyanidin-3-rutinoside.

Sensory evaluation study

The sensory evaluation (60 panelists) showed no preference between the juice samples prepared from FO and TC. Nonetheless, there was a trend showing smaller differences with FO treatment in flavor and overall difference against the control (juice not concentrated) and larger difference with TC samples. These differences in flavor and overall perception, for TC and FO are not significant between each other, p =0.85 and p=0.35, respectively. A trend in preference against control seems to be higher for FO than TC. However, the difference in preference between FO and TC is not significantly different (p=0.5). Additionally, 86% of participants preferred FO against control because of a "better taste"; this preference was significantly different (p=0.001).

Cost analysis

A cost analysis comparison was performed to estimate the feasibility of concentration treatments for a small company that is producing cherry juice locally, from cherries to final product. 114000 L of concentrate was taken as the basis for the estimated annual production of concentrate a year (114,000 L/year). The cost comparison was calculated based on the information provided by two companies: Ederna, that produces the FO equipment EvapEOS EW20000 (commercial unit); and Centriterm, which makes one of the most efficient small scale, thin film evaporators that maintains quality because it minimizes the contact time under high vacuum.

The comparison between these two, scaled up, concentration technologies was to determine if FO process can really be cost effective. From the operating costs, FO was a more cost effective processes, with 31% less operating cost than the Centriterm, providing an opportunity to start exploring a non-thermal technology for very sensitive products. The evaporator is more

efficient but it might require more investment because of the need to have a steam generator. Additionally, there is a 96% energy savings and 33% less investment cost in FO equipment.

Table 11. Cost analysis on concentration treatments.

	Forward Osmosis	Thermal Concentrator
	evapEOs 2.4E8 - EW20000	Thin Film evaporator CT6
Juice (L/h)	473	631
Concentrate (L/h)	59	70
Water removed (L/h)	414	560
Equipment investment ($)	450,000	672,000
Equipment Depreciation [1] ($/year)	45,000	67,200
Steam Cost [2] ($/year)	0	101,096
Electricity Cost [3] ($/year)	3,974	3,397
Energy Cost ($/year)	3,974	106,096
Maintenance ($/year)	-	30,500
Ederna Maintenance Fees ($/year)	90,000	-
Operating cost [4] ($/year)	138,974	203,796
Estimated cost of concentrate ($/L)	1.22	1.79

1 Linear depreciation over 10 years.

2 Steam Cost: 0.028$/L.

3 Electricity Cost: 0.05$/kWh (US industry).

4 Excluding cleaning products, water consumption and labor.

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CHAPTER 3

CONCLUSIONS AND FUTURE WORK

Forward osmosis processing conditions

Based on the condition studied for the concentration of cherry juice by forward osmosis (FO), there was no significant effect of osmotic pressure differential on performance during the FO concentration. Whereas, an increase in temperature from 26 to 35^{o}C resulted in a significant ($p<0.05$) increase of 35% in the average water flux (2.68±0.14; 3.62±0.01 respectively). This is because the increase in temperature lowers the viscosity and increases the diffusion coefficients of the fluids involved in the process, consequently this increases the permeation flux (Petrotos and others 1998). In this study, cherry juice concentration through various process conditions in FO, did not have significant effects ($p>0.05$) in quality parameters (anthocyanin, color, phenolics, viscosity). Petrotos and others (1998), showed that thinner membranes and lower viscosity of draw solution benefit higher water fluxes, thus faster concentration. Additionally, Petrotos and others (1999), observed that the use of ultrafiltration pretreatment to juice improved the performance of the FO concentration instead of performing the concentration of tomato juice as such, since there was a decrease in molecular weight from 200 to 100 kDa, which decreased the rate of internal concentration polarization and resulted in enhanced flux. Herron and others (1994) found higher water fluxes, due to the high turbulence in FO, achieved with the application of 50-85wt% sugar solution. Additionally, Wrolstad and others (1993) used high fructose corn syrup as an osmotic agent solution in FO and no significant changes were seen in sensory characteristics between FO and TC concentration of raspberry juice. Furthermore, Petrotos and others (2010) proposed the use of electrodialysis for the reconcentration of post process diluted osmotic agent, since it is seen as a more viable, more economical alternative than thermal evaporation. Therefore, it is recommended to study the conditions of the membrane more in depth, since it should have a high density of the active

layer for high solute rejection, a thin membrane with minimum porosity of the support layer for low internal concentration polarization, thus higher water flux, high hydrophilicity for improve water flux, and reduced membrane fouling. Moreover, combining low temperature and pretreatment in the form of pressure ultrafiltration of cherry juice prior to forward osmosis process can help to improve the water flux. Furthermore, exploring alternative osmotic agent solutions with a higher osmotic pressure should be explored. Lastly, it is recommended to explore the reconcentration of the diluted osmotic agent with more economical methods such as electrodialysis. FO showed significantly higher retention of anthocyanins (93.4%), red color at 520 nm (increase in 3.9%), than TC (83.3%, decrease of 9.3% respectively). Therefore, the concentration process of cherry juice using FO has advantages over thermal concentration in terms of higher retention of anthocyanins and color. Furthermore, no significant changes in sensory analysis were found in reconstituted samples of FO and TC, the properties of reconstituted juices were found to be comparable to fresh juice.

Anthocyanins stability

Monomeric anthocyanin retention at the end of 12 weeks between reconstituted samples from FO and TC, did not show a significant difference against the control juice (not concentrated). Additionally, the extend of anthocyanin degradation through time, increased with solids content. According to literature (Cemeroglu and others 1994), concentrates have a lower activation energy than juices, thus they degrade more rapidly. Further work on determination of ascorbic acid content during shelf life and comparison between the different treatment samples, is recommended, in other to understand if the loss of ascorbic acid at the end of each treatment significantly influences the degradation rate of anthocyanin over the shelf life. Additionally, exploring the addition of flavonoids extracts, containing quercetin and quercetrin, on reconstituted juice as they can have a protective effect in other to retard the degradation of anthocyanins in the presence of ascorbic acid (Shrikhande and Francis 1974). This is probably

attributed to a competition effect where anthocyanins prefer flavonoids, instead of ascorbic acid, for condensation reactions by intermolecular copigmentation, due to decreased carbinol pseudobase production and increased quinonoidal anhydrobase stabilization (Mazza and Brouillard 1990).

Major anthocyanins stability in reconstituted samples.

In reconstituted samples from FO, cyanidin-3-sophoroside (51% area loss) was significantly more stable than in samples from TC (88% area loss). In reconstituted samples from FO, TC, and in control, cyanidin-3-rutinoside and cyanidin-3-glucosylrutinoside showed no significant differences in retention over time. It would be interesting to investigate the stability of these major anthocyanin compounds in the presence of copigments and to identify the formation of phenolic compounds at the beginning and end of storage. Additionally, the analysis of the concentrations and the possible decline of pyruvic acid and acetaldehyde in different juices during storage to determine any newly formed pyrano-derivatives indicatives of copigmentation with specific major anthocyanins.

Major anthocyanins stability in reconstituted vs. concentrate samples

At the end of 12 weeks at room temperature no significant differences were found in retention of cyanidin-3-sophoroside, cyanidin-3-rutinoside, cyanindin-3-glucosylrutinoside, and cyanidin-3-glucoside between reconstituted vs. concentrated samples from FO. However, cyanidin-3-rutinoside and cyanidin-3-glucosylrutinoside, showed significantly ($p<0.05$) higher retention (60%, 100% respectively) in reconstituted samples from TC than its concentrated form (18%, 22% respectively). The main reason can be that when heat treatment is applied for extended time such as in thermal concentration, fructose has shown to accelerate anthocyanin decay due to the formation of sugar degradation products such as furfural and

hydroxymethylfurfutral (HMF), that proved to favor pigment decay (Hubbermann and others 2006). Therefore, a significant variability occurred at a higher degree in TC samples. Additionally, the interaction with acetaldehyde present in cherries, that is more available in the concentrated form of TC, contributes to the formation of new pigments such as pyrano-cyanidin-3-rutinoside and to the decrease of cyanidin-3-rutinoside. Additionally, Bonerz and others (2006), found that the interaction between cyanidin-3-glucosylrutinoside and pyruvic acid was responsible for the formation of a new pigment, 5-carboxypyrano-cyanidin-3-glucosylrutinoside, and it was rapidly formed during storage time at 20°C. Only cyanidin-3-sophoroside, from reconstituted samples of FO, showed a significant ($p<0.05$) higher retention (49% retention) compared to reconstituted samples from TC (12% retention). No significant differences in retention were seen between concentrated samples from FO vs. TC. In a study done by Navruz and others (2016), it was shown that the addition of gallic acid (37-53%), pomegranate rind extract (22-77%) and green tea extract (44-119%) to sour cherry juice concentrates, increased the stability of cyanidin-3-rutinoside and cyanidin-3-glucosylrutinoside. In this study, green tea extract contained epicatechin at high concentration (1255mg/L) followed by catechin (310 mg/L) and when added to cherry concentrate contributed to higher formation/retention of red color compounds in concentrates through shelf life. Possibly due to a protective action from green tea extract to anthocyanin from oxidative degradation during concentration process due to a higher antioxidant capacity. Additionally, Navruz and others (2016), proved that at 4°C the degradation of anthocyanins in concentrate at 65°Brix was 3.9 times lower than at 20°C. Thus, it is recommended to study the addition of phenolic compounds in concentrates from FO and TC to increase intermolecular copigmentation and improve the stability of major anthocyanins through time. Additionally, it is recommended to explore lower storage temperatures to minimize its degradation over time.

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APPENDIX

Cherry Juice Study Consent Form

You are being asked to take part in a research project defining Cherry Juice. You are being asked to participate because you responded to an e-mail recruiting participants for this study. Please read this form carefully and ask any questions you may have before agreeing to take part in the study.

What the study is about:
The purpose of this study is to determine consumer perception of cherry juice on differences due to the treatments: control, thermal concentration, and forward osmosis; what are the main differences; and preferred treatment(s).

What we will ask you to do: If you agree to be in this study, you will first be asked to taste and evaluate several cherry juices samples and describe their color, appearance, flavor, and overall perception. You will be asked to analyze a total of four (4) samples.

Risks and benefits: The benefits of moderate cherry juice consumption may include: Fighting of Inflammation and Arthritis Pain. Antioxidants in tart cherry juice can reduce pain and inflammation from osteoarthritis.

Compensation: You will be paid $5 for this session (lasting approximately 10-15 min).

Your answers will be confidential. All participants will be assigned a code number, under which all data will be recorded and reported. Panelist names will not be released at any time.

Taking part is voluntary: Taking part in this study is completely voluntary. If you decide not to take part, it will not affect your current or future relationship with Cornell University. If you decide to take part, you are free to withdraw at any time.

If you have questions: The researchers conducting this study are Marcela Patino and Dr. Olga Padilla-Zakour. Please ask any questions you have now. If you have questions later, you may contact Marcela Patino at mp659@cornell.edu. If you have any questions or concerns regarding your rights as a subject in this study, you may contact the Institutional Review Board (IRB) at 607-255-5138 or access their website at http://www.irb.cornell.edu. You may also report your concerns or complaints anonymously through Ethicspoint or by calling toll free at 1-866-293-3077. Ethicspoint is an independent organization that serves as a liaison between the University and the person bringing the complaint so that anonymity can be ensured.

You will be given a copy of this form to keep for your records.

Sensory study of cherry juice

1. **Thinking about this test product COLOR, would you say..?**

Dislike it extremely - Dislike it very much - Dislike it moderately - Dislike it slightly - Neither like nor dislike it - Like it slightly - Like it moderately - Like it very much - Like it extremely

2. **Thinking about this test product APPEARANCE, would you say..?**

Dislike it extremely - Dislike it very much - Dislike it moderately - Dislike it slightly - Neither like nor dislike it - Like it slightly - Like it moderately - Like it very much - Like it extremely

Please taste enough sample to form an opinion. Please make sure to leave a little for the 2nd portion of the study

3. **Thinking about this test product FLAVOR/TASTE, would you say..?**

Dislike it extremely - Dislike it very much - Dislike it moderately - Dislike it slightly - Neither like nor dislike it - Like it slightly - Like it moderately - Like it very much - Like it extremely

4. **Thinking about this test product OVERALL, would you say..?**

Dislike it extremely - Dislike it very much - Dislike it moderately - Dislike it slightly - Neither like nor dislike it - Like it slightly - Like it moderately - Like it very much - Like it extremely

The first product that you tried, code # 738 is a control product. Please retaste it now. The second product at you have tried, code #542 , is a test product. Please retaste it now.

5. **How similar or different is the test product code #738 from the Control?**

Very Different - Moderately Different - Somewhat Different - Not very Different - Essentially Very similar

6. **Which one do you prefer?**

First that you've tried (Control) - Second that you've tried (Test)

7. **Why?**

Better appearance - Dark red color - Looks fresher - Taste better - Taste fresher - Other

Table 12. Anthocyanins, phenolics, color 430nm /520nm from control (C), reconstituted (TD,FD) and concentrate (TC, FC) cherry juice in storage.

Method	WEEK O	WEEK3	WEEK6	WEEK 9	WEEK 12	WEEK O	WEEK3	WEEK6	WEEK 9	WEEK 12	WEEK 0		WEEK 3		WEEK 6		WEEK 9		WEEK 12	
	Anthocyanins					Phenolics					Col 430	Col 520	Col 430	Col 520	Col 430	Col 520	Col 430	Col 520	Col 430	Col 520
C	80.2	57.2	34.7	19.2	28.1	1492	1225	1570	1446	1541	1.8	3.0	1.4	2.4	1.7	2.3	1.2	1.7	1.8	2.1
C	74.6	55.2	34.3	32.9	22.1	1363	1342	1620	1217	1514	1.8	3.0	1.4	2.3	1.7	2.3	1.1	1.6	1.3	1.8
C	72.4	52.5	33.4	28.7	25.5	1294	1331	1598	1470	1432	1.8	2.9	1.6	2.3	1.7	2.3	1.2	1.7	1.5	1.8
TD	55.9	44.6	27.3	17.6	16.0	1361	1341	1648	1455	1546	2.0	2.6	1.4	1.9	2.0	2.1	1.5	1.7	1.3	1.5
TD	56.5	43.0	25.1	18.1	20.1	1453	1385	1617	1399	1508	2.2	2.8	1.3	1.9	2.1	2.3	1.1	1.5	1.3	1.5
TD	61.5	47.6	29.6	25.2	19.7	1369	1366	1723	1355	1646	2.0	2.8	1.3	2.0	1.9	2.3	1.5	1.8	1.4	1.7
TC	40.0	13.5	14.3	13.2	4.6	1847	1579	1673	1455	1470	1.5	3.2	1.2	1.3	2.1	2.4	1.5	1.4	1.5	1.3
TC	39.5	15.7	13.9	11.8	4.8	2022	1620	1286	1179	1541	2.0	3.6	1.4	1.5	1.7	1.8	1.4	1.3	1.5	1.3
TC	35.5	17.8	15.9	12.1	5.7	1872	1598	1667	1005	1523	1.7	3.4	1.4	1.6	1.3	1.3	1.3	1.3	1.4	1.3
FD	67.0	48.0	29.0	25.1	23.7	1297	1379	1286	1133	837	1.6	2.7	1.5	2.3	1.5	2.0	1.6	2.1	1.5	1.9
FD	69.7	46.7	28.2	24.7	20.2	1682	1357	1667	1299	940	2.4	3.5	1.5	2.4	1.4	2.0	1.7	2.3	1.4	1.9
FD	67.2	42.7	28.6	19.4	17.8	1550	1403	1333	1343	880	2.1	3.3	1.8	2.6	1.5	2.1	1.9	2.4	1.5	1.9
FC	79.8	45.1	17.6	11.2	9.6	1343	1683	1442	1318	882	1.8	2.0	1.5	2.5	1.6	1.6	1.8	1.9	1.6	1.6
FC	76.2	26.8	15.9	12.0	9.4	1299	1617	1403	1346	930	1.1	2.0	1.1	1.7	1.3	1.7	1.8	2.0	1.7	1.7
FC	75.1	26.7	15.5	12.0	10.6	1255	1723	1506	1405	870	1.7	1.8	1.2	1.9	1.5	1.9	2.0	2.2	1.9	2.0

Table 13. Water flux and physico-chemical properties from different forward osmosis (FO) and *thermal concentration processes (TC) of cherry juice.

Methods	Pressure bars	Temp ^{o}C	Water Flux	^{o}Brix Concentrate	pH Concentrate	Antho beg	Antho end	Pheno beg	Pheno end	Color CA/ml juice beg at 430nm	Color CA/ml juice beg at 520nm	Color CA/ml juice end at 430nm	Color CA/ml juice end at 520nm	Viscosity (kg/(s*m)) beg	Viscosity (kg/(s*m)) end
FO1	1.7	25.6	3.0	59.2	3.7	79.9	79.8	1178	1343	1.5	3.3	1.5	3.2	40.0	44.0
FO1	1.6	26.3	2.6	58.9	3.7	79.9	79.2	1178	1299	1.5	3.2	2.0	3.6	44.0	45.0
FO1	1.7	26.4	2.8	59.3	3.7	79.6	75.1	1178	1255	1.5	3.3	1.7	3.4	45.0	41.0
FO2	1.6	37.7	3.6	63.0	3.7	56.6	48.1	1387	1364	1.4	2.6	1.6	2.6	44.4	43.0
FO2	1.7	33.4	3.5	61.1	3.7	56.6	48.5	1387	1426	1.4	2.6	1.8	2.7	44.4	42.0
FO2	1.6	35.2	3.8	60.2	3.7	55.1	50.6	1417	1409	1.5	2.7	1.8	2.8	40.3	44.5
FO3	2.7	26.5	2.4	59.6	3.6	53.1	48.0	1351	1393	1.7	2.3	1.5	2.6	40.3	45.5
FO3	2.7	26.7	2.6	60.4	3.5	53.1	49.6	1154	1248	1.7	2.3	1.8	2.9	40.3	44.5
FO3	2.7	24.1	2.7	59.6	3.5	76.3	74.6	1079	1254	1.7	3.6	1.6	3.5	41.7	42.5
FO4	2.7	34.3	3.4	63.1	3.7	74.0	69.5	1155	1172	1.5	3.5	1.8	3.5	50.5	52.8
FO4	2.6	35.3	3.6	63.2	3.7	74.0	72.7	1155	1443	1.5	3.5	1.8	3.6	50.5	53.0
FO4	2.6	34.2	3.8	63.5	3.7	60.3	55.2	1308	1399	1.5	2.9	1.8	3.0	51.7	53.0
TC	0.8	70.0	-	64.7	3.4	47.2	40.0	1859	1847	2.0	2.2	1.8	2.0	42.8	56.8
TC	0.8	70.2	-	63.5	3.4	44.8	39.5	1859	2022	1.2	2.1	1.1	2.0	42.6	56.3
TC	0.8	70.0	-	59.3	3.3	46.0	35.5	1859	1872	1.2	2.1	1.7	1.8	42.8	57.1

Table 14. Area total anthocyanins, cyanindin-3-sophoroside (3S), cyanidin-3-glucosylrutinoside (3GR), cyaniding-3-glucoside (3G), cyanidin-3-rutinoside (3R), over storage at 21 ^{o}C, from control (C), reconstituted (TD,FD) and concentrate (TC, FC) in storage.

	Cyanidin 3S			Cyanidin 3GR			Cyanidin 3G			Cyanidin 3R			Total anthocyanin area		
Sample	W0	W6	W12	W0	W6	W12	W0	W6	W12	W0	W6	W12	W0	W6	W12
C	287.7	120.8	12.8	1323.4	2180.9	644.4	550.8	93.3	6.9	682.6	631.3	121.9	2844.5	3026.3	786
C	244.3	148	11.3	2208.7	2575.2	1331.5	147.7	113	49.3	788	759	319.9	3388.7	3595.2	1712
C	364.3	109.9	77.6	1965.7	1833.6	1059.9	276.3	82.6	41.2	903	556	325.5	3509.3	2582.1	1504.2
TD	155.7	80.8	0.76	899.9	1287.8	988.8	123.5	57.6	36.2	438.2	357.6	226.3	1617.3	1783.8	1252.06
TD	152.5	135	17.4	887.3	2057.8	1053.7	115.1	92	12.2	406.2	568.9	241.2	1561.1	2853.7	1324.5
TD	133.9	147	34	2065.7	1690.5	1706.7	98.6	82.7	87.9	651.8	493.5	442.6	2950	2413.7	2271.2
TC	192	41	64.4	1254.5	489.8	236.4	68.2	26	40.4	404.5	119.3	66.5	1919.2	676.1	407.7
TC	166.9	159.3	56.3	1159.9	1838.8	315.8	82.9	45.1	25.9	353.5	455.4	78.3	1763.2	2498.6	476.3
TC	155.6	37.7	52.6	1699.6	363.2	342.2	92	21.7	27.5	502.9	94	80.7	2450.1	516.6	502.9
FD	151.7	109.5	55.1	1451.1	1423.1	867.5	88.5	38.7	62.9	513.6	386.6	207.6	2204.9	1957.9	1193.1
FD	129.7	132.1	78.8	965.3	970.2	655.3	143	89.3	34.3	366	316.1	146.6	1604	1507.7	915
FD	133.9	63.7	67	914.4	758.4	359.1	138.3	22.1	26.2	356.9	178.6	81.9	1543.5	1022.8	534.2
FC	323.9	61.7	55.1	1325	587.8	125	619.7	15.9	48.5	846.7	138.7	45.3	3115.3	804.1	273.9
FC	249.4	59	53.7	1522.5	336.4	140.8	530.8	13.6	35.1	747.2	87.1	40	3049.9	496.1	269.6
FC	293.7	53.2	46	1552.7	249	95.1	237.3	8.9	45.1	763.9	57.9	49.5	2847.6	369	235.7

Table 15.Water flux over time from different forward osmosis concentration processes of cherry juice.

Time (h)	FO1			FO3			FO2			FO4		
	26°C - 1.7 bars			26°C - 2.7 bars			35°C - 1.6 bars			35°C - 2.6 bars		
0.33	2.28	2.34	2.34	2.28	2.28	2.16	4.5	3.06	3.42	2.76	3.36	3.12
0.5	1.52	1.56	1.56	1.24	1.4	1.32	2.48	2.24	1.88	1.88	2.08	3.24
0.67	1.35	1.35	3.33	0.6	1.17	1.05	1.39	2.61	1.84	1.63	1.56	1.17
0.83	0.98	1.87	0.89	0.86	1.17	0.72	1.39	0.5	0.5	1.11	1.25	0.6
1	0.76	0.75	0.7	0.5	2.46	0.74	0.88	0.68	1.01	0.69	0.78	2.18
1.17	0.65	0.45	0.63	0.65	0.51	0.17	0.5	0.68	1.01	0.56	0.79	0.65
1.33	0.75	0.56	0.51	0.39	0.53	0.45	1.26	1.46	1.11	0.82	0.57	0.65
1.5	0.47	0.43	0.36	0.32	0.29	0.41	0.34	3.33	0.11	0.55	0.48	0.45
1.67	0.47	0.4	0.4	0.37	0.18	0.29	0.34	0.2	0.61	0.45	0.42	0.44
1.83	0.77	0.36	0.32	0.34	0.14	0.35	0.28	0.29	2.5	0.22	0.32	0.27
2	0.11	0.18	0.27	0.15	0.12	0.1	0.34	0.28	0.42	0.12	0.27	0.25
2.17	0.11	0.26	0.45	0.1	0.11	0.41	0.18	0.28	0.23	0.22	0.31	0.39
2.33	0.24	0.15	0.02	0.16	0.15	0.1	0.03	0.21	0.19	0.21	0.22	0.09
2.5	0.26	0.17	0.18	0.17	0.32	0.02	0.18	0.18	0.07	0.12	0.15	0.14
2.67	0.16	0.14	0.16	0.1	0.15	0.13	0.07	0.15	0.1	0.15	0.16	0.17
2.83	0.15	0.13	0.15	0.2	0.11	0.1		0.06	0.08	0.11	0.1	0.1
3	0.13	0.14	0.13	0.08	0.19	0.1		0.06	0.03	0.04	0.09	0.09
3.17	0.09	0.11	0.14	0.06	0.09	0.06				0.01	0.02	0.03
3.33	0.1	0.08	0.09	0.05	0.01	0.07						
3.5	0.07	0.07	0.09	0.04	0.06	0.04						
3.67	0.05	0.08	0.07	0.01	0.03	0.01						
3.83	0.05	0.05	0.06		0.01							
4		0.04	0.05									
4.17		0.04	0.04									
4.33		0.12	0.03									

Table 16. Brix table over time from different forward osmosis concentration processes of cherry juice.

Time (h)	FO1			FO3			FO2			FO4		
	26°C - 1.7 bars			26°C - 2.7 bars			35°C - 1.6 bars			35°C - 2.6 bars		
0.17	13.2	13.6	13.7	13	11.6	13.8	13.1	13.2	13.5	13.5	13.4	13
0.33	14.2	14.2	14.2	13.8	12.3	14.9	14.1	13.3	13.5	14.8	14.30	13.3
0.5	14.9	15	14.95	15	12.9	15.5	15.6	14.2	14.4	15.8	15.40	15.1
0.67	15.7	15.6	15.6	15.7	13.7	16.7	17	16.2	15.5	17.1	16.70	16.3
0.83	16.7	16.8	16.6	17	14.7	17.6	18.6	17.7	17.4	18.6	18.20	17.2
1	19.5	17.9	17.4	18.3	15.8	18.9	20.5	18.8	20.1	19.9	19.80	19
1.17	21.1	18.8	18.6	19.9	17.3	20.2	22.1	19.9	21.9	21.6	21.50	20.9
1.33	22.5	20.3	19.7	21.3	18.6	21.5	26	22.4	24	23.7	23.40	22.8
1.5	24.1	21.6	21.1	22.6	20.3	23.2	29	24.2	26.1	27.1	25.20	24.1
1.67	26.3	22.6	20.8	24.3	21.7	24.4	31.9	27.5	29.2	29.6	27.50	26.9
1.83	27.8	24.4	24	27.3	23	27.4	35.1	29.8	31.8	30.2	29.50	29.7
2	30.1	25.9	25.3	28.5	25.3	28.3	38.6	32.9	35.75	34.6	32.40	31.2
2.17	32.4	27.5	27.2	30.8	26.7	33.6	44.6	35.9	37.3	33.2	36.70	34.1
2.33	29.15	29.4	28.9	32.9	29.3	35.2	49.4	42	41.4	41.5	41.00	37.6
2.5	36.4	31	30.7	35.4	32	37.3	57.1	46.4	45.2	44.8	43.20	40.9
2.67	39.3	32.6	32.4	37.5	34.1	39.5	58.2	50.3	50.4	48.8	47.60	44.1
2.83	41.2	34.5	34.4	42.7	35.6	42.1	61.3	56	54.7	52.6	51.20	49
3	44.1	37.5	36.2	45.6	40.5	45.8		59	58.1	54.7	54.60	52.5
3.17	47.1	40.4	40.5	48.9	44.2	49		61	60.2	59.7	59.10	56.1
3.33	50.5	42.1	42.7	51.9	48	52.3				60.3	60.20	59.4
3.5	53.2	43.7	45.4	54.8	51.4	54.4						60.4
3.67	55.8	46.3	48	59	54.7	58.4						
3.83	59.2	49.1	50.8		57.5	59						
4		51.7	53.3		57.8							
4.17		54.7	56									
4.33		58.9	59.3									