CONCENTRATION OF PINEAPPLE JUICES USING OSMOTIC EVAPORATION

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การทำให้น้ำสับปะรดเข้มข้นด้วยการระเหยแบบออสโมติกผ่านเยื่อแผ่น

จุฬารัตน์ หงส์วลีรัตน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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จุพารัตน์ หงส์วลีรัตน์ : การทำให้น้ำสับปะรดเข้มข้นด้วยการระเหยแบบออสโมติกผ่านเยื่อแผ่น (CONCENTRATION OF PINEAPPLE JUICES USING OSMOTIC EVAPORATION) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.สุเวทย์ นิงสานนท์, 108 หน้า.

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาประสิทธิภาพและสภาวะที่เหมาะสมในการทำให้น้ำสับปะรดเข้มข้น(ทั้งแบบขุ่นและใส)โดยใช้การระเหยแบบออสโมติกผ่านเยื่อแผ่นและประเมินหาสภาวะที่เหมาะสมของการใช้เอนไซม์ในการทำให้น้ำสับปะรดใสด้วยกระบวนการไมโครฟิลเตรชันแบบไหลขวาง

ทำให้น้ำสับปะรดใสโดยนำน้ำสับปะรดพาสเจอไรซ์และน้ำสับปะรดที่เตรียมจากน้ำสับปะรดเข้มข้นมาบ่มด้วยเอนไซม์เพคติเนสก่อนนำไปผ่านเยื่อแผ่นในกระบวนการไมโครฟิลเตรชันแบบไหลขวาง โดยมีตัวแปรต้น 4 ชนิดคือ ความเข้มข้นของเอนไซม์ (0.01-1 มิลลิลิตรต่อลิตร) อุณหภูมิและที่ใช้ในการบ่ม (30-35 องศาเซลเซียสและ 15-60 นาที) และความดันต่างภายในโมดูลเยื่อแผ่น (1.25-2.75 บาร์) จากผลการทดลองเมื่อพิจารณาฟลักซ์หรืออัตราการไหลผ่านเยื่อแผ่นของเพอมิเอทและค่าใช้จ่ายของกระบวนการ อาจกล่าวได้ว่าสภาวะที่เหมาะสมของการใช้เอนไซม์ในการทำให้น้ำสับปะรดใสด้วยกระบวนการไมโครฟิลเตรชันแบบไหลขวางในการทดลองนี้ ได้แก่ การใช้เอนไซม์เพคติเนสความเข้มข้น 0.01 มิลลิลิตรต่อลิตร อุณหภูมิและเวลาที่ใช้ในการบ่มเท่ากับ 30 องศาเซลเซียสและ 15 นาที และความดันต่างภายในโมดูลเยื่อแผ่นที่ 2.25 บาร์ โดยให้อัตราการไหลผ่านเยื่อแผ่นของเพอมิเอท 122 ลิตรต่อชั่วโมงต่อตารางเมตร

ทำให้น้ำสับปะรดแบบขุ่นเข้มข้นด้วยการระเหยแบบออสโมติกผ่านเยื่อแผ่นโดยใช้โมดูลเยื่อแผ่น 2 ชนิดเปรียบเทียบกัน จากผลการทดลองพบว่าโมดูลแบบแผ่นที่ประกอบด้วยเยื่อแผ่นชนิด PTFE/PE ให้ฟลักซ์หรืออัตราการไหลผ่านเยื่อแผ่นของไอน้ำในปริมาณมากกว่าโมดูลแบบท่อที่ประกอบด้วยเยื่อแผ่นชนิด PP ดังนั้นจึงนำน้ำสับปะรดทั้งแบบขุ่นและใสมาทำให้เข้มข้นโดยใช้โมดูลแบบแผ่นโดยมีปัจจัยในกระบวนการ 2 ปัจจัยคือ อุณหภูมิของน้ำสับปะรด (20 และ 35 องศาเซลเซียสและความเร็วของสารละลายแคลเซียมคลอไรด์ (2 และ 3 เมตรต่อวินาที) จากผลของการทำให้น้ำสับปะรดเข้มข้นโดยให้อุณหภูมิของน้ำสับปะรดเท่ากับ 35 องศาเซลเซียสและความเร็วของสารละลายแคลเซียมคลอไรด์เท่ากับ 2 เมตรต่อวินาที พบว่าการระเหยแบบออสโมติกผ่านเยื่อแผ่นในสภาวะดังกล่าวสามารถทำให้น้ำสับปะรดทั้งแบบขุ่นหรือใสเข้มข้นได้ถึง 55 องศาบริกซ์ โดยให้ฟลักซ์อยู่ในช่วง 5.5-8.5 และ 6.6-9.9 กิโลกรัมต่อชั่วโมงต่อตารางเมตรตามลำดับ สรุปได้ว่าการระเหยแบบออสโมติกผ่านเยื่อแผ่นเป็นกระบวนการที่มีประสิทธิภาพในการทำให้น้ำสับปะรดแบบขุ่นเข้มข้นใกล้เคียงกับการทำให้น้ำสับปะรดแบบใสเข้มข้น นอกจากนั้นคุณภาพของน้ำสับปะรด

เข้มข้นที่ได้มีการเปลี่ยนแปลงเพียงเล็กน้อย จึงอาจนำกระบวนการดังกล่าวมาใช้ในการผลิตน้ำสับปะรดแทนการระเหยแบบดั้งเดิม

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PULPY AND CLARIFIED JUICES/CROSSFLOW MICROFILTRATION/ OSMOTIC EVAPORATION.

In this work the concentration of pineapple juice by osmotic evaporation (OE) was evaluated in terms of performance and optimization. For clarification of pineapple juice by crossflow microfiltration (CMF), optimum conditions were determined.

For clarification experiments, the single strength and reconstituted pineapple juices were filtered through crossflow microfiltration (0.1 μm) after enzymatic treatment to select an optimum condition (enzyme concentration, incubation temperature, incubation time and transmembrane pressure) regarding permeate flux. The single strength and reconstituted pineapple juices were treated with pectinase at various concentrations (0.01-1 $ml.l^{-1}$), temperatures (30-35°C), time (15-60 min) and microfiltered at different transmembrane pressures (1.25-2.75 bar). Based on the permeate flux obtained, the optimum condition for clarifying the pretreated reconstituted pineapple juice by microfiltration was: enzyme concentration of 0.01 $ml.l^{-1}$, incubation temperature of 30°C, incubation time of 15 min and transmembrane pressure of 2.25 bar. The average permeate flux at this condition was 198 $l.h^{-1}.m^{-2}$ with total recycling. Moreover, the trial conducted at the optimum condition has produced an average flux as high as 122 $l.h^{-1}.m^{-2}$ at the final VRR (8.5) and the physico-chemical properties of the permeate (clarified pineapple juice) were acceptable.

The concentration experiments were carried out in a laboratory unit composed of two independent circuits, pineapple juice and brine. Calcium chloride solution was used as brine. Two membrane modules, flat and tubular, were compared. The flat module containing one PTFE/PP membrane provided higher flux than the tubular module containing three PP membranes. Concentration of the single strength and clarified pineapple juices was therefore studied using the flat module. Two operating parameters: juice temperature (20 and 35°C) and brine velocity (2-3 $m.s^{-1}$) were investigated. The optimum condition chosen for the next study was juice temperature of 35°C and brine velocity of 2 $m.s^{-1}$. For the concentration of the single strength juice, the evaporation flux ranging from 8.5 $kg.h^{-1}.m^{-2}$ to 5.5 $kg.h^{-1}.m^{-2}$ provided the concentration of the juice up to 55°Brix. The concentration of the clarified juice reached 53°Brix after the osmotic evaporation. In this case, the evaporation flux ranged from 9.9 $kg.h^{-1}.m^{-2}$ to 6.6 $kg.h^{-1}.m^{-2}$. The OE process has demonstrated that high concentration of pulpy pineapple juice is comparable to that of the clarified juice. In addition, the minimal changes of the quality of concentrated juices allow this process to overcome the problem of quality loss occurred under classical concentration technique.

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CHAPTER I

INTRODUCTION

Thailand is the world's leading producer of pineapple (Economic Research Service, www, 2003). Undoubtedly it is also one of the world's leading producers of canned pineapple. As a result, concentrated juice is mainly a by-product of the industry. In 2006, Pineapple juice accounted for approximately 60% of the total export value of fruit and vegetable juices. From 2005-2006, the amount and value of export pineapple juice increased 57 percent and 16 percent, respectively (Department of Export Promotion, www, 2006; Kasikorn Research center, www, 2007). Pineapple juice is commercially concentrated by vacuum evaporation. This technique presents major drawbacks. First is the loss of sensory (color, aroma, taste) and nutritional values of the final product, although flavor restoration has been applied (Arthey and Ashurst, 2001; Lin et al., 2002). Second is the high energy demand, despite the use of energy saving systems: thermocompression, mechanical compression, etc. (Petrotos and Lazarides, 2001). Besides, a trend in consuming healthy foods is increasing around the world. Fruit juices with better conserved nutritional and sensory qualities are therefore in demand.

The applications of various membrane techniques to concentrate the juices have been studied. Osmotic evaporation (OE) is one of these techniques that could be an attractive alternative to the commercial and other membrane processes. This is due to its ability to concentrate solutes to very high levels at low temperature and

pressure, less energy consumption and higher retention of sensory and nutritional attributes, comparing to vacuum evaporation, reverse osmosis (RO) and membrane distillation (MD), respectively. Reverse osmosis is a pressure-driven membrane process that a hydraulic pressure greater than the osmotic pressure must be applied for water to move from high solute to low solute concentration. The mechanism of separation is based on differences in solubility and diffusivity (Girard and Fukomoto, 2000; Mulder, 1996). Membrane distillation is a process in which two aqueous solutions, at different temperatures, are separated by a hydrophobic membrane. The driving force is the vapor pressure difference between the two solution-membrane interfaces due to the existing temperature gradient (Jiao et al., 2004). OE is also a process based on the use of a porous hydrophobic membrane to separate two liquid phases that differ greatly in terms of solute concentrations (Hogan et al., 1998; Kunz et al., 1996; Vaillant et al., 2001a). The operation mode of OE process is similar to that of MD process except for the difference in physical parameters creating the driving force, being either concentration (OE) or temperature (MD).

Although pulpy juices can be successfully concentrated using OE, the removal of the pulp by filtration prior to concentration often leads to significant improvement of process performances (Shaw et al., 2001). Nevertheless, pineapple juice and some other pulpy juices are not clarified commercially. Until recently, various groups of new products based on the clarified fruit juices have appeared in the market. Some of these products are sparking clear beverages (soft drinks, clear juice cocktails, etc.), pastries (natural essences, translucent fruit sauces), uniformly pulpy fruit juice blends (cocktails, ice creams, etc.) and natural translucent jelly products (Vaillant et al., 2001b).

Several researchers have studied concentration of pulpy juices (orange, passion fruit and pineapple) by OE process. However, the evaporation fluxes obtained in the concentration of fruit juice by osmotic evaporation have been low, less than 3.5 L or $kg.h^{-1}.m^{-2}$ (Alves and Coelhoso 2006; Cisse et al. 2005; Nagaraj et al. 2006; Vaillant et al. 2001; Vaillant et al. 2005). Various fruit juices (orange, apple and grape) were concentrated using OE batch process to study the mass and heat transfer mechanisms in the process (Sheng et al., 1991). Pasteurized orange and passion fruit juices clarified by crossflow microfiltration (CMF) and concentrated by OE (pilot scales) were evaluated for flavor quality and compositional changes (Shaw et al., 2001). OE to concentrate clarified passion fruit juice was carried out on an industrial scale (Vaillant et al., 2001a). Pasteurized pineapple juice clarified by CMF and concentrated by OE (a pilot scale) was evaluated for the volatile components retained in the final product (Shaw et al., 2002).

One important parameter influencing the evaporation flux (mass transfer) is membrane module. However, only few works have been conducted to determine the effects of membrane and modules on the OE process. Three types of membranes with the same pore size were compared by Mengual et al. (1993). The composite membrane (PTFE/PP) provided the highest evaporation flux due to its higher porosity and smaller thickness. For modules, Alves et al. (2004) compared the use of two different modules with the same pore size and porosity but different surface area and thickness in the concentration of a sucrose solution used as model juice. The concentration process using the hollow fiber module used less operation time than that using the tubular module due to larger surface area and smaller membrane thickness.

In addition, clarification of pulpy fruit juices by crossflow microfiltration (CMF) with or without enzymatic treatment before OE concentration could improve performance of this concentration process (Cisse et al. 2005; Vaillant et al. 2005). Nonetheless, the direct comparison of evaporation flux between whole juice and the clarified juice has never been reported. Therefore, this work aimed to evaluate the performance of OE in concentration of pineapple juice (both pulpy and clarified) and to optimize the CMF and OE processes in providing a basis to reach industrially competitive flux.

CHAPTER II

REVIEW OF LITERATURE

2.1 Pineapple and pineapple juice concentrate (PJC)

Pineapple [*Ananas comosus* (L.) Merr.] has long been one of the most popular of the non-citrus tropical and subtropical fruits, largely because of its attractive flavor and refreshing sugar-acid balance (Abd Shukor et al., 1998). Pineapple flesh (traditional varieties: Smooth Cayenne and Champaka) consists of about 87% water, 12-13% carbohydrates (most of which are presented as sugars), 0.6% protein, 0.1% lipid, 1% fiber and ascorbic acid of 17 $mg.100g^{-1}$ of edible portion (Hodgson and Hodgson, 1993; USDA National Nutrient Database for Standard Reference, www, 2004). Physico-chemical characteristics of pineapple flesh (cv. Smooth Cayenne) are total soluble solids of 12.5 °Brix, pH of 3.5, acidity of 0.9% w/w (as citric acid) and 4.5-4.6 % sucrose, 1.9-2.2 % fructose and 1.4-1.8 % glucose (Bartolomé et al., 1995; USDA National Nutrient Database for Standard Reference, www, 2004).

The Smooth Cayenne is known as one of the principle cultivars for juice production (Bartolomé et al., 1995; Hicks, 1990). Pineapple juice is often recovered from the ejected skins and cores from cutting step in preparation for canning. Other sources are small pineapples, physically damaged fruits that are not suitable for canning and off-cuts from the canning line (Abd Shukor et al., 1998; Flath, 1980; Rutledge, 2001). Fresh pineapple juice has a soluble solids content averaging around

12-15%, a Brix/acid ratio varying between 14 and 35 and a pH ranging between 3.8 and 4.0, depending on the fruit origin (Hicks, 1990). Physico-chemical properties of fresh pineapple juice (cv. Smooth Cayenne) are total soluble solids of 10 °Brix, pH of 3.6, acidity of 0.8% w/w (as citric acid), viscosity (25 °C) of 6.3 $mPa.s^{-1}$, sucrose of 5.7% w/w and pulp content of 7.4% w/w (Carneiro et al., 2002). Canned pineapple juice (without added ascorbic acid) contains approximately 85-86 % water, 13-14 % carbohydrates, 0.3% protein, 0.1% lipid, 0.1% fiber and 10.7 $mg.100g^{-1}$ ascorbic acid of edible portion (Hodgson and Hodgson, 1993; USDA National Nutrient Database for Standard Reference, www, 2004). Most juice is concentrated to reduce costs of packaging, storage, handling and transportation. The processing steps for concentrating pineapple juice vary upon growing regions, however, thermal concentration (vacuum evaporation) is used commercially for all regions and no membrane concentration has been used (Elkins et al., 1997).

2.2 Microfiltration (MF)

Microfiltration is a pressure-driven membrane process that involves the separation of macromolecules and suspended particles with diameters ranging from 0.05-10 μm (Baker, 2000; Mulder, 1996). Typical pressure range for the system is 5-50 psi (0.3-3.3 bar) (Kramer, 2000). The transport mechanism is mainly a sieving process. The pore sizes of the porous membranes range from 0.1 to 10 μm, making the process suitable for retaining suspensions and emulsions. However, MF membranes possessing pores in the range of 0.1-2 μm are commonly used because they are easy to characterize. Most MF membranes possess an asymmetric structure build up with a top

layer thickness in the order of 1 μm. Both ceramic and polymeric membranes are used, however the former is more frequently used due to its outstanding chemical and thermal resistances relative to the cleaning procedure (Mulder, 1996). The performance of a given membrane is determined by two parameters, selectivity (generally expressed as retention) and flux (or permeation rate). The main problem encountered when MF is applied is flux decline. The major causes of flux decline are concentration polarization and fouling. The latter is the deposition of solutes inside the pores of the membrane (adsorption) or at the membrane surface (pore blocking). There are many ways to depolarize a membrane but the most widespread is crossflow microfiltration (CMF) (Girard and Fukumoto, 2000). In crossflow filtration the feed flow is parallel to the membrane surface so that only part of the retained solutes accumulates.

In recent years, CMF has been an alternative method for clarification, purification, pasteurization and sterilization in several food industries: fruit juices (Cisse et al., 2005; Vaillant et al., 2005; Wang et al., 2005), dairy products (Nelson and Barbano, 2005), olive oil (Bottino et al., 2004), and beer (Gan et al., 2001; Thomassen et al., 2005).

2.2.1 Clarification of pulpy fruit juices by crossflow microfiltration (CMF)

Juice clarification is achieved by the removal of excess pulp (suspended solids) and compounds responsible for high viscosity and haze formation such as soluble polysaccharides (pectin, starch and gums), proteins, polyphenolic compounds (particularly tannins), metal ions and lipids. Centrifugation or finishing with fine screens is used to remove excess pulp; traditional methods (application of enzymes

and fining agents) or membrane processes are used to remove the compounds. In the latter process the juice may be first treated with enzymes to reduce clogging of the membrane and then passed across the membrane under pressure. Addition of enzymes lowers the viscosity because of hydrolysis of soluble polysaccharides and causes the aggregation of the compounds to larger units, which are removed easily by membrane processes. CMF has been a membrane process mainly applied for clarification and sterilization in the fruit juice industry (Girard and Fukumoto, 2000; Mulder, 1996). Commonly, the pore sizes of MF membranes used in the fruit juice industry range from 0.1-2 μm. All yeasts and molds and most bacteria are retained by MF membranes of 0.45 μm or less (Girard and Fukumoto, 2000).

Membrane pores are small enough to hold back tannins and other compounds that cause haze formation in the clarified juice. In addition membrane filter systems are able to remove yeasts, molds and bacteria to a large extent (Arthey and Ashurst, 2001; Baker 2000; Girard and Fukumoto, 2000)**.** Both microfiltration (MF) and ultrafiltration (UF) based on the same separation principle have been used in clarification of fruit juice, also wine and beer (Bailey et al., 2000; Carvalho et al., 1998; Fukumoto et al., 1998; Jiraratananon et al., 1997; Merlin and Shomer, 1999; Mulder, 1996; Rodrigues et al., 2003; Vaillant et al., 1999).

In the traditional process, fruit juice is passed through a series of decantation and diatomaceous filtration steps after enzymatic treatment. By replacing these final filtration steps with CMF, a better quality, sterile clarified juice can be obtained. Because of the high viscosity of pulpy juices, removing pulp (suspended solids) before concentration often enhances performance of the subsequent concentration process such as osmotic evaporation (OE). Various pulpy juices clarified by CMF before

concentrating using OE are passion fruit, pineapple, camu-camu, melon, and orange juices (Cisse et al., 2005; Rodrigues et al., 2004; Shaw et al. 2002; Vaillant et al., 2001; Vaillant et al., 2005). In these studies, enzymes were or were not used as a pretreatment step for MF.

Pineapple is typically low in pectin content (0.06±0.01 mg.100ml^{-1} juice, Carvalho et al., 1998) and in consequence, enzymatic degradation of this pectin can result in rapid clarification (Ashurst, 1995). Various commercial enzymes, especially pectinases have been used with different concentrations and incubation periods. Pectinases are a mixture of enzymes that act on pectic substances (pectins), plant polysaccharides that maintain the integrity of the cell wall or middle lamella (Bigelis 1993). Commercial pectinases are fungal origins, mainly from Aspergillus species. Enzyme preparations are usually mixtures of pectin esterases (PE), polygaracturonases (PG), pectin lyases (PL), hemicellulases, and endo-β-glucanases (Pilnik and Alphon, 1993).

Rapidase pomaliq 2F (0.1% v/v) at 30 ºC for at least 1 h was used in the clarification of six pulpy fruit juices by MF (Vaillant et al., 2001b). Pectinex SP-L and Celluclast 1.5L (0.03% v/v) at 30 ºC for 60 min were applied in the pineapple juice clarification by MF; the enzymatic treatment resulted in reduction of viscosity (29.6%) and pulp content (22%) but did not affect other physical and chemical characteristics including color, sugars and acidity (Carneiro et al., 2002). In addition, pineapple juice was treated with Citrozym Ultra L (0.002% w/v) at 40 ºC for 1 h and a half prior to UF (Barros et al., 2003). The clarification of juices by pectin degradation is also important in the manufacture of high Brix concentrates to avoid gelling and the development of haze (Pilnik and Voragen, 1993).

2.2.2 Effects of CMF on product quality

According to the clarification of the fresh melon juice using MF with prior enzyme treatment before OE concentration, the physico-chemical, nutritional, and microbiological properties of the fresh melon juice (feed, F), the clarified melon juice (permeate, P) and the retentate (R) are shown in Table 1 (Vaillant et al., 2005). Total soluble solids content (TSS) in the permeate was lower than that in the feed and the retentate. This is probably related to the presence of higher suspended solids content in the feed and the retentate that can interfere with the measurement of refractive index (Cisse et al., 2005). The viscosity of permeate was lower than the feed and the retentate due to the removal of suspended solids and compounds responsible for high viscosity i.e. pectin. β-carotene, the main carotenoid compound found in the feed, was completely retained in the retentate. This was probably because it is strongly associated with membrane and wall structures of the cell fragments such as pulp. The result accorded with higher positive a* and b* values, as the color of the retentate was deep orange. A loss of vitamin C (30%) was founded in retentate due to oxygen exposure while vitamin C content in the permeate was not different from that in the feed. The permeate had low counts (< 30 $CFU.ml^{-1}$) for both yeasts and molds and total flora, indicating that crossflow microfiltration (CMF) could insure the stability of the clarified melon juice.

Table 2.1 Main physico-chemical, nutritional, and microbiological characteristics of processed melon juice (in parenthesis, standard deviation from six experiments).

Characteristics	Feed (F)	Permeate (P)	Retentate (R)
Total soluble solids (TSS), $g.kg^{-1}$	88 (1)	70 (1)	91 (1)
Viscosity (25 °C), mPa.s	2.8 (0.1)	1.3 (0.1)	3.5 (0.1)
Turbidity, NTU	3000 (700)	0.61 (0.08)	9000 (900)
Color			
L*	57.1	53.8	53.9
a*	20.4	-2.3	33.2
b*	56.5	21.5	63.4
β-carotene, $g.kg^{-1}$ TSS	0.45	nd	1.45
Vitamin C, $g.kg^{-1}$ TSS	0.89 (0.09)	0.83 (0.07)	0.62 (0.05)
Total flora ($CFU.ml^{-1}$)	$3.5x10^4$	<30	$3.0x10^4$
Yeast and moulds ($CFU.ml^{-1}$)	<30	<30	<30

nd = not detected.

Ref. Vaillant et al., 2005.

The quality of the clarified orange juice (permeate, P) from MF before concentrating using OE was observed (Cisse et al., 2005). The single-strength, pasteurized orange juice (feed, F) was clarified without prior enzyme treatment. The important physico-chemical and nutritional characteristics of the feed, the permeate (P), and the retentate (R) are reported in Table 2.2. The permeate was totally clarified (SIS = 0 $g.kg^{-1}$) and the retentate was enriched with pulp (SIS = 90 $g.kg^{-1}$). This may relate to the swelling capacity of pulp fibers affected by the strong shear stress during constant recirculation thus skewing pulp measurements using the centrifugation method. The viscosity of the permeate was similar to the feed, probably because the feed was not enzymatically treated before clarification thus some compounds causing

high viscosity such as pectin still remained in the feed although the suspended solids was completely removed. The vitamin C and sugar contents in the feed, the permeate and the retentate were not significantly different. No carotenoids were noticed in the permeate but they were retained in the retentate with pulp since these compounds are mainly associated with cell-wall fragments. Subsequently, the permeate was almost colorless (low color purity) whereas the retentate was more yellow than the feed.

Table 2.2 Main physico-chemical and nutritional characteristics of processed orange juice (in parenthesis, standard deviation from six analyses).

Characteristics	Feed (F)	Permeate (P)	Retentate (R)
Total soluble solids (TSS), $g.kg^{-1}$	118 (2)	115 (2)	130 (2)
Viscosity (25 °C), mPa.s	1.1 (0.4)	1.2 (0.3)	1.7 (0.4)
Suspended solids (pulp), $g.kg^{-1}$	80 (3)	0	90 (4)
Color purity (C°)	30	17	37.3
Carotenoids, $g.kg^{-1}$ TSS	0.38 (0.04)	<0.02	0.34 (0.05)
Vitamin C, $g.kg^{-1}$ TSS	3.7 (0.3)	3.6 (0.3)	3.3 (0.2)
Glucose, $g.kg^{-1}$ TSS	186 (1)	185 (2)	188 (2)
Fructose, $g.kg^{-1}$ TSS	220 (2)	220 (2)	221 (2)
Sucrose, $g.kg^{-1}$ TSS	491 (2)	489 (2)	494 (2)

$C° = (a^{*2} + b^{*2})^{1/2}$

Ref. Cisse et al., 2005.

2.3 Osmotic evaporation (OE)

2.3.1 Definition

OE, also called osmotic distillation (OD), is a process based on the use of a porous hydrophobic membrane to separate two liquid phases (most commonly aqueous solutions) that differ greatly in terms of solute concentrations (Hogan et al., 1998;

Kunz et al., 1996; Vaillant et al., 2001a). It is a relatively new technology for concentration of liquid foods such as fruit and vegetable juices and various non-food aqueous solutions such as pharmaceutical products.

2.3.2 Process fundamentals

Driving force is a force that acts on a molecule or a particle, causing it to move across the membrane. The extent of this force is determined by the gradient in potential or approximately by the difference in potential across the membrane divided by the membrane thickness (Mulder, 1996). The potential difference arises as a result of differences in concentration, temperature, pressure or electrical potential. The operation mode of OE process is similar to that of MD process except for the difference in physical parameters creating the driving force, being either concentration (OE) or temperature (MD).

The driving force of OE is the difference in the vapor pressure of the solvent (usually water) between the two solutions, because of the difference in the chemical potential or of the osmotic pressure. Due to the hydrophobicity of the membrane it prevents penetration of the liquids into the pores, creating a liquid-vapor interface at each pore end. The water activity (a_w) difference between two sides of the membrane induces a vapor pressure gradient. Consequently, vapor is transferred across (the stagnant film of air within) the pores. The transport process takes place in three steps:

1. Evaporation of water in the solution of higher water activity at a pore entry,

2. Diffusional or convective transport of water molecules as vapor through the membrane pore and

3. Condensation of water vapor in the solution of lower water activity (Fig. 2.1) (Alves and Coelhoso, 2002; Hogan et al., 1998; Kunz et al., 1996; Nagaraj et al., 2006a; Wong and Winger, 1999). The evaporation of water from the solution of higher vapor pressure into that of lower vapor pressure will result in concentration of the former and dilution of the latter. If the water vapor pressure over the liquid being concentrated drops to a value equal to that over the receiving phase, no further transport will occur. Different transport models have been considered in order to evaluate the vapor flux (J) in l or $kg.h^{-1}.m^{-2}$, across the membrane. There are the molecular diffusion model, the Poiseuille capillary model, and the Knudsen diffusion model. Each of the models has its own limitations, thus, can only be used under certain conditions. However, all three models suggest a linear dependence of volume flux on vapor pressure difference (Kunz el al., 1996; Mengual et al., 1993).

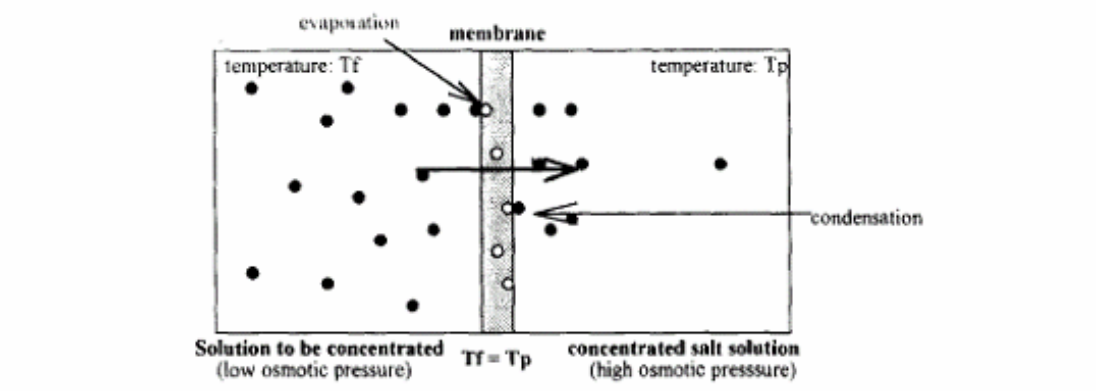


Figure 2.1 Transport process in OE (Kunz et al., 1996).

2.3.2.1 Mass transfer

Diffusion is the main mechanism involved in the mass transfer during OE (Courel et al. 2000b). The main variables influencing mass transfer are water activity

of dilute solution and brine, membrane structure and hydrodynamic circulation conditions in the membrane module (Courel et al. 2000a). Since the separation is based on vapor-liquid equilibrium, only volatile compounds can cross the membrane and the non-volatile solutes such as ions, sugars, macro-molecules, cells and colloids are totally retained in the concentrate (Courel et al. 2001b).

2.3.2.2 Resistances to mass transfer

The overall resistances to mass transfer are of the boundary layers in both the feed and osmotic solution sides and of the membrane itself (Alves and Coelhoso 2002). The boundary layers of the concentrated feed and dilute brine solution are present on either side of the membrane, resulting in significant resistance to mass transfer, which cannot be neglected. Furthermore, heat transfer across the boundary layers could influence the rate of mass transfer and mainly depends on the physical properties as well as hydrodynamic conditions of the solutions (Nagaraj et al. 2006a).

Hogan et al. (1998) stated that boundary-layer resistances are occurred in OE and must be minimized to achieve maximum process performance. The nature and extent of these resistances are rather different from the common pressure-driven membrane processes. Two types of boundary-layer resistances are specified including concentration polarization and viscous polarization. Removal of water from the feed into the strip creates a concentration polarization boundary layer at the upstream membrane surface of increasing solute concentration and the other at the downstream membrane surface of decreasing concentration of salt. This reduces the transmembrane water flux by depressing the vapor pressure of water over the feed solution contacting the membrane but increasing the water vapor pressure over the strip solution contacting the membrane (Fig. 2.2).

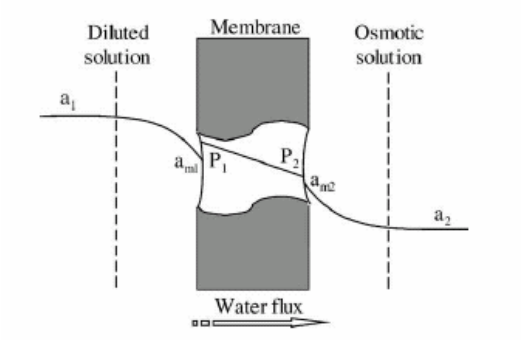


Figure 2.2 Water activity profile in OE (Alves and Coelhoso, 2002).

Since the extent of the concentration polarization is the ratios of the solute concentration at the membrane surface to that in the adjacent bulk liquid and these ratios are dependent upon the ratio of the volume flux of solvent across the membrane to the mass-transfer coefficient of the solute in the feed and strip channels. “Concentration polarization” in OE, thus, is much less important as an additional resistance to water transport than it is in RO because of the low inherent fluxes in OE and economics demand in the use of membrane contactors with the highest possible membrane area per unit volume (high mass transfer coefficients) such as hollow-fiber contactors.

“Viscous polarization” is an unusual boundary-layer resistance developed on the feed side of the membrane when highly concentrated products are desired from OE. This resistance is seldom in other membrane concentration processes and can have a very detrimental effect on process performance. Sheng et al. (1991) reported that the viscous polarization probably caused, in part, the decrease in the water flux as the juice concentration increased. Many of liquid foods (juices and beverages) contain hydrophilic solutes such as sugars, polysaccharides and proteins; when these solutes

are concentrated to high levels, solutions of irregular high viscosity are obtained. As such a solution passes through a membrane-bounded channel, solution near the membrane surface becomes increasingly concentrated until a critical concentration is reached, resulting in a very rapid increase of viscosity with further water removal. The flow rate of this viscous layer along the channel is progressively declined because it is bounded by flowing liquid of lower solute concentration and viscosity. Finally, stagnation of fluid in the boundary layer occurs to the membrane surface on the feed side and the less viscous and more diluted solution extends to the center of the channel with increasing velocity. Reduction of the solution residence time in the membrane module and blockage of the access of the solution to the membrane surface cause considerable decreases in water transport below expected performance. These effects can be minimized by proper fluid management of the feed-side channel of the membrane module such as clarification. An increase in OD flux after UF of single strength Gordo grape juice was reported by Bailey et al., 2000. This increase was attributed to reduction in the viscosity in the juice-membrane boundary layer as the result of protein removal (Fig. 2.3).

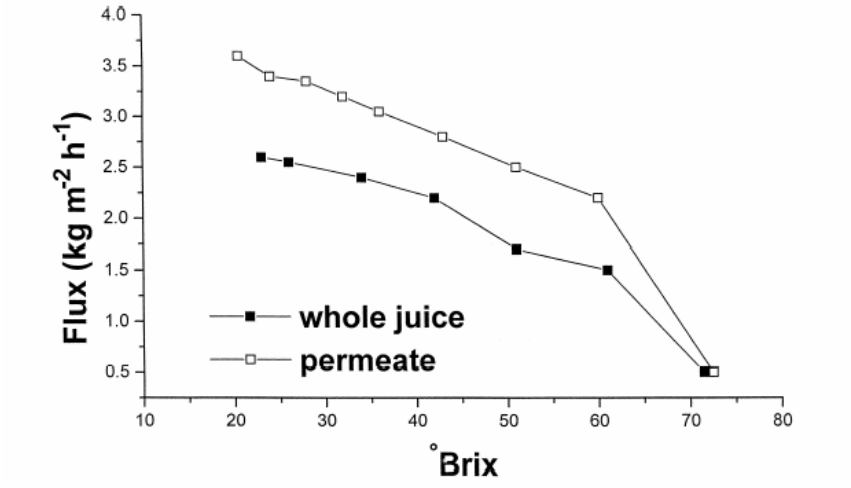


Figure 2.3 Variation of OE flux with concentration for whole juice and juice permeate from UF (Bailey et al., 2002).

Another important characteristic of OE is “temperature polarization” The evaporation process requires the supply of the latent heat of vaporization at the upstream liquid (the solution to be concentrated). In contrast, condensation of water vapor into the downstream liquid (the osmotic agent solution) requires the removal of the heat of the condensation (Fig. 2.4). Supplying or removing this energy by conduction/convection from the bulk liquid phases would cool down the feed and heat up the strip. The temperature differences between the liquids on opposite sites of the membrane, named “temperature polarization”, cause a reduction of the vapor pressure difference and hence a decrease of the driving force for water transport. This difference mainly depends on the heat transfer characteristics, i.e. heat conductivity, of the membrane and module but not the thickness (Gostoli 1999). In practice, this undesirable effect can be regulated by a thermostat and intensive stirring of the two liquids (Kunz et al. 1991). Moreover, the thermal conductance of the membranes used

nowadays is sufficiently high for rapid temperature equilibration near the membrane, resulting in the relatively small temperature difference, seldom greater than 2 °C (Hogan et al., 1998).

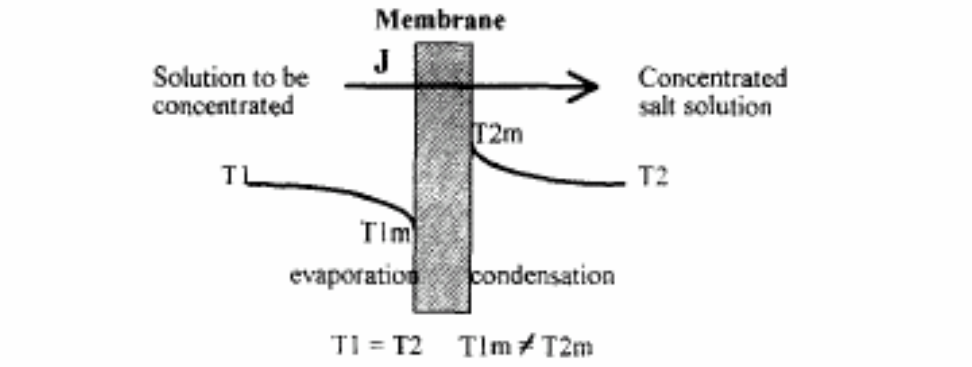


Figure 2.4 Temperature profiles for OE near the membrane (Kunz et al., 1996).

Sheng et al. (1991) reported that the temperature differences (6.24-0.14 °C), corresponding to the values of heat conductivity (0.16-0.70), between the juice and the brine had an effect on the water vapor flux; the flux increased when the temperature decreased while other operating parameters remained constant. This is in accordance with the conclusion of Lefevbre (2002) saying that an increase in heat conductivity reduces the temperature difference, giving a flattening of the temperature profile, whereas the influence of the estimated temperature difference (0.5-0.8 K) considered negligible to the flux decline was reported by Mengual et al. (1993).

2.3.3 Effects of MF pretreatment on the evaporation flux

Osmotic evaporation (OE) involves viscosity-dependent transport of liquid to the upstream surface of a hydrophobic membrane prior to evaporation and diffusion of water vapor across the membrane (Bailey et al., 2000). Clarification of pulpy fruit juices by MF before concentration by OE could improve performance of this concentration process due to complete removal of suspended solids (Cisse et al. 2005) and reduction of viscosity (Vaillant et al. 2005). Nevertheless, the direct comparison of OE flux between whole juice and juice permeate (or clarified juice) from MF in fruit juice concentration has never been reported.

2.3.4 Process parameters

Process factors affecting mass transfer include membranes and modules, osmotic agents and operating conditions: stirring rate (or circulation velocity), temperature and concentration of solutions.

2.3.4.1 Membranes and modules

Since the main requirement of OE is that the membrane must not be wetted in order to maintain the integrity of the gas phase inside the pores, membrane used in OE are made of hydrophobic porous polymer: polyolefins (PE-polyethylene and PP-polypropylene) and perfluorocarbons (PTFE-polytetrafluoroethylene and PVDF-polyvinylidene difluoride) (Hogan et al. 1998). Nonetheless, not only common hydrophobic porous membranes have been used, but also composite membranes in order to improve the prevention of the liquid penetration through the membrane pores (Albrecht et al. 2005). The minimum entry pressure (penetration pressure) for water of 2.9 bar was reported for flat PTFE/PP membranes with a nominal pore size of 2 μm

(Versari et al., 2004). The hydrophobicity of each membrane is determined by its composition, pore size, porosity and surface structure (Durham and Nguyen 1994). When the membrane surface is sufficiently hydrophobic, neither the feed nor the stripper can enter the pores. A highly porous membrane is needed with regard to three flux models: the Knudsen model, the Poiseuille model and the molecular diffusion model, suggesting that flux is proportional to the membrane porosity. The membrane should be as thin as possible because the flux is inversely proportional to the pore length (thickness). Nevertheless, a sufficient amount of material is necessary both for effective heat transfer to minimize temperature polarization and for membrane stability. In addition, the heat conductivity of membrane should be high in order to achieve rapid temperature equilibration near the membrane, resulting in reduction of temperature polarization (Hogan et al. 1998; Johnson et al. 1989; Kunz et al. 1996). This is in agreement with the previous work of Sheng et al. (1991) who reported that the heat conductivity of the membrane indicated the effect on the water flux; the flux increased with the values of heat conductivity. For pore size, it can be as large as practicable, compatible with the requirement that only vapor but not liquid is permitted to pass through the pores (Lefevbre, 1992). In general, the pore size of the membranes range from 0.1-1 μm, the membrane thickness proximately from 10 μm to 300 μm and the porosity is between 70-80 % (Kunz et

al. 1996). Also, Hogan et al. (1998) stated that a pore size of about 0.5 μm or smaller is adequate to prevent liquid penetration.

Various membrane modules have been used for fruit juice concentration. These include hollow fiber module (Bailey et al. 2000; Cisse et al. 2005; Shaw et al. 2001; Shaw et al. 2002; Vaillant et al. 2001a; Vaillant et al. 2005), flat module (Alves and

Coelhoso 2006; Barbe et al. 1998; Nagaraj et al. 2006b; Ravindra Babu et al. 2006; Rodrigues et al. 2004), and tubular module (Alves et al. 2004).

2.3.4.2 Osmotic agents

Since the driving force for water transport through the membrane is given by the difference between the water vapor pressures at the two sides of the membrane, the extractive power of an osmotic agent is represented by the lowering of the water vapor pressure in aqueous solutions. A prerequisite is therefore the high water solubility. Other important properties to be considered include high surface tension (to get high penetration pressure), negligible volatility (to avoid counter-diffusion towards the juice and loss during regeneration), and no toxicity (Celere and Gostoli 2004).

In the OE process the strip solution (the osmotic agent) must be reconcentrated by evaporation in order to be recycled and reused in the process. Therefore, it is important that the osmotic agent itself be thermally stable to quite high temperatures, also non-corrosive. The most attractive strip solutes are water-soluble salts particularly sodium and calcium chloride (Hogan et al. 1998).

The osmotic solution has practically been a high °Brix salt or sugar solution (Shaw et al. 2002). Sodium chloride solution (> 28 °Brix) was used as an osmotic medium in the studies of mass and heat transfer mechanisms in the OE process for concentration of orange, apple and grape juices (Sheng et al. 1991). Calcium chloride (4.6 M, 5.3 M and 40, 45 % (w/w)) has been used as the osmotic agent for various works on concentration of juices using OE. This is due to its non-toxicity, low a_w at saturation (0.33 at 25 °C), ready availability and low cost (Bailey et al. 2000; Barbe et al. 1998; Cassano et al. 2003; Shaw et al. 2001; Shaw et al. 2002; Valliant et al.

2001a). Both sodium chloride and calcium chloride (1-6 M) were used in the study on the effect of osmotic agent's nature and concentration on the OE process; calcium chloride was more effective than sodium chloride at the same concentration. This is due to the higher solubility (osmotic activity) of calcium chloride, resulting in higher vapor pressure gradient across the membrane (Alves and Coelhoso, 2002; Nagaraj et al. 2006b; Ravindra et al 2006). Besides, propylene glycol and glycerol were used as calcium chloride competitors to avoid corrosion of pipes and fittings caused by nearly saturated calcium chloride solution. However, these compounds were less effective than calcium chloride (Alves and Coelhoso, 2002; Celere and Gostoli 2004).

2.3.4.3 Operating conditions

Important operating conditions being investigated include feed and osmotic agent concentrations, circulation velocity (or stirring rate) and operating temperature.

The effect of juice concentration on the vapor flux was studied (Sheng et al. 1991) and was found that the water flux decreased as the juice concentration increased. This was probably due to a boundary-layer resistance on the feed side of the membrane (viscous polarization) or a decrease in osmotic pressure difference between the juice and the brine. These observations agree with the results obtained from sucrose solutions at a laboratory scale (Courel et al. 2000a) and from passion fruit juice at a pilot scale (Vaillant et al. 2001a). Also, the influence of brine (NaCl and $CaCl_2$) concentrations on the vapor flux was evaluated by several researchers: Alves and Coelhoso (2002); Courel et al. (2000a); Mengual et al. (1993); Nagaraj et al. (2006b); Vaillant et al. (2001a). According to their results, the vapor flux increased with the brine concentration. This increase is attributed to an increase of water activity

of brine side, giving higher vapor pressure difference across the membrane, which results in an increase in the driving force for water vapor transport through the membrane. Moreover, the flux as a function of the vapor pressure difference, for all osmotic agents fall into a straight line implying that the vapor flux is only dependent on the vapor pressure difference (Fig. 2.5).

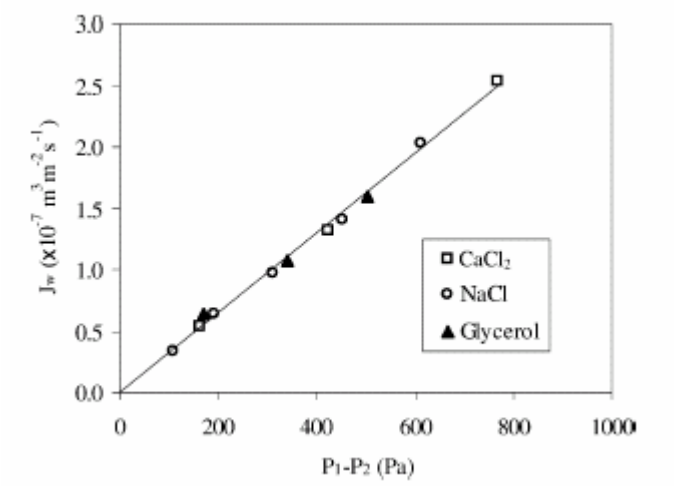


Figure 2.5 Flux variation with the water vapor pressure difference (Alves and Coelhoso, 2002).

The influence of stirring rate on the vapor flux was determined (Mengual et al. 1993) using pure water and NaCl as feed and strip, respectively. The vapor flux increased with stirring rate for all membranes used. This was in accordance with the results from the study of Alves and Coelhoso (2002). Similarly, Courel et al. (2000a) found that the vapor flux increased with circulation velocities of salt solution at low level (0.2-1.7 $m.s^{-1}$) until a plateau was reached. This increase may be due to a decrease in the boundary layer resistance, which is negligible at high circulation velocities (1.7-2.2 $m.s^{-1}$) leading to a constant vapor flux. The similar trend was observed for sugar solution. However, the role of brine velocity has to be integrated

into this flux improvement. Because of the design of the OE experimental device, any increment of sugar solution circulation velocity must be compensated by an increase in brine solution circulation velocity to equalize the pressure drop on both sides of the membrane.

The vapor flux increased with temperature; this was mainly due to the increase in driving force (Alves and Coelhoso 2002; Courel et al. 2000a; Mengual et al. 1993; Sheng et al. 1991; Vaillant et al. 2001a). Higher temperatures give more kinetic energy to the water vapor molecules and reduce the viscosity of feed streams causing an increase in mass transfer coefficient.

2.3.5 Concentration of fruit juices by OE and performance of the process

OE has been successfully applied to the concentration of liquid foods such as milk, fruit and vegetable juices and various non-food aqueous solutions. The process involves the use of a hydrophobic microporous membrane to separate two aqueous solutions at different solute concentrations, a dilute solution such as fruit juice and a hypertonic salt solution such as $CaCl_2$. The difference in solute concentrations, and consequently in water activity of both solutions generates a vapor pressure difference causing a vapor transfer from the dilute solution to the brine solution. This process can be achieved under atmospheric pressure and at room temperature, thus avoiding thermal degradation of the solutions.

Sheng et al. (1991) and Sheng (1993) studied the concentration of fruit juices including orange, apple and grape by OE. The plate and frame module (0.7 and 1 m^2) with PTFE membrane (0.2 μm) was used. The maximum flux obtained was 2.2 $l.h^{-1}.m^{-2}$.

Vaillant et al. (2001) evaluated the potential of OE in concentrating clarified passion fruit juice on an industrial scale. The OE unit (Fig. 2.6) contained a 10.2 m^2 of PP hollow fibers module and the average pore diameter was 0.2 μm.

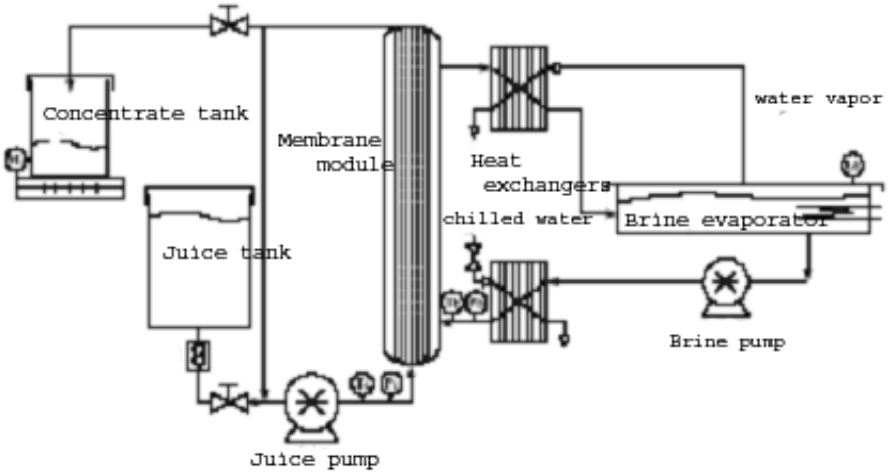


Figure 2.6 Scheme of the industrial pilot plant of OE (Vaillant et al., 2001).

Four sets of experiments were carried out. The first set was conducted with tap water as a feed at around 30 °C to test the evaporation performance of the unit. The obtained evaporation flux ranged between 0.72 and 0.81 $kg.h^{-1}.m^{-2}$. The second set was the concentration of the juice from 14 to 63 g $TSS.100g^{-1}$ without removing concentrate at the same temperature. The evaporation flux obtained during first hour was varied between 0.62 and 0.73 $kg.h^{-1}.m^{-2}$ and tended to decrease after 4 h towards the end of the trial, lasting 12 h; the flux value was 0.50 $kg.h^{-1}.m^{-2}$ at 63 $gTSS.100g^{-1}$.

The third set was the concentration of the juice with continuous extraction of concentrate, lasting 28 h, to show that OE can be continuously conducted. The evaporation flux decreased from about 0.78 to 0.40 $kg.h^{-1}.m^{-2}$ when juice TSS reached 60 g $TSS.100g^{-1}$. The average values of the evaporation flux were around 0.66 and 0.49 $kg.h^{-1}.m^{-2}$ at 40 and 60 g $TSS.100g^{-1}$, respectively. The last set was a multistage

concentration of the juice to obtain a better overall performance during concentration. The process gave the constant evaporation flux of around 0.62 $kg.h^{-1}.m^{-2}$ when the juice was concentrated from 14 to 60 g $TSS.100g^{-1}$. In addition, the production of concentrate at 60 g $TSS.100g^{-1}$ by two-stage process was compared to the one-stage process. The latter process provided the lower evaporation flux of 0.50 $kg.h^{-1}.m^{-2}$ (Fig. 7).

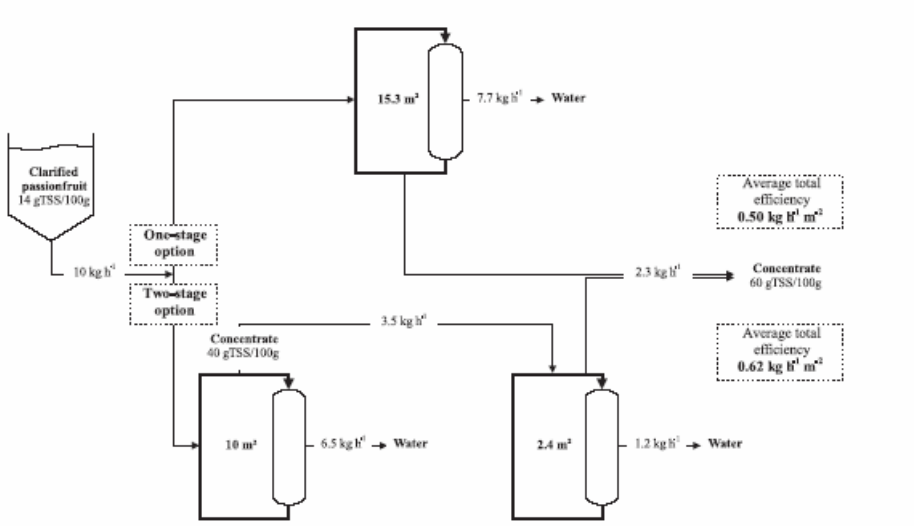


Figure 2.7 Scheme of one- or two-stage continuous-feed OE process and membrane area required (Vaillant et al., 2001).

Recently, Cisse et al. (2005) studied the performance of OE in concentrating the clarified orange juice. The OE pilot plant was similar to those described by Vaillant et al. (2001). The concentration of the clarified orange juice was carried out in two stages with continuous extraction of concentrate (Fig. 2.8). The evaporation flux decreased from 0.7 $l.h^{-1}.m^{-2}$ at the initial TSS (115 $g.kg^{-1}$) to 0.67 $l.h^{-1}.m^{-2}$ when TSS reached 450 $g.kg^{-1}$ (first stage) and to 0.59 $l.h^{-1}.m^{-2}$ when TSS reached 620 $g.kg^{-1}$ (second stage). The decrease in evaporation flux from the initial TSS to the final TSS

was relatively low (16%). Because evaporation flux was mainly correlated to the TSS and did not depend on time, it was stated that no significant membrane fouling occurred during the long-term trial (>30 h). The results confirmed those obtained with passion fruit juice (Vaillant et al. 2001).

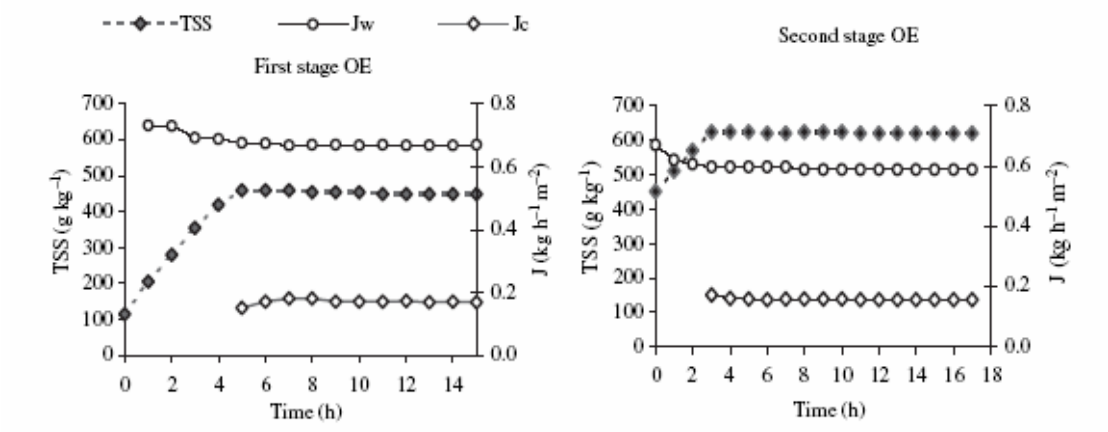


Figure 2.8 Concentration of total soluble solids (TSS), water flux (J_w) and concentrate removal flux (J_c) during OE (T_c = 26-28 °C, T_b = 30-33 °C) (Cisse et al., 2005).

Furthermore, Vaillant et al. (2005) investigated the performance of OE in concentrating the clarified melon juice. The OE pilot plant was the same as described by Cisse et al. (2005). The one-stage concentration with continuous extraction of concentrate was conducted over 12 h. The evolution of evaporation flux was similar to that obtained with passion fruit juice (Vaillant et al., 2001). The evaporation flux reduced approximately 19 % from 0.70 to 0.57 $kg.h^{-1}.m^{-2}$ when juice TSS reached 550 $g.kg^{-1}$.

There is a list of membranes/modules, osmotic agents, operating conditions, and flux values either on the laboratory scale or on a pilot scale shown in Table 3. The evaporation fluxes obtained with different fruit juices were somewhat low and similar,

less than 3.5 $l.h^{-1}.m^{-2}$ or $kg.h^{-1}.m^{-2}$. The same membrane was used thus such fluxes appear to be a characteristic of the membrane rather than of the juice. Nonetheless, trials carried out on the laboratory scale on sucrose solutions (0-65 %w/w) using the flat sheet module and with thinner membrane made of PTFE (60 μm compared to 800 μm) gave rise to much higher evaporation fluxes up to 23 $l.h^{-1}.m^{-2}$ at 35 °C (Courel et al., 2000a).

Table 2.3 Membranes/modules used and fluxes obtained in osmotic evaporation process.

References	Liquids	Modules/Membranes	Conditions		
			Temperatures (°C)	Hydrodynamic conditions	Fluxes obtained (l or kg h^{-1} m^{-2})
Sheng et al. (1991)	Fruit juices (orange, apple, grape)/NaCl solution (>280 g/kg solution)	A Syrinx plate and frame module/PTFE d = 0.2 µm l = 100 µm A = 0.7 m^2	29 and 40	Counter-current flow, Juice flow rate (5.8 l/min) Brine flow rate (1 l/min)	≈ 0-2.2
Mengual et al. (1993)	Pure water (bi-distilled and de-ionized)/NaCl solution (0-5 M)	A Lewis cell/PVDF, PTFE, PTFE/PP d = 0.2, 0.45, 1 µm l = 125-178 µm A = 27.5 cm^2 (0.003 m^2) P = 70-80 %	10-60	Agitation, stirring rates = 0-350 rpm	≈ 0-0.39 or (0.05-10.78) *10^{-8} m^3/m^2 s
Durham and Nguyen (1994)	Tomato puree/NaCl solution (28 %)	PTFE d = 0.2 µm l = 8.5-9 µm P = 78 %	Ambient (20-24)	Counter-current flow	0.6-1.4
Bailey et al. (2000)	Grape juice/$CaCl_2$ solution (62 °B or 40 % w/w)	A liqui-cell hollow fiber contactor/ PP A = 1 m^2	20	Juice flow rate (680 ml/min) Brine flow rate (810 ml/min)	≈ 0-3.5
Courel el al. (2000a)	Sucrose solution (0-65 % w/w)/$CaCl_2$ solution (32.2-45.5 % w/w)	A flat module/ PTFE/PP d = 0.2 µm l = 178 µm P = 80 %	20-35	Co-current flow Sucrose solution circulation velocity (0.1-2.7 m/s) Brine circulation velocity (0.2-2.2 m/s)	0.5-23
Shaw et al. (2001)	Fruit juices (orange and passion fruit) /$CaCl_2$ (4.6 M)	PP hollow fibers d = 0.2 µm A = 10 m^2			Not mentioned

Table 2.3 Membranes/modules used and fluxes obtained in osmotic evaporation process (cont.)

References	Liquids	Modules/Membranes	Conditions		
			Temperatures (°C)	Hydrodynamic conditions	Fluxes obtained (l or kg h^{-1} m^{-2})
Vaillant et al. (2001a)	Passion fruit juice/$CaCl_2$ (5.3 M)	PP hollow fibers d = 0.2 µm l = 800 µm A = 10 m^2	30	Co-current flow Juice circulation velocity (0.24 m/s) Brine circulation velocity ($1.8*10^{-3}$ m/s)	0.50-0.65
Alves and Coelhoso (2002)	Water (de-ionized)/NaCl (1-5 M), $CaCl_2$ (1-3 M), glycerol (3-5.5 M)	A flat module/ PP d = 0.1 µm l = 90 µm A = 11.3 m^2 P = 55 %	20-45	Agitation, stirring rates = 100-600 rpm	≈ 0.09-1.26 or (0.25-3.5) $*10^{-7}$ m^3/m^2 s
Shaw et al. (2002)	Pineapple juice/$CaCl_2$ (4.6 M)	PP hollow fibers d = 0.2 µm A = 10 m^2			Not mentioned
Cisse et al. (2005)	Orange juice/$CaCl_2$ (5.5 M)	PP hollow fibers d = 0.2 µm l = 800 µm A = 10 m^2	26±2 for juice 30-33 for brine	Co-current flow Juice circulation velocity (0.24 m/s) Brine circulation velocity (0.02 m/s)	0.59-0.70
Vaillant et al. (2005)	Melon juice/$CaCl_2$ (5.3-5.6 M)	PP hollow fibers d = 0.2 µm l = 800 µm A = 10 m^2	26±1 for juice 31±2 for brine	Co-current flow Juice circulation velocity (0.24 m/s) Brine circulation velocity (0.02 m/s)	0.57-0.70
Alves and Coelhoso (2006)	Orange juice model solution/ $CaCl_2$ (4.9 M)	PP hollow fibers d = 0.2 µm l = 200 µm A = 0.16 m^2 P = 70 %	25	Counter-current flow	≈ 1.55 or $4.3*10^{-7}$ m^3/m^2 s

Notes: d = pore diameter; l = thickness; A = surface area; P = porosity (All membrane characteristics were specified by the manufacturers.)

2.3.6 Effects of membranes and modules on OE

For OE process, a porous hydrophobic membrane is used for separating the solution to be concentrated from an osmotic agent. In this process, the vapor flux is influenced by only physical parameters like nature, average pore diameter (d), porosity (ε) and tortuosity (τ) of the membranes but not by physico-chemical interactions between the liquids and the membranes like RO. Membranes and modules are critical process parameters influencing mass transfer, expressed as vapor flux, in the OE process. Osmotic evaporation is considered as a mass transfer operation and the impact of the heat transfer due to evaporation and condensation of the water is rather controversial (Kunz et al., 1996). The membranes used in the OE process do not make any contribution to the selectivity. Its only function is the stabilization of the interface between both contacting media (Albrecht et al., 2005). In addition, the membrane itself is present as a barrier to vapor flux. The effect of membrane characteristics on mass and heat transfer in the OE process has been studied by several researchers. According to these studies, the mass transfer coefficients increased with the pore size (0.1, 0.22, 0.45 μm), implying that when the pore size increased, the vapor flux also increased (Alves and Coelhoso, 2004). Whereas, no marked change in the flux was reported between the membranes of pore size 0.2 and 0.45 μm, probably due to insignificant change in mechanism of diffusion. However, there was a significant increase in flux for the membrane of pore size 1 μm, perhaps due to increased contribution of molecular diffusion as compared to Knudsen diffusion (Mengual et al., 1993). Moreover, the flux did not show any dependency on pore size in the smaller range (0.05 and 0.2 μm) because the mechanism of mass

transfer in both cases is in the transient region between Knudsen and molecular diffusion (Nagaraj et al., 2006b; Ravindra Babu et al., 2006).

With higher porosity and smaller thickness of the active layer but the same pore size (0.2 μm), the vapor flux obtained from the composite membrane (PTFE/PP), 8.36 $m^3.m^{-2}.s^{-1}$, was higher than those obtained from the normal membranes (PTFE and PVDF), 7.51 and 5.14 $m^3.m^{-2}.s^{-1}$. Meanwhile, if only smaller thickness was taken into account (the same pore size and porosity), the vapor flux obtained from the PVDF membrane, 5.14 $m^3.m^{-2}.s^{-1}$ was less than that obtained from the PTFE membrane (Mengual et al., 1993). This is unexpected since the membrane mass transfer coefficient is inversely proportional to the membrane thickness. Nonetheless, the thermal conductivity of the PTFE membrane is higher than that of the PVDF membrane, thus temperature polarization as resistance to mass transfer was reduced. As a result, the higher flux was obtained by the PTFE membrane.

Alves et al. (2004) studied the concentration process of a sucrose solution (as a model juice) from 12 to 60 °Brix by OE using two different PP membrane modules: hollow fiber and tubular, with the same pore size and porosity but different surface area and thickness. The concentration process using the hollow-fiber membrane contactor (#I) used less operation time than that of the tubular membrane contactor (#II) due to higher membrane area, higher mass transfer coefficient and thinner membrane of the former contactor. The maximum water fluxes obtained were 0.72 l. $h^{-1}.m^{-2}$ (25 °C) and 0.22 $l.h^{-1}.m^{-2}$ (30 °C) for contactor I and II, respectively.

2.3.7 Effects of thermal concentration on product quality

Concentration of fruit juices can be achieved by several methods: evaporation,

membrane systems, and freezing. The industrial process is multistage vacuum evaporation which can affect the product quality, causing reduction in consumer preference. The process often leads to a considerable loss of volatile flavor compounds (Rao and Vitali, 1999). These compounds are important to the quality of many concentrates, especially for tropical fruits (Barbe et al., 1998; Vaillant et al., 2001). As shown in the work of Lin et al. (2002) an average of 95% of total volatile compounds in the unpasteurized grapefruit juice was lost during thermal concentration (using a thermally accelerated short-time evaporator). Over 84% loss of three dominant volatiles and complete loss of nearly all of the others had been investigated. The color change of pineapple juice as affected by heat treatment was also investigated (Rattanathanalerk et al., 2005). They reported that temperature (55-95 °C) had a significant effect on the color change of pineapple juice in terms of brown pigment formation, hydroxymethylfurfural (HMF), and Hunter color values (L, a, b and ΔE). OE, one of the membrane processes, has the potential to overcome some of these problems. Evaluation of qualities of various pulpy fruit juices concentrated by OE has been reported.

2.3.8 Effects of OE on product quality

Shaw et al. (2001) evaluated the concentrated orange and passion fruit juices prepared by MF followed by OE in terms of retention of flavors and sensorial quality. Both juices were concentrated to 33.5 and 43.5 °Brix, respectively, in a pilot scale osmotic evaporator containing 10.3 m^2 of polypropylene hollow fibers with 0.2 μm pore diameter. Quantitative analysis of 20-35 volatile compounds by headspace gas chromatography indicated about 32% loss in orange juice and 39% loss in passion

fruit juice. The triangle difference test by untrained panelists showed the difference at the 99.9% confidence level between the initial pasteurized orange juice and the juice reconstituted from OE concentrate. In addition, quantitative descriptive test by trained panelists showed slightly lower values for reconstituted orange juice, especially for peel oil flavor, compared to the initial juice. For passion fruit juice, only triangle test was conducted. The result was similar to that reported for orange juice. These results were in accordance with Vaillant et al. (2001) that the sensory scores obtained by the juice reconstituted from OE concentrate with pulp (obtained from pasteurized juice) were very similar to pasteurized juice but higher than thermally concentrated juice in terms of aroma, taste and color. In addition, the vitamin C content was well preserved.

Shaw et al. (2002) evaluated the clarified pineapple juice reconstituted from OE concentrate (51 °Brix) in terms of retention of flavors. Headspace gas chromatography showed that the concentrate retained an average of 62% of the volatile compounds present in the initial pasteurized juice, meaning that about 38% of volatile compounds in pineapple juice lost during processing. This value is similar to the values provided by Shaw et al. (2001).

Approximately 160 volatile compounds have been reported from pineapple including esters, alcohols, aldehydes, ketones and mono- and sesquiterpenoids. Esters constituted over 80% of total volatiles from both green and ripened pineapples. Ethyl acetate is one of the major volatile constituents in both green and ripened pineapples. The others are ethyl 3-(methylthio) propanoate and ethyl 3-acetoxyhexanoate in green pineapple and butane-2-3-diol diacetate and 3-hydroxy-2-butanone in ripened pineapple (Umano et al., 1992).

In 2004, Rodrigues et al. evaluated the application of osmotic evaporation membrane technology to produce concentrated camu-camu juice using a laboratory unit. The clarified camu-camu juice was concentrated in two stages, the first stage reached up to 25 °Brix, and then from 25 to 64 °Brix for the second one. The ascorbic acid loss was about 3% and the color of juice reconstituted from the OE concentrate was not different from the initial clarified juice.

More recently, Cisse et al. (2005) characterized the effect of OE process (2 stages) on the quality of clarified orange juice, including physico-chemical compositions (Table 4), volatile compounds, and sensorial property. A direct comparison of the main solutes (sugar and organic acid contents) expressed in gram per kilogram of TSS showed that no significant differences existed between the initial clarified juice (P) and OE concentrates at 450 and 620 $g.kg^{-1}$ (C^{OE}_{450} and C^{OE}_{620}). The vitamin C content expressed in gram per kilogram of TSS slightly decreased, however, both concentrates (C^{OE}_{450} and C^{OE}_{620}) showed no significant difference with respect to the initial clarified juice. The loss of vitamin C was mainly observed during the first 3 h of concentration, probably due to ascorbic acid oxidation by the residual oxygen entrapped within the pores of the membrane. As residual oxygen contained in the circuit is consumed, vitamin C loss decreased during processing and finally tended towards zero. For the color, after dilution to the same initial TSS (118 $g.kg^{-1}$), no significant difference was noticed for both concentrates (C^{OE}_{450} and C^{OE}_{620}), compared with the initial clarified juice. Some losses of aroma compounds occurred (22-31 %), nonetheless, using sensorial analysis, no significant difference of aroma (at 95% confidence level) was noticed between the initial clarified juice and the clarified concentrate at 620 $g.kg^{-1}$.

Table 2.4 Main physico-chemical and nutritional characteristics of the initial clarified orange juice (P) and the clarified concentrates (in parenthesis, standard deviation from six analyses).

Characteristics	P	C^{OE}_{450}	C^{OE}_{620}
Total soluble solids (TSS), $g.kg^{-1}$	115 (2)	450 (2)	620 (2)
Titratable acidity, g citric $acid.kg^{-1}$ TSS	61 (1)	59 (1)	62 (1)
Glucose, $g.kg^{-1}$ TSS	185 (2)	183 (2)	187 (2)
Fructose, $g.kg^{-1}$ TSS	220 (2)	219 (2)	221 (2)
Sucrose, $g.kg^{-1}$ TSS	489 (2)	490 (2)	491 (2)
Color purity (C°)	17	17[a]	17[a]
Carotenoids, $g.kg^{-1}$ TSS	<0.02	<0.02	<0.02
Vitamin C, $g.kg^{-1}$ TSS	3.6 (0.3)	2.9 (0.3)	3.3 (0.3)

C^{OE}_{450} and C^{OE}_{620} = OE concentrates at 450 and 620 $g.kg^{-1}$

[a]After dilution to 115 $g.kg^{-1}$ TSS

Ref. Cisse et al. 2005.

Moreover, the OE concentrate at 620 $g.kg^{-1}$ was collected at the end of the trial and blended with the MF retentate (R) previously pasteurized to give a pulpy concentrate (R + C^{OE}_{620}) to be compared with the initial single-strength juice (F) and commercially frozen vacuum-evaporated concentrate (C^{VE}_{650}) (Table 5). The composition of R + C^{OE}_{620} was very close to that of the initial juice (F). No significant difference was found for sugars and organic acids. Only 14% of vitamin C was lost. The color of R + C^{OE}_{620} was not different from the initial juice (F). For the commercial concentrate (C^{VE}_{650}), the differences were found compared to the initial juice (F). The significant differences with respect to sugar content and acidity were shown. The vitamin C content was 41% lower in C^{VE}_{650} than in the initial juice (F). Color degradation was observed, indicating an important browning of the commercial concentrate (C^{VE}_{650}). The contents of all classes of aroma compounds in the pulpy concentrates (R + C^{OE}_{620} and C^{VE}_{650}) were lower than those in the initial juice (F),

nevertheless, with the losses being much higher in the commercial concentrate (C^{VE}_{650}) (Table 6). Depending on chemical class, losses in C^{VE}_{650} were 31-70 % whereas losses in R + C^{OE}_{620} were only 17-25 %. The physico-chemical composition, nutritional quality and aroma compounds were thus clearly less affected by the membrane processes than by thermal evaporation. In addition, the sensorial tests indicated that no significant differences (at 95% confidence level) were noticed between the initial juice (F) and the OE concentrate (R + C^{OE}_{620}). Therefore, the membrane process used had no significant effect on the sensorial quality of the juices. On the contrary, the juices reconstituted from the commercial concentrate (C^{VE}_{650}) and the OE concentrate (R + C^{OE}_{620}) were significantly recognized as difference according to aroma, taste, acidity and color.

Table 2.5 Main physico-chemical and nutritional characteristics of the initial single-strength orange juice (F) and the pulpy concentrates: R + C^{OE}_{620} and C^{VE}_{650} (in parenthesis, standard deviation from six analyses).

Characteristics	F	R + C^{OE}_{620}	C^{VE}_{650}
Total soluble solids (TSS), $g.kg^{-1}$	118 (2)	118 (2)	655 (2)
Titratable acidity, g citric $acid.kg^{-1}$ TSS	68 (1)	63 (1)	44 (1)
Glucose, $g.kg^{-1}$ TSS	186 (1)	185 (2)	114 (1)
Fructose, $g.kg^{-1}$ TSS	220 (2)	219 (2)	136 (1)
Sucrose, $g.kg^{-1}$ TSS	491 (2)	488 (2)	291 (2)
Carotenoids, $g.kg^{-1}$ TSS	0.38 (0.04)	0.35 (0.05)	0.24 (0.05)
Vitamin C, $g.kg^{-1}$ TSS	3.7 (0.3)	3.2 (0.3)	2.2 (0.2)

R + C^{OE}_{620} = OE concentrate at 620 $g.kg^{-1}$ blended with the MF retentate (R)

C^{VE}_{650} = commercially frozen vacuum-evaporated concentrate

Ref. Cisse et al. 2005.

Table 2.6 Concentration (in $mg.kg^{-1}$) of the principal classes of aroma compounds in the initial single-strength orange juice (F) and the pulpy concentrates: R + C^{OE}_{620} and C^{VE}_{650} (in parenthesis, standard deviation from six analyses).

Aroma compounds	F	R + C^{OE}_{620}	C^{VE}_{650}
Total alcohols	2405	1946	1649
Total terpenic hydrocarbons	2851	2107	1751
Total aldehydes	112	93	46
Total esters	1810	1363	544
Total terpenols	166	137	102

R + C^{OE}_{620} = OE concentrate at 620 $g.kg^{-1}$ blended with the MF retentate (R)

C^{VE}_{650} = commercially frozen vacuum-evaporated concentrate

Ref. Cisse et al. 2005.

Vaillant et al. (2005) studied the effect of OE on the physico-chemical, nutritional, and microbiological qualities of melon juice previously clarified by MF. The main characteristics of the initial clarified melon juice (Permeate, P) and the concentrate (C) were shown in Table 7. The OE concentrate had very similar values to the clarified juice for acidity and sugars contents. No significant loss of vitamin C was noted, compared with the initial clarified juice (P). Total flora enumeration in the concentrate (C) showed recontamination of the product during handling because the initial clarified juice (P) was almost free of microorganisms. This problem could be easily solved using an aseptic connection between the filter and the concentrator. The color of reconstituted juice from the concentrate (C) was completely reserved, compared with the initial clarified juice (P), indicating the absence of Maillard reactions.

Table 2.7 Main physico-chemical, nutritional, and microbiological characteristics of the initial clarified melon juice and the clarified concentrate (in parenthesis, standard deviation from six analyses).

Characteristics	Clarified melon juice	Clarified concentrate
Total soluble solids (TSS), $g.kg^{-1}$	70 (1)	550 (2)
Titratable acidity, $g.kg^{-1}$ TSS	43 (2)	42 (2)
Glucose, $g.kg^{-1}$ TSS	157 (10)	162 (10)
Fructose, $g.kg^{-1}$ TSS	186 (20)	220 (20)
Sucrose, $g.kg^{-1}$ TSS	400 (40)	410 (40)
Color:		
L*	53.8	52.3[a]
a*	-2.3	-2.2[a]
b*	21.5	19.9[a]
Vitamin C, $g.kg^{-1}$ TSS	0.83 (0.07)	0.85 (0.09)
Total Flora ($CFU.ml^{-1}$)	<30	$0.3*10^4$
Yeast and moulds ($CFU.ml^{-1}$)	<30	<30

[a]After dilution to 70 g kg^{-1} TSS

Ref. Vaillant et al. 2005.

According to several works mentioned above, the qualities of the OE concentrates were not significantly modified by this cold concentration process (OE).

2.3.9 Comparison with other cold membrane processes

The comparative studies between osmotic evaporation (OE) and reverse osmosis (RO) or membrane distillation (MD) were studied.

Rodrigues et al. (2004) evaluated the capability of OE and RO to produce a concentrated camu-camu juice with high nutritional quality, with respect to their performance (flux and maximum content of total soluble solids) and to vitamin C content and color of the concentrates. Camu-camu is a fruit containing high vitamin C (9-50 $g.kg^{-1}$), compared with 0.4-0.9 $g.kg^{-1}$ in orange. Camu-camu fruits obtained

from Brazil were processed and the camu-camu juice was clarified using microfiltration (MF) with previously treated with pectinase. The clarified juice was subsequently concentrated with RO and OE at low temperatures (20-35 °C). The RO trials were conducted using a pilot scale unit with a composite membrane (95% NaCl rejection) in a plate and frame module of 0.72 m^2 of membrane area. The results are shown in Table 8. The average permeate flux obtained ranged from 18-51 $kg.h^{-1}.m^{-2}$ depending on the transmembrane pressure used (20, 40, 60 bar). The maximum total soluble solids content reached only 255 $g.kg^{-1}$ at 60 bar. The ascorbic acid loss was between 8 and 18%. The color of juice reconstituted from the RO concentrate was modified, compared with the initial clarified juice.

The OE trials were carried out using a laboratory unit with a PTFE flat sheet membrane. The effective area of the membrane was 40 cm^2 (0.004 m^2) and the average pore diameter was 0.2 μm. The results are also shown in Table 9. The initial clarified juice was concentrated in two stages with the final concentration of 640 $g.kg^{-1}$. The evaporation fluxes obtained were 12 $kg.h^{-1}.m^{-2}$ at first stage and 9 $kg.h^{-1}.m^{-2}$ at second stage. The ascorbic loss was about 3%. The color of juice reconstituted from the OE concentrate was unchanged, compared with the initial clarified juice.

Table 2.8 Operating conditions, permeate flux and ascorbic acid losses during concentration of camu-camu juice by reverse osmosis.

TMP (bar)	T (°C)	Time (min)	Total soluble solids ($g.kg^{-1}$)		Permeate flux ($kg.h^{-1}.m^{-2}$)			Ascorbic acid loss (%)
			Feed	Concentrate	Initial	Final	Average	
20	21	60	61	148	41.8	4.0	18.2	18.4
40	24	60	64	224	54.8	2.9	24.8	17.3
60	22	36	64	255	76.7	6.8	50.6	7.6

TMP = transmembrane pressure

T = temperature

Ref. Rodrigues et al. 2004.

Table 2.9 Evaporation flux and ascorbic acid losses during concentration of camu-camu juice by osmotic evaporation.

Camu-camu juice*	Total soluble solids ($g.kg^{-1}$)		Evaporation flux ($kg.h^{-1}.m^{-2}$)			Ascorbic acid loss (%)
	Feed	Concentrate	Initial	Final	Average	
First stage	66	247	13.3	11.1	12.0	2.5
Second stage	247	634	12.4	5.8	9.0	3.1

* Operating conditions: Brine conc. (5.2 ± 0.2 $mol.l^{-1}$), Temperature of juice (35 °C) and Temperature of brine (20 °C), Transmembrane pressure < 0.1 bar, Time of first stage (9 h) and Time of second stage (8 h).

Ref. Rodrigues et al. 2004.

Eventually, these two membrane processes could produce high quality concentrates with better retention of vitamin C and color using OE. RO has the advantage of being well developed at the industrial scale, but it has the limitation in reaching high concentration levels. Whereas, OE has the advantage of reaching the concentration levels that obtained with commercial thermal evaporation (up to 600 $g\ kg^{-1}$).

Alves and Coelhoso (2006) investigated the concentration of sucrose solution as a model orange juice by osmotic evaporation (OE) and membrane distillation (MD) in terms of water flux and aroma retention. The mechanism of OE is the same as in MD, but the driving force for water transport is sustained by a vapor pressure difference instead of a temperature difference (Gostoli, 1999; Wong and Winger, 1999). The role of heat transfer in MD is very important, on the contrary, OE is considered essentially a mass transfer operation (Gostoli, 1999). The study of concentration process was carried out in a hollow fiber membrane contactor. The sucrose solution (12 °Brix) was used as a feed (in a shell) for both processes, however, calcium chloride solution (4.9 M) and water were used as a receiving phase (in the fibers) for OE and MD, respectively. Alves and Coelhoso (2006) found that the water flux obtained by OE was two orders of magnitude higher than that obtained with MD despite that the overall driving force for water transport was similar. The cause for the lower water flux obtained in the MD process is the temperature gradient created between the bulk and the membrane interface, reducing the driving force for water transport. Moreover, in the OE process, the feed side mass transfer resistance was not significant as long as its viscosity is relatively low. The same situation can be assumed for the MD process since it started from a similar initial sucrose concentration. Meanwhile, in the OE process, the mass transfer resistance in the fiber (calcium chloride) boundary layer was negligible (Alves et al., 2004). Likewise, there is no concentration polarization in the fiber side of the membrane since pure water was used for the MD process. For the transport of aroma compounds (citral and ethyl butyrate) through the membrane, the model orange juice prepared with sucrose solution 45% (w/w), citral 18 $mg.l^{-1}$ and ethyl butyrate 18 $mg.l^{-1}$ was circulated in one

side of the flat membrane module and a calcium chloride solution (3 M) on the other side. A higher retention per amount of water removal was observed with the OE process. The driving force for the aroma compounds transport depends on their molecular fraction, activity coefficient and saturation vapor pressure, in the feed and in the receiving phase. In the OE process the temperature at both sides of the membrane is similar, leading to equal values of the saturation vapor pressure whereas in the MD process the temperature of the feed is always higher than that of the receiving phase, resulting in higher saturation vapor pressure of the feed compared with the receiving phase. On the other hand, in the OE process the activity coefficient in the feed is less than that in the receiving phase due to salting out effect while in the MD the activity coefficient in the feed is similar to that in the receiving phase. Therefore, the conjugation of the effect of temperature and the relative value of the activity coefficient in the different solutions results in a higher driving force for the aroma compounds transport for the MD process, which explains the aroma retention observed.

2.3.10 Advantages and disadvantages of the OE process

2.3.10.1 Advantages

The primary advantage of the osmotic evaporation process is its ability to concentrate solutes to very high levels at ambient temperature and pressure, with minimal thermal and mechanical damage to the solutes (Hogan et al., 1998). In comparison with conventional thermal concentration and membrane distillation, higher product quality can be obtained due to the lower operating temperatures that minimize volatile loss and heat degradation effects (Gostoli, 1999; Kunz et al., 1996;

Petrotos and Lazarides, 2001; Shaw et al., 2001; Shaw et al., 2002; Sheng et al., 1991; Vaillant et al., 2001a;). Besides, the energy consumption of the OE is much lower than reverse osmosis because there is no substantial hydraulic involved, hence the energy cost is quite low (Kunz et al., 1996; Petrotos and Lazarides, 2001). It also does not suffer from osmotic pressure limitations like reverse osmosis thus concentration levels close to the values currently obtained by conventional method (vacuum evaporation) can be reached.

2.3.10.2 Disadvantages

A drawback of the osmotic evaporation process for foods is its relatively low flux values, less than 5 $l.h^{-1}.m^{-2}$ (Kunz et al., 1996; Petrotos and Lazarides, 2001). However, this problem could be overcome by further development of industrial modules with more suitable hydrophobic membranes characterizing improved diffusion (Petrotos and Lazarides, 2001; Vaillant et al., 2001a). Another problem related to commercial application of OE in concentrating fruit juice is the management of diluted osmotic agents such as brines. For economic reason, the brine should be reused several times before it is removed from the process. The suggested use of evaporation would negatively affect the operational cost of the process. Several alternative methods, such as electrodialysis, have been experimented for the concentration of the exhausted brine (Jiao et al. 2004; Petrotos and Lazarides, 2001). Recently, Cisse et al. (2005) used the method called “cold regeneration” to reconcentrate the brine ($CaCl_2$ solution) in order to restore its osmotic ability. This was achieved by adding $CaCl_2$ crystals into the diluted brine and mixing under room temperature until the desired concentration was reached.

2.3.11 Industrial applications

By far the successful applications of OE in a commercial scale are the production of grape juice concentrate for winemaking and low-alcohol wines in Australia (Durham and Nguyen 1994; Hogan et al. 1998). Nevertheless, the process is a hybrid process, involving preconcentration of the feed by RO followed by further concentrating the RO retentate by OE.

The potential applications include the selective removal of a volatile solute from an aqueous solution in the drug industry, the production of other fruit juice concentrates, and the preconcentration of heat-sensitive pharmaceutical and biological products such as vaccines.

Table 2.3 Membranes/modules used and fluxes obtained in osmotic evaporation process.

References	Liquids	Modules/Membranes	Conditions		
			Temperatures (°C)	Hydrodynamic conditions	Fluxes obtained (l or kg h^{-1} m^{-2})
Sheng et al. (1991)	Fruit juices (orange, apple, grape)/NaCl solution (>280 g/kg solution)	A Syrinx plate and frame module/PTFE d = 0.2 µm l = 100 µm A = 0.7 m^2	29 and 40	Counter-current flow, Juice flow rate (5.8 l/min) Brine flow rate (1 l/min)	≈ 0-2.2
Mengual et al. (1993)	Pure water (bi-distilled and de-ionized)/NaCl solution (0-5 M)	A Lewis cell/PVDF, PTFE, PTFE/PP d = 0.2, 0.45, 1 µm l = 125-178 µm A = 27.5 cm^2 (0.003 m^2) P = 70-80 %	10-60	Agitation, stirring rates = 0-350 rpm	≈ 0-0.39 or (0.05-10.78) *10^{-8} m^3/m^2 s
Durham and Nguyen (1994)	Tomato puree/NaCl solution (28 %)	PTFE d = 0.2 µm l = 8.5-9 µm P = 78 %	Ambient (20-24)	Counter-current flow	0.6-1.4
Bailey et al. (2000)	Grape juice/$CaCl_2$ solution (62 °B or 40 % w/w)	A liqui-cell hollow fiber contactor/ PP A = 1 m^2	20	Juice flow rate (680 ml/min) Brine flow rate (810 ml/min)	≈ 0-3.5
Courel el al. (2000a)	Sucrose solution (0-65 % w/w)/$CaCl_2$ solution (32.2-45.5 % w/w)	A flat module/ PTFE/PP d = 0.2 µm l = 178 µm P = 80 %	20-35	Co-current flow Sucrose solution circulation velocity (0.1-2.7 m/s) Brine circulation velocity (0.2-2.2 m/s)	0.5-23
Shaw et al. (2001)	Fruit juices (orange and passion fruit) /$CaCl_2$ (4.6 M)	PP hollow fibers d = 0.2 µm A = 10 m^2			Not mentioned

Table 2.3 Membranes/modules used and fluxes obtained in osmotic evaporation process (cont.)

References	Liquids	Modules/Membranes	Conditions		
			Temperatures (°C)	Hydrodynamic conditions	Fluxes obtained (l or kg h^{-1} m^{-2})
Vaillant et al. (2001a)	Passion fruit juice/$CaCl_2$ (5.3 M)	PP hollow fibers d = 0.2 µm l = 800 µm A = 10 m^2	30	Co-current flow Juice circulation velocity (0.24 m/s) Brine circulation velocity ($1.8*10^{-3}$ m/s)	0.50-0.65
Alves and Coelhoso (2002)	Water (de-ionized)/NaCl (1-5 M), $CaCl_2$ (1-3 M), glycerol (3-5.5 M)	A flat module/ PP d = 0.1 µm l = 90 µm A = 11.3 m^2 P = 55 %	20-45	Agitation, stirring rates = 100-600 rpm	≈ 0.09-1.26 or (0.25-3.5) $*10^{-7}$ m^3/m^2 s
Shaw et al. (2002)	Pineapple juice/$CaCl_2$ (4.6 M)	PP hollow fibers d = 0.2 µm A = 10 m^2			Not mentioned
Cisse et al. (2005)	Orange juice/$CaCl_2$ (5.5 M)	PP hollow fibers d = 0.2 µm l = 800 µm A = 10 m^2	26±2 for juice 30-33 for brine	Co-current flow Juice circulation velocity (0.24 m/s) Brine circulation velocity (0.02 m/s)	0.59-0.70
Vaillant et al. (2005)	Melon juice/$CaCl_2$ (5.3-5.6 M)	PP hollow fibers d = 0.2 µm l = 800 µm A = 10 m^2	26±1 for juice 31±2 for brine	Co-current flow Juice circulation velocity (0.24 m/s) Brine circulation velocity (0.02 m/s)	0.57-0.70
Alves and Coelhoso (2006)	Orange juice model solution/ $CaCl_2$ (4.9 M)	PP hollow fibers d = 0.2 µm l = 200 µm A = 0.16 m^2 P = 70 %	25	Counter-current flow	≈ 1.55 or $4.3*10^{-7}$ m^3/m^2 s

Notes: d = pore diameter; l = thickness; A = surface area; P = porosity (All membrane characteristics were specified by the manufacturers.)

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

3.1.1 Experimental materials

Pineapple juices used were single strength pasteurized pineapple juice (SJ) and pineapple juice concentrate (JFC). The SJ was bought from a Carrefour, Montpellier, France. The JFC in a 25-kg aseptic package (the Smooth Cayenne variety) was supplied by the Siam Agro Industry Pineapple Public Co. Ltd. (SAICO, Rayong Thailand) and stored at –20 °C until use. The JFC was commercial pineapple juice concentrated to 65 ºBrix on an industrial scale by an evaporator, featuring three effects (the temperature of the first effect was 74 °C) and an aroma recovery unit.

3.1.2 Enzymes

Commercial pectinase, Pectinex Ultra SP-L, was supplied by Novo Nordisk, Switzerland. Pectinex Ultra SP-L is a multi-component enzyme preparation produced by a selected strain of *Aspergillus acucatus*. This enzyme preparation contains pectolytic (polygalacturonase) and hemicellulolytic activities. The standard activity is 26,000 $PG.ml^{-1}$ at pH 3.5 and 20 °C.

3.1.3 Osmotic agent

Calcium chloride (CASO HT food grade pearls 93-97%, Solvay S.A., Belgium) was used as osmotic agent for osmotic evaporation. The concentration of calcium chloride solution ranged approximately from 5.5 to 6.0 M containing a_w values from 0.329 to 0.435. A_w values of calcium chloride solution at 5.5 M evaluated in this experiment were between 0.412 and 0.427 at 25 °C.

3.1.4 Membrane units

3.1.4.1 Microfiltration (MF) unit (TIA, Bollène, France):

The lab scale used features four modules of tubular ceramic membranes assembled as shown in Fig. 3.1. The total effective area of the membrane was 0.02 m^2 and the average pore diameter was 0.1 μm (SCT-USF, Bazet, France) with the total feed tank volume of 3 l.

Figure 3.1 Microfiltration unit.

3.1.4.2 Osmotic evaporation (OE) unit:

Two membrane modules, tubular and plane, of laboratory scale were used. The tubular module contained three polymeric membranes made of polypropylene (PP) with 0.2 μm average pore diameter (Figure 3.2). The internal diameter was 5.75 mm and the length was 0.65 m. The total effective area of the membrane was 0.035 m^2. The flat module (Fig. 3.3) contained one flat sheet membrane made of thin porous polytetrafluoroethylene (PTFE) supported by PP net (TF-200, Pall-Gelman, USA) with 0.2 μm average pore diameter, 60% porosity and a thickness of 178 μm. The effective area of the membrane was 0.005 m^2.

Figure 3.2 Tubular module and membranes.

Figure 3.3 Flat module and membranes.

3.2 Methods

3.2.1 Clarification experiments

3.2.1.1 Optimization of enzymatic treatment and crossflow microfiltration (CMF)

The parameters to be optimized were: enzyme concentration (0.01, 0.025, 0.05, 0.1, 0.5, 1.0 $ml.l^{-1}$ or 0.001, 0.0025, 0.005, 0.01, 0.05, 0.1 %), incubation time (15, 30, 60 min), incubation temperature (30, 35 °C), and TMP (1.25, 1.75, 2.25, 2.75 bar) for CMF. The temperature of enzymatic treatment was monitored using a water bath with agitation by magnetic stirrer. The microfiltration unit used (TIA, Bollène, France) features four modules of tubular ceramic membranes placed (T1-70, SCT, Bazet, France) with a total effective area of 0.02 (4*0.005) m^2 and 0.1 μm average pore diameter.

The SJ and JFC were treated with each specified amount of Pectinex Ultra SP-L at 30 °C for 1 h and immediately microfiltered without enzyme inactivation. For each concentration level, a feed tank was filled with 2.5 l of enzyme-treated pineapple juice. The juice was clarified through the MF unit at constant pressure (2 bar) and cross-flow velocity (7 $m.s^{-1}$) and at room temperature (19±1 °C). The permeate was measured for permeate flux determination and returned to the feed tank to keep a constant concentration factor. At the same time, the effect of TMP on permeate flux was observed. The MF unit composed of four membrane modules as mentioned earlier. Each module (Module 1, M 1 to Module 4, M 4) was hypothesized to perform the different TMP as the following: 2.75, 2.25, 1.75 and 1.25 bar. The membrane was thoroughly cleaned after each run. The flow rate of each permeate channel was measured in order from Module 1 to Module 4 every 5 minutes for 2 h to obtain the permeate flux (J_p) from the following equation.

Permeate flux (J_p) = flow rate/ area = volume/time*area $l.h^{-1}.m^{-2}$

From this set of experiments, optimum enzyme concentration and TMP could be obtained. The experiments were repeated using only JFC with the optimum enzyme concentration to cover different incubation times and temperatures. Consequently, optimum incubation time and temperature could be identified.

3.2.1.2 CMF of the JFC at the optimum conditions using a larger membrane area (to confirm the flux value)

The JFC was treated with optimum enzyme concentration, incubation temperature and time (0.01-$ml.l^{-1}$ Pectinex SP-L at 30 °C for 15 min) before clarification. A feed tank was filled with 3 l of the enzyme-treated juice (13 °Brix). The juice was clarified using these conditions: TMP 2.25 bar, room temperature (21 °C), feed velocity 7 $m.s^{-1}$. For the first trial, the permeate was recirculated to the feed tank to keep a constant concentration factor. The flow rate of all permeate was measured every 5 min for 4 h to obtain the permeate flux. For the second trial, the permeate was collected for quality analysis.

3.2.1.3 VRR study: average flux and juice characteristics

1) Effects on initial SJ and JFC

The feed tank was filled with 3 l of SJ (~ 12.2 °Brix) or JFC (13°Brix). The juice was clarified using these conditions: TMP 2.25 bar, room temperature (22±1 °C), feed velocity 7 $m.s^{-1}$. The time was noted every 100 ml of permeate obtained. The permeate was collected every 500 ml and then the same amount of the juice was added to the feed tank to keep a constant concentration factor. The total permeate

collected was 7.3 l in 8.8 h and 8.8 l in 7.1 h of processing time for SJ and JFC, respectively. Permeates at different VRR were analyzed.

2) Effects on the JFC at optimum conditions

The JFC was treated with 0.01 $ml.l^{-1}$ Pectinex SP-L at 30 °C for 15 min before clarification. A feed tank was filled with 3 l of the enzyme-treated juice (13 °Brix). The juice was clarified using these conditions: TMP 2.25 bar, room temperature (25 °C), and feed velocity 7 $m.s^{-1}$. Permeate was collected every 500 ml and then the same amount of the enzyme-treated juice was added to the feed tank to keep a constant concentration factor. The permeate volume of every 100 ml and the time at that point were recorded to obtain permeate fluxes. Total permeate collected was 15 l in 6.2 h processing time. For quality analysis, initial juice (JFC), enzyme-treated juice (feed), permeate (P), and retentate (R) were analyzed.

After each process, the MF unit was cleaned using the method modified from the recommended method from TIA (Bellène, France) as shown in the appendix A. The cleaning solutions used were sodium hydroxide (2%), nitric acid (0.2%) and sodium hypochloride (0.025%).

3.2.2 Concentration experiments

The OE unit consisted of two independent circuits, one for the juice and the other for the brine. The 2-l juice tank was placed on a digital balance connected to a computer where the decay of the juice mass was continuously registered allowing further evaporation flux calculations. The 5-l brine tank was used to maintain a nearly constant salt concentration during the experiment. The volume of the brine was about three times higher than that of the juice to prevent a significant dilution with

consequent decrease in the driving force (Alves and Coelhoso, 2004; Courel et al., 2000a). Both solutions were circulated co-currently in the membrane module using two independent gear pumps. The temperatures of the juice and the brine were controlled by two thermostat circulating water systems. Rotameters were used for the circulation flow rate in each circuit. Manometers were used for indicating the pressure difference between both circuits (TMP). By adjusting the circulation flow rates of the circuits, the TMP was maintained at a negligible level (< 0.1 bar) to prevent liquid transfer through the pores. Juice conductivity was measured before and after each concentration trial to ensure integrity and hydrophobicity and to detect possible salt leakage through the membrane. For brine regeneration, $CaCl_2$ pearls were added to the diluted brine until the desired concentration (as a_w value) was obtained (Cisse et al, 2005). After each trial, the OE unit was cleaned with deionized water for the brine tank and with sodium hydroxide (1%: 50 ml of 30.5% NaOH) and then deionized water (until reach pH 7) for the juice tank.

3.2.2.1 Process performance of the osmotic evaporation (OE) process

Prior to optimization, the process efficiency of two membrane modules (tubular and plane) were investigated. Single strength pasteurized pineapple juice (SJ) at six concentration levels (10, 20, 30, 40, 50, 60 °Brix) was concentrated to simulate the concentration process. These experiments were carried out using pre-concentrated juices (20-60 °C) obtained from thermal concentration (T = 35-40 °C, time = 2.5-3 h). The following operating conditions were used regarding the results of Courel et al. (2000a).

Juice temperature: 35 °C

Brine temperature: 20 °C

Juice velocity: 0.32 $m.s^{-1}$ (for tubular module), 1.25 $m.s^{-1}$ (for flat module)

Brine velocity: 0.26 $m.s^{-1}$ (for tubular module), 2.00 $m.s^{-1}$ (for flat module)

Transmembrane pressure (TMP) : < 0.1 bar

3.2.2.2 Optimizing conditions for OE

The parameters to be optimized were juice temperature (20 and 35 °C) and brine velocity (2-3 $m.s^{-1}$). At the optimal conditions chosen, the SJ and its clarified juice were concentrated in two stages of 8 h each using the flat module. Since the membrane surface of the flat module was small, the juice was concentrated in a closed concentration loop (shown in the appendix B) continuously fed with the raw juice. On the first stage (day), each juice was concentrated with OE from the initial Brix to reach about 30 °Brix. On the second stage (day), the juice previously concentrated with thermal evaporation at around 30 °Brix was concentrated with OE up to 55 °Brix. The pre-concentrated juice with thermal evaporation was needed because the amount of the concentrated juice obtained from the first stage of OE was not enough for the subsequent stage of concentration.

In addition, the effect of the juice concentration on the flux behavior was investigated. Both the SJ and its clarified juice (using CMF) were concentrated under steady-state condition using the flat module. Due to the small effective area of the membrane surface compared with the large volume of juice in the OE system, concentration did not change during 3 h of operation. Six different concentrations (10-60 °Brix) were evaluated.

3.2.3 Analytical procedures

Total soluble solids (TSS) content was measured using handy refractometers (Model N1 and N2, ATAGO, Japan) at room temperature. The pH was determined using a pH meter (Model CG 842, SCHOTT, GERMANY). Titratable acidity (TA) was determined according to the indicator method (AOAC 1990, section 942.15 p.918), using phenolphthalein indicator to establish the end point. Total polyphenols was determined using the rapid method described by Georgé et al. (2005) as shown in the appendix C. Vitamin C was evaluated with HPLC, using the method modified from Rojas-Gonzalez et al. (2006) as shown in the appendix D. Flavor analysis was performed using GC-MS as shown in the appendix E.

Suspended solids (SS) were determined in relation to total juice weight (% w/w). A 10-ml juice was transferred to a pre-weighed tube, weighed and centrifuged at 20000 rpm (48400×g) for 1 h at 20 °C. After removing the supernatant, the weight of settled solids was then determined. Further, the settled solids (in the tube) were oven dried at 60±2 °C overnight (16 h) and weighed.

Turbidity was determined using a bench turbidity meter (Model LP 2000, HANNA Instruments, Hungary) and is reported as Nephelometric Turbidity Units (NTU). The initial juice and the retentate were diluted 5 and 10 times, respectively, before each measurement.

Color was determined using a MINOLTA chroma meter (Model CR-300), Japan. The color values are expressed as chroma and hue.

Viscosity was determined at room temperature (25-26 °C) using a SCHOTT capillary viscometer (Schott-Geräte Gmbh, Germany). All samples were filtered through the standard filter paper before measuring. The amount used for each

measurement was 8 ml. Distilled water was used as the reference for obtaining the relative viscosity according to the following equation:

$$\mu_s = \mu_w (t_s/t_w)$$

where μ_s and μ_w = viscosity of sample and water

t_s and t_w = flow time of sample and water

The viscosity of water at different temperatures was taken from Table 5-A1 (Okechukwu and Rao, 1999).

Water activity of both juice and brine were measured in an aw-meter Aqualab (Series 3 Model TE, Decagon Devices, Inc., USA) with a mean error of 0.05. The equipment was daily calibrated using salt standard solutions with water activity of 0.243, 0.504 and 0.760.

Conductivity values of juice and brine were performed in the HANNA Instruments conductivity equipment, calibrated with standard solutions ranging from 1413 to 12880 $\mu S.cm^{-1}$. The juice conductivity was always monitored during concentration to ensure membrane integrity and hydrophobicity, and to detect possible salt leakage through the membrane. The brine conductivity was evaluated regarding dilution problems during the concentration trials but it was verified that the $CaCl_2$ concentration did not change more then 10% after an eight hour experiment.

3.2.4 Statistical analysis

Data of the main characteristics of the single strength and clarified pineapple juices before and after OE was statistically analyzed by t-test.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Clarification experiments

4.1.1 Preliminary study

The reproducibility of the microfiltration (MF) unit used was evaluated by conducting three trials of clarification of single strength commercial juice (SJ, 12.8 °Brix) at 20 °C and TMP of 2 bar ($2*10^5$ Pa). The reproducibility of the MF unit was satisfying (coefficient of variation of average fluxes obtained < 5%, shown in Table 4.1).

Table 4.1 The reproducibility of each membrane module of the MF unit expressed as coefficient of variation (cv) of average permeate flux (J_p, $l.h^{-1}.m^{-2}$).

	Trial 1	Trial 2	Trial 3	J_p (SD)	cv
Module 1	64.5	61.8	60.5	62.3 (2.0)	3.21
Module 2	63.5	59.6	58.7	60.6 (2.6)	4.21
Module 3	60.3	59.5	58.3	59.4 (1.0)	1.70
Module 4	62.7	59.8	57.9	60.1 (2.4)	4.01

4.1.2 Optimization: enzyme treatment and CMF conditions (with total recycling)

The results are shown in two parts. The first part is the flux behavior with time of single strength commercial juice (SJ) and juice from commercial concentrate (JFC)

diluted to the same Brix as SJ. The second one is the effect of each operating parameter on permeate flux.

4.1.2.1 Flux behavior vs. Time according to enzyme concentration, incubation time and TMP

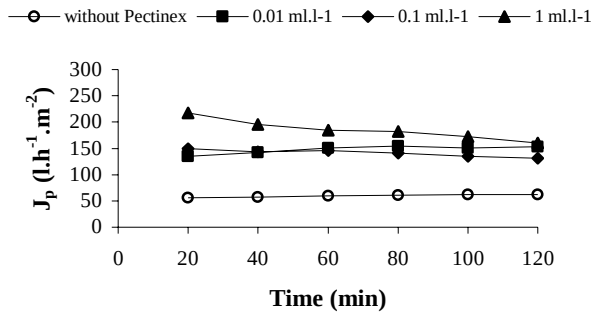
According to enzyme concentration and TMP, four distinct groups of curves were observed for single strength commercial juice (SJ). The first group was SJ without Pectinex treatment (SJ_0). The second group was SJ treated with Pectinex at 0.01 $ml.l^{-1}$ ($SJ_{0.01}$), the third group was SJ treated with Pectinex at 0.025-0.50 $ml.l^{-1}$ ($SJ_{0.025}$-$SJ_{0.50}$), and the last group was SJ treated with Pectinex at 1 $ml.l^{-1}$ (SJ_1). Two distinct groups of curves were also observed for juice from commercial concentrate (JFC). The former was JFC without Pectinex (JFC_0) and the latter was JFC treated with Pectinex at 0.01-0.10 $ml.l^{-1}$ ($JFC_{0.01}$-$JFC_{0.10}$).

Flux behaviors of SJ at each enzyme concentration were similar for all transmembrane pressures except at 1 $ml.l^{-1}$ (Fig. 4.1). The flux of SJ_0 stabilized with time. The flux of $SJ_{0.01}$ increased with time whereas the fluxes of $SJ_{0.025}$-$SJ_{0.50}$ decreased with time and may be later stable at different periods of time for different TMP. The classical behavior can be explained by the fouling establishment at the beginning of the process and then reaching the steady state. The flux of SJ_1 decreased with time for lower TMP (1.25 and 1.75 bar) but increased with time and then either stabilized or decreased for higher TMP (2.25 and 2.75 bar).

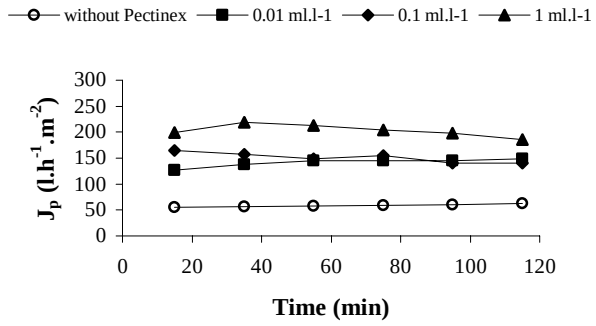
Flux behaviors of JFC at each enzyme concentration were also similar for all transmembrane pressures (Fig. 4.2). The flux behavior of JFC without Pectinex

stabilized with time. The flux of JFC treated with Pectinex decreased with time at all concentration levels (0.01-0.10 $ml.l^{-1}$).

Both juices provided similar behaviors at the same enzyme concentration for all TMP except for 0.01 $ml.l^{-1}$ enzyme. According to the results, the effect of enzyme concentration was more pronounced than that of TMP. This agreed with Vaillant et al. (1999) stating that flux depended mainly on enzyme concentration and little on TMP in the microfiltration of passion fruit juice after enzymatic treatment.



(a)



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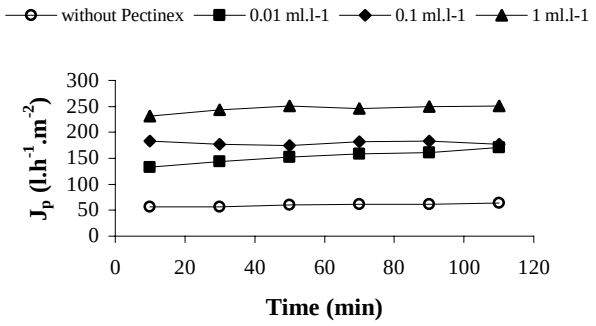

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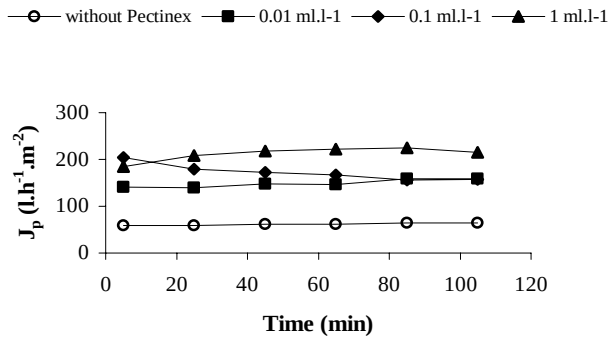
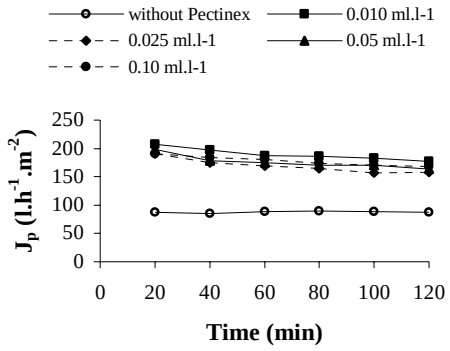
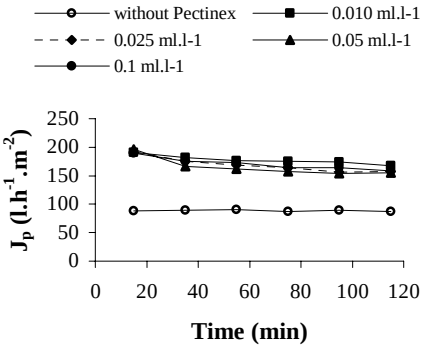


(d)

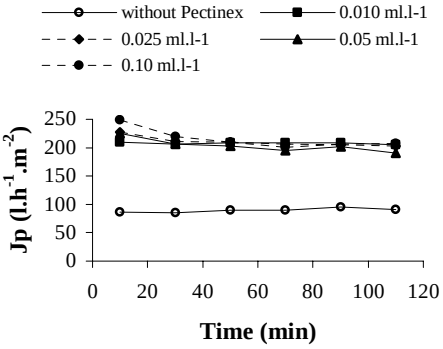
Figure 4.1 Permeate flux (J_p) versus time during microfiltration of single strength pineapple juice (SJ) pretreated with Pectinex Ultra SP-L at various concentrations at TMP of 1.25 bar (a), 1.75 bar (b), 2.25 bar (c) and 2.75 bar (d) (temperature, 19±1 °C; cross flow velocity, 7 m.s^{-1}).



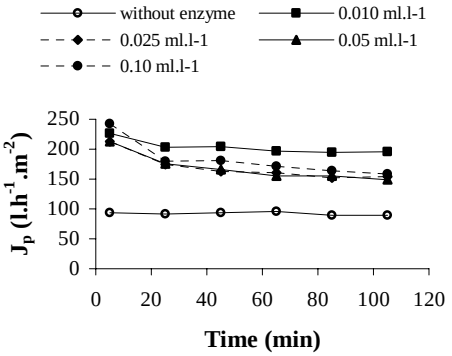
(a)



(b)



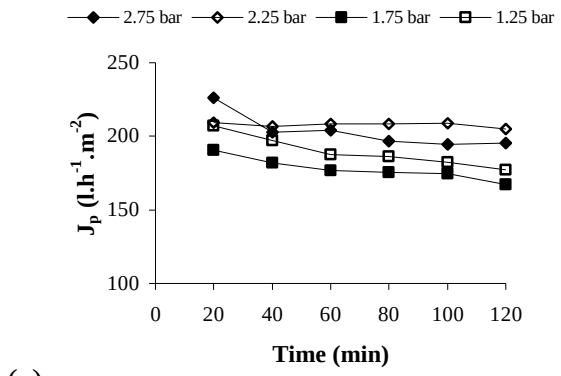
(c)



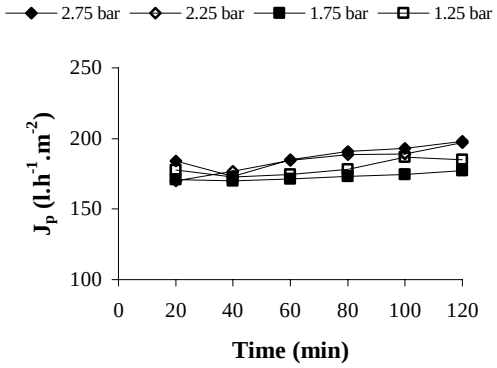
(d)

Figure 4.2 Permeate flux (J_p) versus time during microfiltration of juice from concentrate (JFC) pretreated with Pectinex Ultra SP-L at various concentrations at TMP of 1.25 bar (a), 1.75 bar (b), 2.25 bar (c) and 2.75 bar (d) (temperature, 19±1 °C; cross flow velocity, 7 $m.s^{-1}$).

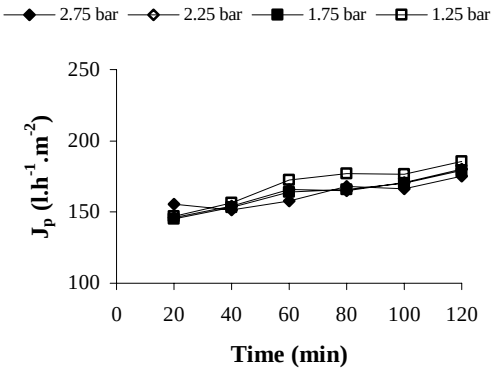
According to TMP and incubation time of the enzyme (Fig. 4.3), the flux of the JFC treated with the 0.01 ml.l^{-1} enzyme for 60 min decreased with time at all TMP



(a)



(b)



(c)

Figure 4.3 Permeate flux (J_p) versus time during microfiltration of juice from concentrate (JFC) pretreated with 0.01 ml L^{-1} Pectinex Ultra SP-L for three incubation times: 60 min (a), 30 min (b) and 15 min (c), at different TMP (tempereature, 19±1 °C; cross flow velocity, 7 m.s^{-1}).

(1.25, 1.75, 2.25, and 2.75 bar). However, at 2.25 bar the flux decreased at a slower rate. For 30-min incubation time, the flux of the JFC increased with time at all TMP and the fluxes at higher TMP (2.25 and 2.75) increased at higher rates. For 15-min incubation time, the flux of the JFC increased with time for all TMP at a similar rate. At the lower incubation times (15 and 30 min), the increase in flux may be due to the existing enzyme reaction. It means that pectin degradation still occurred, leading to a reduction of water holding capacity, and consequently, free water was released to the system and reduced the viscosity and thus facilitating the MF process (Lee et al., 2005).

4.1.2.2 Effects of enzyme concentration and TMP

Effects of enzyme concentration at each TMP

Average fluxes were determined from the values obtained after 30 min processing time until the end of the process (2 h).

The average flux of the enzyme-treated SJ was higher than that of the untreated SJ at all TMP (Fig. 4.4). Since pectinase hydrolyzes soluble polysaccharides such as pectin, resulting in decreasing in viscosity and facilitating the MF process (Lee et al., 2005). At lower TMP (1.25 and 1.75 bar) the increase in enzyme concentration levels from 0.01 to 0.1 $ml.l^{-1}$ did not enhance the flux, ranging from 138 to 152 $l.h^{-1}.m^{-2}$, whereas at higher TMP (2.25 and 2.75 bar) with enzyme addition the flux slightly increased from 160 to 196 $l.h^{-1}.m^{-2}$ and from 153 to 175 $l.h^{-1}.m^{-2}$, respectively. The juice was also enzymatically treated with higher enzyme concentrations, 0.5 $ml.l^{-1}$ and 1 $ml.l^{-1}$ where the maximum fluxes obtained were 167 and 211 $l.h^{-1}.m^{-2}$, respectively. This result was agreed with the study of Vaillant et al.

(1999) stating that the permeate flux was noticeably enhanced according to enzyme concentration at medium (about 0.5 $ml.l^{-1}$) and high (>0.5 $ml.l^{-1}$) levels in CMF of passion fruit juice. However, in this study, the average flux of the juice enzyme-treated with 0.5 $ml.l^{-1}$was in the range of the average flux obtained using lower enzyme concentrations (0.01-0.1 $ml.l^{-1}$).

In addition, the similar trial was investigated using JFC. The average flux of enzyme-treated JFC was higher than that of untreated JFC at all TMP (Fig. 4.5). Nevertheless, the increase in enzyme concentration up to 0.1 $ml.l^{-1}$ did not enhance the flux at all TMP. This was probably due to that pineapple contained low amount of pectin thus the hydrolysis could be completed using the 0.01-$ml.l^{-1}$ enzyme hence increasing in the concentrations of enzyme did not provide more efficiency.

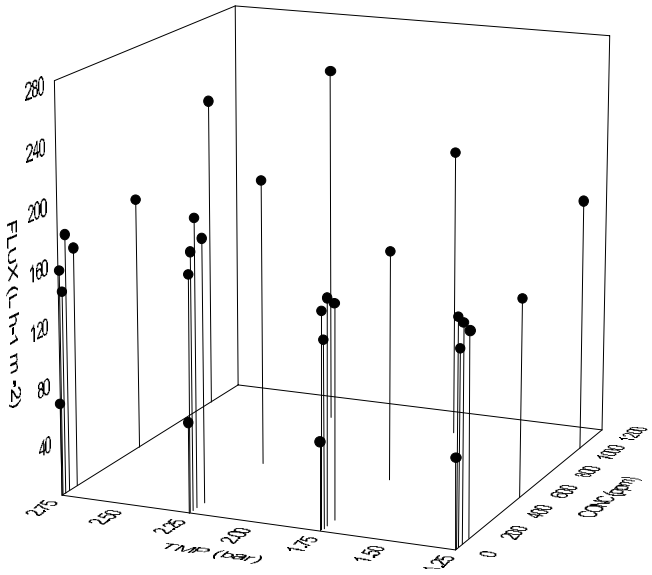


Figure 4.4 An effect of Pectinex Ultra SP-L concentration on average permeate flux (J_p) of SJ during microfiltration at various TMP with total recycling (temperature, 19±1 °C; cross flow velocity, 7 $m.s^{-1}$; VRR, 1; incubation temperature and time, 30 °C and 1 h).

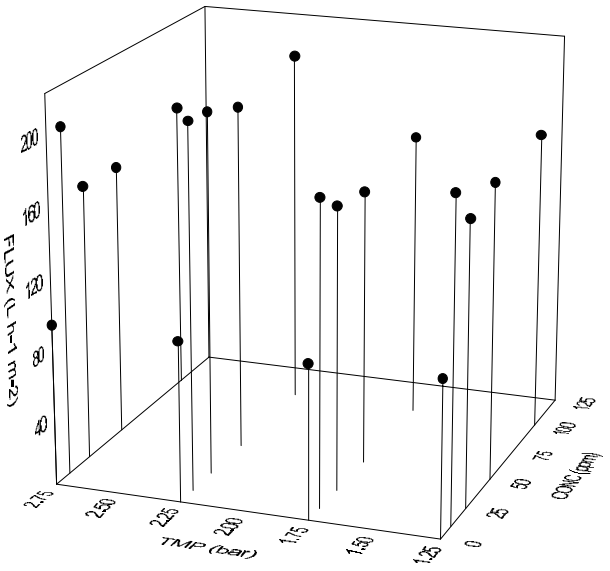


Figure 4.5 An effect of Pectinex Ultra SP-L concentration on average permeate flux (J_p) of JFC during microfiltration at various TMP (temperature, 19±1 °C; cross flow velocity, 7 $m.s^{-1}$; VRR, 1; incubation temperature and time, 30 °C and 1 h).

Based on the results and an economic reason, the 0.01 $ml.l^{-1}$ enzyme was chosen as the optimum.

Effects of TMP at each concentration

The average flux of untreated SJ did not increase with TMP. The values were 60-63 $l.h^{-1}.m^{-2}$. The fluxes of enzyme-treated SJ at all concentration levels increased with TMP higher than 2.25 bar and the highest fluxes were obtained at this TMP. The values were 160, 175, 196 and 179 $l.h^{-1}.m^{-2}$ for 0.01, 0.025, 0.50 and 0.1 $ml.l^{-1}$ enzyme, respectively (Fig. 4.6). The results were supported by the finding of Vaillant et al. (1999) that TMP had a slight positive effect on the permeate flux at low enzyme concentration (<0.5 $ml.l^{-1}$). This significant difference of behavior of the permeate flux according to the TMP before and after the enzymatic treatment prove clearly that

the fouling properties of the juice were completely modified by the pectin hydrolysis. For the untreated juice, the results are in contradiction with the Darcy's law: the increase in driving force (TMP) is counterbalanced by the increase of the hydraulic

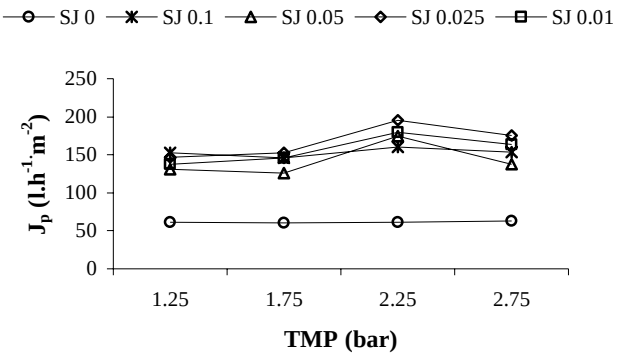


Figure 4.6 An effect of Transmembrane pressure (TMP) on average permeate flux (J_p) of SJ treated with various enzyme concentrations during microfiltration (temperature, 19±1 °C; cross flow velocity, 7 $m.s^{-1}$).

resistance of the fouling layer that can be compressed when the pressure increases. For the treated juice, the fouling layer is more compressible and so its hydraulic resistance is more sensitive to the pressure.

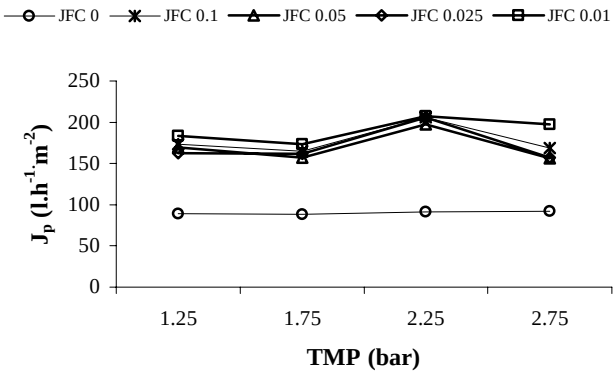


Figure 4.7 An effect of Transmembrane pressure (TMP) on average permeate flux (J_p) of JFC treated with various enzyme concentrations during microfiltration (temperature, 19±1 °C; cross flow velocity, 7 $m.s^{-1}$).

In the same manner, the average flux of untreated JFC did not change with TMP. The values were 88-92 $l.h^{-1}.m^{-2}$. The similar trend was observed for the flux of enzyme-treated JFC at all concentration levels. The highest fluxes were also obtained at 2.25 bar. The values were 208, 206, 198 and 206 $l.h^{-1}.m^{-2}$ for 0.01, 0.025, 0.50 and 0.1 $ml.l^{-1}$ enzyme, respectively (Fig. 4.7).

According to the results, the TMP of 2.25 bar ($2.25*10^5$ Pa) was chosen as the optimum.

4.1.2.3 Effects of incubation time and TMP

Effects of incubation time at each TMP

This study was carried out using only JFC enzyme-treated (0.01 $ml.l^{-1}$) at 30 °C with three incubation times: 15, 30 and 60 min. As shown in Table 4.2, the average flux of the juice did not increase noticeably with incubation time. It was constant at lower TMP (1.25 and 1.75 bar) and increased only of 20% at higher TMP (2.25 and 2.75 bar). These results showed that the kinetics of the pectin analysis are fast and the reaction rate decreases very rapidly. Fourfold increase in incubation time from 15 to 60 min improved the average flux for only 0.25 times. Hence, the 15-min incubation time was chosen as the optimum. This short period is more favorable to the quality preservation of the juice avoiding oxidation phenomena and limiting the risk of fermentations. Furthermore, it limits the time needed to process the juice without decreasing the filtration performances.

Table 4.2 An effect of incubation time on average permeate flux (J_p) of enzyme-treated JFC (0.01 ml.l^{-1}) during microfiltration at various TMP with total recycling (temperature, 19±1 °C; cross flow velocity, 7 m.s^{-1}).

Incubation Time (min)	TMP (bar)/ J_p (l.h^{-1}.m^{-2})			
	1.25	1.75	2.25	2.75
15	178	169	171	167
30	181	174	190	192
60	183	173	208	198

Effects of TMP at each incubation time

This study was carried out using only JFC enzyme-treated (0.01 ml.l^{-1}) at 30 °C with three incubation times: 15, 30 and 60 min. Fig. 4.8 shows that the average flux of enzyme-treated JFC for 15 min decreased with TMP. In contrast, the fluxes of enzyme-treated JFC for 30 and 60 min increased with TMP higher than 2.25 bar. However, the highest fluxes were obtained at different TMP. The highest flux of enzyme-treated JFC for 30 min obtained at 2.75 bar was 192 l.h^{-1}.m^{-2} and the highest flux of enzyme-treated JFC for 60 min obtained at 2.25 bar was 208 l.h^{-1}.m^{-2}.

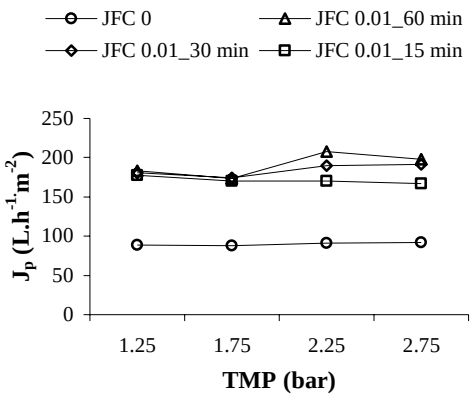


Figure 4.8 An effect of transmembrane pressure (TMP) on average permeate flux (J_p) of enzyme-treated JFC (0.01 ml.l^{-1}) at various incubation times during microfiltration (temperature, 19±1 °C; cross flow velocity, 7 m.s^{-1}).

4.1.2.4 Effects of incubation temperature and TMP

Two incubation temperatures, 30ºC and 35 °C, were studied using only enzyme-treated JFC (0.01 $ml.l^{-1}$) for 15 min incubation time. The average flux increased with temperature (Table 4.3), nonetheless, only 2-8%. Thus, the temperature of 30 °C was chosen as the optimum because it limits quality damages and energy consumption.

Table 4.3 An effect of incubation temperature on average permeate flux (J_p) of enzyme-treated JFC (0.01 $ml.l^{-1}$) during microfiltration at various TMP with total recycling (temperature, 19±1 °C; cross flow velocity, 7 $m.s^{-1}$).

Incubation temperature (°C)	TMP (bar)/ J_p ($l.h^{-1}.m^{-2}$)			
	1.25	1.75	2.25	2.75
30	178	170	171	167
35	185	182	187	179

Overall, the optimal conditions of enzyme preparation and MF for the juice are 0.01-$ml.l^{-1}$ enzyme concentration, 15-min incubation time, 30 ºC and 2.25-bar TMP, regarding the permeate flux and economic reason. Clarification of the reconstituted juice using the optimal enzyme preparation and CMF condition was conducted to collect the clarified juice for quality evaluation.

4.1.2.5 Permeate flux and juice quality

At the optimum conditions using a larger membrane area (0.02 m^2), the average flux obtained from 4 modules was 198 $l.h^{-1}.m^{-2}$ at 21°C. The value was slightly higher than the average flux obtained from one module (171 $l.h^{-1}.m^{-2}$) at 20 °C. These results confirm the potential of the clarification conditions in obtaining the

high permeate flux. The comparisons of permeate fluxes obtained among different works are presented in Table 4.4.

Table 4.4 Comparison of permeate fluxes obtained in this work and from others

Ref.	Raw materials	Enzymes	membrane&module	Operating conditions				Permeate fluxes
				TMP (bar)	T (°C)	Time (h)	v ($m.s^{-1}$)	($l.h^{-1}.m^{-2}$)
This work	pasteurised PJ (12.8°B)	no	ceramic tubular 0.1 µm	2	19±1	2	7	61
	pasteurised PJ (12.8°B)	Pectinex ultra SP-L 0.1 $ml.l^{-1}$ at 30°C for 1 h	(Membralox 1T1-70, SCT, Bazet, France) & a MF unit (TIA, Bollène, France)	2	19±1	2	7	157
	recon.PJ (12.8°B)	no	ceramic tubular (0.1 µm)	2	19±1	2	7	90
	recon.PJ (12.8°B)	Pectinex ultra SP-L 0.1 $ml.l^{-1}$ at 30°C for 1 h	(Membralox 1T1-70, SCT, Bazet, France) & a MF unit (TIA, Bollène, France)	2	19±1	2	7	179
Carvalho et al. (1998)	recon.PJ (12°B) (pulp removed prior to MF)	no	ceramic tubular (0.22 µm) & a Millipore Ceraflo tubular pilot system	1	25	1	-	52
Carneiro et al. (2002)	PJ 10 °B (from fruits) (depulped prior to MF)	Pectinex ultra SP-L & Celluclast 1.5 L 0.3 $ml.l^{-1}$ each at 30°C for 1 h	polysulfone tubular 0.3 µm & Koch membrane systems	1	25	1.5	6	100
Other juices:								
Fukumoto et al. (1998)	apple juice (from fruits)	Pectinex Ultra SP-L (0.12 $ml.l^{-1}$) & Pectinex 100 L (0.06 ml.l-1) at 50 °C for 2 h	ceramic tubular 0.2 µm (SteriloxTM 1P19-40, U.S. Filter Corp., Warrendale, PA, USA) & a membrane filtration unit (APV Crepaco Inc., Tonawanda, NY, USA)	4	50	-	8	200

For the optimum conditions, the permeate (P) was collected within 40 min (VRR = 2.5). As shown in Table 4.5, the permeate was totally clarified (SS = 0%), however, the retentate (R) contained the similar amount of SS as the initial juice (JFC). Due to the dilution of the feed by the remained cleaning water in the MF unit at the beginning of the clarification process, the TSS contents of P and R were lower than that of the JFC. The similar trend was observed for acidity and viscosity. Nevertheless, the Brix/acid ratios of JFC, P and R were not different, indicating that the tastes of all juices were the same. This agreed with Cisse et al. (2005) stating that the clarification did not affect the sugar/acid balance of P. The total polyphenol content of JFC was reduced up to 27.5% after clarification. Nonetheless, the decrease in the total polyphenol content was lower (up to 15%) during CMF of vinegars (López et al. 2005). The vitamin C contents of P and R were significantly lower than those of JFC, because of the dilution mentioned earlier. Moreover, Wang et al. (2005) found that the use of similar membrane (0.14 μm tubular ceramic membrane) allowed the clarified West Indian cherry juice to retain the chemical composition i.e. glucose, fructose, vitamin C and pH, approximately close to its origin.

Table 4.5 Physico-chemical properties of juice from concentrate (JFC), clarified juice (CJ) and retentate (R) (mean (SD)).

Properties/ Juices	JFC	P	R
pH	3.9 (0)	3.9 (0.02)	3.9 (0)
TSS (°Brix)	13 (0)	10 (0)	10.4 (0)
Acidity (g citric acid.100 ml^{-1})	0.46 (0)	0.34 (0)	0.36 (0)
Brix/acid ratio	28 (0.2)	29 (0.3)	29 (0.2)
Turbidity (NTU)	1890 (30)	2.5 (0.1)	2523 (76)
Suspended solids, SS (%)	0.8 (0.04)	0	0.7 (0.04)
Viscosity (mPa.s) at 25 °C	1.66 (0.01)	1.41 (0.03)	1.43 (0.02)
Total polyphenols (mg gallic acid.100 g^{-1})	43.65 (0.54)	31.64 (0.61)	33.86 (1.75)
Vitamin C (mg.100 ml^{-1})	7.9 (0.27)	4.0 (0.01)	3.1 (0.03)

The numbers of samples evaluated were 2-4 for each characteristic.

4.1.3 Effects of VRR on average flux and juice characteristics

4.1.3.1 Influence of the VRR on flux

The microfiltration unit was constantly fed with previously enzyme-treated JFC to keep the feed concentration constant meanwhile permeate was collected periodically. The results in Fig. 4.9 indicated that the average flux decreased by increasing the VRR. At the beginning the flux decreased at higher rate and then at slower rate towards the final VRR (8.5). The average flux obtained at the final VRR was 122 $l.h^{-1}.m^{-2}$. Interestingly, only 19% decrease in the average flux was found. However, the different behavior was previously observed on enzyme-treated passion fruit and mango juices, probably due to the different pore size of the membrane used and the different suspended solid content of the initial juices. The initial pulp contents of both passion fruit and mango juices were 3-4 times higher than that of pineapple, according to Vaillant et al. (2001b). Additionally, in comparison with the same juice

but untreated, the similar pattern was found but with higher rate of the flux reduction at the beginning of the filtration process. The average flux (62 $l.h^{-1}.m^{-2}$) obtained at the final VRR (5.0) was 2 times lower than that of the enzyme-treated juice. The VRR effect was also examined on the single strength pasteurized juice (SJ). As shown in Fig. 4.10, the same behavior as the enzyme-treated juice was observed. The average flux obtained at the final VRR (4.3) was 41 $l.h^{-1}.m^{-2}$ and the decrease in flux (18%)

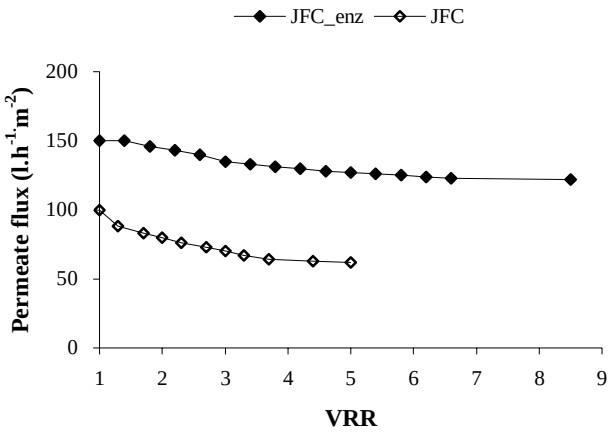


Figure 4.9 Permeate flux versus volumetric reduction ratio (VRR) for JFC and enzyme-treated JFC (JFC_enz).

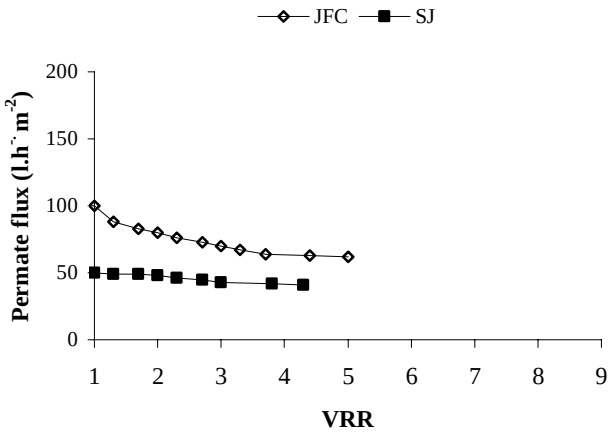


Figure 4.10 Permeate flux versus volumetric reduction ratio (VRR) for JFC and single strength pasteurized juice (SJ).

was similar to that observed in the enzyme-treated JFC. Therefore, the preset value for VRR of the enzyme-treated JFC could be as high as 8.5 in case that retentate is considered as a by-product or waste.

4.1.3.2 Characterization of the juices regarding to VRR

The physico-chemical properties of initial juices (SJ, JFC), permeate (P) at different VRR and retentate (R) are shown in Fig. 4.11. By increasing VRR, pH and Brix/acid ratio were unchanged. However, total soluble solids (TSS) and acidity of permeates at all VRR levels were lower than the initial juices (VRR = 1). This did not cause by the process itself but by the dilution of the feed at the beginning of the process due to cleaning water left in the MF unit (ca. 150 ml). Nonetheless, it could be negligible because both TSS and acidity of permeates tended to reach the initial levels at the end of the process (the final VRR = 4.3 and 5 for SJ and JFC, respectively). All permeates were totally clarified (SS = 0%), supporting by the turbidity values close to 0 NTU and the retentates of both juices were about two times enriched with pulp. The SS contents of the SJ increased from 1.0±0.2 % to 1.8±0 % and the SS contents of the JFC increased from 0.6±0.1 to 1.4±0 %.

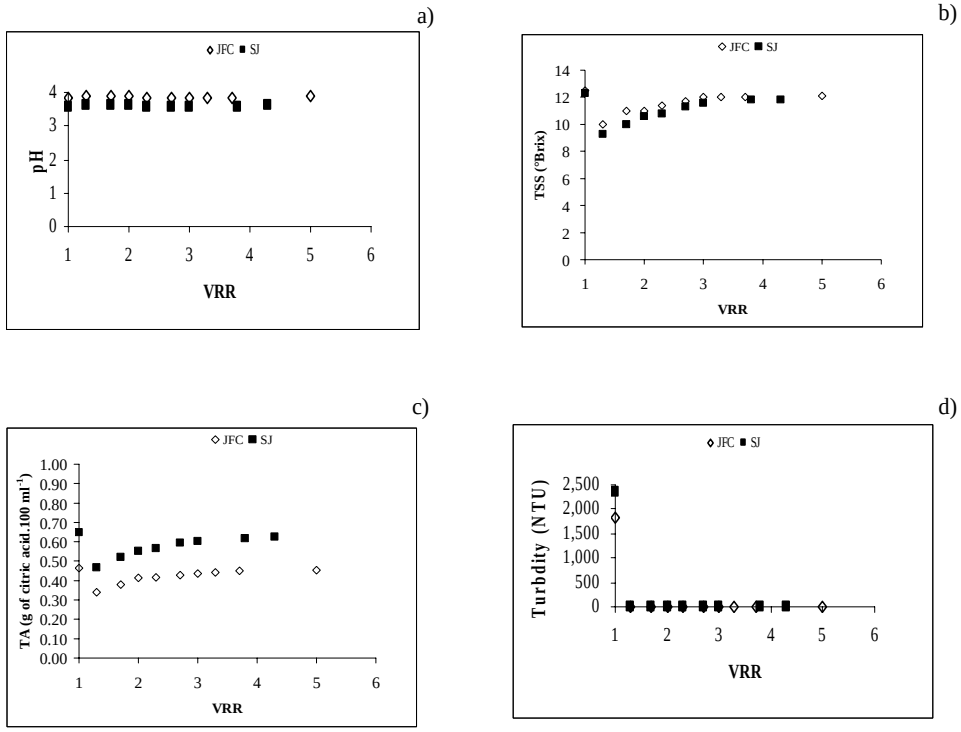


Figure 4.11 An effect of VRR on properties (pH, TSS, TA, Turbidity) of SJ and JFC.

The physico-chemical properties of initial JFC (I), enzyme-treated JFC (Feed, F), permeate (P) and retentate (R) at a VRR of 8.5 are reported in Table 4.6 Permeate was totally clarified (SS = 0%) and the retentate was enriched with pulp (2% SS). The TSS content and acidity of retentate were higher than those of permeate, however, the Brix/acid ratio, an indicator for juice taste, were not different. The vitamin C contents of permeate and retentate were lower than the initial and the feed, although it is relatively stable in acidic foods (Fourie, 2001). This reduction was probably due to oxidative damage (because of dissolved and headspace oxygen) during the long processing time (6 h). Interestingly, the viscosity value of the permeate was the same as that of the feed although the former contained no pulp and the latter contained

0.9% SS. The similar trend was observed from the viscosity of the initial JFC and the retentate containing 1.1% SS and 2.0% SS, respectively. Furthermore, the viscosity of the feed was lower than that of the initial JFC despite that the pulp contents of both sample juices were not different. According to these findings, it seemed that low amount of pectin had a stronger effect than the pulp on the CMF of the pineapple juice. This was in accordance with the result obtained from the MF of orange juice (Cisse et al., 2005).

Table 4.6 Physico-chemical properties of initial JFC (I), enzyme-treated JFC (Feed, F), permeate (P) and retentate (R) (mean (SD)).

Properties/ Juices	**I**	**F**	**P**	**R**
VRR	1.0	1.0	8.5	8.5
pH	3.85 (0.01)	3.83 (0.01)	3.83 (0.01)	3.82 (0)
TSS (°Brix)	13.0	13.0	13.0	14.0
Acidity (g citric acid.100 ml^{-1})	0.46 (0.03)	0.47 (0.01)	0.45 (0)	0.51 (0.01)
Brix/acid ratio	28 (2)	28 (1)	29 (0)	28 (0)
Turbidity (NTU)	1880 (9)	1780 (26)	0.15 (0.06)	12167 (103)
Suspended solids, SS (%)	1.1 (0.1)	0.9 (0)	0	2 (0.1)
Viscosity (mPa.s) at 26 °C	1.41 (0.01)	1.29 (0.02)	1.29 (0)	1.41 (0)
Vitamin C (mg.100 ml^{-1})	3.4 (0.07)	2.4 (0.01)	0.3 (0.0)	0.6 (0.01)

The numbers of samples evaluated were 2-4 for each characteristic.

4.2 Concentration experiments

4.2.1 Process performance of OE using two membrane modules (tubular and plane)

The preliminary test using deionized water was conducted for both tubular and flat module. The operating temperatures for both sides of membrane were equal at 25 °C. The average evaporating fluxes were 0.3 and 5.2 $kg.h^{-1}.m^{-2}$, respectively. Concentration of SJ at six concentration levels (10-60 °Brix) by OE was determined to simulate the concentration process. The evaporation fluxes obtained from the juice of 10-60 °Brix using the tubular module ranged from 0.49 to 0.23 $kg.h^{-1}.m^{-2}$ whilst the evaporation fluxes obtained from the same juices using the flat module were between 8.86 and 3.67 $kg.h^{-1}.m^{-2}$ (Table 4.7). This was probably due to thinner membrane implying higher membrane mass transfer coefficient (Alves and Coelhoso, 2004) and turbulent flow (Re = 5618) that was promoted in juice side of the flat module but not in any side of the tubular module. In addition, the membrane used for the flat module (PTFE) is more hydrophobic than that used for the tubular module (PP) according to surface energy values between both materials (18 vs.29 $dynes.cm^{-1}$).

Table 4.7 Evaporation fluxes (J) obtained during OE of SJ by different membrane modules.

Membrane modules	Total soluble solids (° Brix)					
	10	20	30	40	50	60
J (tubular) $kg.h^{-1}.m^{-2}$	0.49	0.45	0.37	0.34	-	0.23
J (flat) $kg.h^{-1}.m^{-2}$	8.64	7.63	6.48	4.68	3.96	3.67

4.2.2 Optimization: juice temperature and brine velocity

4.2.2.1 Effect of operating conditions

According to the results in 4.2.1,the evaporation fluxes obtained from the flat module were much higher than those obtained from the tubular module. Therefore, the optimization of OE was carried out on the flat module using the SJ. Two operating parameters, juice temperature (20 and 35 °C) and brine velocity (2 and 3 $m.s^{-1}$), were investigated. The juice velocity was fixed at 1.25 $m.s^{-1}$. The increase in temperature enhanced the evaporation fluxes about two times from 4.5 to 8.6 $kg.h^{-1}$ $.m^{-2}$ for the lower brine velocity and from 3.9 to 9.1 $kg.h^{-1}.m^{-2}$ for the higher brine velocity, whereas the increase in velocity slightly improved the evaporation flux (5%).

The results are in accordance with the findings of Courel et al. (2000a). They found that the vapor flux increased two times for a temperature different of 12°C between the two circulating solutions, water and brine, whereas the evolution of the evaporation flux was hardly noticeable at high values of brine velocity (1.7-2.2 $m.s^{-1}$) since the role of concentration polarization becomes negligible due to strong sheer stress along the concentration side of the membrane. The increase of flux with temperature was mainly due to the increase in driving force (Alves and Coelhoso 2002; Courel et al. 2000a; Mengual et al. 1993; Sheng et al. 1991; Vaillant et al. 2001a). Higher temperatures give more kinetic energy to the water vapor molecules and reduce the viscosity of feed stream causing an increase in mass transfer coefficient. Therefore, the optimum conditions for further studies of OE were the juice temperature at 35ºC and the brine velocity of 2 $m.s^{-1}$.

4.2.2.2 Two-step concentration

At the conditions chosen, the SJ and its clarified juice were concentrated using the flat module. The concentrations were carried out in two stages of 8 h each. The OE allowed the concentration of the pasteurized juice from 12.5 °Brix to 28 °Brix at the first stage and from 33 °Brix to 55 °Brix at the second stage. The average evaporation fluxes during these trials ranged from 8.5-5.5 $kg.h^{-1}.m^{-2}$. When the clarified juice was concentrated by OE, the similar behavior was observed. The average evaporation fluxes obtained ranged from 9.9 to 6.6 $kg.h^{-1}.m^{-2}$ and the juice concentration reached 53 °B (Table 4.8). These values were lower than those (12 to 9 $kg.h^{-1}.m^{-2}$) obtained by Rodridges et al. (2004) who used the same membrane module and similar operating conditions but the juice (camu-camu) contained lower initial total soluble solids (6.6 vs. 11 °Brix). With different membrane and module (PP hollow fibers), the flux values obtained in this experiment were much higher than those (0.5-0.7 $kg.h^{-1}.m^{-2}$) obtained with other clarified juices, melon, orange, and passion fruit (Cisse et al. 2005; Vaillant et al. 2001a; Vaillant et al. 2005).

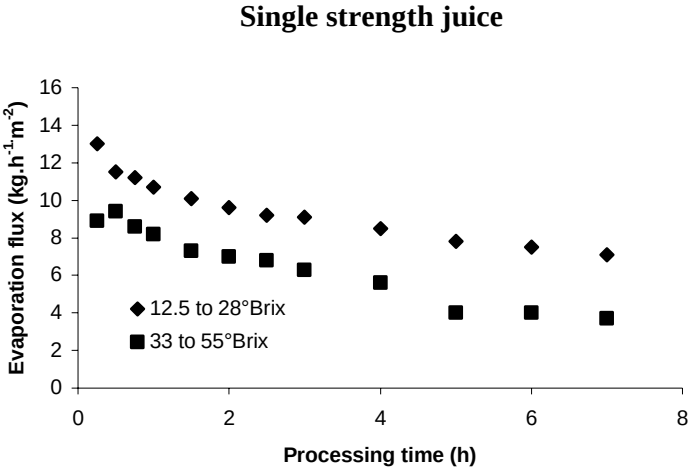
Table 4.8 Total soluble solids (TSS), a_w and average evaporation flux of the single strength juice and the clarified juice during OE trials.

	Single strength juice					Clarified juice				
	TSS (°Brix)		a_w		Flux (kg. $h^{-1}.m^{-2}$)	TSS (°Brix)		a_w		Flux (kg. $h^{-1}.m^{-2}$)
	F	C	Initial	Final		F	C	Initial	Final	
1st stage	12.5	28	0.35	0.39	8.5	11	28	0.38	0.42	9.9
2nd stage	33	55	0.38	0.41	5.5	32	53	0.35	0.38	6.6

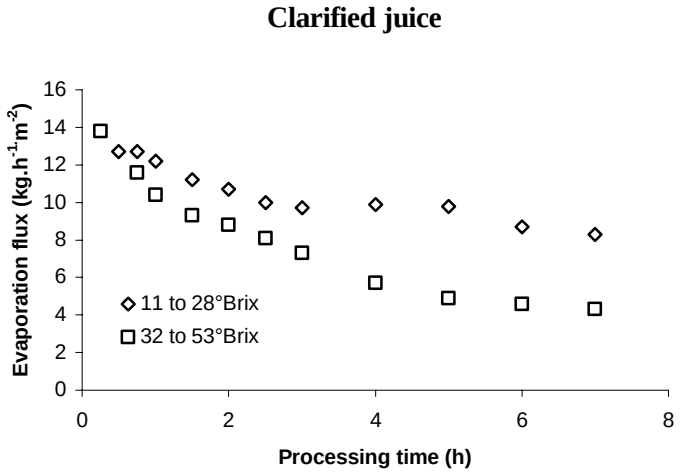
F: Feed, C: Concentrate

The evaporation flux was slightly higher for the concentration of the clarified juice than that for the single strength juice. This was probably attributed to less concentration polarization in the juice-membrane boundary layer because of the lower initial TSS of the clarified juice, 11 °Brix compared to 12.5 °Brix for the single strength juice and the complete removal of suspended solids or pulp (Cisse et al., 2005). From the result, however, pulp content had only little effect on the flux regarding the small increase (15%) in the flux.

The evaporation flux decreased during the processing time (Fig. 4.12) for both clarified and single strength juices. In general, the flux decay during membrane filtration is attributed to the concentration polarization and fouling phenomena due to solute retention on the membrane surface. However, in the case of osmotic evaporation this decay could be related to the concentration of the juice itself, resulting in the increase in juice viscosity and consequently the increase in resistance to mass transfer in the liquid phase and also in the decrease in the driving force, the water activity difference between both sides of the membrane (Alves et al., 2004). As mentioned earlier, the juices were concentrated in two steps of 8 h each. The high volume of the brine tank resulted in a minimum change in a_w of the brine during this period (around 10%). Therefore, the impact of brine dilution on the decline of the driving force during the process could be neglected.



(a)



(b)

Figure 4.12 Evolution of the evaporation flux during the concentration of single strength (a) and clarified (b) pineapple juices by OE.

4.2.2.3 Effect of juice concentration on flux behavior

In order to understand the effect of the juice concentration on the flux behavior, the experiments under steady state (constant feed concentration) were investigated (Fig. 4.13). As expected, the evaporation flux decreased when the juice concentration increased. The same behavior was observed for both the single strength juice and the clarified one. These observations agree with the results obtained for

sucrose solutions at a laboratory scale (Courel et al., 2000a) and for passion fruit juice at a pilot scale (Vaillant et al., 2001a). This phenomenon can be mainly attributed to an increase in the viscosity of the juice that affects the transfer coefficient in the liquid phase. A reduction of the driving force due to a decrease in the vapor pressure of the juice can also be mentioned.

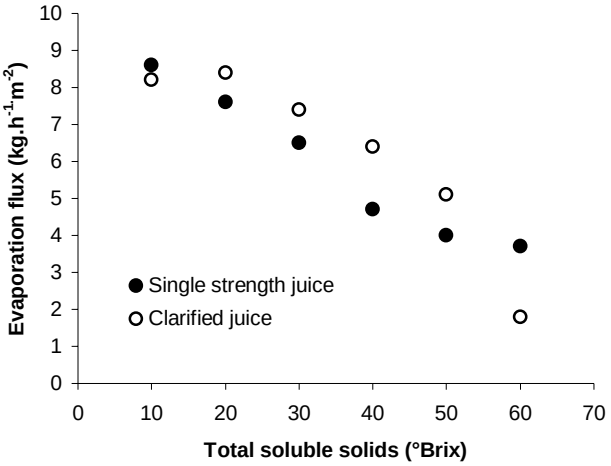


Figure 4.13 Evolution of evaporation flux during the concentration of clarified and pulpy pineapple juices by OE.

4.2.2.4 Physico-chemical characteristics of OE concentrate at optimum conditions

Main characteristics of single strength and clarified juices before and after the concentration by OE are shown in Table 4.9.

Table 4.9 Main characteristics of the single strength and clarified pineapple juices before and after concentration by OE.

Characteristics	Single strength pineapple juice				Clarified pineapple juice			
	1st stage		2nd stage		1st stage		2nd stage	
	Feed	Conc.	Feed	Conc.	Feed	Conc.	Feed	Conc.
TSS (g.100 g^{-1})	12.6	29.0	31.3	56.7	10.6	27.8	30.2	55.5
pH ^{ns}	3.77	3.71	3.70	3.68	3.96	3.92	3.88	3.85
Chroma ^{ns}	4.95	5.84	4.38	3.44	2.91	4.14	5.86	3.22
Hue ^{ns}	-1.20	-1.32	-1.27	-1.35	1.52	1.47	1.49	1.00
Ascorbic acid (mg.100 ml^{-1})	11.2 a	4.3 b	12.9 a	8.0 b	3.9 a	1.0 b	8.7 a	6.6 a
Total polyphenols (mg.100 g^{-1})	18.6	46.3	61.3	106.2	4.9	42.9	47.2	112.3

The characteristics of feed and concentrate (Conc.) are compared in the same row within each stage.
a-b the different letters indicate significant difference
^{ns} non-significant difference

The pH of the juices did not change due to their buffer property. The color of the juices in terms of chroma and hue values did not significantly change because the temperature used in the OE process was low (35°C). The results were supported by the findings of Rodrigues et al. (2004) and Vaillant et al. (2005). On the other hand, the color change of pineapple juice in terms of Hunter parameters a and b values during heat treatment (55-95°C) was found by Rattanathanalurk et al. (2005). Ascorbic acid content significantly decreased in both juices except for the concentration of clarified juice at the second stage. This was probably due to oxidation by the residual oxygen entrapped within the pores of the membrane (Cisse et al., 2005), dissolved oxygen in the juices (Reley and Kajda, 1994),

headspace oxygen in the feed tank, and the oxygen entrapped in the concentration loop of the system. However, these losses can be reduced by better control system such as pre-conditioning the membrane with the juice and flushing nitrogen gas into the feed tank before starting the concentration process. Moreover, several researchers reported that no significant loss of ascorbic acid was noted in the clarified juice concentrates, compared with the initial clarified juices (Cisse et al., 2005; Rodrigues et al., 2004; Vaillant et al., 2005). Noticeably, the losses of ascorbic acid at the second stage (25-38%) of both juices were lower than those at the first stage (62-69%), probably due to less dissolved oxygen (higher feed concentration) at the beginning of the concentration process. The total polyphenols increased proportionally to concentration factor especially in the single strength juice.

Table 4.10 shows the major volatile compounds found in both feed and concentrate along with their retention percentage of area normalization.

Table 4.10 Main volatile flavor compounds of single strength pineapple juice before and after OE at the first stage in terms of area normalization (%).

Compounds	Feed	Concentrate
	Aera normalization (%)	
Ethyl acetate	67.82	34.84
Ethyl butyrate	8.45	2.93
3-Hydroxy-2-butanone (acetoin)	0.15	0.23
Methyl-3-(methylthio) propionate	11.70	9.24
Ehyl-3-(methylthio) propionate	27.21	16.96
Ethyl-3-acetoxy hexanoate	5.02	3.29

Area normalization (%) = peak area of a compound/peak area of all compounds

Ethyl acetate and 3-hydroxy-2- butanone (acetoin), the major compounds in ripened pineapple (Umano et al., 1992), and the other important compounds were lost less than 50% (21-49%) after osmotic evaporation at the first stage. Likewise, loss of volatile compounds (22-39%) of the clarified juices (pineapple, orange and passion fruit) after osmotic evaporation was reported by Cisse et al. (2005), Shaw et al. (2001 and 2002) and Vaillant (2001), compared with considerable loss (95-100%) of volatile compounds in the unpasteurized pineapple and grapefruit juices during thermal concentration (Lin et al., 2002).

Moreover, Cisse et al. (2005) investigated the effect of OE process (2 stages) on the volatile compounds of orange juice. They compared the contents of all classes of aroma compounds in the pulpy OE concentrate with the commercial one. The pulpy OE concentrate was obtained by blending the clarified OE concentrate with the MF retentate previously pasteurized. Depending on chemical classes, losses in the OE concentrate were only 17-25% whereas losses in the commercial concentrate were 31-70%. This obviously indicated that the aroma compounds were less affected by the membrane processes than by thermal evaporation.

Table 4.7 Comparison of permeate fluxes obtained in this work and from others

Ref.	Raw materials	Enzymes	membrane&module	Operating conditions				Permeate fluxes
				TMP (bar)	T (°C)	Time (h)	v ($m.s^{-1}$)	($l.h^{-1}.m^{-2}$)
This work	pasteurised PJ (12.8°B)	no	ceramic tubular 0.1 µm	2	19±1	2	7	61
	pasteurised PJ (12.8°B)	Pectinex ultra SP-L 0.1 $ml.l^{-1}$ at 30°C for 1 h	(Membralox 1T1-70, SCT, Bazet, France) & a MF unit (TIA, Bollène, France)	2	19±1	2	7	157
	recon.PJ (12.8°B)	no	ceramic tubular (0.1 µm)	2	19±1	2	7	90
	recon.PJ (12.8°B)	Pectinex ultra SP-L 0.1 $ml.l^{-1}$ at 30°C for 1 h	(Membralox 1T1-70, SCT, Bazet, France) & a MF unit (TIA, Bollène, France)	2	19±1	2	7	179
Carvalho et al. (1998)	recon.PJ (12°B) (pulp removed prior to MF)	no	ceramic tubular (0.22 µm) & a Millipore Ceraflo tubular pilot system	1	25	1	-	52
Carneiro et al. (2002)	PJ 10 °B (from fruits) (depulped prior to MF)	Pectinex ultra SP-L & Celluclast 1.5 L 0.3 $ml.l^{-1}$ each at 30°C for 1 h	polysulfone tubular 0.3 µm & Koch membrane systems	1	25	1.5	6	100
Other juices:								
Fukumoto et al. (1998)	apple juice (from fruits)	Pectinex Ultra SP-L (0.12 $ml.l^{-1}$) & Pectinex 100 L (0.06 ml.l-1) at 50°C for 2 h	ceramic tubular 0.2 µm (SteriloxTM 1P19-40, U.S. Filter Corp., Warrendale, PA, USA) & a membrane filtration unit (APV Crepaco Inc., Tonawanda, NY, USA)	4	50	-	8	200

CHAPTER V

CONCLUSIONS

All operating parameters (enzyme concentration, incubation temperature, incubation time and TMP) differently affect permeate flux. Using permeate flux as the index, the optimum set of the operating variables are obtained regarding economic reason and product quality. Interestingly, the enzyme concentration as low as 0.01 $ml.l^{-1}$ (0.001%) provides the permeate flux values up to 208 $l.h^{-1}.m^{-2}$ therefore the cost of enzyme treatment could be reduced. In addition, the trial carried out at the optimum conditions has produced the average flux as high as 122 $l.h^{-1}.m^{-2}$ at the final VRR (8.5) and the physico-chemical properties of the permeate (clarified pineapple juice) is of economic value.

The concentration of both single strength and clarified pineapple juices could easily reached 55 °Brix using osmotic evaporation. Pineapple juice could be efficiently concentrated without the prior clarification since pulp (suspended solids) content had low effect on the evaporation flux, regarding the small difference of flux values between the single strength juice and the clarified one. The minor changes in quality of concentrated juices make this process overcome the problem of quality loss occurred under vacuum evaporation.

Further clarification and concentration experiments should be carried out to allow sensory evaluations of both MF clarified juice and OE concentrate and other membrane modules that could be scaled up easily should be investigated.

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APPENDIX A

Cleaning method for the microfiltration unit

Cleaning method for microfiltration unit (modified from TIA, Bollène, France)

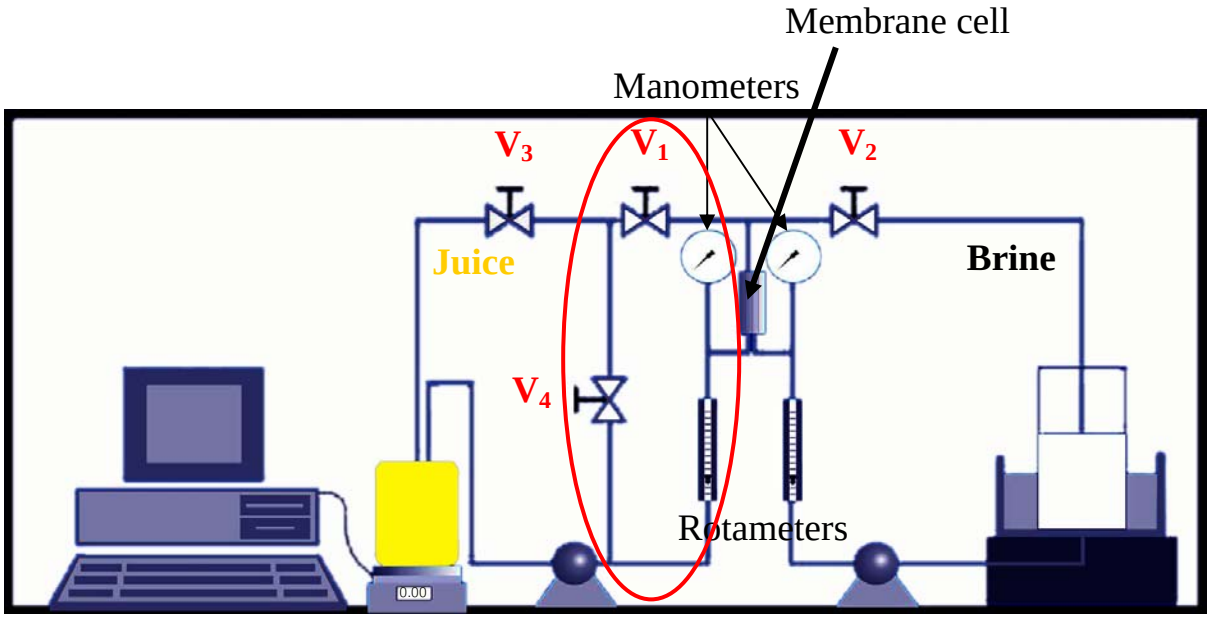
1. Empty all permeate channel and place them into a volumetric flask
2. Rinse a feed tank with water and fill it with water (3 L)
3. Check that a pressure valve must be completely opened (TMP = 0)
4. Turn on a MF unit and turn it off when 200 ml permeate is drained out
5. Empty the feed tank and repeat steps 2-4 for two more times
6. Empty the feed tank and place all permeate channel back to the feed tank
7. Fill the feed tank with water (1.5 L) and add 100 ml of NaOH and 3 ml of NaOCL
8. Check that the pressure valve must be completely opened (TMP = 0)
9. Turn on the MF unit and wait for 20 min
10. Increase TMP to be 2 bar, wait for 10 min and decrease TMP to be 0 bar
11. Turn off the MF unit and drain
12. Fill the feed tank with water (1.5 L) and add 10 ml of HNO_3
13. Turn on the MF unit and wait for 5 min
14. Increase TMP to be 2 bar, wait for 5 min and decrease TMP to be 0 bar
15. Turn off the unit and drain
16. Fill the feed tank with water and turn on the MF unit
17. Recirculate until a pH of drainage = 7

Note The 1^{st} 20 min is for breaking cake on membrane surface.

The 2^{nd} 10 min is for cleaning inside pores with higher TMP.

APPENDIX B

A closed concentration loop of the osmotic evaporation unit

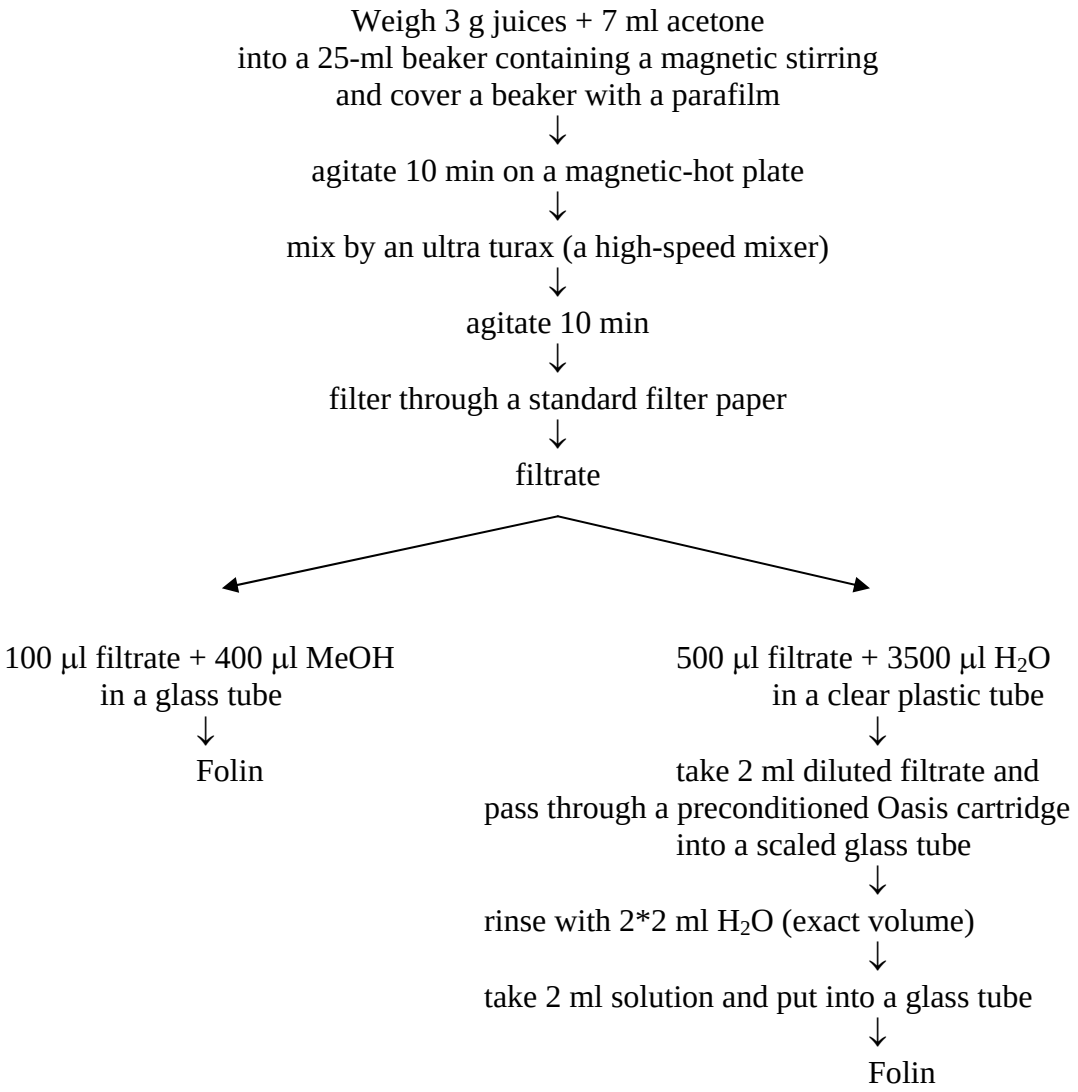

Membrane cell
Manometers
V3
V1
V2
Juice
Brine
V4
Rotameters
Juice pump
Brine pump

APPENDIX C

Rapid determination of total polyphenols

Determination of total polyphenols (Georgé et al., 2005)

Protocol of total polyphenols and vitamin C



Note
A precondition for an Oasis cartridge: rinse with 3 ml MeOH and 2*3 ml H_2O.
A cleaning method between each sample: rinse with 4*3 ml MeOH and 2*2 ml H_2O.
1 sample = 3 extraction and each extraction = 2 tubes, so total = 6 sub-samples

Folin protocol

1. add 2.5 ml Folin-Ciocalteu reagent (diluted with H_2O, 1:10) and incubate 2 min at ambient temperature
2. add 2 ml Na_2CO_3 (75 $g.L^{-1}$), homogenize and immediately incubate at 50 °C for exactly 15 min
3. cool down in ice-water bath about 5 min
4. transfer each sample into a PS cuvette (1.5 ml)
5. read at 760 nm

APPENDIX D

Vitamin C analysis by HPLC

HPLC analysis of V.C (Rojas-Gonzalez et al., 2006)

System conditions were specified as the following:

Device	AGILENT 1100 Series
Software	Agilent Chemstation
Column	PR 18 E 5 µms (250*4.6 mm) MERCK
Solvents (isocratic)	Phosphate tampon solution pH 2.5
Flow rate	0.7 ml / min
Temperature	25 °C
Detection	UV 245 nm
Injection	20 µl

Preparation of tampon solution pH 2.5

1. Prepare 1 L of 2% of potassium dihydrogen phosphate
2. Prepare 1 L of 5% of meta-Phosphoric acid
3. Transfer 0.5 L of the phosphate solution into a 1L beaker and gradually added the acid (ca. 120 ml) into the beaker until a pH of a tampon solution reaches 2.5 using a pH meter
4. Keep the tampon solution in a 1L brown bottle

Preparation of standard solutions

1. Weight 50 mg of L-ascorbic acid, dilute with the tampon solution and bring up to 100 ml final volume
2. Prepare 5 levels of standards: 1.25, 2.50, 5, 10 and 20 mg/ 100 ml by diluting with the tampon solution

Sample preparation

1. Dilute a juice sample to an initial Brix if needed
2. Homogenize 3 ml sample with 3 ml tampon in a plastic tube using a mixer (5 times)
3. Filter a solution through a 0.45 µm syringe driven filter unit into a 25-ml beaker

Materials and chemicals

Materials:

1. Automatic pipette (1-5 ml) "FINNPIPETTE® " V34442, 4500 Thermo ELECTRON CORPORATION
2. Sterile syringe (10 ml) BD Discardit™ II, Becton Dickinson S.A., Spain
3. 0.45 µm syringe driven filter unit
4. Plastic tube
5. Mixer
6. Beaker (25 ml)
7. Syringe "Agilent" LC 50 µl FN, Australia

Chemicals:

1. L-ascorbic acid (99% A.C.S. Reagent) 50 mg, $C_6H_8O_6$ = 176.12, ALDRICH, Spain
2. Meta-phosphoric acid (33.5-36.5%) 120 ml, assay ≥ 33.5% (T), Fluka 79613, USA
3. Potassium dihydrogen phosphate 500 ml, KH_2PO_4 = 136.09, Fluka 60220, USA

APPENDIX E

Flavor analysis by GC-MS

GC-MS analysis of juice

Sample preparation by headspace solid-phase microextraction (SPME)

A 2.5-ml juice sample was diluted with 7.5-ml water in a 15-ml vial. An SPME holder (Supelco, Bellefonte, PA, USA) was used to perform the experiments. A fused silica fibre, coated with a 100 μm layer of PDMS (polydimethylsiloxane), was chosen to extract the volatile components of the juices. A 5-min incubation time, 30-min extraction time at 60 °C and 1-min desorption time were operated.

Gas chromatography–mass spectrometry (GC–MS)

Samples were analyzed by GC-MS using an Agilent 6890 gas chromatograph coupled to a HP 5973 quadrupole mass spectrometer with electron ionization mode (EI) generated at 70 eV. The ion source and quadrupole temperatures were 230 and 150 °C, respectively. Volatile compounds were separated on a DB-Wax (column A, J&W Scientific, Folson, CA, USA) fused silica capillary column (30 m*0.25 mm i.d., 0.25 μm film thickness). The on-column injector was heated to 250 °C. Helium was used as carrier gas at a flow rate of 1 $ml.min^{-1}$. The oven temperature was increased from 40 °C at a rate of 3 $°C.min^{-1}$ up to 210 °C where it was held for 10 min.

BIOGRAPHY

Miss Chularat Hongvaleerat was born on June 16, 1967 in Rayong Province, Thailand. She received her Bachelor's Degree in Agriculture (Soil Science) from King Mongkut's Institute of Technology, Chaokhunthaharn Ladkrabang, Thailand in 1989 and received her Master's degree in Agriculture (Food Science and Technology) from the University of Tennessee, Knoxville, USA in 1994. After graduation, she has been served in position of lecturer at Department of Food Science, Faculty of Science, Burapha University, Chonburi from 1995 until present. She continued with her graduate study in the Food Technology Program, Institute of Agricultural Technology, Suranaree University of Technology.