Stabilization of Pineapple Juice and Coconut Water Using Microfiltration and Ultrafiltration : Process Development and Performance Improvement

Aporn Laorko

A Thesis Submitted in Fulfillment of the Requirements for the Degree of
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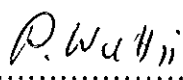**2010**
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i

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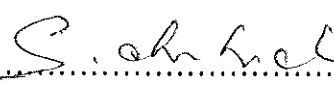
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ii

ชื่อวิทยานิพนธ์	การทำน้ำสับปะรดและน้ำมะพร้าวให้คงตัวโดยการกรองแบบไมโคร ฟิลเตรชันและอัลตราฟิลเตรชัน: การพัฒนากระบวนการผลิตและ ปรับปรุงสมรรถนะ
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บทคัดย่อ

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาการทำน้ำสับปะรดและน้ำมะพร้าวให้คงตัวโดย กระบวนการกรองระดับไมโครฟิลเตรชันและอัลตราฟิลเตรชันเพื่อสามารถรักษาคุณภาพของน้ำ ผลไม้รวมถึงการศึกษาการปรับปรุงสมรรถนะของกระบวนการ

จากการศึกษาผลของขนาดรูพรุนของเมมเบรนขนาด 0.1 และ 0.2 μm และ MWCO ขนาด 30 และ 100 kDa ต่อค่าฟลักซ์ ฟาวลิ่ง และคุณภาพของน้ำสับปะรดในกระบวนการ กรองระดับไมโครฟิลเตรชันและอัลตราฟิลเตรชัน พบว่าขนาดรูพรุนที่แตกต่างกันไม่มีผลต่อความ แตกต่างกันของค่า pH, ปริมาณของแข็งที่ละลายได้, น้ำตาลรีดิวซิ่งและค่ากรดในขณะที่ไม่มีสาร แขวนลอยและการเจริญของจุลินทรีย์อยู่ในส่วนของเพอมิเอท จากการทดลองพบว่าเมมเบรน ขนาด 0.2 μm มีความเหมาะสมต่อกระบวนการกรองระดับไมโครฟิลเตรชันของสับปะรดมาก ที่สุด ทั้งนี้เนื่องจากให้ค่าฟลักซ์สูงและยังคงรักษาคุณค่าทางพฤษเคมี คือ ปริมาณวิตามินซี ปริมาณฟีนอลิกทั้งหมดและการต้านอนุมูลอิสระมากกว่าการใช้เมมเบรนขนาดอื่น สภาวะที่ เหมาะสมในการกรองแบบกะด้วยเมมแบรนขนาด 0.2 μm คือความเร็วตามขวางเท่ากับ 3.4 m/s และความดันเท่ากับ 0.7 bar ได้ค่าฟลักซ์เฉลี่ยเท่ากับ 37 l/m^{2}h

จากการศึกษาอายุการเก็บในผลิตภัณฑ์น้ำสับปะรดชนิดใสและปลอดเชื้อโดยการ ใช้เมมแบรนระดับไมโครฟิลเตรชันและอัลตราฟิลเตรชัน พบว่าคุณภาพของผลิตภัณฑ์ไม่มีความ แตกต่างกันระหว่างน้ำสับปะรดที่ผ่านการกรองทั้งสองแบบทั้งในสภาวะการเก็บที่ระยะเวลาและ อุณหภูมิการเก็บเดียวกัน นอกจากนี้ไม่พบเชื้อจุลินทรีย์ในผลิตภัณฑ์ตลอดการเก็บรักษา ผลิตภัณฑ์ สับปะรดที่เก็บที่อุณหภูมิ 4 $^\circ$C ยังคงรักษาคุณภาพของน้ำสับปะรดได้ดีกว่าการเก็บที่อุณหภูมิ 27 และ 37 $^\circ$C ปริมาณวิตามินซีลดลงเมื่ออุณหภูมิและเวลาในการเก็บเพิ่มขึ้น ซึ่งบ่งชี้โดยค่าคงที่ (k) และค่าพลังงานกระตุ้น (Ea) สีของผลิตภัณฑ์มีการเปลี่ยนแปลงน้อยที่สุดเมื่อเก็บที่สภาวะ 4 $^\circ$C

จากการศึกษาพบว่าอายุการเก็บของน้ำสับปะรดชนิดใสและปลอดเชื้อโดยการใช้เมมเบรนระดับไม โครฟิลเตรชันและอัลตราฟิลเตรชัน ประมาณ 3.5 เดือน เมื่อเก็บที่ 4 °C โดยใช้เกณฑ์ปริมาณ วิตามินซีที่ลดลง 50 %

จากการศึกษาการปรับปรุงสมรรถนะของกระบวนการกรองน้ำสับปะรดโดยระดับ ไมโครฟิลเตรชัน พบว่าเมื่อเพิ่มความเร็ว จาก 1.5 เป็น 3.4 m/s ส่งผลให้ค่าฟลักซ์วิกฤติ เพิ่มจาก 25.4 เป็น 40.2 l/m^2h และค่าฟลักซ์คงที่เพิ่มขึ้นจาก 36.4 เป็น 56.5 l/m^2h การใช้เทคนิคการพ่น แก๊สไนโตรเจนระหว่างการทดลองส่งผลให้ค่าฟลักซ์วิกฤติและค่าฟลักซ์คงที่มีค่าเพิ่มขึ้น และพบว่า ประสิทธิภาพการเพิ่มค่าฟลักซ์มากที่สุดเมื่อใช้การพ่นแก๊สในสภาวะความเร็วที่ต่ำ (1.5 m/s) โดย ประสิทธิภาพค่าฟลักซ์วิกฤติเพิ่มขึ้น 55-128% และค่าฟลักซ์คงที่เพิ่มขึ้น 65-95 % เมื่อเพิ่มสัดส่วน การพ่นแก๊ส (gas injection factor, ε) จาก 0 เป็น 0.35 การพ่นแก๊สไม่มีผลต่อคุณภาพของน้ำ สับปะรดในด้านการต้านอนุมูลอิสระ ค่า pH, ปริมาณของแข็งที่ละลายได้และค่าสี แต่จะส่งผลให้ ปริมาณวิตามินซีลดลง

จากการศึกษาการคัดเลือกขนาดรูพรุนของเมมเบรนต่อค่าฟลักซ์ ค่าฟาวลิ่งและ คุณภาพของน้ำมะพร้าวระหว่างการกรองที่ขนาดรูพรุนแตกต่างกันคือ ขนาด 0.1 และ 0.2 μm และ MWCO ขนาด 30 และ 100 kDa พบว่าขนาดรูพรุนไม่มีผลกระทบต่อค่า pH ปริมาณของแข็งที่ ละลายได้ ปริมาณน้ำตาลรีดิวซิ่ง ค่ากรด ค่าสีและปริมาณฮอร์โมนเอสโตรเจน ไม่พบเชื้อจุลินทรีย์ ในน้ำมะพร้าวที่ผ่านการกรองจากเมมเบรนทุกขนาด การกรองโดยใช้เมมเบรนระดับไมโคร ฟิลเตรชันจะให้ค่าฟลักซ์ที่สูงกว่าและค่าฟาวลิ่งน้อยกว่าระดับอัลตราฟิลเตรชัน จากการทดลอง พบว่าเมมเบรน ขนาด 0.1 μm เป็นเมมเบรนที่มีความเหมาะสมต่อกระบวนการกรองน้ำมะพร้าว ทั้งนี้เนื่องจากให้ค่าฟลักซ์สูงและค่าฟาวลิ่งต่ำกว่าเมมเบรนชนิดอื่น ในขณะที่ไม่มีความแตกต่าง ของคุณภาพของเพอมิเอท

จากการศึกษาอายุการเก็บของผลิตภัณฑ์น้ำมะพร้าวชนิดใสและปลอดเชื้อโดยการ ใช้เมมเบรนระดับไมโครฟิลเตรชันและอัลตราฟิลเตรชันเป็นเวลา 6 เดือน ที่อุณหภูมิการเก็บที่ 4, 27 และ 37°C พบว่าไม่มีความแตกต่างของคุณภาพน้ำมะพร้าวในด้านความเป็นกรดด่าง ปริมาณ ของแข็งที่ละลายได้ และปริมาณฮอร์โมนเอสโตรเจนในทุกสภาวะการเก็บรักษา นอกจากนี้ยังมี การศึกษาการปรับปรุงสมรรถนะของกระบวนการกรองน้ำมะพร้าว พบว่าเมื่อเพิ่มความเร็ว จาก 1.6 เป็น 3.5 m/s จะส่งผลให้ค่าฟลักซ์วิกฤติ เพิ่มจาก 97.3 เป็น 145.3 l/m^2h และค่าฟลักซ์คงที่เพิ่มขึ้น จาก 145.5 เป็น 176.5 l/m^2h การใช้เทคนิคการพ่นแก๊สจะส่งผลให้ค่าฟลักซ์วิกฤติและค่าฟลักซ์ คงที่มีค่าเพิ่มขึ้นและมีประสิทธิภาพการเพิ่มค่าฟลักซ์มากที่สุดเมื่อใช้การพ่นแก๊สในสภาวะความเร็ว ที่ต่ำกว่า (1.6 m/s) โดยประสิทธิภาพค่าฟลักซ์วิกฤติเพิ่มขึ้น 20-63% และค่าฟลักซ์คงที่เพิ่มขึ้น 65-

95 % เมื่อเพิ่ม ε จาก 0 เป็น 0.35 การพ่นแก๊สที่สภาวะต่างๆระหว่างการกรองไม่มีผลต่อคุณภาพ
ของน้ำมะพร้าว

      จากการศึกษาผลของการพ่นแก๊สต่อการเปลี่ยนแปลงค่าการเกิดฟาวลิ่งและกลไก
การเกิดฟาวลิ่งระหว่างการกรองของน้ำสับปะรดและน้ำมะพร้าวพบว่า กลไกการเกิดฟาวลิ่งเริ่มต้น
ด้วยการเกิดฟาวลิ่งแบบปิดรูพรุนสมบูรณ์ (complete blocking) ตามด้วยการเกิดฟาวลิ่งแบบปิดรู
พรุนและแบบซ้อนทับบางส่วน (intermediate blocking) และสุดท้ายจะเป็นการเกิดฟาวลิ่งแบบชั้น
เค้ก (cake filtration) การพ่นแก๊สส่งผลให้เกิดการเปลี่ยนแปลงระยะเวลาและความแน่นของการเกิด
ฟาวลิ่งที่แตกต่างกัน การเกิดฟาวลิ่งแบบปิดรูพรุนสมบูรณ์เกิดในช่วงประมาณ 5-6 นาที ของการ
กรอง เวลาเริ่มต้นของการเกิดชั้นเค้กในน้ำสับปะรดลดลงจากชั่วโมงการกรองที่ 1.3 เป็น 0.9
ในขณะที่เวลาเริ่มต้นของการเกิดชั้นเค้กในน้ำมะพร้าวลดลงจากชั่วโมงการกรองที่ 1.0 เป็น 0.67
เมื่อใช้ ε เพิ่มจาก 0 ถึง 0.35 การเพิ่มขึ้นของ ε ส่งผลต่อการลดลงของการเกิดฟาวลิ่งรวม (R_t) ทั้ง
แบบผันกลับได้ (R_{rf}) และผันกลับไม่ได้ (R_{if}) อย่างมีนัยสำคัญ แต่ไม่พบความแตกต่างของการเกิด
ฟาวลิ่งแบบภายในรูพรุนของเมมเบรน ($R_{if\text{-}in}$)

      จากการศึกษาความเป็นไปได้ทางเศรษฐศาสตร์ของการผลิตน้ำสับปะรดและน้ำ
มะพร้าวแบบใสและปลอดเชื้อโดยใช้กระบวนการระดับไมโครฟิลเตรชัน โดยการศึกษานี้ใช้ข้อมูล
และสภาวะที่เหมาะสมการจากการศึกษาข้างต้นเพื่อใช้ในการคำนวณและประเมินค่าการลงทุนของ
เครื่องจักรและอุปกรณ์ พบว่าต้นทุนของเมมเบรนที่ใช้เป็นต้นทุนหลักในการลงทุน หากประมาณ
กำลังการผลิต 20,000 ลิตรต่อวัน พบว่าโรงงานการผลิตสับปะรดสามารถคืนทุนภายใน 2.6 ปี และ
โรงงานการผลิตน้ำมะพร้าวสามารถคืนทุนได้ภายใน 4.4 ปี

Thesis Title   Stabilization of Pineapple juice and Coconut Water Using Microfiltration and Ultrafiltration: Process Delvelopment and Performance Improvement

Author   Ms. Aporn Laorko

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ABSTRACT

In order to preserve the quality of pineapple juice and coconut water, the membrane technology was developed to produce the sterilized-clarified juice without the effect of heat treatment. The improvement of process performance during membrane filtration was also studied.

To select the suitable membrane, the effects of membrane pore size on the permeate flux, membrane fouling and quality of clarified pineapple juice were studied. Microfiltration (membrane pore size of 0.1 and 0.2 μm) and ultrafiltration (membrane molecular weight cut-off (MWCO) of 30 kDa and 100 kDa) membranes were employed. Membrane filtration did not have significant effects on the pH, reducing sugar and acidity of clarified juice whereas the suspended solids and microorganism were completely removed. The 0.2 μm membrane gave the highest permeate flux, total vitamin C content, total phenolic content and antioxidant capacity as well as the highest value of irreversible fouling. Regarding these results, the membrane with pore size of 0.2 μm was considered to be the most suitable membrane for the clarification of pineapple juice. The optimum operating conditions for clarifying pineapple juice by membrane filtration was a cross-flow velocity (CFV) of 3.4 m/s and transmembrane pressure (TMP) of 0.7 bar. An average flux of about 37 l/m^2h was obtained under the optimum conditions using batch concentration mode.

To study the shelf-life of the clarified juice, the quality of microfiltration (MF) and ultrafiltration (UF)- clarified juice during storage for 6 months at the temperature of 4, 27 and 37°C were investigated. The results showed that there was no significant difference in the quality between the clarified juice by

MF and UF during storage at 4 and 27 compared with 37 °C at the same storage time. No microbial growth was found after 6 months of storage. The storage time and temperature did not affect the total soluble solid and pH. The clarified juice stored at 4 °C had the best quality comparing to the other juices. The vitamin C content was the most affected by storage time and temperature as indicated by kinetic constant and activated energy respectively. The colour (L*) of clarified juice stored at 4 °C was lighter than the juices stored under others temperatures. The shelf-life of clarified pineapple juice base on the reduction by 50 % of vitamin C was 3.5 mounts, at storage temperature of 4 °C.

According to the membrane property and the quality of the clarified juice, the membrane pore size of 0.2 µm was selected for studying the process improvement. The effects of CFV and gas sapraging on the critical and limiting flux during cross flow microfiltration of pineapple juice were investigated. It was observed that the critical and limiting flux increased as the CFV increased. The critical flux varied from 25.4 to 40.2 l/m^2h and limiting flux varied from 36.4 to 56.5 l/m^2h while CFV increased from 1.5 to 3.4 m/s without gas sparging. The use of gas sparging led to the remarkable improvement of both critical and limiting flux but it was more effective when the lower CFV of 1.5 m/s, compared to those at higher CFV(2.0 and 2.5 m/s). When the gas injection factor at 0.15, 0.25 and 0.35 was applied with a fixed CFVof 1.5 m/s, the permeate flux improvement of 55.6 %, 75.5 % and 128.2 % were achieved for critical flux while 65.8%, 69.7% and 95.1% were achieved for limiting flux, respectively. In addition, the CFV and gas sparging did not affected the pH, total soluble solid, colour, total phenolic content and DPPH free radical scavenging activity of clarified juice. However, L-ascorbic acid and total vitamin C were significantly decreased after using the higher CFV and higher of gas injection factor.

In the case of coconut water, the selection of membrane pore size and operating parameters was also investigated. The MF- membrane with pore size of 0.1 and 0.2 µm and UF- membrane with MWCO of 100 and 30 kDa were used. The effect of membrane pore size and MWCO on quality of clarified juice, permeate flux and fouling were studied. It was found that the MF and UF-clarified juice did not

different in pH, total soluble solid, reducing sugar, estrogen hormone and minerals. The results from microbiological analysis of the clarified coconut water showed that sterilized of coconut water was obtained using either MF or UF membranes. The permeate flux of MF was much higher than those of UF while the fouling resistance of UF membrane was much higher than those of MF membrane. The irreversible fouling resistance of 0.1 μm membrane was the lowest and most of this irreversible fouling was external irreversible fouling, formed on the membrane surface. According to these results, it could be concluded that 0.1 μm membrane was the most suitable membrane for clarification and sterilization of coconut water.

The quality of MF and UF-clarified coconut water during storage were investigated. The storage time and temperature did not affect the total soluble solid, pH and estrogen hormone. The $0.1 \mu m$ membrane was selected to study the enhancement of process performance. The effects of CFV and gas sparging with various gas injection factor on the critical and limiting flux during cross flow microfiltration of coconut water were studied. It was observed that the critical and limiting flux increased as the CFV increased. The critical flux varied from 97.3 to 145.3 l/m^2h and limiting flux varied from 145.5 to 176.5 l/m^2h while the CFV increased from 1.6 to 3.5 m/s without gas sparging. The use of gas sparging with various gas injection factor led to an increase in both critical and limiting flux during microfiltration of coconut water. The improvement of 20.6 %, 51.4% and 63.0% were achieved for critical flux while 10.2%, 17.4 % and 22.6% were achieved for limiting flux with the gas injection factor of 0.15, 0.25 and 0.35, respectively. In addition, the CFV and gas sparging did not affect the pH, total soluble solid, colour and estrogen hormone during microfiltration process.

The effect of gas sparging on fouling and fouling mechanism during microfiltration of pineapple juice and coconut water were also studied. The experiments were performed at the CFV of 1.5 m/s, TMP of 0.7 bar for pineapple juice and CFV of 1.6 m/s, TMP of 0.6 bar for coconut water with gas sparging at different gas injection factors. The fouling mechanism during the microfiltration of both pineapple juice and coconut water started with complete blocking, followed by an intermediate blocking and then cake filtration. Gas sparging affected both intensity

and duration of fouling mechanism. The duration of complete blocking stage was about 5-6 min at the beginning of the microfiltration for both feed. The initial points of defined cake filtration stages reduced from 1.3 to 0.9 h for pineapple juice and 1.0 to 0.67 h for coconut water as the gas injection factor varied from 0 to 0.35. In the case of fouling resistance, increase in gas sparging could significantly reduce the R_t, R_{rf} and R_{if-ex} but the R_{if-in}.

The technical and economical feasibility of pineapple juice and coconut water production by using cross flow microfiltration were study. The data for production plant designed, based on the experimental results from the previous study was used. The estimated production of clarified juice is about 20,000 liter/day for each juice. The outline of the calculation of investment cost and the operating cost is summarized. The membrane cost is one of the largest in the fixed capital cost. The economic assessment of pineapple juice by microfiltration were accomplished for production of 5,000 ton/year, yielding an interest rate of return of 38.3-53.6 % and payback period of 1.9-2.6 years for pineapple juice while the yielding an interest rate of return of 19.2-23.2 % and payback period of 3.9-4.4 years for coconut water, depending on the operating condition.

ACKNOWLEDGEMENT

CONTENTS

CONTENTS (Continued)

CONTENTS (Continued) Page

CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

CHAPTER 1

INTRODUCTION AND REVEIW OF LITERATURE

1.1 Introduction

Tropical fruit juice is a popular product with increasing demand in the world and Thailand exported more than 225,000 ton of tropical fruit juice which counted for more than US$ 200 million (Nation Food Institute, 2006). The pasteurized and concentrated pineapple juices are exported for more than a half of total volume in the world. Pineapple juice is marketed world-wide, principally because of theirs attractive aroma, flavour and other beneficial components for human health that are generally indicated as antioxidants such as vitamin C, carotenoid, phenolic compound etc. These can reduced not only the risk of oxidative damage related to the presence of free radicals but also can reduced risk of contracting different types of cancer, cardiovascular and neurological diseases. Coconut water is also a very popular product. It is considered as natural refreshing and highly isotonic drink with delicate aroma and flavour.

Conventional thermal processing ensures safety and extends the shelf life of fruit juice, but it often leads to detrimental change in the sensory and nutritional qualities of the product. Many researchers have a common aim to find the best conditions and processing techniques to keep and improve the nutritional and sensory quality of fruit juice. Nowadays a simple cold preservation technology with refrigeration is applied in small and medium-sized agro-industries to produce bottled tropical fruit juice and make it still fresh for from 10 days to three weeks which is long enough to satisfy domestic retail markets. The productivity of this cold preservation technology is relatively low and limits the scale-up of production. Membrane technology may be an alternative for fruit juice preservation and conservation due to its operational advantages such as mild temperature, the ease of scaling up and simplicity of operation. Membrane technology could provide two fractions of fruit juice, the retentate (solution rejected by membrane) and permeate

1

(solution passed through membrane). The permeate is considered to be the clarified and sterilized fruit juice while most microbes are separated and concentrated in the retentate. This fraction process allows a small volume of juice that is the retentate to be sterilized for the elimination of microbes while most of the flavor and nutritional compounds are preserved in the permeate. Hence it is a simple way to process a large amount of juice and avoid the loss of phytochemical compounds due to high temperature (Torregrosa *et al.*, 2006; Alwazeer *et al.*, 2003). According to their separation capacities, membrane technology is suitable for cold sterilization. Furthermore, the process could combine clarification and sterilization in one single continuous operation. However, the effect of the membrane pore size and MWCO may possibly influence the permeate flux and quality of the clarified fruit juice. Moreover, the process performance of membrane filtration is limited by membrane fouling which results in flux decline and a possible change in product characteristics. Present work is to apply membrane technology for stabilization of tropical fruit juice and improve the performance of filtration process by fouling mechanism analysis and hydrodynamic manipulation for long-term low-cost operation.

1.2 Review of Literature

1.2.1 Fruit juice

1.2.1.1 Pineapple

Thailand is now one of the major producers and exporters of pineapple in the world. During the past five years, the average annual production amounted to two million tones. While the total production area was approximately 100,000 hectare spread over thirteen provinces. Most of the pineapple farms are located along the East and the West Coasts of the Gulf of Thailand. Smallholders, generally occupying between 1 to 5 hectare of land, constitute more than 95% of all producers. Roughly 80% of the production is destined for processing (especially canning and juice), while the rest is mainly domestic consumption (Anupunt *et al.*, 2007). The pineapple is a native American product, first found in Central and South America. From these countries, plants have been taken to all tropical sections of the world. The *Smooth*

Cayenne variety is known as one of the best for juice production and most growth in Thailand. The physical and chemical characteristic of pineapple juice is shown in table 1.

Table1. Average physical and chemical characteristics of single strength pineapple juice

	Juice
Total solids content, w/w%	10.1
pH	3.6
Acidity, w/w % citric acid	0.8
Soluble solids, Brix	10.0
Viscosity, mPa.s	6.3
Sucrose, w/w%	5.7
Glucose, w/w%	2.1
Fructose, w/w%	2.0
Pulp content, w/w%	7.4
L_{Hunter}	16.8
a_{Hunter}	-0.6
b_{Hunter}	6.8
Haze	97.2

Source: Carneiro *et al.* (2002)

The 'Smooth Cayenne' is well suited to the peeling machine that, in a series of operations to turn a cleaned, crown and root-free, whole pineapple into an intact cylinder (subsequently sliced into rings), core and extracted flesh from the residual side peel and 2 ends. Several sizes of Ginacas accommodate inspected and sized uniformly cylindrical fruit at the rate over 90 fruits /min while off shape fruits are routed to other uses for instance juice. The juice was extent still is a by-product of solid pack operations. A fresh whole fruit or the cored and peeled flesh has the highest market value, but a limited shelf-life up to three weeks under proper conditions. Large slices in syrup or juice are next in value. Broken slices and small fruit can be cut into spears and chunks. The odd pieces are diced into ~1 cm cubes as crush. These operations generate a large amount of juice. The eradicator flesh (scooped from the peel or shell and ends), together with peeled off-size/shape fruit and core, are

comminuted and pass through a finisher or screw press. Screening and centrifugation of these fractions is necessary to remove skin specks or eyes and adjust the pulp level for blending with other juice streams. Pineapple juice with a pH of ~3.5 can tolerate moderate thermal processing. Filling temperature of 70 °C followed by rapid heating to 95°C or a hot fill at ~90°C with rapid cooling could maintain quality. The juice can be concentrated to 60-65 °brix and has different of products including UHT and frozen. The concentrated juice has a global market as reconstituted juice or a major blending stock. Pineapple is either the base or component of many juice and beverage blends. The producing process step of pineapple juice is shown in Figure 1.
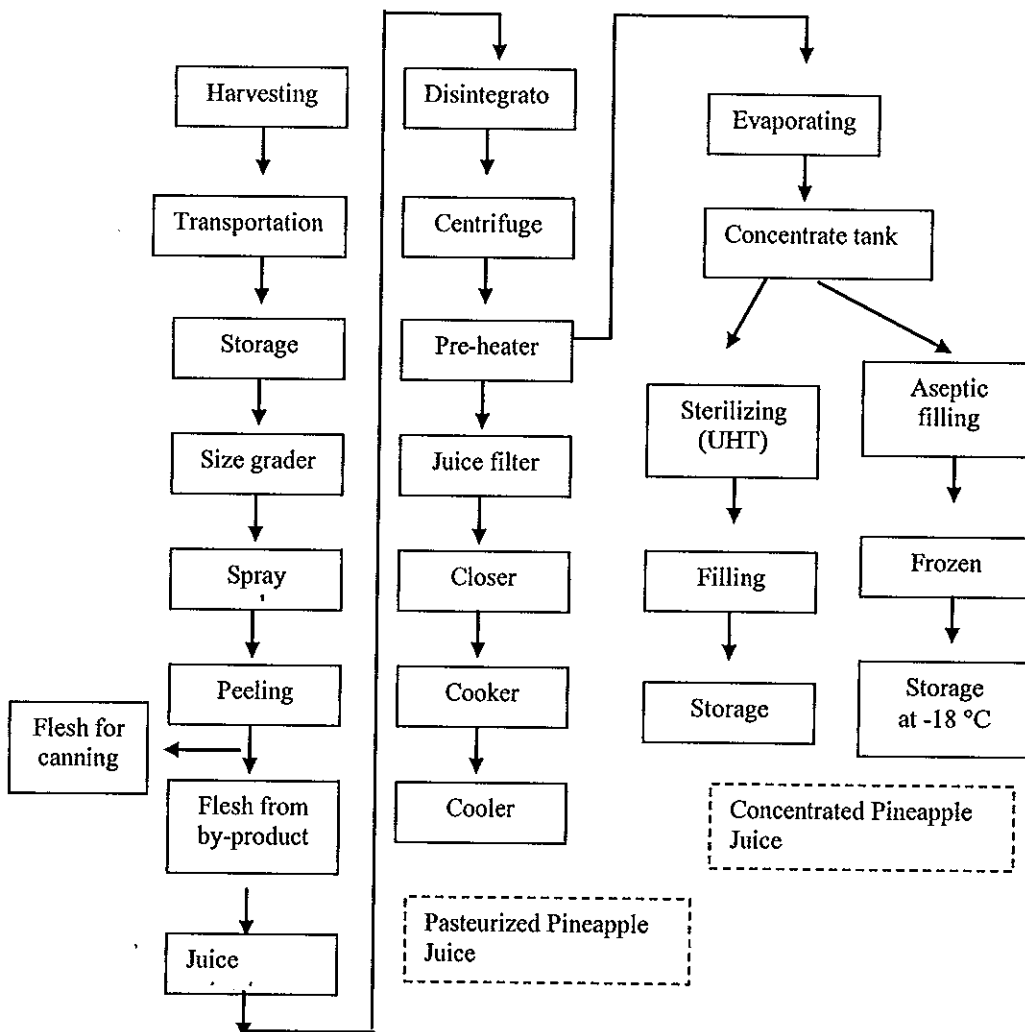
Figure 1. Process of pineapple juice and pineapple juice concentrate

Source: Modified from Downing (1996)

1.2.1.2 Coconut water

Coconut water (*Cocos nucifera L.*), the liquid endosperm obtained from immature coconuts, in its natural form is a refreshing and nutritious beverage. Nowadays, coconut water is becoming more widely consumed around the world due to its beneficial health properties, naturally fat-free and low in food energy (16.7 cal or 70 kJ per 100 g) (FAO, 2007). Coconut water contains a complex of vitamins and minerals, which make it a nutritious beverage. It is high in potassium, chloride, calcium and magnesium and it is also an essential fat free. While the mineral content remains fairly constant, the sugar and protein concentration increase as the nut matures. The nutritional of coconut water is shown in Table 2.

Table 2. Physical and chemical compositions of coconut water

	Mature Coconut water	Tender Coconut water
Total solid%	5.4	6.5
Reducing sugar%	0.2	4.4
Minerals%	0.5	0.6
Protein%	0.1	0.01
Fat%	0.1	0.01
Acidity (mg) %	60.0	120.0
pH	5.2	4.5
Potassium%	247.0	290.0
Sodium (mg) %	48	42.0
Calcium (mg) %	40	44.0
Magnesium (mg) %	15.0	10.0
Phosphorous (mg) %	6.3	9.2
Iron (mg) %	79.0	106.0
Copper (mg) %	26.0	26.0

Source: Krishnankutty (1987)

Coconut water has been successfully used as liquid in intravenous therapy in emergency situations. Coconut water contains many active compounds which have different therapeutic properties; it is non-allergenic and readily accepted by the body. Coconut water was considered as a safe and useful means of rehydration, particularly to the patient suffering from potassium deficiency. In fact, coconut water

has been shown to be as effective as commercial electrolyte solutions for prolonging survival times in sick patients. Researchers have demonstrated that coconut water can be given through intravenous infusing as much as one fourth to one third of the patient's body weight without complications. For centuries, coconut water has been used as a "temporary contraceptive" drink for both Thai and Indonesian people. They said that people in Java are afraid of drinking coconut water as it causes to diminish fertility. With this background, young coconut juice (YCJ), presumably containing phytoestrogen, is investigated for its possibly beneficial effect on accelerating wound healing in ova rats, a model for postmenopausal women. The investigations are continuing on the possibility that YCJ can be used to halt Alzheimer's disease (Radenahmad et al., 2006). Furthermore, coconut water contains estrogen hormone such as estradiol (17β-estradiol) that improves synapse formation on dendritic spines in the hippocampus of oophorectomized rats (Monk and Brodaty, 2000; McEwen and Alves, 1999). Estrogen also may improves cerebral blood flow and glucose metabolism and it may in some way acts as an antioxidant (Monk and Brodaty, 2000; McEwen and Alvews, 1999; Gibbs and Aggarwal, 1998; Birge, 1996).

Coconut water is also highly recommended as a means for oral rehydration. Athletes and sports enthusiasts use coconut water to replenish electrolytes lost in perspiration. It works ever better than some popular commercial sports drinks. The nutritional characteristics of coconut water and sport drink are compared in Table 3.

Table 3. The nutritional comparison between coconut water and sport drink

Parameter	Coconut water	Sport drink
	In mg/100 ml	
Carbohydrate	2100	5800
Calcium	60	1
Phosphorus	10	9
Sodium	3.8	45.8
Potassium	2.1	8
Magnesium	10	3

Source: FAO (2004)

In addition, coconut water has shown to act as an antioxidant activity in many types of destructive free radicals and protecting hemoglobin in blood from nitrite-induced oxidation. These effects are most significant when using fresh coconut water. They diminish significantly when the coconut water is heated or processed. Phytochemicals provided in coconut water such as ascorbic acid 0.7 mg/100g and antioxidant capacity 11.5mg /100g (Leong and Shui, 2002)

Tender coconuts after removal from the tree can be kept for 15 days without spoilage in ambient conditions. After that, fermentation takes place and coconut water becomes unfit for consumption if the water is taken out from the nut it spoiled within a day because of external contamination by microorganisms and rapidly loses most of its organoleptic and nutritional characteristics. It has been reported that microbial contamination may be in ranged of 10^6 cfu per ml in the traditional way of collection.

1.2.2 The effect of heat treatment on fruit juice quality

Conventional thermal processing in fruit juice are pasteurization and sterilization that use high heat treatment process to ensure safety and extend shelf–life of the product. However, it often leads to detrimental change in the quality, especially the sensorial and the nutritional.

1.2.2.1 Thermal process for food preservation

Thermal processing is one of the method by which appropriate food are preserved and made available to the consumer. Pasteurization, low temperature long time (LTLT) 63 °C 30 min and high temperature short time (HTST) 73.2°C 15 s are wildly used as mild treatment process for fluid foods to specifically inactivate certain pathogenic vegetative with low heat resistance. The process can be delivered either by batch or continues heating. It is important to note that the heat treatment is not intended or sufficient to inactivate all spoilage-causing vegetative cells or activated any heat resistant spore, if present. This fact determines a short keeping quality period can raise up to about 2 to 3 weeks under refrigerated conditions. In other words, the finished product (low acid) is not commercially sterile (David *et*

*al.,*1996). However, pasteurized high acid fluid packed via the hot-fill-hold method in a hermitically sealed container may yield a commercially sterile shelf–stable product. In the pasteurization of juice it is necessary to not only destroy microorganisms, but also to inactivate pectic enzyme. Generally, very high-temperature short time thermal process are used for commercial sterilization of foods and for aseptic packaging. HTST processes obtaine products with the best possible characteristics from the standpoints of flavour, aroma and colour. Typical of temperatures and times for commercial sterilization (UHT) of aseptically packaged low–acid food are 135-149 °C for 1 to 30 s. For high acid foods those parameters typically are 93-96°C for 15-30 s (Lopez, 1987)

Standard canning procedures specify filling cans or jars with hot juice at least 71 °C, sealing and processing at 100 to 105°C for up to 10 minutes and cooling immediately. This is rarely done in a still (stationary or motionless) retort, since slow heating and cooling would ruin the quality. Instead, a continuous rotary retort provides rapid heating and cooling as a result of the juice being stirred inside the can by the headspace bubble movement during rotation. Another rapid system is the spin cooker/cooler where the spinning action provides good internal and external surface contact (Fao, 2007).

1.2.2.2 Effect of thermal process on phytochemical and nutritional properties.

A phytochemical compound is a natural bioactive substance found in plant foods, acts as a natural defense system. It provides food color, flavour and natural disease resistance where works with nutrients and dietary fiber against diseases. Several studies suggest that phytochemical compounds with nutrients found in fruits, vegetables and nuts, may help slow the aging process, reduce cell damage, stimulate the immune system and reduce the risk of many diseases, including cancer, heart disease, stroke, high blood pressure, cataracts, osteoporosis and urinary tract infections (Gil-Izquierdo, 2002; Kurowska, 2000). Pineapple is an important sources of health promoting constituents and good source of vitamin C and other phytochemicals, such as phenolic compounds. Wen and Wrolstad (2002)

characterized phenolic content in pineapple juice and found that phenolic compounds in pineapple juice include sinapyl-L-cysteine, N-γ-L-glutamyl-S-sinapyl-L-cysteine, S-sinapyl glutathione, and p-coumaric like compounds (Figure2). Pineapple juice also contains phytosterols such as ergostanol and stigmastanol (Ng and Hupé, 1999). These phytosterols have been reported to have cholesterol lowering effect by reducing absorption of cholesterol. However, many researchers found that the heat treatment could be affected many phytochemical compounds.
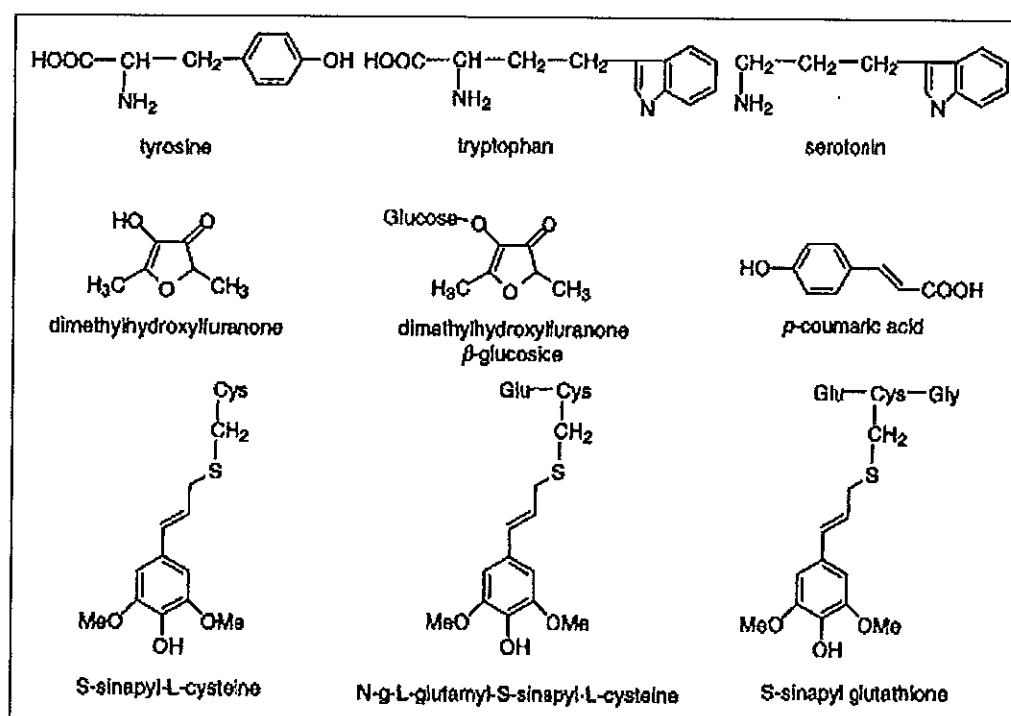
Figure 2. Chemical structures of the identified phenolic peaks in pineapple juice Souece : Wen and Wrolstad (2002)

Several studies reported that phenolic compounds decreased during heating process. For example, pasteurization of yellow banana peppers (*Capsicum annuum*) could reduce 45% of quercetin and 63% of luteolin and ascorbic acid content also decreased (Lee and Luke, 1999.) In additions, Polydera *et al.* (2004) suggested that the rates of degradation of ascorbic acid were lower for orange juice

treated with high pressure than the pasteurized juice and this led to a better retention of its antioxidant activity.

Additionally, previous study also reported a short time/high temperature process recommending for optimum pigment retention (Markakis, 1974). However, only a few studies dealt with the mechanistic aspects of anthocyanin degradation. Markakis *et al.* (1957) postulated opening of the heterocycle and chalcone formation as the first degradation step and heating shifted the equilibrium toward the chalcone with the chalcone-flavylium reversion being very slow. The first investigation on the degradation products of anthocyanins upon heating were carried out by Adams (1973). Hrazdina (1971) reported that anthocyanin would decompose upon heating into a chalcone structure; the latter might further transformed into a coumarin glucoside derivative with a loss of the B-ring. Moreover, the most common change occurring in thermal processing of green vegetable juice is the loss of its bright green color. The stability of chlorophylls is affected by both temperature and pH (Ryan-Stoneham and Tong, 2000). The central magnesium atom is easily removed during thermal processing, particularly under acidic condition and replaced by hydrogen to form the unappealing olive-brown pigments, pheophytins (Schwartz and Lorenzo, 1990). The effects of cooking (98 °C for 30 min) on carotenoid content of cassava cultivars were studied by Penteado and Almeida (1988). Provitamin A activity expressed as retinol equivalents/100 g ranged from 2.8 to 13.9 for raw and 4.9 to 10.7 for cooked samples at 98 °C for 30 min. They also reported that cooking decreased the provitamin A activity by 20–55%. The antioxidant capacity of orange juice with thermal process treatment (90 °C 1 min) was decreased from 39.3% to 35.4 % comparison to untreated juice (Elez- Martinase and Martin-Belloso, 2007). Gil-Izquierdo *et al.* (2002) studied pasteurization of orange juice with mild pasteurization (75°C 30s) and standard pasteurization (95°C 30s) which led to degradation of several phenolic compounds, that are caffeic acid derivative, vicenin 2 (apigenin 6-8-di-C-glucoside,) and narirutin (5,7,4,'-trihydroxyflavonone-7-rutinoside) with losses of 35, 31, and 28%, respectively. The carotenoids of orange – carrot juice heating at 98°C for 21s using heat exchanger decreased 9-cis–violaxanthin and neoxanthin (32.9%), antheraxanthin (3.9%) crytoxanthin (15.5%) 9-cis 2 carotene (25.9%) and 9-cis-B-carotene (27.3%) (Torregrosa *et al.*, 2006). In addition, pasteurization of yellow

passion fruit juice at 85 °C 30 min resulted in a 25 % loss in L-ascorbic acid (Talcott *et al.*, 2003). However, some studies reported that the thermally process foods might have higher antioxidant capacity than fresh and unprocessed foods due to physicochemical change that occurred during heating, and these changes might occur before, during or after processing depending on phytochemicals composition and storage condition.

1.2.3 Shelf-life stability of fruit juice during storage

Shelf-life stability of fruit juice is a measurement of how long the juice retains optimal quality. In thermal process ambient stable food deterioration is restricted, for the most part, to the cause by enzyme activity, chemical change and microbiological change.

1.2.3.1 Enzymatic activity

In general terms the thermal process to which these products are subjected during manufacture are sufficient to inactive all enzyme and it is rare for residual enzymic activity or enzyme regeneration to cause storage problems.

Enzymes from fruit juice such as peroxidase (POD) and poly phenoloxidase (PPO) contracting with oxygen causes nutritional and color losses. POD and PPO are wildly detected in many fruit and vegetable and are closely linked to enzymatic colour change with consequent loss of sensorial properties and nutritional quality. Different naves have been associated with PPO including tyrosinase, cresolase, cathecolase and phenolase and generally reflect the ability of this enzyme to utilize many different phenolic compounds as substrate (Michael and Robinson, 1991). The enzymatic browning is one of the most important reactions in food chemistry (Figure 3).

o-dihydroxyphenol   o-quinone   brown polymer
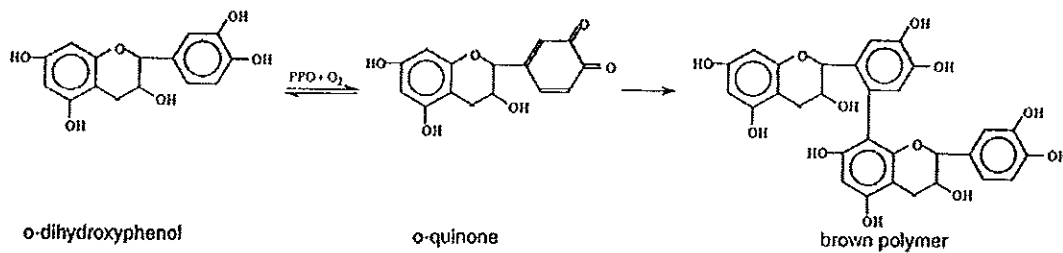
Figure 3. Enzymatic browning reactions in fruit juice

Source: Borneman *et al.* (2001)

PPO and POD are very resistant to heat and therefore are considered biological indicators of thermal processing. To prevent negative effect from enzyme fruit juice can undergo difference process such as ultra-high temperature (UHT), conventional pasteurization and freezing. To solve this problem packaging of fruit juice and its preservation has been attempted by a number of workers. As thermal sterilization will grossly alter the taste, various treatments like filtration pasteurization, adjustment of sugar, pH and total solid, concentration by reverse osmosis, addition of preservatives, carbonation etc., in various combinations have been tried for its preservation (Matsui *et al.,* 2007)

1.2.3.2 Chemical changes

Chemical changes that take place during storage are those related to oxidation, non-enzymic browning (i.e. Maillard reaction) or resulting from nutrient breakdown.

-Oxidation reactions are many and complex. They can use either headspace oxygen, trapped oxygen or free radical oxygen released by enzymic activity or thermal treatment. They can be initiated photochemical. They are, in common with all chemical reaction, dependent on temperature and time, and are often catalyzed by common food constituents such as trace metals. The results of these reactions are similarly varied but most are observed as 'off' colour and flavour. Under normal ambient storage conditions, i.e. 15- 25 °C, oxidation reactions are probably the most common cause of quality deterioration during storage.

-Non-enzymic browning or Maillard reaction takes the general form of a condensation reaction between amino acids and reducing sugars and has the potential to occur in any system where these two substrates are present. Although the Maillard reaction is extremely complex, the factors which control the reaction are reasonably well understood. The application of thermal energy has a complex effect on the reaction. As with all chemical reactions, heat may initiate and accelerates. Maillard reaction, the nature of the substrate materials also affects the reaction. Proteins are less reactive than pure amino acids. Polymeric carbohydrates such as starch do not take part in the reaction but pure reducing sugars such as lactose are very reactive. Many other chemical constituents of foods have either positive or negative effects on non-enzymic browning and this complex series of reactions can affect off quality in three ways. Firstly it can produce undesirable 'off' colour and flavour the brown discoloration and bitter notes. Nutrient breakdown is strongly influenced by the severity of the applied heat process and by the time and temperature of storage (Michael and Robinson, 2001). The scheme of the Maillard reaction adapt from Hodge, (1953) is shown in Figure 4.
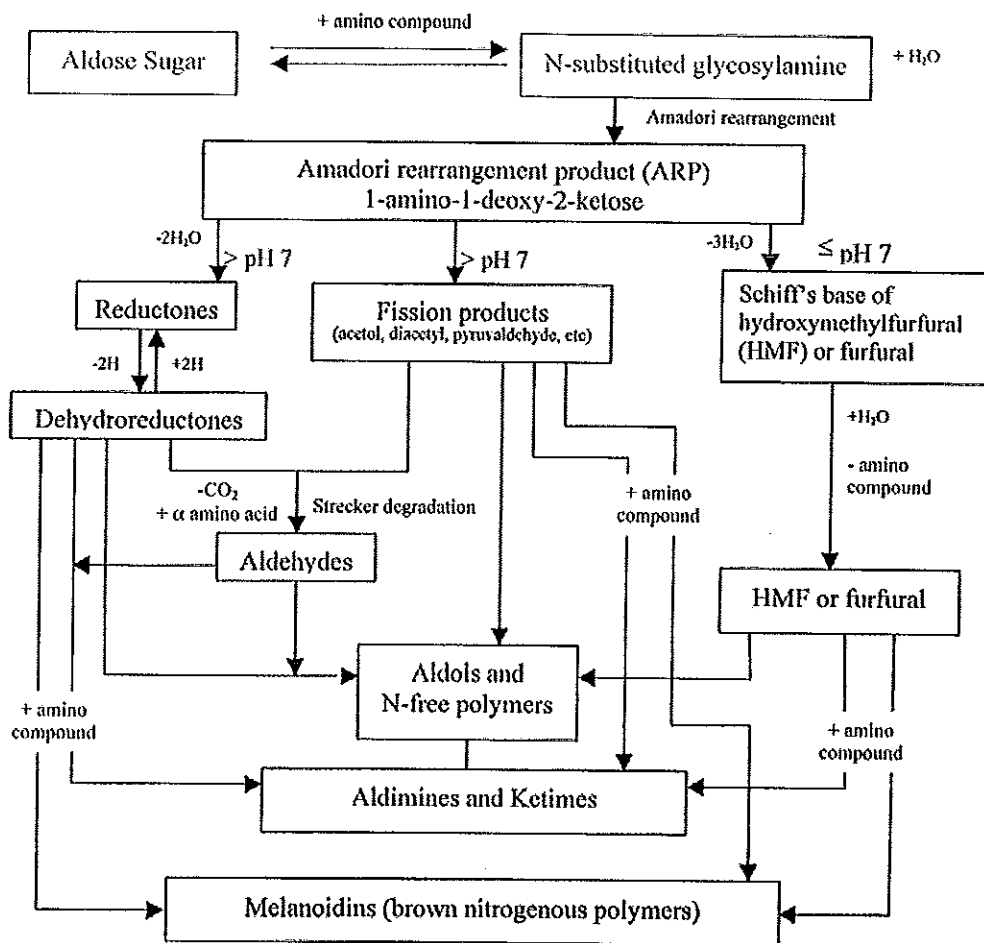
Figure 4. Malliard reaction

Source: Martin *et al.* (2001)

-Nutrient breakdown, loss of nutrient from processed food is strongly influenced by the severity of the applied heat process and by the time and the temperature storage. Polydera *et al.* (2004) studied the effect of storage on the antioxidant activity of pasteurized reconstituted orange juice at different temperatures 0, 5, 10, 15 and 30 °C. It was found that the total antioxidant activity of orange juice decreased with increasing temperature. The increasing of storage temperature also led to a decrease of ascorbic acid. Polydera *et al.* (2005) studied thermal pasteurized (condition 80°C 60 s) orange juice and storage at different temperature at 0,5,10,15 and 30 °C. It was found that the shelf-life of orange juice was 88, 58, 39, 26 and 9 days based on 50% ascorbic acid loss and 111, 66, 60, 24 and 6 days based on sensory

evaluation respectively. Ros-Chumillas *et al.* (2007) found that orange bottled juice stored at 4 °C has better preserved ascorbic acid than those stored at 25 °C. However, vitamin C is oxidized and lost during the storage period of the juice. The rate of degradation of the vitamin C highly depends on the storage conditions temperature, dissolved oxygen and oxygen barrier provide by container materials are major factors affecting vitamin C loss in packaged orange juice.

The other factors may need to be considered when setting up a storage protocol. There may be a need to consider and allow for the effect of light. This is certainly the case for product packed in different package. Belinet *et al.* (2006) studied the l-ascorbic acid content of orange juice storage in various packaging after 9 months at 20 °C. They found that the glass enabled the best preservation of ascorbic acid. In plastic packaging, the loss of ascorbic acid was correlated with oxygen permeability of plastics.

1.2.3.3 Microbiological change

In determining the influence of microorganism on the shelf life of foods, the rates of microbial growth as a function of various environmental factors must be known. Microbes have the ability to multiply at high rate when favorable conditions are present. Prior to harvest, fruit and vegetables good defense mechanisms against microbial attacks, however after separation from the plant, they can easily succumb to microbial proliferation. Microbial growth in foods results in food spoilage with the development of the undesirable sensory characteristics and in certain cases the food may become unsafe for consumption.

Since thermal pasteurization could cause some undesirable organoleptic changes in addition to some detrimental affects to the nutritional quality of the juice. Alternatively, non-thermal processes have been investigated for their efficiency to extend shelf- life and protect organoleptic and nutritional qualities of the juice. Non-thermal processes are including, ultraviolet light, high-pressure treatment and pulsed electric field. These various processes are described as their effectiveness against spoilage and pathogenic microorganisms as well. For example, pulsed electric field affected the cell membrane and may cause irreversible membrane leakage of

microorganism. High pressure has the potential to inactivate microorganisms and certain enzymes and to modify the functional properties of some food constituents; but the nutritional and sensorial properties of high pressure processed foods are preserved. Because high pressure acts by disrupting secondary and tertiary bonds without affecting the covalent bonds, no deterioration of essential vitamins, phytochemicals, aroma compounds, etc. occurs. Therefore high pressure processing is a safe and consumer friendly physical method, meeting the consumers' growing demand for freshly, minimally processed, additive-free (clean-label) and nutritious food (Smelt, 1998a; Membrane technology, microfiltration/ ultrafiltration can be an alternative to fruit juice preservation and conservation, because it dose not involve the use of severe for heat treatment.

1.2.4. Membrane Technology in fruit juice production

Membrane processes are today consolidated system in various productive sectors, since the membrane process is a non-thermal with out phase change or chemical agents. The introduction of these technologies in the industrial transformation cycle of fruit juice represents one of the technological answers to the problem of the production of juice with high quality, natural fresh taste and additive free. The primary motivations for using membrane technology to replace traditional thermal processing are to substantially reduce the thermal damage to thermally labile flavor compounds and improve sensory profiles of juice product. The second reason for using membrane technology is energy saving and enzyme can be reduced (Girard and Fukomoto, 2000). However, many membrane processes incur high capital and operational costs related to membrane replacement and cleaning so the overall economics should be considered for evaluating membrane technology (Liu, 2003). In addition, the propose of the membrane filtration of fruit juice is to remove suspended solids as well as haze since the product needs to be clear without sediments, haze or turbidity during storage and free from microorganism. Specifically, the polymerization of phenolic compounds and their interaction with other components (e.g. protein) could causes haze formation and turbidity in fruit juice (de Brujin and Borquez, 2006)

Microfiltration (MF) and ultrafiltration (UF) are basically similar in that the mode of separation is molecular sieving through increasingly fine pores. MF is used in a number of applications as either a pre-filtration step or a process to separate fluid from a process steam with a membrane pore size typically of 0.2-2 μm and is able to retain particle with molecular weight 100 kDa. MF has been successfully used in the food industry to remove bacteria and particulate substances from liquid food steams. UF is the most common membrane process used in the dairy industry and it involves the use of membranes with a pore size ranging between 0.01-0.2 μm. Applications of UF in food processing can mostly likely be found in situations that require the separation of one or more desirable food constituents that have a larger molecular weight of >10 kDa from a liquid mixture. The role of UF in postharvest processing of fruit and vegetable juices is prominent in fruit juice clarification. UF unit is often found in a fruit juice depectinization operation where UF is used to recover depectinization enzymes such as pectin methylesterase and polygalacturonase. The most important qualities of a membrane are high selectivity, high permeability, mechanical stability, temperature and chemical resistance. Selectivity, the measurement of the ability of the membrane to retain or reject targeted food components, is considered as the first criterion when considering using membrane processes to perform a giving separation task (Liu, 2003).

Many studied on UF and MF for clarification of fruit juices had examined the effect of pore size on flux and retention of components. In general, the flux increases as the pore size because the membrane permeability coefficient. For the solution of given size, retention will generally decrease with pore size increases. Flux should be as high as possible to be economical, but potential haze precursors should be retained to obtain a quality product. Fukumoto *et al.* (1998) suggests that flux may not necessarily increase with pore size. Membrane with larger pore size tend to be more susceptible to fouling, as the proportion of smaller particles and colloids in juice increase and can leads to pore blocking and plugging. For the quality of fruit juice with filtration by using different pore size found that the low molecular weight compound such as minerals acid, vitamin and sugar have a very low retention while the larger component such as pulp, starch and pectin had a very high retention.

Several studies have examined the effects of temperature, cross flow velocity, transmembrane pressure (TMP) and pore size on the MF and UF of various juices (Table 4). The optimum conditions found in each of the studies were dependent on the juice processed, the equipment and the procedure. The optimum operation parameters for production fruit juice by membrane filtration are summarized as follow.

Table 4. Optimum operation parameter for membrane clarification of various fruit juice

| Juice | Membrane | Optimum parameter | | | Reference |
		TMP (bar)	CFV (m/s)	T (°C)	
Passion fruit	30 kDa polysulfone hollow fiber	1.17	72l/h	40	Jiraratananon and Chanchai, 1996
Apple Juice	0.2,0.02 µm ceramic tubular membrane	4.14	8	50	Fukumoto et al,1998
Cushew Nut	0.3µm ceramic membrane	2	-	30	Campos et al., 2002
Apple Juice	15,50 kDa ceramic tubular	1.4,4	2,7	50-55	de Bruijn et al., 2002
Pineapple juice	0.3µm tubular polyestersulfone	1	6	25	Carnerio et al.,2002
Carrot–juice	15 kDa tubular membrane PVDF	1.03	0.14	23.5	Cassano et al., 2003
Apple juice	0.01µm, 30 kDa polysulfone	1.47	12l/h	-	Youn et al., 2004
Lemon Juice	0.2 tubular ceramic membrane	1.5	7	35	Vaillant et al 2005

Juice	Membrane	Optimum parameter			Reference
		TMP (bar)	CFV (m/s)	T (°C)	
Lemon juice	0.2 µm 15% PVDF, 5% PMMA 5% PVP in dimethylformamide (DMF)	0.6	1	20	Espamer, et al., 2006
Kiwi fruit juice	15 kDa tubular membrane PVDF	0.9	-	25	Cassano et al., 2007
Apple juice	50 kDa polyethersulfone plate membrane	2.5	2	23-50	He et al., 2007
Mosambi Juice	50 kDa a thin film composite polyamide	4.14	1200rpm	42	Rai et al., 2007
Orange juice	15kDa PVDF tubular membrane	0.85	800l/h	25	Cassano et al., 2007
Kiwi fruit juice	30 kDa cellulose plate sheet	0.65	933ml/min	30	Cassano et al.,2008
Mosambi juice	50 kDa plate sheet polyethersulfone	3.6	1.2	-	Sarkar etal 2008
Red fruit juice	45 kDa hollow fiber	4	1-1.2	25-30	Soroknai-et al.,2008
Water lemon	0.2µm hollow fiber membrane	2.78	1200rpm	30	Chhaya et al., 2008

TMP = transmembrane pressure, CFV= cross-flow velocity, T = temperature

1.2.4.1 Cold sterilization and stabilization of fruit juice by using membrane filtration

Production of cold sterilization by MF and UF with aseptic processing and packaging is the method that can be prevented microbial spoilage. Heatherbell et al. (1977) filtrated apple juice ($3.8x10^4$ cfu/ml) with a 50 kDa MWCO polysulfone membrane to a two folds concentration. A permeate had low counts (<1 cfu/ml), while the concentrate reached $1x10^5$ cfu/ml. No evidence of spoilage was

detected in aseptically bottled product after storage at room temperature for 6 months. Carnerio *et al.* (2002) sterilized and clarified pineapple juice by MF with 0.3 µm tubular polyethersulfone membrane the result showed that the process can reduce haze, viscosity, microorganism and showed no significant changes in pH, acidity, sugar and soluble solid content of the juice and the product can kept under refrigerator (8 °C) for a period of 28 days. Youn *et al.* (2004) studied filtration of apple juice by using membrane with MWCO of 30,000 and pore size of 0.01 µm the result found that the quality of apple juice membrane filtration improved colour without deterioration changes of pH, total acidity, organic acid and vitamin C, which are important quality.

Reddy *et al.* (2005) studied green coconut water produced in developed two stage laboratory scale constant pressure filtration system. The method of this studied using pre-filtration unit by ordinary filter paper for removal of suspended particles and a micro filtration unit by cellulose nitrate membrane with pore size of 0.2 µm for removal of microorganism. Cassono *et al.* (2007) clarified kiwifruit juice by using 15 kDa polyvinylidenefluoride membranes. The quality of permeate product permitted a good level of ascorbic acid.

1.2.4.2 Basic concepts of membrane filtration

Filtration can be defined as a method of separating particulate matter in a continuous liquid using the permeable barrier. The permeation flux of particle-free water across a clean membrane can be described by Darcy's law as:

$$J = \frac{TMP}{\mu R} \tag{1-1}$$

Where J (m^3/m^2s) is the permeation flux, TMP is the transmembrane pressure (bar) µ (Pa.s) is the absolute viscosity of water, and R (1/m) is the hydraulic resistance to the fluid.

The TMP, known as a transmembrane pressure across the membrane is calculated as:

$$TMP = \frac{P_{in} + P_{out}}{2} - P_p \qquad (1\text{-}2)$$

Where P_{in} is the pressure in to the membrane, P_{out} is the pressure at the outlet of the membrane and P_p is the permeate pressure. The permeate pressure is very close to 0, so often is ignored.

For MF and UF, the fouling by concentration polarization may be negligible due to the large size of the particles retained. Thus, in the case of the permeation flux through a filtration unit treating suspensions, R, can be given, by modifying Equation (1-1), as:

$$J = \frac{TMP}{\mu(R_T)} \qquad (1\text{-}3)$$

Where R_T is total hydraulic resistance, comprising the membrane resistance (R_m) and the fouling resistance (R_f) :-

$$R_T = R_m + R_f \qquad (1\text{-}4)$$

R_m is a memebrane resistance, R_f can be broken down to reversible fouling resistance (R_{rf}) and irreversible fouling resistance (R_{if}):-

$$R_f = R_{rf} + R_{if} \qquad (1\text{-}5)$$

R_{if} is estimated after the membrane was fouled, by replacing the feed with water to eliminate reversible fouling resistance. The water flux of the fouled membrane was then determined to estimate the irreversible fouling resistance by the following equation:-

$$R_{if} = \frac{TMP}{\mu_p J_{wf}} - R_m \qquad (1\text{-}6)$$

Where J_{wf} is the water permeate flux of the fouled membrane. R_{rf} at the end of run was calculated by using equations (1-5) and (1-6) (Youravong, 2001). Most large solute and particles are retained in the retentate during membrane filtration. The observed solute solution (or rejection) coefficient (R_j) is given by

$$R_j = 1 - \frac{C_p}{C_b} \qquad (1\text{-}7)$$

Where C_p and C_b are the solute concentration in the permeate and in the bulk solution (or the feed) respectively. If the solute completely rejected by the membrane ($C_p=0$), then R_j is 1 if the solute freely passes though the membrane, then the R_j is zero.

The volumetric concentration factor (VCF) is defined as the initial volume divided by the retentate volume at any time. The retentate is determined by the difference between the initial feed and permeate volume.

$$\text{VCF} = \frac{\text{Initial feed volume}}{\text{Retentate volume}} \qquad (1\text{-}8)$$

1.2.4.3 Concentration polarization and fouling

During a membrane filtration process the permeate flux can decrease with time. This behavior is often observed as given in Figure 5. The flux declines at first rapidly with time; then the speed of flux decline decreases, and finally a steady state is reached where the flux does not decrease anymore. The decrease in flux is commonly ascribed to two phenomenas: concentration polarization and fouling. The distinction between these two phenomena is not always clear, and often the two phenomenas are linked together.
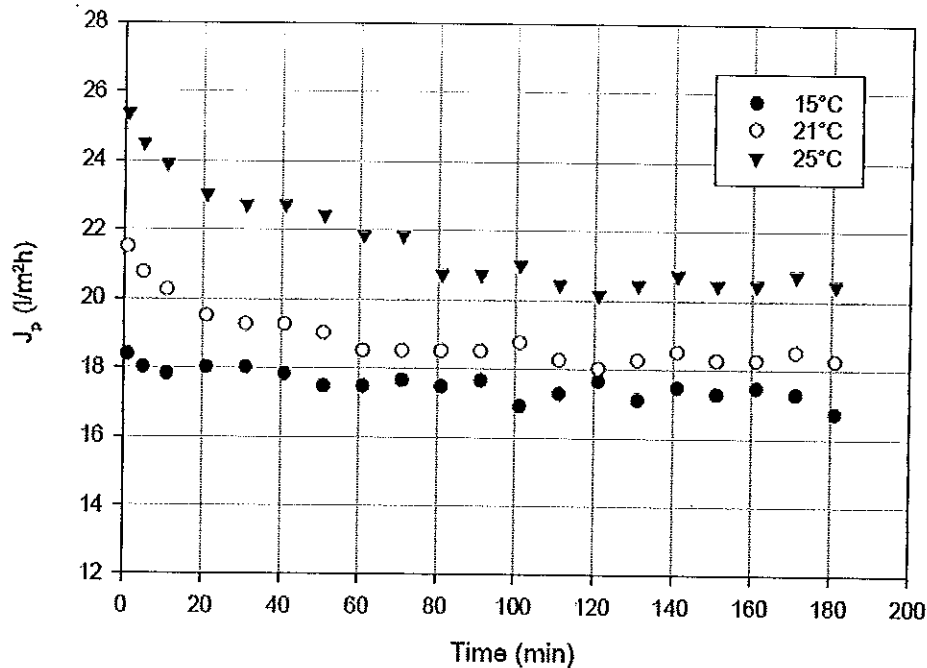
Figure 5. Permeate flux during a microfiltration process of orange juice at different
temperature

Source : Cassano *et al.* (2007)

When filtering a solution or suspension, the membrane retains
dissolved molecules and/or suspended particles (here after generally referred to as
solutes). The solute concentration near the membrane will therefore gradually
increase. Such a concentration build-up will generate a diffusive flow back to the bulk
of the feed. After some time a steady state can be reached where the convective solute
transport towards the membrane equals the diffusive solute transport away from the
membrane (Figure 6) this build-up of a concentration boundary layer near the
membrane surface, governed by convective and diffusive transport is referred to as
concentration polarization. Concentration polarization is thus a phenomenon which
takes place is the solution. Fouling is based on direct contact between solutes and the
membrane surface or within the pores, blocking of the pores by particles, and the
formation of a cake layer of particles on top of the membrane. All these processes
increase the hydraulic resistance against permeate flow, and thus reduce the capacity
of the microfiltration process
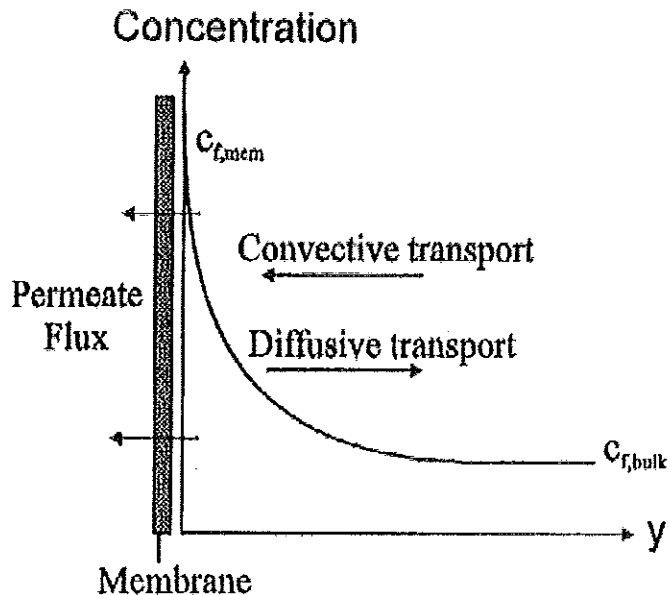
Figure 6. Schematic representation of a concentration polarization layer

Source : Huisman (1998)

Concentration polarization can lead to a reduction of flux through two mechanisms: osmotic pressure effects and concentration polarization induced fouling. The increased concentration of solutes near the membrane causes an increased osmotic pressure at the feed side of the membrane surface and thus decreases the driving force for permeate flux. This mechanism is especially important for reverse osmosis and UF, where osmotic pressures in the concentration polarization boundary layer can be high. The particles normally retained in microfiltration do not cause any significant (and in many UF applications) concentration polarization leads to a flux decline because concentration polarization increases the amount of fouling. The increased concentration of solutes near the membrane surface causes a higher rate of solute adsorption; wall concentrations may be ever so high that effectively a gel layer or cake layer is formed. All the phenomena cause an increased hydraulic resistance to the permeate flow (Huisman, 1998). These two phenomena are aspects of the same problem, which is the build-up of retained components in the boundary layer of the

membrane-solution interface. Both phenomena induce additional resistances on the free side to the transport across the membrane, and at the same time, they are responsible for the gradual reduction of the permeate flux through the membrane, and for the change of the selectivity of the process.

Concentration polarization is a reversible phenomenon, while fouling is irreversible and can be caused by several mechanisms: adsorption pore blocking and/or formation of a gel layer. The two phenomena are not completely independent of each outer since fouling can also result from polarization phenomena.

The extent of these phenomena is strongly dependent on the type of membrane processes involved and the feed employed. The flux decline is very severe in MF and in UF and, very often, the process flux is less than 5% of that for pure water. Figure 7 shows a schematic representation of the various resistances that can arise during a separation process.
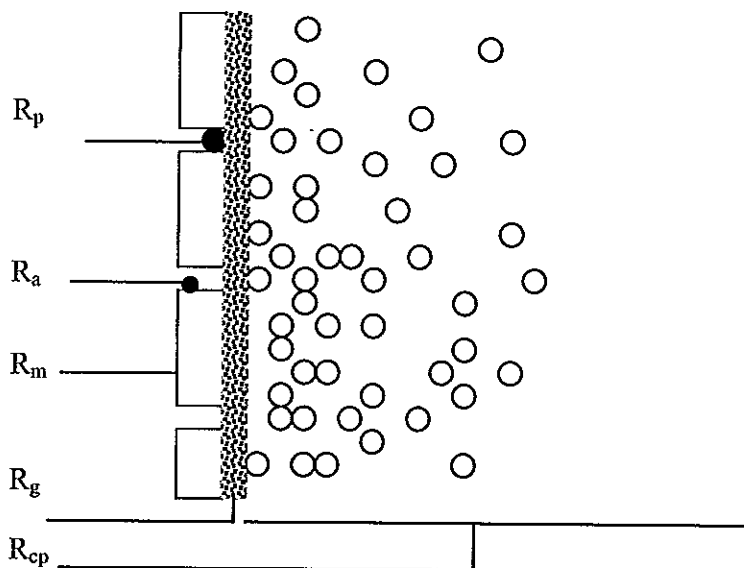
R_p = pore blocking, R_a = adsorbtion, R_m = membrane, R_g = gel layer formation
R_{cp} = concentration polarization

Figure 7. Overview of various types of resistance toward mass transport across a membrane

Source: Mulder (1991)

1.2.4.4 Fouling mechanism

An important limitation in the performance of membrane processes is that the permeate flux is adversely affected by transient build-up of a layer of rejected species at the membrane upstream interface. The general effect of these phenomena, known as concentration polarization, is a rapid permeate flux decay during the early period of filtration, followed by a long and gradual flux decline towards a steady or nearly steady-state limit value. However, a more important aspect of concentration polarization phenomena, which has to be considered, is related to the physicochemical interactions of the accumulated material with the membrane. In this case a fouling mechanism such as adsorption on the membrane pore walls and pore plugging by solute penetration occurs rather than the build-up of a particle cake layer at the interface. The various modes of pore blocking are a function of the solid/solute size and shape in relation to the membrane pore size distribution: • complete pore blocking: the pore entrance is sealed; •pore bridging: partial obstruction of the entrance; • internal pore blinding: material not rejected by the pore entrance is adsorbed or trapped on the pore wall or in the membrane support. For process engineers designing systems it may be useful to classify fouling as in-depth pore fouling, pore plugging and cake formation (de Barros *et al.* 2003). The models are illustrated in Figure 8.
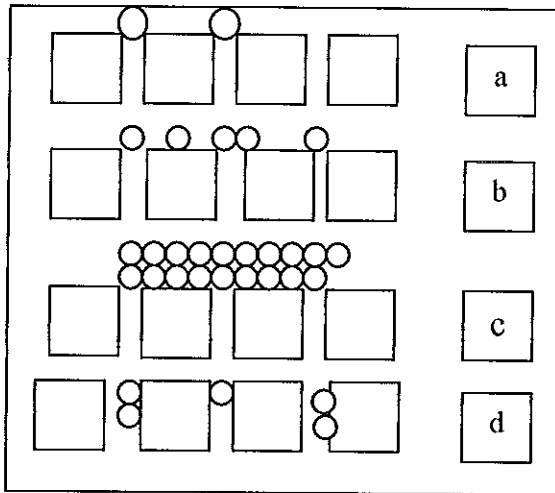
Figure 8. Mechanism for membrane fouling: (a) complete pore blocking; (b) partial pore blocking; (c) cake filtration; (d) internal pore blocking

Source: de Barros *et al.* (2003)

The ability of simple cake filtration analysis to predict the variation in flux rate with time during cross-flow filtration has let to various fouling mechanisms to be proposed to better characterize the flux performance. The various fouling mechanisms that have widely used are cake filtration, intermediate law, standard pore blocking and complete pore blocking. By combining various developments on the filtration models, the various correlations in each mechanism and reformulated in terms of flux per unit time (Hu and Scott, 2008).

a. Complete pore blocking

$$\ln(J^{-1}) = \ln(J_0^{-1}) + k_b t \qquad (1\text{-}9)$$

b. Gradual pore blocking (or sometime called standard pore blocking)

$$J^{-0.5} = J_0^{-0.5} + k_s t \qquad (1\text{-}10)$$

c. Intermediate filtrati

$$J^{-1} = J_0^{-1} + k_i t \qquad (1\text{-}11)$$

d. Cake filtration

$$J^{-2} = J_0^{-2} + k_c t \qquad (1\text{-}12)$$

In these models, k_s, k_i, k_b, k_c are fouling coefficients relating to each model respectively. t is the filtration time and J_0 is the initial permeate flux. The fouling mechanism can be analyzed by fitting experimental data to Equations 1-(9-12). The linear stages in the figures based on these equations indicate the type and duration of the fouling.

1.2.4.5 Membrane cleaning disinfectant and sterilization

Membrane fouling is referring to the flux decline of the membrane filter caused by the accumulation of certain constituent in the feed water on the surface of the membrane use in the membrane matrix. Certain fouling material can be removed by hydraulic means such as filter back wash or scrubbing. Most can be removed by chemical means. Chemical cleaning is an integral part of membrane process operation at a profound and economic of the membrane process (Liu, 2003). A large number of different cleaning solutions have been developed for specific application. Optimize the cleaning process requires knowledge of how the operating condition affect cleaning and subsequent performance as well as the stability of cleaning agent. Some of the commonly used cleaners are acid base and proprietary surfactant mixtures (Kim *et al.*, 1993). Acid are most effective at removing calcium salt (carbonate and phosphate) and metal oxide. In both cases, these components are dissolved by reaction with the acid to form a soluble salt (Zeman and Zydney, 1996). When the membrane is fouled by iron oxide, citric acid is very effective because it not only dissolves iron oxide precipitate but also form complex with iron (Hong and Elimelch, 1997). Caustic is typically used to clean membrane fouled by organic and microbial foulants. The fraction of caustic is two-fold (1) hydrolysis (2)

solubilization. There are a numbers of organic materials including polysaccharides and protein can be hydrolyzed by caustic. The hydrolysis of polysaccharides is the reason why cellulose-based (cellulose, a simple polysaccharide, consists of thousands of glucose linked by 1,4 -β-glycoside bounds) membranes have to be used in a limited pH range. Tertiary structures of proteins are likely to be disrupted and proteins are reduced to peptides. Fats and oils also react with caustic through saponification, generating water- soluble soap micelles. A very important function of caustic is to increase negative charges of humic substances. Therefore, they are easier to be removed from membranes.

The technology corporation company (A/G) recommends that the process of juice and beverage clarification the cleaning procedure will be fallow:

A) Flash with clean water

B) Circulate 0.5 N NaOH at 50 °C for 1 hour

C) Flash with clean water optional

D) Circulate NaOCl at 50 °C pH 10- 12 for 1 hour

E) Flash with clean water

In addition, disinfectant destroyed all living pathogenic microorganism while sterilization also eliminate very highly resistance bacterial spore. Membrane system in the food industrials are typically disinfected on a daily basis. Hypochlorite (NaOCl) is commonly used for the chemical disinfectant of membrane system and probably kills bacteria through oxidation of critical elements. The concentration of sodium hypochlorite for sanitization is usually use at 100 ppm. Sodium bisulfite (NaHSO$_3^-$) is a strong reducing agent and is thus compatible with many membrane systems that might be degraded by strong oxidizing agent like hypochlorite. The effectively of bisulfite solution is also pH dependent better activity is obtained in acidic solution (pH <4). However, it been reported that NaHSO$_3$- can cause swelling of cellulose acetate membrane and lead to an increase in flux and solute passage.

Steam sterilization is used extensively for membrane system. Minimum requirement for effective steam sterilization are 15 min and exposure to steam at 121 °C and 1 bar, pressure. Steam sterilization can be performed on the disassembled system in an autoclave, but the membrane unit must then be aseptically attached to the remainder of the pasteurized system. The preferred method of

sterilization is known as steam in place or SIP. In this case the membrane unit is exposed to flowing steam with in the completely assemble filtration system (Zeman and Zydney, 1996).

1.2.5 Factors affecting the process performance during microfiltration or ultrafiltration

A number of experiments have been carried out to investigate the influence of hydrodynamic factors on membrane filtration process. The key hydrodynamics factors in membrane processing are temperature, TMP and cross flow velocity.

1.2.5.1 Cross flow velocity

Feed velocity or shear stress at the membrane surface is key factor influencing membrane flux and fouling, especially, for reduction of concentration polarization or reversible fouling resistance. High shear rates generated at the membrane surface tend to shear off deposit material and thus reduce the hydraulic resistance of the fouling layer. Fouling may be more severe when a solution filtered at low feed flow rate (Tores et al., 2002). Cassano et al. (2007) studied the effect of axial flow rate on UF of kiwi fruit juice by vary the feed flow rate from 300-700 l/h. The resulted shown that the flux increased with increasing feed flow rate.

1.2.5.2 Temperature

It is known that increasing feed temperature increases the permeate flux in membrane filtration due to a decrease in permeate viscosity, which enhances permeate flow, and increases diffusivity, which enhances dispersion of the polarized layer (Cheryan,1977; Nichole and Cheryan,1981; Eckner and Zottola, 1993; Marshall et al.,1993; Youravong, 2001). Jiraratananon and Chanachai (1996) studied the membrane filtration of passion fruit juice at different process temperature. The result shown that, the flux increased with temperature from 30 to 40 °C and then decrease at 50 °C. The reason for a drop of permeate flux at 50 °C was probable formation of a true gel on the membrane surface. Fukumoto et al.,1998 clarified apple juice with

various temperature from 30 to 50 °C. The result found that the temperature increase improve flux due to viscosity reduction and/or an increase in soluble solid. Temperature of 50 °C is often used for UF and MF for fruit juice to maximize flux and minimize microbial growth.

1.2.5.3 Transmembrane pressure (TMP)

TMP is a key operating parameter for pressure driven membrane processes. During membrane filtration, two distinct operation-regions exist regarding to permeate flux. The region in which the permeate flux increase with increasing TMP is called the pressure-dependent region. Under conditions where the permeate flux does not increase with increasing TMP, it is called the pressure-independent region (Grandison and Lowis, 1996).

1.2.6 Improvement of membrane process performance

For an efficient filtration system, concentration polarization and fouling should be reduced to minimize flux decline. There are some methods for improving flux during fruit juice clarification.

1.2.6.1 Critical flux

During membrane filtration as soon as a separation of solute occurs, an accumulation of matter appears on the membrane. Field *et al.* (1995) introduced the concept of critical flux for microfiltration, stating that there is a permeate flux below which fouling is not observed. The critical flux results in a force balance between drag forces and surface interaction in a mass boundary layer and then depend on surfaced interactions the hydrodynamics and the position along the membrane. As the concentration in the boundary layer increases along the membrane, in cross flow filtration this critical flux appears where the boundary layer is the thickest (Espinass *et al.*, 2006)

Above the critical flux, the fouling phenomenon is self-regulated. An increase of pressure leading to a flux is higher than the critical flux generates a growth in the deposit until a decrease in flux reaches its critical value. On the other hand, the

limiting flux is the maximum flux that can be achieved at steady state in with measuring TMP an operation. It is clear that the concept of critical flux is a very powerful optimization tool for this membrane filtration.

However, some authors pointed out that operation below the critical flux may not be sufficient to avoid long-term fouling. These authors introduced the concept of sustainable flux, at which the desired separation can be operated in profitable manner, only minimizing but not elimination fouling entirely (Stoller and Chianese, 2006). There are two types of critical flux. A 'strong form' of critical flux exists if the flux of a suspension is identical to the flux of clean water at the same the transmembrane pressure. In the second definition, A 'weak form' of the critical flux exists if the relationship between membrane transpressure and flux is linear, but the slope of the line is differ from that of clean water (Wu *et al.*, 1999).

The method of critical flux determination was carried out using the step by step technique. The TMP is increased at fixed intervals in time steps of 30 min prior to the onset of non-linearity in the increase in permeate flux, which is indicative of critical flux, thereafter 15 min time steps were used, the critical flux is the average of the last time independent flux step and the first time dependent step. The critical flux detection is shown in Figure 9. Although the disadvantage of this method is a lesser degree of control over the initial fouling this can be overcome by starting the experiment at as low a TMP as possible followed by gradual small TMP increment of 0.1×10^5 Pa (0.1 bars). In order to as certain the effect of reversibility of deposition an alternative method of determining critical flux was used and the results of these experiments are in full agreement with those obtained using the step by step method (Chiu and James, 2006).
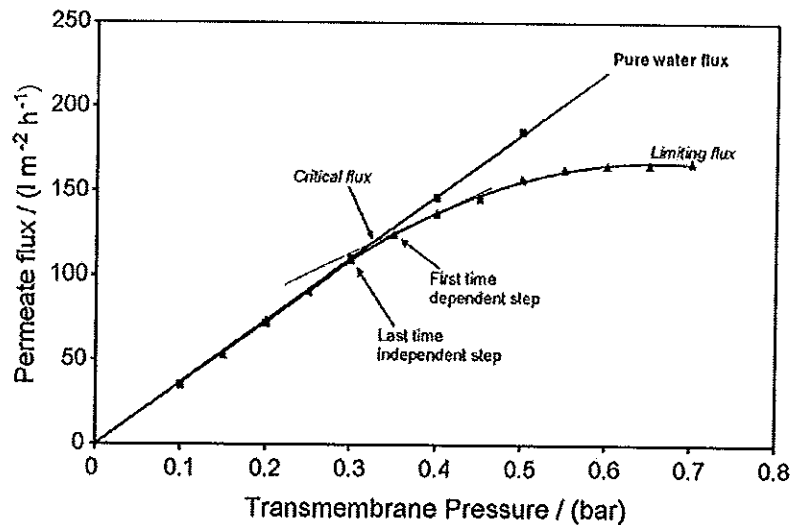
Figure 9. Critical flux determination

Source: Chiu and James (2006)

There are several factors affecting critical flux such as thermodynamic, membrane properties, consequences of critical flux on process efficiency.

Thermodynamic at the membrane surface have a major influence on variations in critical flux values: an increase in the strength of the hydrodynamics being synonymous with a critical flux rise. Furthermore, the sensitivity of critical flux to hydrodynamic conditions can explain the distribution of critical fluxes (and then of fouling) along the membrane surface. Tangential flow at the membrane surface induced a variation of critical flux, which has typically been repressed as a power law of Reynolds number in numerous papers dealing with critical flux. Such a trend is found in all studied dealing with effect of cross flow velocity on the critical flux but a common exponent for this power laws cannot be deduced. Madaeni *et al.* (1999) found that a large cross flow velocity can cause a small increase in critical flux if the pressure drop is along the membrane surface become significant. For the same TMP, the transmembrane pressure at the inlet of the membrane surface when the velocity and hence feed-side pressure gradient are high is it self high. This leads to a local permeate flux, which can be superior to the critical value and hence local fouling. Chiu and James (2006) study the effect of gas sparging on critical flux on microfiltration. The result found that the critical flux increase with increasing gas

flow velocity. The overall critical flux improvement in the presence of gas can be attributed to the increased mean velocity of the fluid which in turns increases the wall shear stress and Reynolds number.

Effect of membrane properties, membrane properties such as porosity and pore size (or molecular weight cut off) have been experimentally investigated in addition to the effect of the membrane material properties. Wu *et al.*(1999) observed for a PES membrane a decrease of the critical flux when the membrane cut off is increased as proposed by the authors, the change in critical flux could be the difference in surface properties (such a charge) but could also be the result of a change in local porosity and hence in local permeate velocity. The effect of a membrane material, membrane surface being hydrophobic or even the effect of a membrane cleaning did not show consequence for the determination of the critical flux (Manttari *et al.*, 2000)

Stoller and Chianese (2006) studied the best method for operating batch membrane processes in the presence of fouling. The case was the purification of olive washing wastewater. The result showed that adopting a permeate flux around the predicted value of the critical flux at the end of the specific membrane batch process seems to be the best procedure to assure the recovery target and extend the membrane's life. Currently common to control membrane processes by maintaining the permeate flow rate constant and manipulating the operating pressure. In batch processes the pollutant concentration in the feed stock changes continuously during operation because of batch concentration, leading to a reduction of the critical flux along the time. As a consequence, operating the batch process at a permeate flux equal to the critical flux at initial feed conditions leads to heavy fouling.

1.2.6.2 Gas Sparging

A promising and simple method by which the efficiency of pressure membrane process can be upgraded seems to be gas bubble entrainment into the feed of the membrane system. Cui *et al.* (1997) indicated that gas sparging by air injection into the UF feed could produced a gas–liquid two-phase flow and limited the formation of a polarizing layer in the course of macromolecular separation by UF.

Injection of air bubbles into the lumen of tubular and hollow fibre membranes, to enhance permeate flux in UF processes was firstly introduced by Cui (1998). There has been a strong trend towards the gas-sparging in submerged membrane bioreactors (MBR) systems where air is injected outside the fibres rather than inside the lumens of the fibres. Also, it has been reported that permeate flux enhancement is more pronounced in upward flow vertical tubular modules than that in the horizontally installed membranes. It is generally believed that slug flow pattern is the most suitable regime to enhance UF processes (Taha *et al.*, 2006). Chiu and James (2006) studied the effects of various superficial gas and liquid velocities and the use of different nozzles. The resulted shown that two–phase flow can produce a critical flux of up to 1.7 times grater that the single-phase flow. Increasing superficial gas and liquid velocities increased the critical flux. The best results were found in the slug flow regime. Cabassud *et al.* (2001) investigated how tangential (gas-liquid) two-phase flow in hollow-fibre modules contributed to the formation of a solid layer (from retained bentonite particles) by varying the wall shear stress. It was observed that gas sparging upgraded the efficiency of macroparticle UF at maximum air flow velocity (1.0 m/s).

These are attributed to the increase in mean velocities of the fluid, the increase in shear stress number, the secondary flow and wakes created by the slugs and most importantly the ability of gas slugs to increase the faction of filtration area exposed to cross flow by reducing the extent of the stagnated regions. Psoch and Schiewer (2006) focused on permeate flux enhancement by air sparging. The results showed that air sparging over several weeks significantly increased permeate flux.

The flow patterns were categorized on the basis of the visual and video observation and still photography, as well as the time-spatial characteristic map of interfaces obtained from previous experiments (Furukawa, 1995). The flow patterns were defined as follows:

(1) Bubble flow: Small gas bubbles dispersed in a continued of flowing liquid.

(2) Slug flow: This flow pattern is characterized by large bullet shaped bubbles having smooth gas-liquid interface and length longer than a tube diameter, and flowing intermittently with liquid slugs which contain small gas bubbles.

(3) Annular flow: In annular flow the liquid flow on the tube wall as liquid film and the gas phase flow in the center. Usually some of the liquid phase is contained as entrained droplets in the gas core (Furukawa *et al.*, 2001).

In membrane system using two-phase flow within module to overcome concentration polarization and membrane fouling, the most likely flow patterns are bubble flow and slug-flow due to the relatively low gas flow rate applied. Bubble flow occurs when the bubbles are significant less than (< 60%) the tube or channel size. The bubble behavior is similar to the bubbles in a stationary liquid. Slug-flow (also called plug flow) occurs when the gas flow as large bullet-shaped bubbles approaching the diameter of the tube or channel size. There may be small bubbles following the slug (Figure 10).

| Bubble flow | Slug flow | Churn flow | Annular flow |
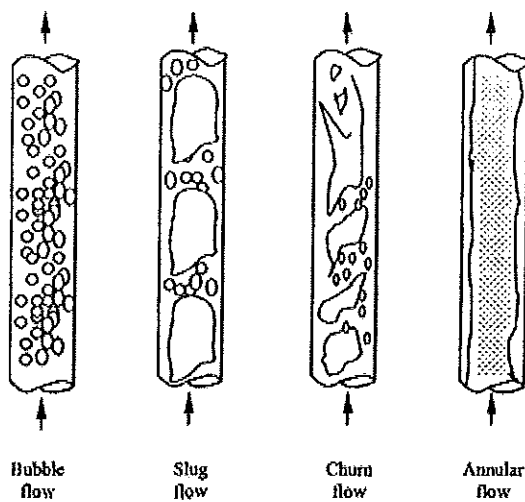
Figure 10. Gas–liquid two-phase flow patterns
Souce: Modified from Whalley (1999).

The interface for this gas-liquid two-phase flow in tubular membranes follows a variety of flow patterns. The predominant factor determining flow regime is the void fraction (gas volume/total volume) in the pipe, which depends directly on the gas and liquid phase velocities. With increasing void fraction, the flow pattern changes from bubble flow ($0<\varepsilon<0.2$) over slug flow ($0.2<\varepsilon<0.9$) to annular and churn flow ($0.9<\varepsilon<1.0$). Slug flow is the most effective flow pattern for reducing cake layer

build up; this is due to high shear stress induced by water and air slugs, according to studies of Li *et al.* (2008). The injection ratio, ε, is:

$$\varepsilon = \frac{U_g}{U_l + U_g}$$
(1-13)

where U_l and U_g are superficial liquid and gas flow velocities, respectively.

The flux enhancement ratio with gas sparging is depend on the type of membrane module, membrane orientation, and operating parameters such as transmembrane pressure, feed concentration, bubble size and frequency (or gas flow rate), liquid cross flow velocity, etc.

Sur and Cui (2001) conducted a detailed study of the effects of operation parameters on flux in bubble enhanced cross flow MF of barkers yeast using 5 mm diameter tubular membranes (0.15 μm pores). The operating parameters examined in this study included the feed suspension concentration, transmembrane pressure, feed suspension cross flow velocity and gas superficial velocity. The effects of concentration and liquid flow on flux enhancement for a relatively low fixed gas superficial velocity (0.18 m/s) and a pressure of 4.0 bar. The flux enhancement was most significant when polarization or cake formation was more severe, namely at high concentration and low liquid velocity. At 4.0 bar the enhancements ranged from 40 to 135% and data at the less polarized 0.5 bar ranged from 10 up to 70%. These results suggest that the flux enhancement is due to disruption of the deposited cake of rejected particles. Similar to the effect observed in UF, bubbling was most effective at low liquid flow rates. Thus as the gas velocity increased from 0 to 0.18 m/s, there was a large change in the observed flux but further increase in velocity, up to five times more, had a rather minor effect. This indicates that gas sparged MF could be a cost-effective operation from the energy consumption point of view. However, with MF applications, the flux decline caused by membrane fouling often cannot be fully recovered by gas sparging, presumably because internal pore fouling is not reversed by surface shear.

Yu *et al.* (2003) studied critical flux base on the TMP increase is the flux below no or negligible membrane fouling occur. A method was tested for enhancing the critical fluxes by injecting air into a shell-side feed organic hollow fiber membrane module. A range of aeration intensities was tested to filtrate the biologically treated wastewater. Air sparging promotes turbulence, resulting significant enhancements of critical flux.

1.2.6.3. Backpulsing

Transmembrane pressure pulsing or backpulsing is an effective technique for reducing fouling phenomena in membrane, improving the overall filtration rate and extending interval (the time between two consecutive membrane cleanings). Backpulsing is an in-situ method for cleaning the membrane by periodically reversing the transmembrane pressure. When transmembrane pressure is reversed, permeate liquid is forced back through the membrane to the feed side. This flow reversal dislodges deposited foulants, which are then carried out of membrane module by the tangential flow of retentate. It should be noted that, backpulsing is most effective in removing deposits on the membrane surface. It severe pore plugging occur, backpulsing would most likely be ineffective in preventing precipitous flux decline. This type of irreversible fouling may only be corrected by chemical cleaning. (Sondhi and Bhave, 2001)

For, theory of blackpulsing, during filtration, particle accumulation on the membrane surface, forming a cake or gel layer at the same time, some particle may absorb on or block the surface pores. It is believed that the black pulsing process restores the flux by dislodging the particles blocking the membrane pores and those particles forming a cake on the membrane surface (Figure 11). It is assumed that the cake layer is instantly lifted and swept into the retentate flow. Thus, only particle fouling on the membrane surface (external fouling) is considered and internal pore plugging effect is assumed to be minimal (Cakl *et al.*, 2000). If the above assumption is valid, then for complete membrane cleaning, the pore-blocking and the cake-forming particles should be push back into the cross flow and swept away into the retentate flow.
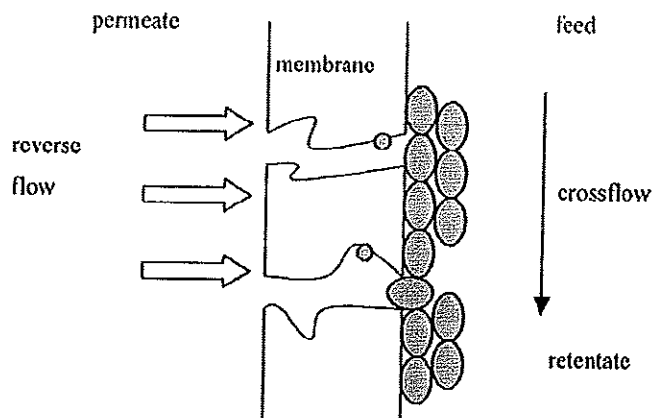
Figure 11. Schematic representation of membrane cleaning during backplusing
Source : Sondhi and Bhave (2001)

Backpulsing should be distinguished from the more familiar technique of backflushing or (backwashing). The fundamental difference between a backpulse and backflusing is the speed and force utilized to dislodge accumulated matter on the membrane surface. In backflushing, flow reversal through the membrane occurs for 5-30 s once every 30 min to several hours. In backpulsing, flow reversal occurs every few min and reversed high-pressure pulses (up to 10 bar) are applied for very short periods of time (typically <1 s). In addition, backpulsing is a dynamic process and introduces transient effects which can not be found in conventional backflushing.

The simplest backpulse device is a pump and bladder assembly. The bladder assembly holds the permeate volume and includes a membrane barrier to prevent direct contact of pressurizing air with permeate. The pump (gear or diaphragm) is connected to the air intake and generates the required air pressure for an effective backpulse. A variation of this approach uses a tank and air compressor. The tank is filled with permeate and pressurized to 80-100 psi. the tank is sized to deliver adequate volume based on the total filtration area. The frequency is set with a timer. The disadvantage of this type of device is the relatively slower speed of permeate discharge, inconsistent discharge volume and potential leaks.

The backpulse valve assembly containing a fixed volume reservoir (such as that used in the laboratory scale unit) is more effective due to the ability to

deliver consistent permeate volume at high pressure almost instantaneously. Backpulse devices are available is sizes that provide from 100 ml to 5.7 l of reverse flow. A single assembly can be used to backpulse several modules at one time, whether connected in series or parallel. Backpulsing is of special significance in ceramic membrane filtration because unlike polymeric membranes, ceramic membranes are able to with stand the high pressures associated with backpulsing.

Redkar *et al.* (1996) studied rapid back pulsing on yeast suspended in deionized water with a flat sheet cross flow MF module and cellulose acetate membrane in 0.07 μm. average pore diameter. The optimum forward filtration time were found to be 1.5, 3, and 5 s, respectively, for backpulsing duration of 0.1, 0.2 and 0.3 s. The experimental gave net fluxes with backpulsing of about 85% of clean membrane flux (790 l/m^2 h) whereas the long-term flux in the absence of blackpulsing is an order- of –magnitude lower (94 l/m^2 h). Sondhi and Bhave (2001) studied effect of backpulsing on cross flow filtration of difference process streams on synthetic electroplating wastewater containing $Cr(OH_3)$ suspension with various pore size 0.05-5.0 μm. The result showed that backpulsing is effective in minimizing membrane fouling. Up to five-fold increase steady states permeate flux and 100% flux recovery. The result also shown that, the larger of pore diameter the greater is the effective of blackpulse. Meacle *et al.* (1999) observed the implementation of membrane backpulsing significantly improved the performance of this membrane based purification step for removal of unreacted polysaccharide from the conjugate vaccine product. Buffer requirement and cycle time were appreciable reduced without affecting product quality or product yield and backpulsing was successfully scaled-up from the lab scale. The authors also observed that backpulsing was most effective at low shear rates, when the protein gel-layer was expected to be thickest and sieving was significantly better at low shear rates when backpulsing was used. The summary of some techniques to improve process performance during membrane filtration process is shown in Table 5

Table 5. The summary of some techniques to improve process performance

Technique	Type of fouling removed	Mechanism to reduce fouling	Suitable type of feed	Example of application
1.Critical flux	Avoid the formation of severe fouling	The drag force on the solute molecules concentrated over the membrane surface are equal to the dispersive force, (Stoller and Chainese, 2006)	All various fluids: critical flux decreases with increasing feed concentration and increases with increasing solute size; (Bacchin *et al.*, 2006)	Olive wastewater (Stoller and Chainese, 2006) Yeast cell suspension (Field *et al.*,1995) Skim milk (Youravong *et al.*, 2003)
2.Gas sparging	Effective to remove concentration polarization and delay the formation of external fouling	The bubble motion generates secondary flow, to promote local mixing, and then reduce concentration polarization and fouling (Cui *et al.*, 2003)	Most effective with high concentration of fluid, low liquid flow velocity and larger particle size (Cui *et al.*, 2003)	Yeast suspension (Sur and Cui, 2005) Wastewater (Psoch and Schiewer, 2006) Pineapple wine (Youravong *et al.*, 2010)
3.Backpulsing	Effective to remove external fouling layer and minimal internal pore blocking	Liquid is forced in reverse direction from permeate side to pass though the membrane, thereby lifts the boundary layer and wash it out of membrane surface and remove solutes which blocks the pores (Cakl,2000)	Effective for the treatment of feed stream containing relative non adhesive suspended particle (Jose and Davis 1998)	Synthetic electroplating waste water suspension (Sondhi and Bhave, 2001) Oil emulsion (Cakl,2000) Suspension of latex breads (Ma *et al.*, 2001)

1.2.6.4 Enzymatic treatment

For the fruit juice, the fouling materials are mainly composed of cell wall polysaccharides such as pectin, cellulose lignin and hemicelluloses. Several pectinase are known to exert a clarifying action on fruit juices. These enzyme breakdown the pectin in the juice, have change solubility and precipitation properties of pectin. The quantity of pectinase required depends on the conditions of the treatment and the relative activity of the enzyme. The supplier can advise as to the approximate amounts to use and the optimum temperature and time for the reaction. To enhance filtration performance, fruit juice are usually treated before filtration with enzyme. Carneiro et al. (2002) used enzymatic treated with 0.03% (v/v) of two enzymatic preparations (pectinex SP-L and Celulast 1.5 l, from Novo Nordisk), at 30 °C for 60 min. The resulted shown that enzymatic treatment reduce the viscosity and the suspended solid (pulp) content of the juice, precipitating part of it and rendering part of it soluble. Vaillant et al. (1999) studied the effect of high-rate enzymatic treatment for degradation of suspended solid prior to microfiltratiom of passion fruit juice. It was found that a synergistic effect between pectinase and cellulose activities enhanced the permeate flux

All of these reviews give the information to improve flux enhancement on membrane filtration. Each technique has its advantages and suitable for each type of raw materials. For this research will be studied several technique to improve efficiency of membrane filtration such as critical flux, gas sparging and combination of critical flux with gas sparging on pineapple juice and coconut water. These techniques should be able one operation to choose the operating parameters in order to control the fouling of membrane and low cost long-term operation.

1.2.7 Economic assessment of membrane process for fruit juice

Economic assessment of membrane applications involves evaluation of costs associated with the application with the resulting benefits in comparison to competitive technology or other-non technological alternatives. The cost of membrane

applications include of capital amortization, membrane replacement, energy use, cleaning chemicals, and operating labour. The benefits in process applications include reduce operating costs relative to competitive technology, saving the product, recovery of by products, saving of water, energy, chemicals etc. In effluent reduction applications saving in disposal costs become important.

Juice clarification involves separation of suspended particles and colloidal matter that cause cloudiness. Centrifugation is the technology of choice to separate large particles but it becomes increasingly expensive when particles are smaller and when density difference is smaller. Filtration is relatively less sensitive to these factors. Media filters of rotary vacuum and pressure leaf type dominate the technology for fine filtration. However, membrane filtration is more attractive than media filtration under most circumstances.

1.2.7.1 Membrane and membrane system cost

The cost of a membrane depends on its type while the cost of membrane systems depend on types, size and degree of automation of the design. The cost of the membrane system alone cannot be used in the decision making process. Permeate flux for the same feed differs significantly among different systems. Spiral system which are extremely cost effective have little tolerance for suspended solids hence required elaborate and costly pretreatmemt. Hollow fiber and tubular system can accomudate more suspended and particulates. Polymeric systems have limited chemical were tolerance compared to ceramic systems. These factors should be considered before comparing costs.

Membrane systems are modular in mature. Therefore, the capital cost of membrane systems increase almost linearly with size. System size scale factors for seawater and brackish water desalination applications are reported to around 0.85 to 0.95 (Ray, 1992).

Energy Costs

Cross-flow filtration is driven by pressure and assisted by velocity. Both pressure and velocity are generated by pumps driven by electrical energy.

Membrane filtration is one of most energy efficient means of separating solutes like salt and sugar from water.

The energy consumption is optimally designed ultrafiltration systems is about 50 W/m^2 of membrane area (Eycamp, 1995). When the overall efficiency is 50% and the average permeate flux is 20 l/m^{2}h, the energy consumption in and optimally designed system is about 5 kWh/ m^3.

Other Costs

Membrane replacement, cleaning chemicals, and labor are the other costs associated with membrane systems. The cost of membrane replacement is inversely proportional to membrane life is about 12 to 18 months. Hollow fiber ultrafiltration membranes have been used for about 4 years in vinegar clarification. Ceramic membranes have extra long life span extending beyond 8 years.

The cost of cleaning is highly variable, depending strongly on severity of fouling. Specific cleaning cost of $0.10/ m^2 –year has been reported for fermentation broth clarification in a 4000 h/yr operation (Bemberis and Neely, 1986). Membrane cleaning is more effective at high temperatures. Steam, gas, or electricity can be used to heat water depending on availability. This is a relatively minor operating cost but capital cost of steam or gas pipe work can be significant. In general, cleaning costs range from 10 to 20% of the total operating costs of a membrane system. Membrane systems do not require full-time operators. Most of the regular labor requirement is during startup and cleaning. About 2 h/d is a typical labor requirement.

1.2.7.2 Type of capital investment decisions

The basic capital investment decision models can be classified into two major categories; non-discounting models and discounting models. Non-discounting models ignore the time value of money, whereas discounting models explicitly consider it. Although many accounting theorists disparage the non-discounting models because they ignore the time value of money, many firms continue to use these models in making capital investment decisions. However, the use of discounting models has increased over the years, and few firms use only one model-indeed, firms seem to use both types. The payback period, in particular, seems to be the most widely used non-discounting method while the accounting rate return is employed much less. The use of both types of models suggests that both types of models suggest

that both categories supply useful information to mangers as they struggle to make a capital investment decision.

The typical of capital investment decisions can be divided into 2 types: discounting and non-discounting models.

Non-discounting models

-Payback Period

One type of non-discounting model is the payback period. The payback period is the time required for a firm to recover its original investment. One way to use the payback period is to set a maximum payback period for all projects and to reject any project that exceeds this level.

-Accounting rate of return

The accounting rate of return is the second commonly used non discounting model. The accounting rate of return measures the return on a project in terms of income, as opposed to using a project's cash flow.

Discounting Models

-The Net Present Value (NPV)

Discounting models explicitly consider the time value of money and therefore incorporate the concept of discounting cash inflows and outflows. Two discounting models will be considered: net present value (NPV) and internal rate of return (IRR). The net present value method will be discussed first; the internal rate of return method is discussed in the following section.

Net present value measures the profitability of an investment. If the NPV is positive, it measures the increase in wealth. For a firm, this means that the size of a positive NPV measures the increase in the value of the firm resulting from an investment. To use the NPV method, a required rate of return must be defined. The required rate of return is the minimum acceptable rate of return. It is also referred to as the discount rate, the hurdle rate, and the cost of capital.If the net present value is positive, it signals that (1) the initial investment has been recovered, (2) the required rate of return has been recovered, and (3) a return in excess of (1) and (2) has been received. Thus, if NPV is greater than zero, the investment is profitable and, therefore, is acceptable. If NPV equals zero, the decision maker will find acceptance or rejection of the investment equal because the investment will earn exactly the required rate of

return. Finally, if NPV is less than zero, the investment should be rejected. In this case, it is earning less than the required rate of return.

Internal Rate of Return

Another discounting model is the internal rate of return (IRR) method. The internal rate of return is defined as the interest rate that sets the present value of project's cash inflows equal to the present value of the project's cost. In other words, it is the interest rate that sets the project's NPV at zero. The internal rate of return is the most widely used of the capital investment techniques. One reason for its popularity may be that it is a rate of return, a concept that managers are comfortable with using. Another possibility is that managers may believe (in most cases, incorrectly) that the IRR is the true or actual compounded rate of return being earned by the initial investment. Whatever the reasons for its popularity, a basic understanding of the IRR is necessary (Hansen and Mowen, 2007).

1.3 Objectives

1. To develop a membrane filtration process for production of clarified pineapple juice and coconut water.

2. To study the quality of clarified pineapple juice and coconut water during storage.

3. To improve membrane process performance for production of clarified pineapple juice and coconut water by varieties of techniques during membrane filtration.

4. To study the fouling mechanism during membrane filtration process of pineapple juice and coconut water.

5. To evaluate the economic assessment of membrane filtration process for pineapple juice and coconut water production.

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CHAPTER 2

EFFECT O MEMBRANE PROPERTY AND OPEATION CONDITIONS ON PHYTOCHEMICAL PROPERTIES AND PERMEATE FLUX DURING CLARIFICATION OF PINEAPPLE JUICE

2.1 Abstract

The effects of membrane property on the permeate flux, membrane fouling and quality of clarified pineapple juice were studied. Both microfiltration (membrane pore size of 0.1 and 0.2 µm) and ultrafiltration (membrane molecular weight cut-off (MWCO) of 30 kDa and 100 kDa) membranes were employed. Membrane filtration did not have significant effects on the pH, reducing sugar and acidity of clarified juice whereas the suspended solids and microorganism were completely removed. The 0.2 µm membrane gave the highest permeate flux, total vitamin C content, total phenolic content and antioxidant capacity as well as the highest value of irreversible fouling. Regarding these results, the membrane with pore size of 0.2 µm was considered to be the most suitable membrane for the clarification of pineapple juice. The optimum operating conditions for the clarification pineapple juice by membrane filtration was a cross flow velocity (CFV) of 3.4 m/s and transmembrane pressure (TMP) of 0.7 bar. An average flux of about 37 l/m^2h was obtained during the microfiltration of pineapple juice under the optimum conditions using batch concentration mode.

2.2 Introduction

Pineapple juice is a popular product with increasing demand in many countries. Thailand is one of the biggest countries for the production of pineapple and exports more than a half the total of world volume annually (Nation Food Institute, 2008). Pineapple juice is marketed world-wide because of its attractive aroma, flavour

and other beneficial components. The nutritional compounds in pineapple juice for human health are generally identified as phytochemicals, such as vitamin C, carotenoid and phenolic compounds. These components not only reduce the risk of oxidative damage related to the presence of free radicals but also the risk of contracting different types of cancer and cardiovascular and neurological diseases (Collins and Harrington, 2002).

Phenolic compounds, one of the most widely occurring sources of phytochemical nutrient, have been associated with the health benefits derived from consuming high levels of fruits and vegetables (Hertog et al., 1993; Parr and Bolwell, 2000). The beneficial effects derived from phenolic compounds have been attributed to their antioxidant activity (Heim et al., 2002). Phenolic compounds, such as flavonoids, phenolic acids and tannins, could contribute greatly to the antioxidant activity of foods (Parr and Bolwell, 2000). Wen and Wrolstad (2002) analyzed phenolic compounds in pineapple juice and found that the phenolic compounds included sinapyl-L-cysteine, N-γ-L-glutamyl-S-sinapyl-L-cysteine, S-sinapyl glutathione and a p-coumaric-like phenolic compound. Vitamin C is another major phytochemical compound, considered as important water soluble antioxidant. It protects compounds in extracellular and intracellular spaces in most biological systems and reduces tocopherol radicals back to their active form at cellular membranes (Kaur and Kapoor, 2001). In pineapple juice 2 forms of vitamin C is found, L-ascorbic and dehydroascobic acid. L-ascorbic acid is the main biologically active form of vitamin C. It is reversibly oxidized to form dehydroascorbic acid, which also exhibits biological activity. Hernández et al. (2006) reported that total vitamin C content in ripe pineapple is about 26 mg/100g fresh weight.

However, previous studies reported that many phytochemical compounds are reduced during a conventional heating process. For example Gil-Izquierdo et al. (2002) studied the pasteurization of orange juice by mild pasteurization (75°C, 30 s) and standard pasteurization (95°C, 30 s). Both processes led to the degradation of several phenolic compounds, including caffeic acid derivative, vicenin 2 (apigenin 6-8-di-C-glucoside,) and narirutin (5,7,4,'-

trihydroxyflavonone-7-rutinoside). The reduction of these components varied from 28 to 34%.

As mentioned above, conventional thermal processing ensures safety and extends the shelf- life of fruit juice, but it often leads to detrimental change in the sensorial and nutritional qualities of the product. Membrane technology may be an alternative for fruit juice preservation and conservation because of its operational advantages such as mild temperature, the ease of scaling up and simplicity of operation. It has been reported that the use of ultrafiltration (UF) in kiwi fruit juice processing permitted a good level of clarification and reduced the small levels of antioxidant activity compared with the fresh juice. The reduction can be attributed to a 16 % degradation of the initial content of ascorbic acid (Cassano *et al.*, 2007a).

In the case of blood orange juice, after clarifying it with UF, the quality of the polyphenols was well preserved (Cassano *et al.*, 2007b). However, it has been found that the maximum turbidity may develop with the formation of particles reaching to 0.3 to 1.0 μm during storage. Particles larger than 0.5 μm may settle out and form a precipitate (Girard and Fukumoto, 2000). The potential source of particle formation can be pectin, protein, phenolic compounds and microorganisms. These compounds cause changes in the chemical and physical properties of clarified fruit juice. To prevent or reduce these problems, the suitability of the membrane pore size and operating conditions, as well as the pretreatment of the fruit juice, must be studied.

There have been a few studies of membrane filtration in fruit juice processing. Carneiro *et al.* (2002) successfully clarified pineapple juice with a 0.3 μm ceramic membrane. de Barros *et al.* (2003) studied the fouling mechanism of pineapple juice and found that complete pore blocking predominated in the ceramic membrane while cake formation predominated in hollow fiber membranes. Rai *et al.* (2007) clarified mosombi juice with different pretreatment methods. They found that the best condition for pretreatment was enzymatic treatment followed by adsorption with bentonite. This condition gave the highest permeate flux of 23 l/m^2h. Cassano *et al.* (2008) studied the membrane filtration of kiwifruit juice using a 30 kDa cellulose

membrane. They found that a steady flux was about 18 l/m^{2}h during filtration using the batch concentration mode (VRF=2.76). Moreover, they also found that the formation of a cake layer covering the entire surface of the membrane was the main cause of the membrane fouling.

In general, flux increases with membrane pore size while retention generally decreases as a membrane pore size increases (Girard and Fukamoto, 2000). The retention of sugar in the process of clarified pineapple juice by MF and UF was studied by de Carvalho et al., (2008). It was observed that the membrane pore size and MWCO as well as the geometry of the module influenced the sugar content in clarified juice. However, there was no study on the effect of membrane pore size and MWCO on phytochemical compounds of pineapple juice.

Membrane technology could provide two fractions of fruit juice, the retentate (solution rejected by membrane) and permeate (solution passed through membrane). The permeate is considered to be the clarified and sterilized fruit juice while most microbes are separated and concentrated in the retentate. This fraction process allows a small volume of juice, that is the retentate, to be sterilized for the elimination of microbes while most of the flavor and nutritional compounds are preserved in the permeate. Hence it is a simple way to process a large amount of juice and avoid the loss of phytochemical compounds due to high temperature (Torregrosa et al., 2006). According to their separation capacities, MF and UF are suitable for cold sterilization. Furthermore, the process could combine clarification and sterilization in one single continuous operation. However, the effect of the membrane pore size and MWCO may possibly influence the permeate flux and quality of the clarified fruit juice. Moreover, the process performance of membrane filtration is limited by membrane fouling which results in flux decline and a possible change in product characteristics. This present study aimed at employing MF and UF for the sterilization and clarification of pineapple juice. This was done to study the effect of membrane pore size on the permeate flux, fouling and the quality of clarified juice, including the chemical, physical, microbiological, and phytochemical properties. Furthermore, the

effects of the operating conditions (TMP, CFV) on permeate flux and phytochemical properties were also investigated.

2.3 Materials and methods

2.3.1 Preparation of pineapple juice

Fresh pineapples (*Ananus Comosus L. Merr.*) were cleaned by tap water. After the shells were peeled by a stainless steel knife, the fresh pineapples were chopped into pieces of 1 cm^3 and the juice was extracted by a hydraulic press. The total soluble solid and pH values of the juice were in the range of 12.2-14.2 °Brix and 3.5-4.0 respectively. The fresh pineapple juice was stored at 4 °C before use. Before using the membrane filtration process, the pineapple juice was treated with 0.03 % (V/V) of commercial pectinase (Pectinex® ultra SP-L),(PA(EN)) at room temperature (25±3°C) for 60 min (Carneiro *et al.*, 2002).

2.3.2 Microfiltration and ultrafiltration

The membrane system used was a polysulfone hollow fiber module (Amersham Biosciences, UK) with a fiber diameter and length of 1 mm. and 30 cm. respectively. The effective membrane area was 0.011 m^2.The membrane pore size and MWCO were 0.1 and 0.2 μm for MF and 30 and 100 kDa for UF. The membrane system consisted of an 8 liter stainless steel jacket-feed tank and a variable-feed pump (Leeson, USA) and transducers (MBS 3000, Danfoss, Denmark) were used for measuring the pressure of the feed, retentate and permeate. The temperature of the feed was controlled by circulating cooling water through a jacket-feed tank. The CFV and TMP were controlled using a needle permeate valve and a variable speed-feed pump. A digital balance (GF-3000, A&D, Japan) connecting the computer was used to measure the permeate flux. The schematic diagram of the experimental set-up is shown in Figure12.
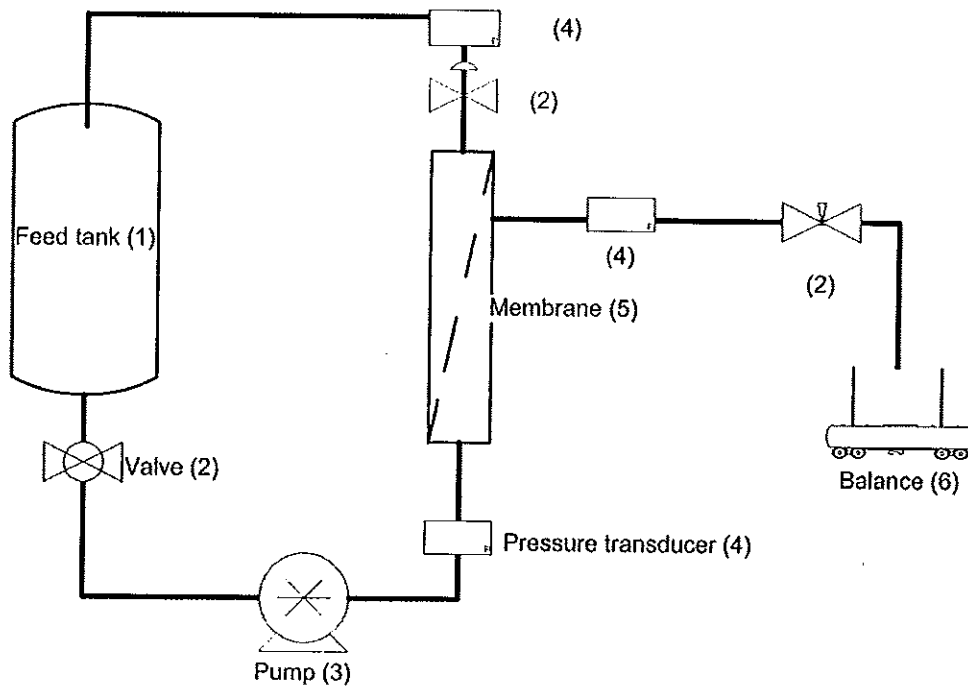
Figure 12. Schematic of the membrane experimental set-up

In studying the effect of membrane pore size and MWCO on the quality of clarified juice, permeate flux and fouling, the experiments were carried out using a total recycle mode (both retentate and permeate were returned to the feed tank). Three liters of juice were used for each test. The experimental operating conditions included a constant CFV of 1.2 m/s, temperature of 20±2 °C and TMP of 1.0 (for MF) and 2.0 bar (for UF). The effect of TMP (0.05-1.0 bar) and CFV (1.5-3.4 m/s) on the permeate flux in a total recycle mode were also studied using the most suitable membrane pore size or MWCO obtained from the previous experiments. The optimum condition obtained was then employed for clarification and sterilization of the pineapple juice under batch concentration mode. Note that the % recovery was defined as the percentage of permeate volume to the initial feed volume.

2.3.3 Membrane fouling and resistances analysis

The membrane filtration process can generally be described by Darcy's law as follow:

$$J = \frac{TMP}{\mu R_t} \qquad (2\text{-}1)$$

where J (m/s) is the permeation flux, TMP is the transmembrane pressure (Pa), μ (Pa.s) is the viscosity of the permeate and R_t (m^{-1}) is the total resistance to the permeate.

R_t is classified by equation (2-2) as follow:

$$R_t = R_m + R_{rf} + R_{if} \qquad (2\text{-}2)$$

where R_t is the sum of R_m (membrane resistance), R_{rf} (the resistance caused by reversible fouling) and R_{if} (the resistance caused by irreversible fouling). In this study, R_{rf} was defined as the fouling which could be removed by water flushing. The residual fouling after water flushing was R_{if} and it was further cleaned by chemical cleaning.

The resistance defined by equation (2-2) could be evaluated by measuring the water flux during the cleaning process. R_m was determined using the slope of cleaned water flux versus TMP and equation (2-1). After the filtration of the pineapple juice, the water was flushed through the membrane surface to removed R_{rf} while the permeate valve was closed. Water flushing was undertaken using clean water at a CFV of 1.4 m/s and a TMP of 0.3 bar for 15 min. After the first water flushing, the permeate valve was opened and the water flux was measured to determined the residual fouling resistance (that is $R_m + R_{if}$). A chemical cleaning process was applied by circulating 0.5 N NaOH solution at 50 °C, TMP of 0.3 bar and CFV of 1.4 m/s for 40 min, followed by 50 ppm. Of NaOCl solution at the same condition to remove the irreversible fouling. After the chemical cleaning solution was removed by water flushing, the water flux was then measured to evaluate the residual resistance (that is $R_m + R_{if}$). With the R_t obtained after the filtration of pineapple juice, the use of equation (2-1) and the results from the cleaning procedure combining with equation (2-2), all types of resistances could be worked out.

2.3.4 Pineapple juice analysis

The samples of fresh pineapple juice (PA(F)), enzymatic treated pineapple juice (PA(EN)), and clarified pineapple juice obtained by membrane filtration, were collected and stored at -20 °C before analysis of chemical, physical and phytochemical properties.

The total solid, titrable acidity as citric acid, total sugar and reducing sugar in the samples, were analyzed by the methods of AOAC (2002). The total soluble solid was measured by a hand refractometer (Atago, Japan). The pH was measured by a pH meter (PB-20, Sartorius, Germany) and the colour was measured by a colorimeter (Colour Quest XT, Hunter lab, USA). The viscosity was measured by a U-tube capillary viscometer (Kapillarviskosimeter 50904, Schott, Germany) at 20°C. The suspended solid content was determined according to the method of Cassano et al. (2007b). The protein content was determined by the Lowry method (Lowry et al., 1951). Microbiological analyses were performed by the method described in the Bacteriological Analytical Manual (BAM, 2002). The content of pectic materials was measured in terms of alcohol insoluble solid (AIS) (Rai et al., 2006).

L-ascorbic and dehydroascorbic acid were determined by high performance liquid chromatography (HPLC). The method was based on that of Zapata and Dupour (1992) with some modifications.

The DPPH free radical scavenging was determined by the method of Singh et al. (2002) with some modifications. The results were expressed as the mg of L-ascorbic acid equivalent per 100 ml fruit juice (mg AAE/100ml).

The total phenolic content was determined by spectrophotometric determination using Folin-Ciocalteu's phenol reagent (Kim et al., 2002). The total phenolic content was expressed as the mg gallic acid equivalent per100 ml fruit juice (mg GAE/100 ml).

Ib

The oxygen radical absorbance capacity (ORAC) was determined using a FLUO star Galaxy plate reader (Fluostar optima software user manual, BMG Labtech, Germany) with some modification by using the method of Wu *et al.* (2004). The oxygen radical absorbance capacity (ORAC) was expressed as a micromole Trolox equivalent (μmol TE/100 ml).

The data obtained were subjected to analysis of variance (ANOVA) and the mean comparisons were carried out using Duncan's Multiple Range Test (DMRT).

2.4 Results and discussion

2.4.1 Effect of enzymatic treatment and membrane filtration on chemical and physical properties of pineapple juice

All chemical and physical properties of PA(F) and PA(EN) are shown in Table 6. The results show that there were no significant differences in pH, acidity, total soluble solid, total solid, total sugar and reducing sugar between PA(F) and PA(EN). However, suspended solid, viscosity, colour and pectic materials (AIS) significantly decreased after the juice was treated with enzyme. The reason of reduction in suspended solid and viscosity was probably that pretreatment of pineapple juice with pectinase caused hydrolysis and subsequent degradation of pectin, consequently removed pectinious materials (Vaillant *et al.*, 2001). The enzymatic treatment of fresh juice also reduced the macromolecules or colloidal species which play important roles in fouling of membrane leading to flux decline. In addition, the enzymatic treated juice could improved the permeate flux during membrane filtration (Girard and Fukamoto, 2000). Therefore, PA(EN) was used as feed for all membrane filtrations.

Table 6. Chemical and physical properties of fresh pineapple juice (PA(F)) and enzymatic treated pineapple juice (PA(EN))

Properties	PA(F)	PA(EN)
Total solid (w/w %)	13.75 ± 0.64^{ns}	13.68 ± 0.58^{ns}
Total sugar (w/w %)	13.49 ± 0.64^{ns}	13.25 ± 0.51^{ns}
Reducing sugar (w/w %)	4.28 ± 0.47^{ns}	4.45 ± 0.33^{ns}
Total soluble solid (°Brix)	13.60 ± 0.53^{ns}	13.57 ± 0.51^{ns}
pH	3.75 ± 0.13^{ns}	3.67 ± 0.08^{ns}
Acidity (w/w % as citric acid)	0.77 ± 0.02^{ns}	0.77 ± 0.03^{ns}
Viscosity (mPa s) at 20 °C	2.16 ± 0.01^{a}	2.07 ± 0.02^{b}
Density (kgm^{-3}) at 20 °C	1021.9 ± 3.5^{ns}	1024.2 ± 3.3^{ns}
Suspended solid (w/w %)	1.82 ± 0.17^{a}	1.52 ± 0.21^{b}
Color		
L*	79.64 ± 3.79^{b}	81.66 ± 2.06^{a}
a*	0.27 ± 0.64^{b}	0.45 ± 0.09^{a}
b*	27.92 ± 0.04^{a}	24.52 ± 1.00^{b}
Protein (g/100 ml)	0.409 ± 0.009^{ns}	0.409 ± 0.005^{ns}
Pectic materials(AIS) (w/w%)	0.22 ± 0.01^{a}	0.11 ± 0.01^{b}

Same letters in the same row present no statistical differences according to Duncan's multiple range test at P<0.05

Table 7 illustrates the chemical and physical properties of juices before and after membrane filtration. It was observed that reducing sugar and pH between PA(EN) and clarified juice were not significant different while total sugar, acidity, density and total soluble solid in clarified juice slightly decreased. The suspended solid in the pineapple juice was completely removed by membrane filtration. The decrease in total soluble solid was probably due to the removal of suspended solid. As reported by Schott et al. (1960) and Rai et al. (2007), the presence of suspended and soluble pectin in fruit juice caused an increase in refractometric reading. The brightness of clarified juice, indicated by the L* value were lighter and clearer when the smaller pore size membrane was used. The juice clarified by 30 kDa membrane gave the lowest value of acidity and protein content. The trend of protein content was slightly reduced with decreasing membrane pore size. Since protein content in pineapple juice is the precursor of Maillard reaction which is the reason for darkening

of fruit juice during storage (Campos *et al.*, 2002). The reduction of protein content might be benefit for preservation of colour during storage of the product.

Table 7. Chemical and physical properties of enzymatic treated pineapple juice (PA(EN)) and clarified pineapple juice with various membrane pore size and MWCO.

Properties	Treatments of pineapple juice				
	PA (EN)	0.2 μm	0.1 μm	100 kDa	30 kDa
Total solid (w/w%)	13.62 ± 0.76^a	13.02 ± 0.32^{ab}	12.62 ± 0.15^{bc}	12.46 ± 0.49^{bc}	12.20 ± 0.20^{bc}
Total sugar (w/w%)	13.35 ± 0.56^a	12.66 ± 0.48^b	12.58 ± 0.43^b	12.29 ± 1.19^b	11.72 ± 0.51^{bc}
Reducing sugar (w/w%)	4.45 ± 0.33^{ns}	4.28 ± 0.38^{ns}	4.09 ± 0.22^{ns}	3.94 ± 0.14^{ns}	4.10 ± 0.09^{ns}
Total soluble solid (°Brix)	13.57 ± 0.51^a	12.87 ± 0.50^b	12.83 ± 0.15^b	12.80 ± 0.92^b	12.57 ± 0.60^b
pH	3.67 ± 0.08^{ns}	3.63 ± 0.29^{ns}	3.62 ± 0.17^{ns}	3.63 ± 0.03^{ns}	3.65 ± 0.02^{ns}
Acidity (w/w % as citric acid)	0.78 ± 0.02^a	0.72 ± 0.01^b	0.74 ± 0.02^b	0.74 ± 0.01^b	0.71 ± 0.00^b
Viscosity (mPa s) 20 °C	2.07 ± 0.02^a	1.44 ± 0.01^b	1.44 ± 0.01^b	1.42 ± 0.01^b	1.38 ± 0.01^b
Density (kgm^{-3}) 20 °C	1024.58 ± 4.84^a	1026.63 ± 2.48^a	1018.31 ± 1.72^b	1019.71 ± 2.65^b	1005.88 ± 1.35^c
Suspended solid (%)	1.52 ± 0.21^a	0.00 ± 0.00^b	0.00 ± 0.00^b	0.00 ± 0.00^b	0.00 ± 0.00^b
Color					
L*	81.66 ± 2.06^b	99.22 ± 0.07^a	99.41 ± 0.11^a	99.50 ± 0.15^a	99.44 ± 0.11^a
a*	0.45 ± 0.09^a	-2.47 ± 0.10^b	-2.53 ± 0.05^b	-2.11 ± 0.12^b	-2.46 ± 0.15^b
b*	24.52 ± 1.00^a	7.26 ± 0.52^c	6.52 ± 0.25^{bc}	6.20 ± 0.03^{bc}	6.64 ± 0.18^d
Protein (g/100 ml)	0.409 ± 0.005^a	0.375 ± 0.009^b	0.365 ± 0.085^b	0.255 ± 0.157^{bc}	0.199 ± 0.021^d

Same letters in the same row present no statistical differences according to Duncan's multiple range test at $P < 0.05$

2.4.2 Effect of membrane filtration on phytochemical properties of pineapple juice L-ascorbic acid, dehydroascorbic acid and total vitamin C

Figure 13. shows the L-ascorbic acid, dehydroascorbic acid and total vitamin C contents in PA(EN) and clarified pineapple juice. The minor loss of these components was observed after membrane filtration. The highest contents of L-ascorbic acid (10.36 mg/100 ml) and total vitamin C (19.95 mg/100 ml) were

obtained after membrane filtration by 0.2 μm membrane. However, the vitamin C contents in the clarified juice clarified by 0.2 μm membrane did not different from the vitamin C in PA(EN). The 30 kDa membrane yielded the lowest contents of L-ascorbic acid (7.68 mg/100 ml), dehydroascorbic acid (8.06 mg/100 ml) and total vitamin C (15.73 mg/100 ml). The 0.1 μm and 100 kDa membrane showed the similar effect on these contents. In addition, the 0.2 μm membrane gave the best preservation of vitamin C. In general, vitamin C in the fruit juice is sensitive to the conditions such as high temperature, light exposure and ascorbate oxidase. All of these conditions have been reported to promote the transformation of L-ascorbic acid to dehydroascorbic acid. However, the dehydroascorbic acid still exhibits biological activity (Hernández *et al.*, 2006)
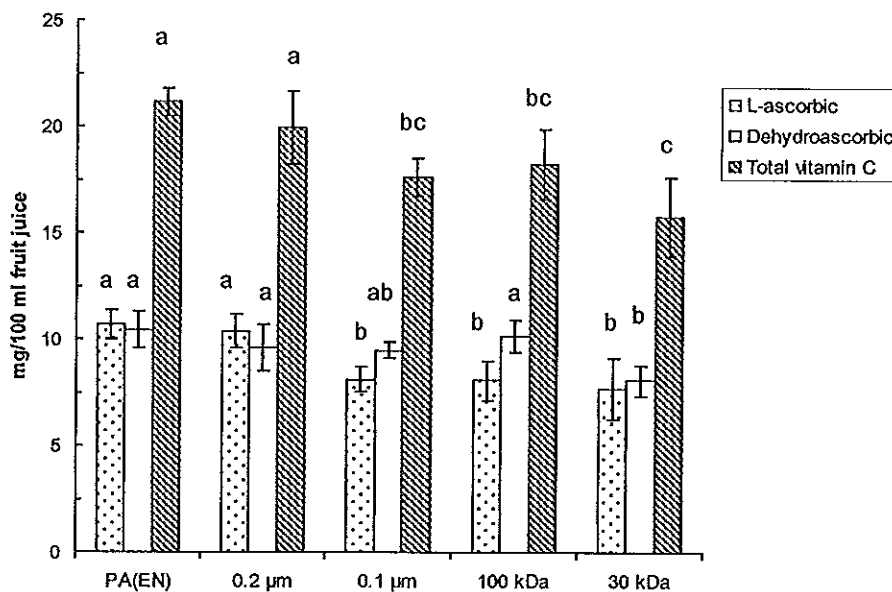
Figure 13. L-ascorbic acid, dehydroascorbic acid and total vitamin C content in enzymatic treated pineapple juice (PA(EN)) and clarified pineapple juice with various membranes pore size and MWCO (a-d: means in value of each method with in each juice with difference letters are significantly different according to Duncan's multiple range test at P<0.05, ns: no significantly different)

2.4.3 Total phenolic content and antioxidant capacity

The content of antioxidant compounds, including vitamin C, carotenoids and phenolic acid, varies greatly among various fruits. Table 8 shows the effect of membrane filtration on total phenolic content and the antioxidant capacity of pineapple juice. The highest values of total phenolic content (69.34 mg GAE/100 ml) and DPPH free radical scavenging capacity (25.76 mg AAE/100 ml) were obtained by 0.2 μm membrane. These results did not significantly different from the total phenolic content and DPPH free radical scavenging in PA(EN). There was no significant difference in total phenolic content among clarified juice obtained from 0.1 μm, 0.2 μm and 100 kDa membranes. The lowest value of total phenolic content was identified from the juice treated by 30 kDa membrane. In this study, the total phenolic content in clarified juice decreased with pore size. It could be due to that some polyphenol in pineapple juice probably associated with the other components, then the membrane with smaller pore size could reject the phenolic compounds. In addition, there was no significant difference in DPPH free radical scavenging between 0.2 μm and 100 kDa membrane while the results from 0.1 μm and 30 kDa were less than those membranes. There was no significant difference in oxygen radical absorbance capacity (ORAC) between PA(EN) and clarified pineapple juice. The MF membrane with a pore size of 0.2 μm gave the highest recovery of phytochemical compounds including vitamin C (94.3%), total phenolic content (93.4%) and DPPH free radical scavenging capacity (99.6%). These results indicated that 0.2 μm membrane could effectively maintain the antioxidant capacity of the juice.

Table 8. Total phenolic content and antioxidant capacity in pineapple juice and clarified pineapple juice

Treatments	Total phenolic content (mg GAE/100ml)	DPPH radical scavenging capacity (mg AAE/100ml)	Oxygen radical absorbance capacity (μmol TE/100ml)
PA(EN)	74.21 ± 3.61^{a}	25.86 ± 1.13^{a}	330.36 ± 10.34^{ns}
0.2μm	69.34 ± 1.36^{a}	25.76 ± 0.71^{ab}	325.30 ± 8.23^{ns}
0.1μm	59.59 ± 5.40^{ab}	24.02 ± 0.48^{b}	318.69 ± 7.31^{ns}
100 kDa	62.93 ± 4.88^{b}	23.79 ± 1.02^{b}	314.38 ± 9.15^{ns}
30 kDa	55.93 ± 5.40^{c}	19.40 ± 0.51^{c}	308.28 ± 7.90^{ns}

Same letters in the same column present no statistical differences according to Duncan's multiple range test at $P<0.05$

2.4.4 Effect of enzymatic treatment and membrane filtration on microbiological property of pineapple juice

For microbiological properties (Table 9), the total variable count of PA(EN) was higher than PA(F). The reason was probably that the treated time of one hour at room temperature led to activate the growth of bacteria. Microbiological analyses of clarified juice showed that the product met the Thai requirement for juice and drinks. Total variable cells, mold & yeast and coliforms were completely removed by membranes filtration.

Table 9. Microbiological quality of fresh pineapple juice (PA(F)), enzymatic treated pineapple juice (PA(EN)) and clarified pineapple juice with various membranes pore size and MWCO.

Microbiological quality	Treatments of pineapple juice					
	PA(F)	PA(EN)	0.2 μm	0.1 μm	100 kDa	30 kDa
Total plate count (CFU/ml)	1.53×10^{4}	3.34×10^{6}	<25	<25	<25	<25
Yeast&Mould (CFU/ml)	225±25	352±84	<15	<15	<15	<15
Colifroms (MPN/ml)	<3	<3	<3	<3	<3	<3

2.4.5 Permeate flux profile and resistances during membrane filtration
Effect of membrane pore size and MWCO

The permeate flux during membrane filtration of pineapple juice with total recycle mode is illustrated in Figure 14. In general, the permeate flux rapidly declined at the initial stage of the process. Afterward, the smoother and slower decline toward a quasi-steady state tended in turn, to be attributed to fouling due to pore blocking and cake built up (Yasan et al., 2007). In the case of fruit juice, the foulants were probably composed of cell wall, polysaccharides such as pectin, cellulose lignin and hemi- celluloses (Yu et al.,1986; de Barros et al., 2003). The permeate flux at the end of the process obtained from 0.2 μm membrane was 24.2 l/m²h and it was the highest flux compared with other membranes. Although the pore size of membrane varied doubly, the flux of 0.2 μm membrane did not significantly higher than that of 0.1 μm membrane (22.0 l/m²h). Girard and Fukumoto (2000) suggested that the flux may not necessarily increase with the pore size. The membrane with larger pore size tends to be more susceptible to fouling because more severe pore blocking occurring in the larger membrane pores. It also can be expected that more particles can accumulate in larger pore volume (Hwang et al., 2008). In the case of UF membranes, the flux (8.9 l/m²h) of 30 kDa membrane was much lower than that of 100 kDa membrane (18.7 l/m²h). Considering the small pore of UF membrane, most fouling phenomena could occur on the membrane surface. Therefore R_m could significantly affect the flux. In this study, R_m of 30 kDa membrane was much higher than the R_m of 100 kDa membrane (Table 10). Consequently, the flux from 30 kDa membrane was lower than that of 100 kDa membrane.

Table 10. Permeate resistance during membrane filtration of pineapple juice at CFV of 1.2 m/s temperature of 20±2 °C and TMP 1 bar for MF and 2 bar for UF

Pore size/MWCO	$R_m(\times 10^{12})$ (m^{-1})	$R_t(\times 10^{12})$ (m^{-1})	$R_{rf}(\times 10^{12})$ (m^{-1})	$R_{if}(\times 10^{12})$ (m^{-1})
0.2 μm	0. 069	26.4	16.09	10.29
0.1 μm	0.23	29.7	28.05	1.58
100 kDa	1.30	31.9	25.70	4.88
30 kDa	4.80	69.55	57.67	7.07
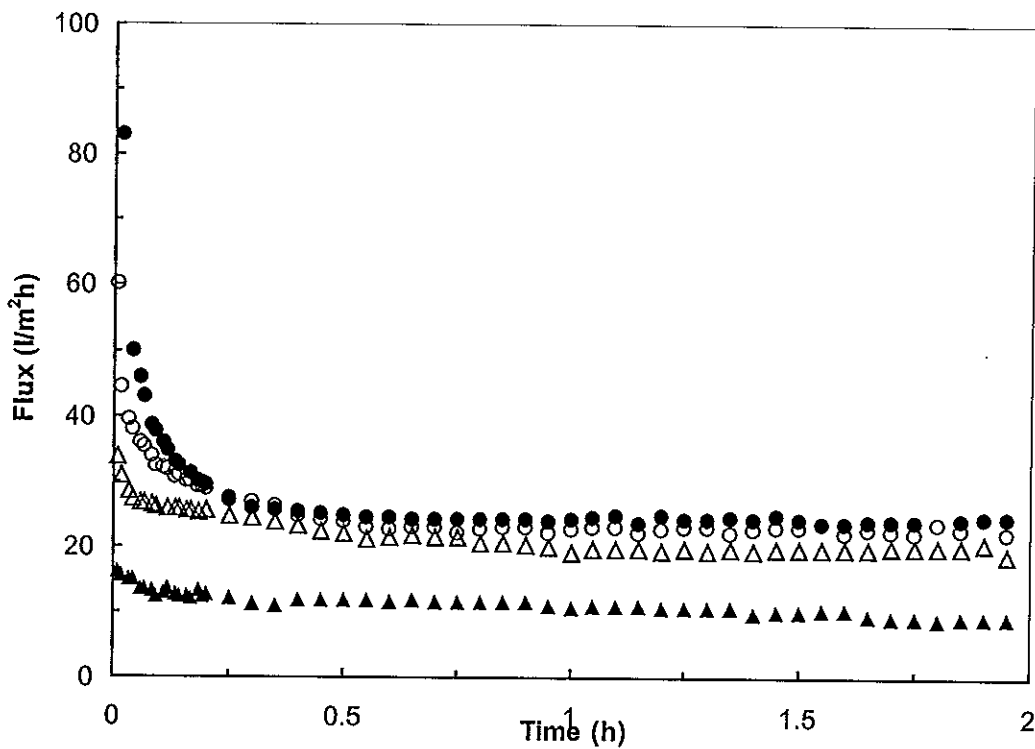
Figure 14. Permeate flux during membrane filtration of pineapple juice with total recycle mode (● 0.2 μm, o 0.1 μm, Δ 100 kDa, ▲ 30 kDa, at CFV = 1.2 m/s, temperature = 20±2°C, TMP = 1 bar for MF and TMP = 2 bar for UF)

R_t during membrane filtration were 26.4 $\times 10^{12}$, 29.7 $\times 10^{12}$, 31.9 $\times 10^{12}$ and 69.5 $\times 10^{12}$ m^{-1} for 0.2 μm, 0.1 μm, 100 kDa and 30 kDa membranes respectively. In the case of MF, R_t of 0.1 μm membrane was higher than 0.2 μm membrane. Referring to UF, R_t of 30 kDa was higher than 100 kDa membrane. The fouling resistances R_t, R_{rf} and R_{if} are shown in Table 10. In general, the R_{rf} was much higher than the R_{if} at all membranes used. The R_{if} of 0.2 μm membrane was higher than the other membranes. It could be due to the higher permeate flux leading to higher concentration polarization and more attached solute to the membrane surface. The results were in agreement with Hwang et al. (2008). They found that the larger pore may have more opportunities to be blocked by particles. The R_{if} of 0.1 μm membrane was the lowest value. The R_{if} of 0.2 μm membrane was the highest but it can be reduced by modifying hydrodynamic operation such as gas sparging (Li et al., 2008).

As mention above, not only the best recovery of phytochemical properties i.e. vitamin C, total phenolic content, and antioxidant capacity were achieved by 0.2 μm membrane, but also the highest value of permeate flux was obtained by this membrane. Therefore, the 0.2 μm membrane was selected to be the optimal membrane pore size for clarification of pineapple juice in this study.

2.4.6 Effect of operating condition

The 0.2 μm membrane was selected to investigate the effect of TMP and CFV on permeate flux and phytochemical properties during microfiltration. The experiments were carried out under total recycle mode.Figure. 15 shows the flux versus TMP at CFV of 3.4 m/s. Under low TMP (TMP < 0.4 bar), the flux increased linearly as TMP increased. When high TMP (TMP > 0.4 bar) was applied, the flux curve bend and showed deviation from a linear flux-TMP behavior and it becomes independent to the pressure. This pressure independent flux value is referred to the limiting flux. In this study, the limiting flux (56.4 l/m^{2}h) was obtained at TMP of 0.7 bar.
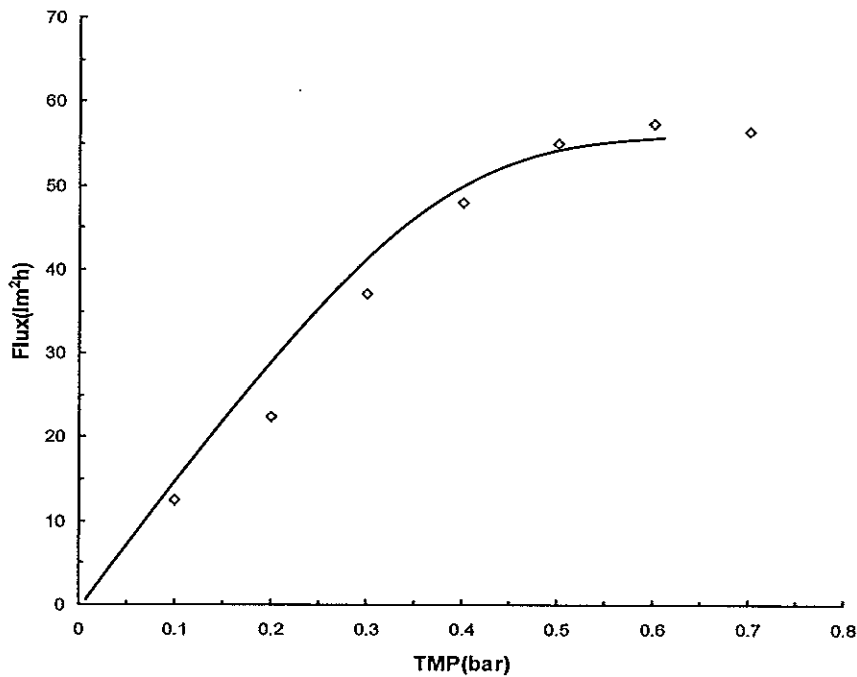
Figure 15. Effect of TMP on the permeate flux (membrane pore size 0.2 µm, CFV = 3.4 m/s, temperature = 20±2°C)

Figure 16 shows the permeate flux as varying of CFV during microfiltration. It was observed that the permeate flux increased linearly with increasing CFV. The permeate flux increased from 33.2 to 54.8 l/m^2h while the CFV increased from 1.5 to 3.4 m/s. Increasing of CFV would enhance wall shear stress on the membrane surface. Higher wall shear stress is helpful to reduce concentration polarization and reversible fouling on the membrane surface (Vadi and Rizvi, 2001). In order to compare the effect of TMP and cross- flow velocity on the phytochemical properties of pineapple juice clarified by 0.2 µm membrane, various cross-flow velocities, a TMP of 0.3 bar which was represented as low TMP (low fouling condition) and a TMP of 0.7 bar which was represented as high TMP (high fouling condition) were selected for analysis (Table 11). The results showed that CFV and TMP did not have significant effect on the phytochemical properties of clarified pineapple juice. According to these results, the CFV of 3.4 m/s and TMP of 0.7 bar were selected for batch concentration experiment.
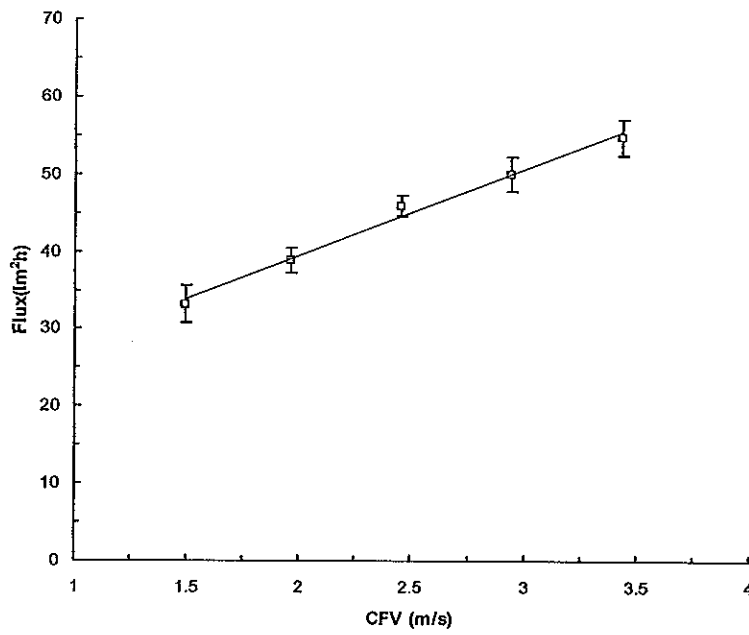
Figure 16. Effect of CFV on the permeate flux (membrane pore size 0.2 µm, TMP = 0.7 bar, temperature = 20± 2°C)

Table 11. Phytochemical properties of clarified pineapple juice at different cross-flow velocity and TMP with 0.2 µm membrane

TMP (bar)	Properties	Cross- flow velocity (m/s)				
		1.5	2.0	2.5	3.0	3.4
Low TMP (0.3)	L-ascorbic acid (mg/100ml)	10.90±0.39	10.63±0.23	10.62±0.24	10.46±0.28	10.30±0.17
	Dehydroascorbic acid (mg/100ml)	10.77±0.27	10.51±0.04	10.65±0.30	10.62±0.19	10.80±0.20
	Total vitamin C (mg/100ml)	21.67±0.65	21.15±0.23	21.27±0.27	21.08±0.40	21.10±0.36
	Total phenolic content (mg GAE/100ml)	65.50±2.65	64.85±2.34	66.77±2.14	66.67±1.65	65.52±1.05
	DPPH(mg AAE /100ml)	25.35±0.75	24.63±1.51	24.76±0.95	24.80±0.36	25.55±0.36
	ORAC (µmol TE/100ml)	325.30±6.29	319.90±9.33	325.52±9.36	323.13±8.32	322.34±6.30
High TMP (0.7)	L-ascorbic acid (mg/100ml)	10.56±0.21	10.34±0.23	10.62±0.24	10.36±0.11	10.28±0.18
	Dehydroascorbic acid(mg/100ml)	10.68±0.36	10.60±0.17	10.71±0.23	10.62±0.19	10.49±0.38
	Total vitamin C (mg/100ml)	21.24±0.30	20.94±0.25	21.33±0.37	20.98±0.08	20.76±0.22
	Total phenolic (mg GAE/100ml)	66.33±2.89	65.85±2.34	66.77±2.90	66.67±2.11	67.19±2.81
	DPPH(mg AAE / 100ml)	25.05±0.55	24.81±1.33	24.51±1.00	25.03±0.70	25.55±1.15
	ORAC (µmol TE/100ml)	323.02±6.90	321.90±9.81	320.39±9.92	316.13±6.10	323.35±5.89

The data of all parameters were no significantly difference in various CFV

2.4.7 Flux profile and phytochemical properties of clarified pineapple juice in batch concentration mode

Regarding the practical application in fruit juice processing, batch concentration mode was also performed by 0.2 µm membrane with CFV of 3.4 m/s and TMP of 0.7 bar. Figure.17 shows the permeate flux and percentage of recovery during MF with batch concentration mode. The permeate flux was sharply decreased in the first ten minutes of the filtration then the flux gradually deceased to 30 l/m^{2}h at recovery of 85 %. An average flux of about 37 l/m^{2}h was obtained after the membrane filtration of 5 hours. The phytochemical properties of clarified pineapple juice at the first hour and at the end of MF under batch concentration mode is

illustrated in Table 12. It is evident that all phytochemical properties of clarified pineapple juice were still preserved after 5 hours of microfiltration.
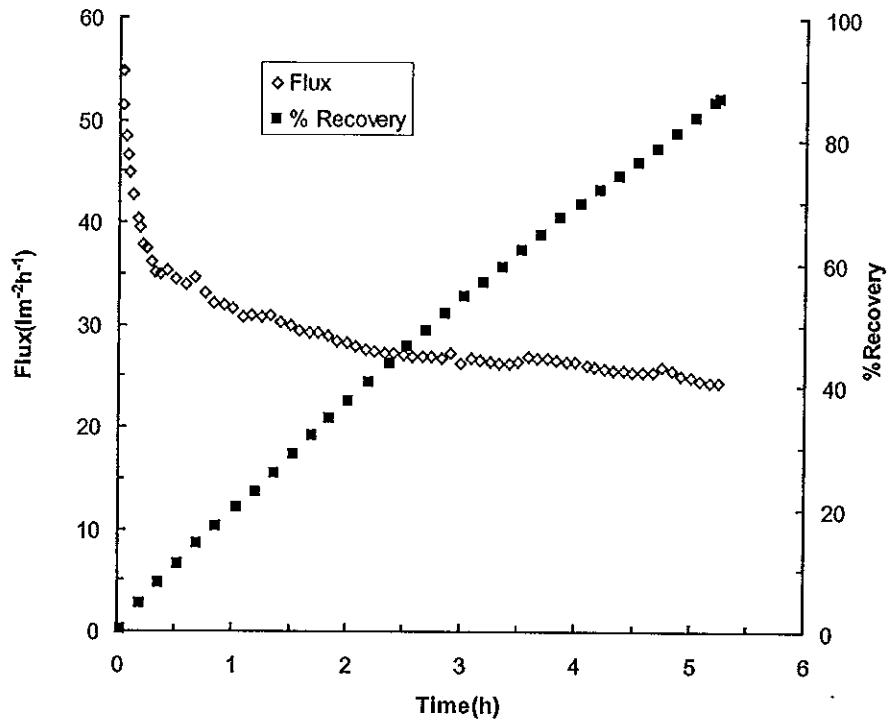
Figure 17. Time versus permeate flux and percentage of recovery during microfiltration of pineapple juice with batch concentration mode (membrane pore size 0.2μm, CFV = 3.4 m/s, TMP = 0.7 bar, temperature = 20±2 °C)

Table 12. Phytochemical properties of clarified pineapple juice after performed with batch concentration mode at CFV of 3.4 m/s and TMP 0.7 bar

Properties	1 hour	5 hours
L-ascorbic acid (mg/100ml)	10.46±0.30	10.28±0.18
Dehydroascorbic acid (mg/100ml)	11.06±0.64	10.81±0.22
Total vitamin C (mg/100ml)	25.58±1.05	21.09±0.43
Total phenolic content (mg GAE/100ml)	66.76±1.20	66.43±2.73
DPPH radical scavenging capacity (mAAE/100ml)	25.58±1.05	25.92±0.55
Oxygen radical absorbance capacity (µmolTE/100ml)	323.06±6.71	324.72±9.25

2.5 Conclusions

Cold sterilization of pineapple juice was performed by MF and UF membranes. The MF membrane with a pore size of 0.2 µm gave the highest recovery of phytochemical compounds including vitamin C (94.3%), total phenolic content (93.4%) and DPPH free radical scavenging capacity (99.6%). The membrane pore size and MWCO did not affect the oxygen radical absorbance capacity. Total variable count, yeast & mold and coliforms were removed completely by all membranes employed. The results indicate that membrane filtration with a pore size of 0.2 µm could serve as a cold sterilization process which could achieve the preservation of phytochemical compounds. This gives perfect clarification and sterilization in one step.

The highest permeate flux was obtained from a 0.2 µm membrane while the highest irreversible fouling (9.79×10^{12} 1/m) was obtained from this membrane as well. However there was no difference in permeate flux between 0.2 and 0.1 µm membranes. The lowest irreversible fouling (1.58×10^{12} 1/m) was observed from a 0.1 µm membrane. According to the highest permeate flux, total phenolic content and antioxidant capacity, a membrane with a pore size of 0.2 µm was considered to be the most suitable membrane in this study. The CFV and TMP did not have significant effect on the phytochemical properties of clarified pineapple

juice. The optimal operating condition of the 0.2 μm membrane was a CFV of 3.4 m/s and TMP of 0.7 bar. In a further study, the changes in the chemical, physical, phytochemical compounds and microbiological properties during storage will be studied. In addition, the improvement of the process performance of microfiltration with a 0.2 μm membrane will be studied.

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CHAPTER 3

COLD STERILIZATION OF PINEAPPLE JUICE BY MEMBRANE FILTRATION: QUALITY CHANGES DURING STORAGE AND THEIR SHELF-LIFE

3.1 Abstract

Membrane filtration is one of non-thermal processing technique for fruit juice processing. It could provide a better preservation of the nutritional properties and flavour of the juice. This study aimed to investigate the quality changes including vitamin C, total phenolic content, antioxidant capacity (2-Diphenly-1-picrylhydrazyl: DPPH, free radical scavenging capacity and Oxygen Radical Absorbance Capacity: ORAC assays) microbial and chemical-physical properties (colour, browning index, pH and total soluble solid) of clarified pineapple juice during storage under differences temperatures (i.e. 4, 27 and 37°C). The juices were filtrated by microfiltration (MF) and ultrafiltration (UF) under the transmembrane pressure (TMP) of 1 and 2 bar respectively. The results showed that there was no significant difference in the quality between the clarified juice by MF and UF during storage at 4, 27 compared with 37 °C at the same storage time. No microbial growth was found after 6 months of storage. The storage time and temperature did not affect the total soluble solid and pH. The clarified juice stored at 4 °C had the best quality comparing to other juice samples. The vitamin C content was the most affected by storage time and temperature as indicated by kinetic constant and activated energy respectively. The colour (L*) of clarified juice stored at 4°C was lighter than the juices stored under others temperatures. The shelf-life of clarified pineapple juice base on the reduction by 50 % of vitamin C was 3.5 mounts, at storage temperature of 4 °C.

88

3.2 Introduction

Pineapple juice is highly consumed in many countries. Thailand is a world exported leader of both concentrate and single strength pineapple juice for decade. The pineapple juice is becoming popular product since it contains attractive aroma, flavour and beneficial component that playing primary role in avoiding the risk of chronic diseases. Pineapple juice is one of the fruit that contain high content of antioxidant and phenolic compounds. Wen and Wrolstad (2002) characterized phenolic compounds in pineapple juice and found that the phenolic compounds in pineapple juice are sinapyl-L-cysteine, N-γ-L-glutamyl-S-sinapyl-L-cysteine, S-sinapyl glutathione, and p-coumaric like compound. Pineapple juice also contains phytosterols such as ergostanol and stigmastanol (Ng and Hape',1999). These phytosterols have cholesterols lowering effect by reducing absorption of chloresterol. Vitamin C, water soluble vitamin, plays an important role in antioxidant activity. It reduced risk of heart disease by preventing the oxidation of low- density lipoprotein (LDL) cholesterol.

It is well known that the conventional thermal processes of fruit juice including pasteurization and sterilization ensure safety and extend shelf-life of the product. However, the process often leads detrimental change in the quality of the product because of high heat treatment. Membrane technology is an alternative method to avoid loss of these components. The membrane filtration process could potentially combine the clarification and sterilization in one step. Microfiltration (MF) and ultrafiltration (UF) are non thermal processes for production of fruit juice with high quality, natural fresh taste and additive free; beside there are simple concept of operation and characterized as low energy consumption (Cassano, *et al*, 2007a). It has been reported that the use of membrane filtration process in fruit juice permitted a good level of recovery of vitamin C and antioxidant capacity (Cassano *et al.*, 2008; Cassano *et al.*, 2007b)

During storage, fruit juice suffers from an importance number of deterioration reactions such as microbial spoilage, phytochemical properties degradation and the change in colour, texture and appearance that produce an important quality loss (Cortés *et al.*, 2008). The study of shelf-life leads to understand

behavior of product characteristics during storage and may help the producers in identifying not only the optimal condition but also the most significant characteristic, limiting the shelf-life. Determination of the quality changes of fruit juice in the real time is a lengthy process that would severely delay market introduction of new product. Therefore, a standardized test was developed to accurately the environmental effect of storage on a clarified fruit juice during its expected usable shelf-life.

A number of authors have studied the clarification of fruit juice by MF and UF processes. On the other hand, there is no report about the quality changes of clarified pineapple juice during storage regarding the phytochemical properties. The *being forld* aim of this study was tend to investigate the changes of microbial, physical and phytochemical properties of MF and UF-clarified pineapple juice during 6 months of storage at 4, 27 and 37°C. This information was then used for determination of clarified pineapple juice shelf-life.

3.3 Materials and methods

3.3.1 Preparation of pineapple juice

Fresh pineapples (*Ananus Comosus L. Merr.*) were rinsed with the tap water. After peeling, the fresh pineapples were cut into 1 cm^3 pieces and the juices were extracted by hydraulic press. Total soluble solid (TSS) and pH values of the juice were in the ranged of 12.2-14.2 °Brix and 3.5-4.0 respectively. The fresh pineapple juice was kept at 4 °C before used. The pineapple juice was treated by 0.03 % (V/V) of commercial pectinase (Pectinex® ultra SP-L (25±3°C) for 60 minutes before introducing to membrane system (Carneiro *et al.*, 2002).

3.3.2 Microflitration and ultrafiltration

The membrane system used was a polysulfone hollow fiber module (Amersham Biosciences, UK) with a fiber diameter and length of 1 mm. and 30 cm. respectively.

The effective membrane area was 0.011 m^2. The pore size and MWCO of the membranes were 0.2 μm and 100 kDa for MF and UF respectively. The membrane system consist of a 8 liter stainless steel jacket-feed tank, variable-feed pump (Leeson, USA) and transducers (MBS 3000, Danfoss, Denmark) for pressure of the feed, retentate and permeate measurement. The temperature of the feed was controlled by circulating chilling water through a jacket-feed tank. The cross-flow velocity (CFV) and transmembrane pressure (TMP) were controlled using needle permeate valve and variable speed-feed pump. The digital balance (GF-3000, A&D, Japan), connecting the computer was used to measure the permeate flux. The schematic diagram of the experimental set-up is shown in Figure12.

The experiments were carried out under batch concentration mode (the retentate return to the feed tank) at constant CFV of 1.2 m/s, ×temperature of 20±2 °C and TMP of 1.0 bar (for MF) and 2.0 bar (for UF). The permeate sample was filled into the sterilized glass bottles directly under aseptic conditions inside a laminar flow cabinet. The bottles were sterilized by hot air oven at 180°C for 3 hours before use. The laminar flow cabinet was sprayed with 70 % alcohol and exposal to germicidal uv light, uv-c 254 nm. with the intensity at 76 $\mu m/cm^2$ for overnight. A HEPA air filter system with 0.3 μm pore size and a 0.1375 m^2 filtration area was installed to provide positive pressure of bacteria free air in the laminar flow cabinet.

3.3.3 Storage conditions

The clarified juice obtained from MF and UF were filled in sterilized glass bottles and stored at 4, 27 and 37 °C. Samples were analyzed in triplicate at 0, 1, 2, 3, 4, 5 and 6 months of storage time.

3.3.4 Pineapple juice analyses

The sample colour was measured by a colourimeter (Colour Quest XT, Hunter lab, USA). It is classified by CIE (Comission Internationale l'Eclairage) into

three dimension; L*, Brightness, a*, red to green colour and b*, yellow to blue colour. The determination of the total colour difference (ΔE) was carried out using the measured colour attribute with the following equation:

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \qquad (3\text{-}1)$$

ΔE indicates the magnitude of the colour difference between clarified juice at initial time and after storage period (Cortés et al., 2008). Chroma, a quantify of colour intensity was determined using equation (3-2)

$$Chroma = (a^{*2} + b^{*2})^{1/2} \qquad (3\text{-}2)$$

Non-enzymatic browning index was determined using an absorbance at 420 nm with spectrophotometer (Thermo Spectronic, 4001/4, USA), according to the method of Maydave et al., (1997).

The pH values were measured using pH meter (PB-20, Sartorius, Germany). The total soluble solid were measured by hand refractometer (ATAGO, Japan)

The Microbiological analyses of clarified juices were performed by the method described in Bacteriological Analytical Manual (BAM, 2002).

Total vitamin C (L-ascorbic acid and dehydroascorbic acid) content was determined by high performance liquid chromatography (HPLC). The method was based on Zapata and Dupour, (1992) with some modifications. The juice 10 ml were homogenized with a 10 ml of extraction solution (0.1M citric acid, 0.05% ethyldiaminetretraacetic acid (EDTA) in 5% aqueous methanol) for 2 min. An internal standard of isoascorbic acid was added at 20 mg/100g of fruit juice. The homogenated was then centrifuged for 10 min at 10,000 × g and 2 °C. After calibrating the pH with cold buffer, the pH of the supernatant was adjusted to 2.35-2.40 with 6 N HCl. The sample was passed through a sep-pack C -18 cartiladge (Verti-pack) which had been preconditioned with 10 ml HPLC grade methanol followed by 10 ml of ultrapure water. The residual water in the cartridge was expelled with air before being used.

The first 5 ml of eluent was discarded and the next 3 ml was retained for analysis. One ml of o-phenylenediamine (3.33 mg/ml) was added and the vial was placed in ice tray in darkness for 80 min before injection. After 80 min, the mixture was passed through a 0.45 μm filter (Vertipure Nylon syling, USA) into an amber vial and then was injected into HPLC system.

The HPLC system consists of reverse phase C_{18} column (Symmetry® C_{18} 5μ 4.6x250 mm, Waters,Ireland). The mobile phase was methanol-water (5:95, v/v) containing 5mM hexadecyltrimethylammonium bromide (CTAB) and 50 mM potassium dihydrogen phosphate, with pH adjusted to 4.59. The flow rate was 1.0 ml/min. Detection was at 261 nm for reduced L-ascorbate and isoascorbate and at 348 mm for L-dehydroascorbate. The retension times were 5.6, 10.8 and 13.5 min for L-dehydroascorbate, reduced L-ascorbate and isoascorbate respectively. Standards of L-ascorbate, L-dehydroascorbate and isoascorbate were purchased from Sigma Chemical Company (St.Louis, MO). The results of vitamin C content were expressed as mg/100ml of fruit juice.

Total phenol content was determined by spectrophotometric determination using Folin-Ciocalteu's phenol reagent (Kim et al., 2002). Total phenolic content was expressed as milligram gallic acid equivalents per 100 ml pineapple juice (mg GAE/100g fruit juice).

The DPPH free radical scavenging was determined according to the method of Gil-Izquierdo et al., (2001). The results were expressed as milligrams of L-ascorbic acid equivalent per 100 ml pineapple juice. L-ascorbic acid was used as antioxidant standard reference compound.

The oxygen radical absorbance capacity (ORAC) assay were carried out on a FLUO star Galaxy plate reader (fluostar optima solfware user manual, BMG Labtech, Germany) by using modified method of Wu et al., (2004).

3.3.5 Kinetic considerations and determination of shelf- life

Zero and First order model have been used to evaluate the degradation of vitamin C, total phenol content and antioxidant capacity. This kinetic is presented by the following equations (Ross, 1998).

$$C = C_0 - kt \hspace{4cm} (3\text{-}3)$$

$$C = C_0 \exp(-kt), \hspace{3.5cm} (3\text{-}4)$$

where C is the content of vitamin C (mg/100g), C_0 is the initial content of vitamin C (mg/100g), k is the reaction rate constant (month^{-1}) and t is the storage time (month).The Arrhenius relationship was assumed for the temperature dependence for the reaction rate constant k as follow :

$$k = A_0 \exp(-E_a/RT) , \hspace{3cm} (3\text{-}5)$$

where E_a is the activation energy of the reaction (cal/mol), R is the gas constant (1.986 cal/mol K), T is the absolute temperature (K), and A_0 is the pre exponential constant. A plot of the log of rate constant for the test temperature versus the reciprocal of the absolute temperature gives the straight line if the Arrhenius relation applies to the specific reaction. The energy of the activation (E_a) was derived from the slope (E_a/R). The intercept, however, gave the exponential constant. To study the influence of temperature on reaction rate, the Q_{10} values were calculated according to the following relationship:

$$Q_{10} = (k_2/k_1)^{10/T2-T1} \hspace{3cm} (3\text{-}6)$$

Obtained data were subjected to analysis of variance (ANOVA) and mean comparison were carried out using Duncan's Multiple Range Test (DMRT).

3.4 Results and Discussion

3.4.1 Change in total soluble solid, pH and colour during storage

The physicochemical properties of clarified pineapple juices during storage at various temperatures are shown in Table 13. The total soluble solid in MF and UF clarified pineapple juice range from 12.5-12.8 and 12.2-12.7 °Brix while the

pH range from 3.56-3.69 and 3.57-3.68 respectively. It was observed that the storage time and temperature did not affect the total soluble solid and pH of clarified juices. The same results were observed by other authors (Cortés *et al.*, 2008; Esteve *et al.*, 2005; Martin *et al.*, 1995).

Table 13. Total soluble solid and pH of clarified pineapple juice during 6 months of storage at 4, 27 and 37 °C

Storage conditions		Total soluble solid		pH	
Temperature (°C)	Time (month)	MF	UF	MF	UF
4	0	12.8(0.1)*	12.4(0.2)	3.64(0.04)	3.68(0.04)
	1	12.8(0.2)	12.7(0.1)	3.61(0.07)	3.68(0.04)
	2	12.8(0.2)	12.3(0.1)	3.61(0.07)	3.65(0.08)
	3	12.7(0.2)	12.4(0.2)	3.69(0.08)	3.58(0.06)
	4	12.5(0.2)	12.5(0.2)	3.68(0.04)	3.65(0.12)
	5	12.5(0.1)	12.4(0.2)	3.66(0.03)	3.61(0.06)
	6	12.5(0.1)	12.2(0.2)	3.58(0.08)	3.62(0.03)
27	0	12.8(0.1)	12.4(0.2)	3.64(0.04)	3.68(0.04)
	1	12.7(0.2)	12.5(0.1)	3.65(0.01)	3.62(0.04)
	2	12.5(0.3)	12.4(0.2)	3.64(0.01)	3.65(0.08)
	3	12.5(0.1)	12.4(0.1)	3.62(0.04)	3.58(0.06)
	4	12.5(0.1)	12.4(0.1)	3.60(0.03)	3.62(0.08)
	5	12.5(0.1)	12.3(0.2)	3.59(0.04)	3.62(0.03)
	6	12.6(0.2)	12.4(0.1)	3.59(0.05)	3.57(0.03)
37	0	12.8(0.1)	12.4(0.2)	3.64(0.02)	3.68(0.05)
	1	12.6(0.1)	12.4(0.2)	3.61(0.05)	3.67(0.06)
	2	12.6(0.3)	12.3(0.1)	3.61(0.02)	3.64(0.11)
	3	12.6(0.2)	12.5(0.1)	3.58(0.04)	3.62(0.02)
	4	12.7(0.1)	12.4(0.1)	3.56(0.06)	3.58(0.04)
	5	12.7(0.1)	12.2(0.1)	3.63(0.01)	3.60(0.05)
	6	12.6(0.2)	12.3(0.1)	3.61(0.07)	3.60(0.06)

*standard deviation

The change in colour of clarified pineapple juice stored at 4, 27 and 37 °C were monitored during 6 months. For the fresh clarified juice (0 month storage), there were no significant difference in the colour between MF and UF-clarified juice. The changes in colour of clarified pineapple juice across the duration of the shelf- life study are shown in Figure 18. There were no significant difference in L* a* and b* between the MF and UF clarified pineapple juice, stored at the same temperature. The L* value of clarified juice (indicating the lightness), stored at 4 °C was much higher than that the juice stored at 27°C and 37 °C. The falling in L*values indicated that the juice were turning darker due to the non-enzymatic browning reaction during storage. The change in a* value (indicating the redness) was not much during storage at

experiment temperatures whereas the b*value (indicating the yellowness) gradually increased with storage time and temperature. An increase in yellowness was in accordance with the decrease of L* values
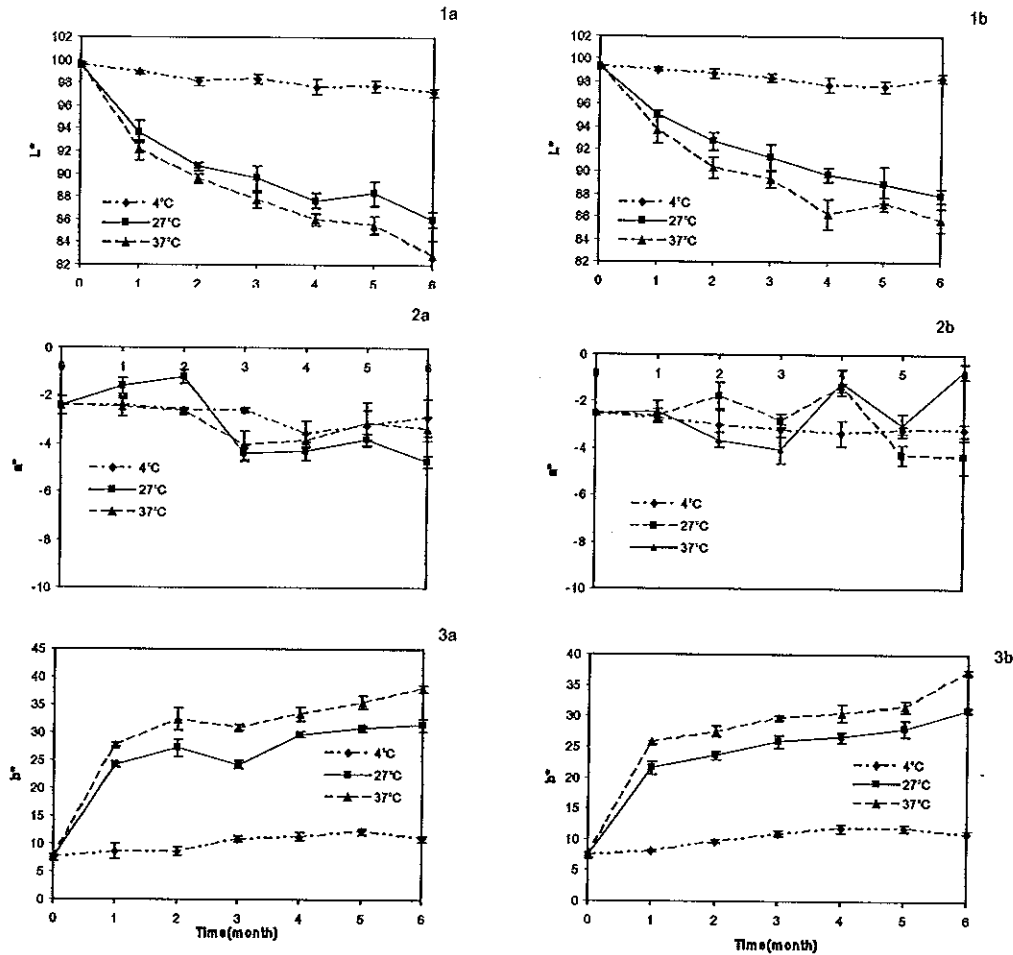
Figure 18. L*(1) a*(2) and b*(3) values of MF clarified pineapple juice (a) and UF clarified pineapple juice (b) during 6 months of storage at 4, 27 and 37 °C

The overall colour change of clarified juice stored at 4 °C was much less than that stored at 27 and 37 °C. Table 14. shows the chroma and the total colour differences (ΔE) of clarified juice during storage. The chroma (indicating the quantifies the intensity of colour) of the clarified juice, stored at 27 and 37 °C increased significantly. The total colour differences (ΔE), indicating the magnitude of the colour difference between clarified pineapple juice at the initial time and after

storage period, was significantly increased as the storage time and temperature increased. This was due to the non-enzymatic browning reaction. Choi *et al.* (2002) recommended that ΔE of 2 would be noticeable visual difference. In general, the ΔE of MF- clarified juice was higher than the UF-clarified juice, stored at the same temperature during for 6 months storage. The reason was probably due to the MF–clarified juice had more remaining substrate (amino acid) than the UF–clarified juice therefore it had more occurring of Millard reaction, leading to increase of ΔE.

Table 14. Chroma and colour difference (ΔE) of clarified pineapple juice during 6 months of storage at 4, 27 and 37 °C

Storage conditions		Chroma		Colour difference (ΔE)	
Temperature (°C)	Time (month)	MF	UF	MF	UF
4	0	7.85	7.73		
	1	8.91	8.51	1.24	0.85
	2	9.02	10.10	1.83	2.48
	3	11.20	11.43	3.62	3.87
	4	11.81	12.24	4.37	4.83
	5	12.63	12.21	5.14	4.87
	6	11.34	11.43	4.21	3.87
27	0	7.85	7.73		
	1	24.25	21.71	17.73	14.88
	2	27.23	23.67	21.66	17.62
	3	24.62	26.04	19.54	20.26
	4	29.99	26.63	25.24	21.57
	5	31.00	28.31	25.88	23.23
	6	31.74	31.29	27.56	26.37
37	0	7.85	7.73		
	1	27.90	25.76	21.63	19.20
	2	32.48	27.72	26.88	22.12
	3	31.16	29.93	26.27	24.55
	4	33.48	30.49	28.68	26.65
	5	35.59	31.67	30.85	27.12
	6	38.05	37.15	34.23	32.85

The colour change due to non enzymatic browning during storage of clarified pineapple juice was determined by measurement of absorbance at 420 nm., known as browning index. Figure 19. shows the absorbance of 420 nm. of MF and UF- clarified juice. The browning index of clarified juice increased with the storage

time. In addition, the storage temperature also affected the browning index during storage. Since it was evident that the browning index of the juice stored at 27 and 37 °C were higher than that of the juice stored at 4 °C. However, there were not much different in browning index of the clarified juice stored at 27 and 37°C. Similar results were observed during storage of peach juice at 3 15 30 and 37 °C (Buedo *et al.*, 2001). In addition, Lee and Chen (1998) found that the results of browning measurement are in accordance with vitamin C reduction.
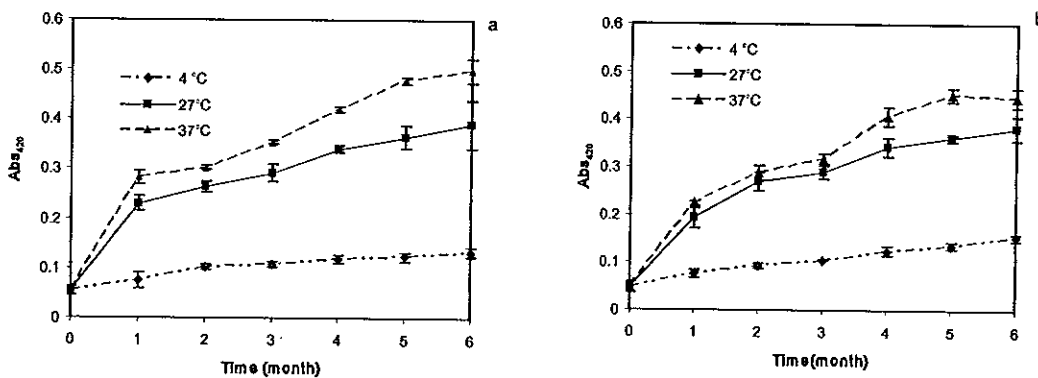
Figure 19. Browning index of MF clarified pineapple juice (a) and UF clarified pineapple juice (b) during 6 months of storage at 4, 27 and 37 °C

Nevertheless, there are several numbers of deterioration reactions leading to the change in colour of fruit juice during storage such as ascorbic acid degradation, microbial spoilage, HMF formation and off flavour etc (Nagy and Randall, 1973). However, it is important to bear in mind that the advances stages of Millard reaction can also give rise to compounds responsible for the development of off flavour and colour change that could affect the sensorial and quality of pineapple juice during storage.

3.4.2 Changes in total phenol and antioxidant capacity during storage

To the best of our knowledge, this is the first study in which the changes in phytochemical properties of MF and UF clarified pineapple juice during storage were investigated. Variation in the amount of total phenol and antioxidant capacity of clarified pineapple juice are shown in Figure 20. and 21. The antioxidant

capacity of pineapple juice was evaluated using DPPH free radical scavenging, based on electron transfer and oxygen radical absorbance capacity (ORAC) assay based on hydrogen transfer. The initial total phenol content of clarified pineapple juice obtained by MF and UF were 68.71±1.67mg /100 ml and 65.05±1.36 mg /100 ml (Figure 19). The content of total phenol in MF- clarified juice was slightly higher than that in UF-clarified juice. However, there was no statistical difference. During 6 months of storage at 4, 27 and 37 °C, the total phenols content obtained from MF and UF-clarified juice were slightly decreased with storage time. It was probably due to polyphenolic oxidation and polymerization reaction, reducing the number of free hydroxyl groups measured by the Folin- Ciocalteu-assay (Klopotek et al., 2005; Pacheco-Palencia et al., 2007). Similar result was reported by Klimczak et al., (2007). However, the colder storage temperature (4°C) could preserved the total phenol content than those stored at higher temperatures (27, 37°C). During 6 months of. storage at 4, 27 and 37°C, the lost of total phenol content in MF-clarified juice were 11.2, 14.9 and 15.3% respectively while the lost in UF- clarified juice were 10.9, 12.8, 14.3 % respectively.
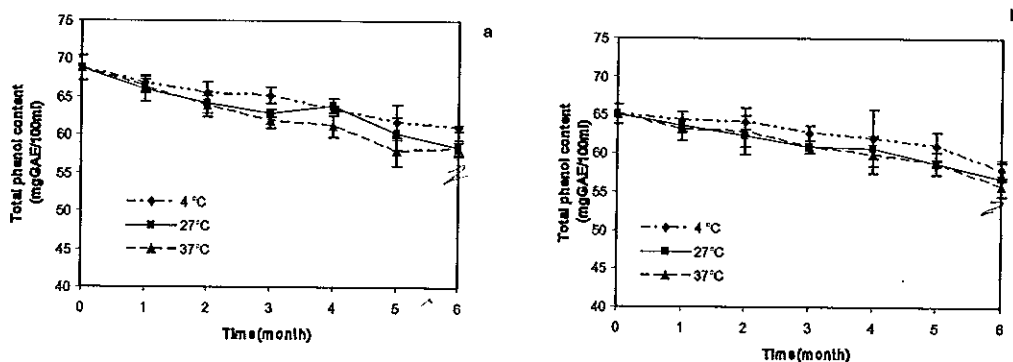
Figure 20. Total phenol of MF-clarified pineapple juice (a) and UF-clarified pineapple juice (b) during 6 months of storage at 4, 27 and 37 °C

The antioxidant capacity of clarified pineapple juice was also determined by the DPPH free radical scavenging and oxygen radical absorbance capacity (ORAC assay). The initial content of DPPH free radical scavenging of MF and UF clarified juice were in the range of 28.70±0.78 and 26.84±0.93

mgAAE/100ml fruit juice while the content of ORAC assay were in the range of 321.57±5.81 and 319.35±6.72 μmTE/ 100ml fruit juice, respectively. The results showed that there were no significantly difference in antioxidant capacity of the samples, stored at the same temperature between MF and UF-clarified pineapple juice. The antioxidant capacity of all samples   slightly decreased with storage time. The presented results are in the line with the data obtained by Klimczak *et al.*, (2007). They found the decrease in antioxidant of orange juice, after 6 months of storage at 18, 28 and 38°C were 18, 45 and 84 % respectively. The decrease in antioxidant capacity was related to the observed losses of total vitamin C. Figure 20. presents the change in oxygen radical absorbance capacity of MF and UF clarified pineapple juice. There was a slight decrease in antioxidant capacity during 6 months of storage. The trends of decreasing in ORAC result was similar with the result of DPPH free radical scavenging. In addition, the antioxidant also had positive correlation with vitamin C content. This result was in accordance with the study of Saxena *et al.*, (2009), who studied the changes of phytochemical properties in jackfruit during storage. The correlation of vitamin C between DPPH scavenging activity and ORAC assay is shown in Figure 22 a and b. The loss of vitamin C during the first month of storage could not be detected by DPPH but ORAC. It was evident that the loss of vitamin C content at the first month of storage was due to a sharp decrease in L-ascorbic acid (data not shown). This result suggested that the DPPH assay could be indicated the loss of L-ascorbic acid rather than the ORAC method.
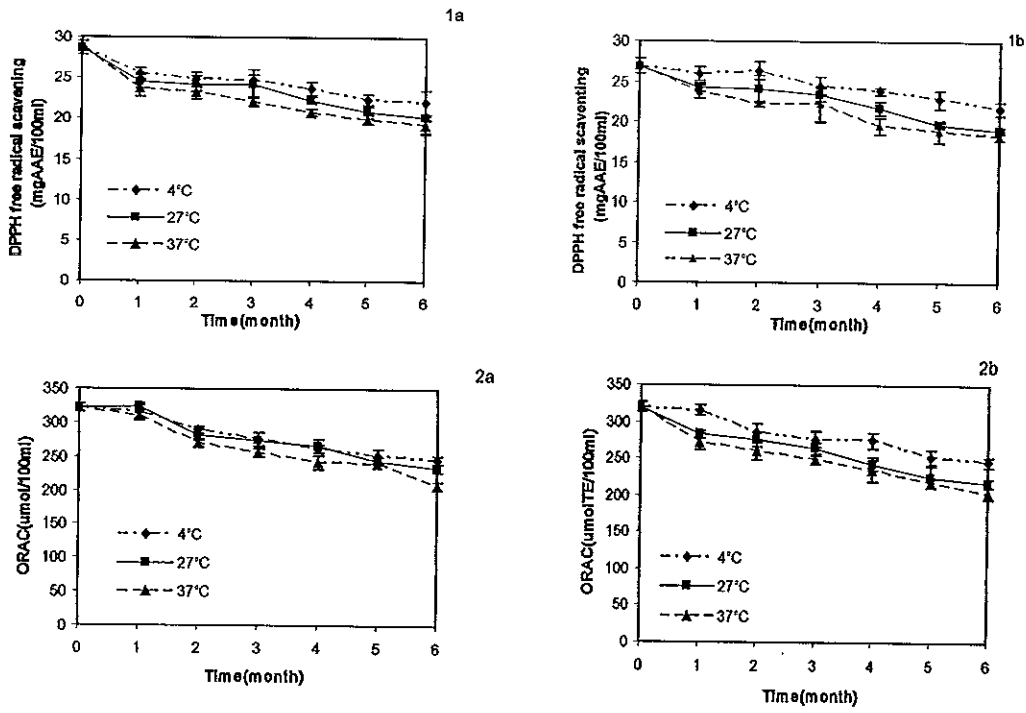
Figure 21. Antioxidant capacity (DPPH(1), ORAC(2)) of MF- clarified pineapple juice (a) and UF- clarified pineapple juice (b) during 6 months of storage at 4, 27 and 37 °C

a   b
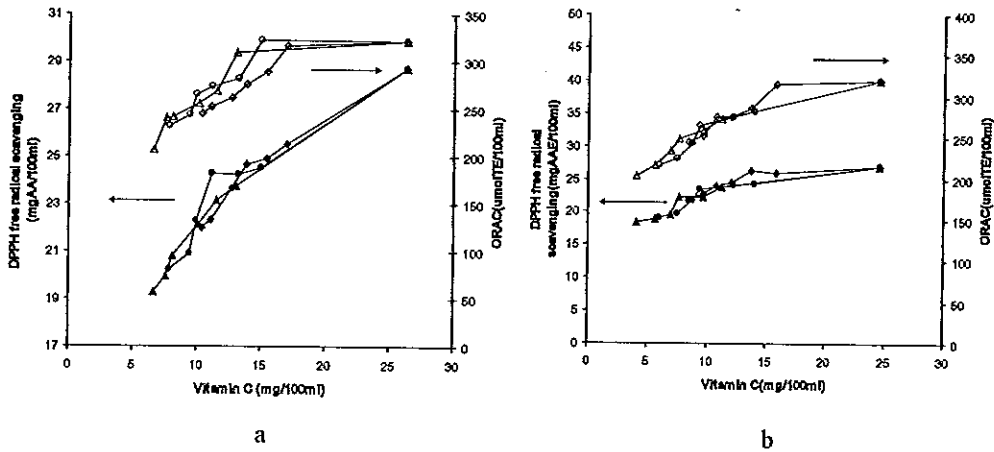
Figure 22. The correlation between vitamin C and DPPH scavenging activity and ORAC assay of MF- clarified pineapple juice (a) and UF- clarified pineapple juice (b) during 6 months of storage at 4($\lozenge$), 27(o) and 37(Δ) °C

3.4.3 Changes in total vitamin C during storage

At the initial of storage time, there were no significant difference in total vitamin C between MF and UF clarified pineapple juice and the content of vitamin C were in the range of 26.32±1.32 and 24.56±0.20 mg/100 ml respectively. These values were slightly less than the fresh pineapple juice (28.67±1.8 mg/100 ml). This result indicated that the membrane filtration process could be effectively preserved vitamin C in clarified pineapple juice. Vitamin C content sharply decreased during the first month of the storage (Figure. 23). The reason was due to the degradation of L-ascorbic acid to the dehydroascorbic acid. Choi *et al.* (2002) found similar results when they studied the ascorbic retention of blood orange juice during refrigerated storage. They found that the L-ascorbic acid completely degraded within 5 weeks. The reduction of vitamin C content, stored at 4, 27 and 37°C of MF-clarified pineapple juice were 60.7, 70.3 74.8 % respectively and UF- clarified pineapple juice were 65.7, 75.6 and 80.2 % respectively. The storage temperature at 4 °C could preserve total vitamin C more than the other temperatures. It is important to note that the storage temperature did not affect the rate of reduction of vitamin C content during 6 months of storage. The decrease in vitamin C content during storage was observed by many studies (Polydera *et al.*, 2003; Klimczak *et al.*, 2007; Piljac-Zegarac *et al.*, 2009; Lee and Chen, 1998). According to the literature, the vitamin C content in the juice decreased during storage was dependent of the storage conditions such as temperature, oxygen, and light access. On the other hand, the great reduction of vitamin C might be due to the present of oxygen in the head space of the glass bottle. The oxygen is usually responsible for the loss of vitamin C during storage. Vitamin C retention has been used as indicator of shelf-life for fruit juice. It has been accepted that the shelf –life of the fruit juice could be determined based on 50% loss of the vitamin C (Shaw, 1992; Odriozola-Serrano *et al.*, 2008).
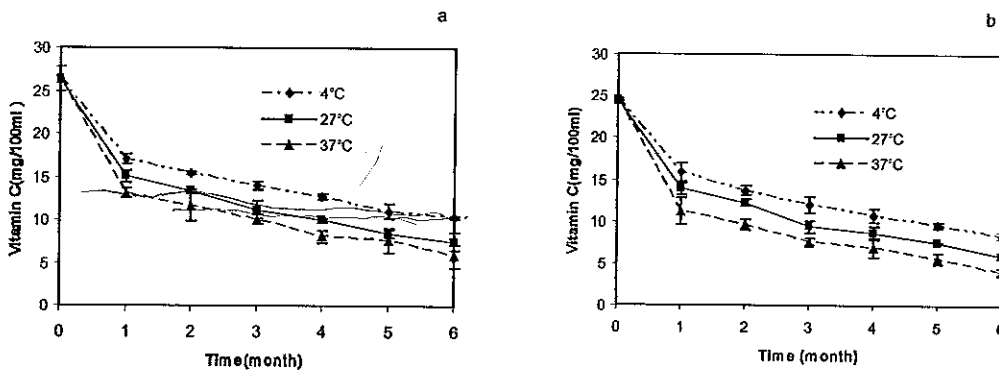
Figure 23. Vitamin C of MF-clarified pineapple juice (a) and UF-clarified pineapple juice (b) during 6 months of storage at 4, 27 and 37 °C

3.4.4 Kinetic study of vitamin C, total phenol content, antioxidant capacity and colour

The changes in colour, vitamin C, total phenol and antioxidant capacity (DPPH and ORAC assay) during storage were chosen for the kinetic study. The reaction was first determined by plotting the amount of remaining parameter values versus times (in month) at different temperatures. A plot yielding a straight line was taken, meaning that the degradation is of zero order; or the first order. The degradation of all parameters was fitted to a first order kinetic model (Eq. 3-4) for both MF and UF- clarified pineapple juice. Figure 24 (1a) and (1b) show the example of the degradation plots of vitamin C. The rate of deteriorative reaction (k) was likewise determined using the Eq. 3-4. In addition, the Arrhenius plots of vitamin C in MF and UF- clarified juice are shown in Figure 23 (2a) and (2b) as well. Table 15. presents the kinetic constant (k), activation energy (E_a) and Q_{10} of vitamin C, total phenol, antioxidant capacity and colour at different storage temperatures. As expected, the rate constant degradation of clarified juice increased with storage temperature. In the case of activation energy, the higher activation energy means that the reaction is more temperature-dependent, i.e. the reaction become faster as the temperature increase. The lower degradation rate gives the longer shelf-life of the

juice than the higher degradation rate. In general, the highest (positive) kinetic constant, at the same storage temperature of clarified juice was vitamin C followed ORAC, DPPH and total phenol respectively while the kinetic constant of clour (b*) was higher than that of colour (L*). It was evident that the highest activated energy (E_a) was vitamin C followed ORAC, DPPH and total phenol respectively, suggesting that vitamin C is more temperature dependent than the others while the activated energy of clour (L*) was much higher than that of colour (b*). It is also important to note that both kinetic constant, at the same temperature and activate energy between MF-clarified juice and UF- clarified juice were comparable. The Q_{10} values of clarified juice, calculated in the temperature of 27 and 37 °C are also shown in Table 15. The Q_{10} values of all parameters were in the range of 1-1.5. The higher Q_{10} values indicated that the parameter was more temperature dependent. The antioxidant capacity (DPPH and ORAC) had the Q_{10} values of 1, indicating that the temperature did not much affect the antioxidant capacity during storage for 6 months.

Table 15. Kinetic constant (k), activated energy (E_a) and Q_{10} for vitamin C, total phenol and antioxidant capacity in clarified pineapple juice storage at 4, 27 and 37 °C

Parameters	T(°C)	k (month^{-1})		E_a (kcalmol^{-1})		Q_{10}(27-37°C)	
		MF	UF	MF	UF	MF	UF
Vitamin C	4 °C	-0.1037	-0.1237				
	27°C	-0.1417	-0.1660	2.14	2.38	1.2	1.2
	37°C	-0.1630	-0.1974				
Total phenol	4 °C	-0.0186	-0.0194				
	27°C	-0.0224	-0.0217	1.96	1.08	1.2	1.1
	37°C	-0.0275	-0.0240				
DPPH	4 °C	-0.0318	-0.0381				
	27°C	-0.0430	-0.0541	1.84	2.05	1.0	1.0
	37°C	-0.0440	-0.0545				
ORAC	4 °C	-0.0497	-0.0468				
	27°C	-0.0602	-0.0575	1.65	1.32	1.0	1.0
	37°C	-0.0683	-0.0593				
Colour (L*)	4 °C	-0.0031	-0.022				
	27°C	-0.0151	-0.0153	10.25	11.18	1.3	1.1
	37°C	-0.0196	-0.0168				
Colour (b*)	4 °C	-0.0585	-0.0631				
	27°C	-0.0623	-0.0672	0.77	0.49	1.1	1.1
	37°C	-0.0685	-0.0692				
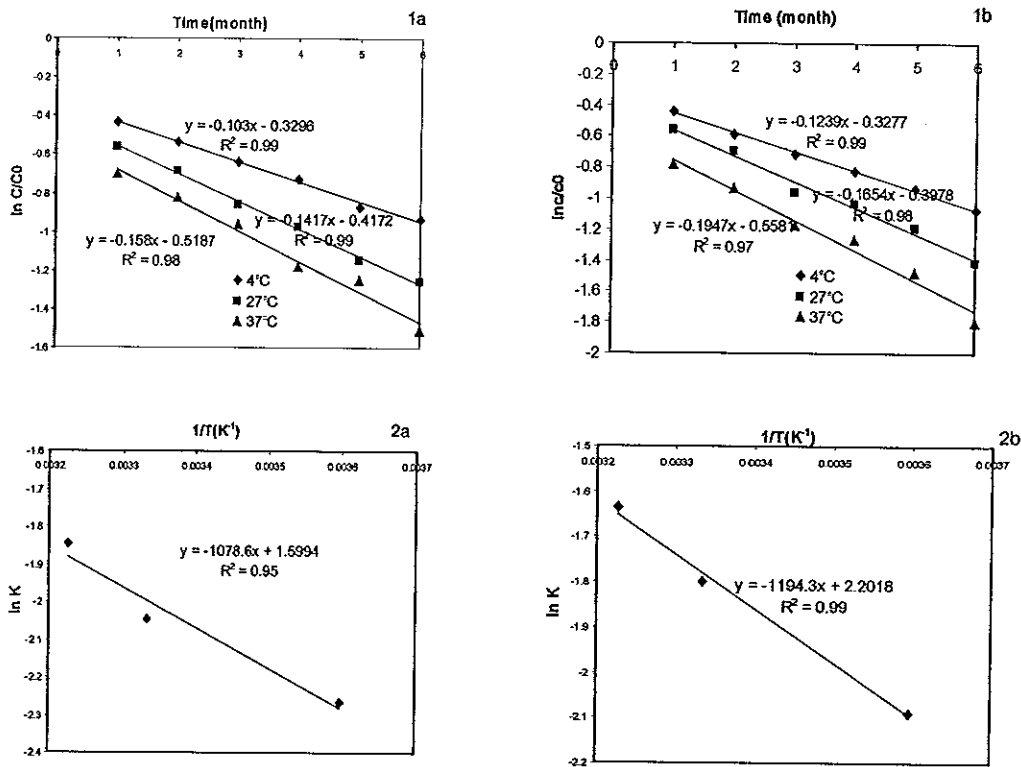
Figure 24. Vitamin C degradation (1) and Arrhenius approach (2) of MF-clarified
pineapple juice (a) and UF-clarified pineapple juice (b) during 6 months
of storage at 4, 27 and 37 °C

3.4.5 Shelf-life determination

In practice, survived microbial count is the important indicator of
sterilized product. In this study, it was found that no microbial growth was observed
during storage of either MF or UF-clarified pineapple juice until the 6 months of
storage (data not shown). Generally, all yeast & molds and most bacteria are retained
by MF with pore size of 0.4 μm or smaller (Girard and Fukomoto, 2000). Therefore,
in this study the microbiological result did not used for indicating the shelf- life of
clarified juice. The shelf-life of clarified pineapple juice was estimated based on the
time taken at 50 % reduction of vitamin C, total phenol content, DPPH and ORAC
(Table 16). It can be seen that the self-life based on the reduction of total phenol,
DPPH and ORAC for both MF and UF- clarified juice, stored at 4-37 °C was longer

than 6 months. However, the shelf- life of MF and UF clarified juice based on 50% reduction of vitamin C were in the range of 2.9-3.5 months at 4°C, 2 months at 27 °C and 0.8-0.9 months at 37 °C. It is important to note that the clarified juice stored at colder temperature had a longer shelf- life higher than the higher temperature.

Table 16. Shelf-life[a] (months) of clarified pineapple juice at various storage temperatures (base on Vitamin C, total phenol antioxidant capacity)

Index	Storage temp (°C)	Shelf- life (months)	
		MF	UF
Vitamin C	4	3.5	2.9
	27	2.0	2.0
	37	0.8	0.9
Total phenol content	4	> 6	> 6
	27	> 6	> 6
	37	> 6	> 6
DPPH	4	> 6	> 6
	27	> 6	> 6
	37	> 6	> 6
ORAC	4	> 6	> 6
	27	> 6	> 6
	37	> 6	> 6

a* calculated base on vitamin C, total phenol, DPPH and ORAC decreasing by 50 %

3.5 Conclusion

No microbial growth was observed in the clarified juice after 6 months of storage. Storage time and temperature did not affect the pH and total soluble solid of MF and UF clarified pineapple juice. There were no significant difference in L* a* and b* between the MF and UF clarified pineapple juice. However, the clarified pineapple juice stored at 4°C gave the less values of total colour difference (ΔE) and browning index than that of the juice stored at 27 and 37 °C. For the total vitamin C, total phenol and antioxidant capacity, there were no statically difference between clarified juice form MF and UF. During 6 months storage of MF-clarified juice, the loss of total phenol content were 11.2, 14.9 and 15.3% while the loss of UF-clarified juice were 10.9, 12.8, 14.3 %, stored at 4, 27 and 37°C, respectively. The vitamin C

contents (L-ascorbic acid) was most affected by storage time and temperature, whereas the antioxidant capacity (DPPH and ORAC) were slightly decreased during 6 months of storage. The rate constant (k) of all parameters of the juice stored at 4°C was less than those stored at 27 and 37 °C. The shelf-life of clarified juice based on 50 % vitamin C reduction ranged between 0.8 month at 37 °C, 2.0 months at 27 °C and 3.5 months at 4 °C. However, the shelf-life based on total phenol and antioxidant capacity reduction by 50% was more than 6 months. The storage temperature at 4°C was the best condition to retain appreciative quality of the juice.

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CHAPTER 4

EFFECT OF GAS SPARGING ON FLUX ENHANCEMENT AND QUALITY
OF CLARIFIED PINEAPPLE JUICE BY MICROFILTRATION

4.1 Abstract

Membrane fouling is a major obstacle in the application of microfiltration. Several techniques have been proposed to enhance the permeate flux during microfiltration. Gas sparging is a novel hydrodynamic method for improving the performance of membrane process. In this study, the effects of cross flow velocity (CFV) and gas injection factor (ε) on the critical and limiting flux during microfiltration of pineapple juice were investigated. The 0.2 μm hollow fiber microfiltration membrane was performed under total recycle mode. It was observed that the critical and limiting flux increased as the CFV increased. The critical flux varied from 25.4 to 40.2 l/m^{2}h and limiting flux varied from 36.4 to 56.5 l/m^{2}h while CFV was increased from 1.5 to 3.4 m/s without gas sparging. The use of gas sparging led to the remarkable improvement of both critical and limiting flux but it was more effective at the lower CFV (1.5 m/s), compared to those at higher CFV (2.0 and 2.5 m/s). When the gas injection factor was applied at 0.15, 0.25 and 0.35 with a CFV of 1.5 m/s, the enhancement of 55.6%, 75.5% and 128.2% were achieved for critical flux while 65.8%, 69.7% and 95.1% were achieved for limiting flux, respectively. The results also indicated that the use of gas sparging was an effective method in reducing reversible fouling and external irreversible fouling but internal irreversible fouling. In addition, the CFV and gas sparging did not affect pH, total soluble solid, colour, total phenolic content and DPPH free radical scavenging activity of clarified juice. Although, L-ascorbic acid and total vitamin C were significantly decreased when the higher CFV and higher gas injection factor were applied, the use of gas sparging at lower CFV was beneficial for flux enhancement while most of the quality of the clarified juice was preserved.

4.2 Introduction

Thailand is one of the world's leader producers of pineapple. During the last two decades, pineapple production in Thailand stood at approximately 2 million tons, annually (Anupunt, et al., 2000). The pineapple juices, major product from pineapple are in the form of the concentrate and pasteurized juice products. Conventionally, both products are produced by heat treatment process leading to the loss of flavor and nutritional value such as vitamin C and phenolic compounds. Microfiltration is one of the alternative methods for pineapple juice production to avoid the heat- treatment degradation effects. This process separates the juice into two fractions i.e. fibrous concentrate pulp and clarified juice, free of spoilage microorganisms. It is a simple process to produce a large amount of juice and avoid the loss of phytochemical compounds (Koroknai et al., 2008). In addition, it can be potentially combined clarification and sterilization in one single continuous operation.

However, the process performance of microfiltration is limited by membrane fouling which results in flux decline. There are several techniques to enhance the permeate flux or reduce the fouling such as backpulsing, gas sparging and critical flux etc. The critical flux method seems to be one of the most used approaches to overcome fouling problem (Sotler and Chianese, 2006). The critical flux was first introduced by Field et al., (1995). They defined that the critical flux is "a flux below which a declined of flux of time does not occur; above it fouling is observed". At the critical flux the drag forces on the particles and solute molecules over the membrane surface are equal to the dispersive forces. Thus, it is possible to control and maintain the constant flux when starting–up the process at a low permeate flux. Under this condition, no stagnant cake layer was observed (Sotler and Chianese, 2006). However, microfiltration operation below the critical flux is not favorable since large membrane areas would be necessary and this subsequently results in higher investment cost (Field et al., 1995). Because of this limitation, the techniques that can be employed to enhance the critical flux are critical need. The critical flux, in fact is influenced by several factors such as hydrodynamic condition (e.g. CFV) feed properties (e.g. particle size and concentration) etc. These factors are related to the rate of accumulation and removal of solutes or particles on the membrane surface.

Increasing in CFV (enhance mass transfer) lead to an increase in critical flux. In milk component suspension, the critical flux is influenced by modification of feed properties (e.g. adjusting pH or ionic strength) (Youravong *et al.*, 2003). However, modification of pH or ionic strength techniques does not applicable to some products (e.g. fruit juice).

Alternatively, gas sparging is a technique that can be employed to reduce concentration polarization during microfiltration. The gas is introduced into the membrane module to promote the local mixing near the membrane surface. The gas-liquid or two-phase flows systems, the mixture can adopt various dynamic structure known as flow patterns, corresponding to the gas injection factor (ε). The ε is the ratio of the superficial gas flow velocity (U_g) to the sum of superficial gas velocity (U_g) and superficial liquid flow velocity (U_l). The superficial velocity is defined as the velocity if only gas or liquid is in the pipe. The dual flow pattern changes from bubble flow ($0 < \varepsilon < 0.2$), over slug flow ($0.2 < \varepsilon < 0.9$) to annular flow ($0.9 < \varepsilon < 1.0$) (Psoch and Schiewer, 2006). It is generally believed that the slug flow pattern is the most suitable regime to enhance membrane filtration process (Cabussaud *et al.*, 2001; Li *et al.*, 2008). Chiu and James (2006) studied the effects of various superficial gas and liquid velocities and the use of different nozzles. The results showed that two-phase flow with the injection factor of 0.63 can produce a critical flux of up to 1.7 times greater than that of the single-phase flow. It was also found that increasing superficial gas and liquid velocities lead to an increase in the critical flux. Cabussaud *et al.*, (2001) investigated the effect of tangential (gas-liquid) two-phase flow in hollow fiber modules contributed to the formation of a solid layer (from retained bentonite particles) by varying the wall shear stress. They found that flux enhancement was due to mixing and turbulence created by gas bubble and linked to cake porosity and resistance. Bellara *et al.*, (1996) studied the effect of gas-liquid two-phase flow on the permeate flux and membrane sieving coefficient. The result showed that the use of gas sparging led to a reduction of membrane sieving coefficient. These observed effects agreed with Cui *et al.*, (2003). With increasing permeate flux, the observed membrane rejection is also increased for partially retentive membrane when gas bubble are introduced. Li *et at.* (2008) employed gas sparging to enhance permeate flux during separation of protease using ultrafiltration.

They found that the permeate flux did not remarkable increase and the protease activity reduced when the gas sparging was employed.

A few researchers have investigated the effect of gas sparging on the permeated flux and fouling using various types of feed but fruit juice. This work was aimed to study the effect of CFV and gas sparging on flux (critical flux and limiting flux) enhancement and fouling during microfiltration of pineapple juice. In addition, their effects on physical and phytochemical properties of clarified juice were also studied. It was hope that the obtained information and knowledge will be helpful for the pineapple juice industry.

4.3 Materials and Methods

4.3.1 Preparation of pineapple juice

Fresh pineapples (*Ananus Comosus L. Merr.*) were cleaned by tap water. After the shells were peeled by a stainless steel knife, the fresh pineapples were chopped into pieces of about 1 cm^3. The juice was extracted by a hydraulic press. The total soluble solid and pH values of the obtained juice were in the range of 12.2-14.2 °Brix and 3.5-4.0 respectively. The fresh pineapple juice was stored at 4 °C before use. The pineapple juice was pre-treated with 0.03 % (V/V) of commercial pectinese (Pectinex® ultra SP-L),(PA(EN)) at room temperature (25±3°C) for 60 min before being introduced to microfiltration system (Carnero *et al.*, 2002).

4.3.2 Microflitration system

The membrane system used was a 0.2 μm polysulfone hollow fiber module (Amersham Biosciences, UK) with a fiber diameter and length of 1 mm. and 30 cm. respectively. The effective membrane area was 0.011 m^2. The membrane system consisted of a 8 liter stainless steel jacket-feed tank, variable-feed pump (Leeson, USA) and transducers (MBS 3000, Danfoss, Denmark) for pressure measurement of the feed, retentate and permeate measurement. The temperature of the feed was controlled by circulating cooling water through a jacket-feed tank. The

CFV and transmembrane pressure (TMP) were controlled using needle permeate valve and variable speed-feed pump. The digital balance (GF-3000, A&D, Japan), connecting the computer was used to measure the permeate flux.

4.3.3 Critical flux determination

In studying of the effect of CFV, gas sparging on the critical flux, limiting flux and the quality of clarified juice, the experiments were carried out under total recycle mode and batch concentration mode respectively. The critical flux and limiting flux were investigated by a "step by step" technique (Chui and James, 2005). The initial TMP was 0.1 bar and TMP was increased at fixed interval of 0.05 bar in time step of 30 min prior to the onset of non-linearity in the increase of permeate flux, which was the indicative of critical flux, thereafter time steps of 20 min were used. Figure 25 shows an example of critical flux detection. The critical flux is the flux that the point where the deviation from the straight line starts and the limiting flux is the flux that it was independent on the pressure. The critical flux at various CFV (1.5-3.4 m/s) was determined.
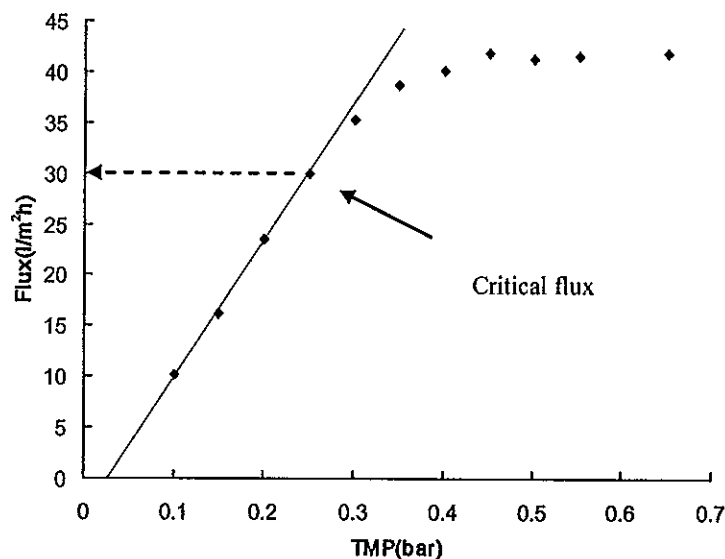
Figure 25. Detection of critical flux by a 'step by step' method in total recycle mode at CFV of 2.0 m/s

4.3.4 Gas sparging during microfiltration

The compressed nitrogen gas was injected into the inlet of feed pipe through a Y tube tubular piece. The CFV was varied from 1.5-2.5 m/s. The gas flow rate was controlled and measured by a gas flow meter (RMB- 50D–SSV, Dwyer, USA) combined with pressure gauge (2419-2C-P, CKD, Japan). In this study, the ε (ε) applied were 0, 0.15, 0.25 and 0.35, varying from bubble flow to slug flow. The schematic set-up during microfiltration is shown in Figure 26.
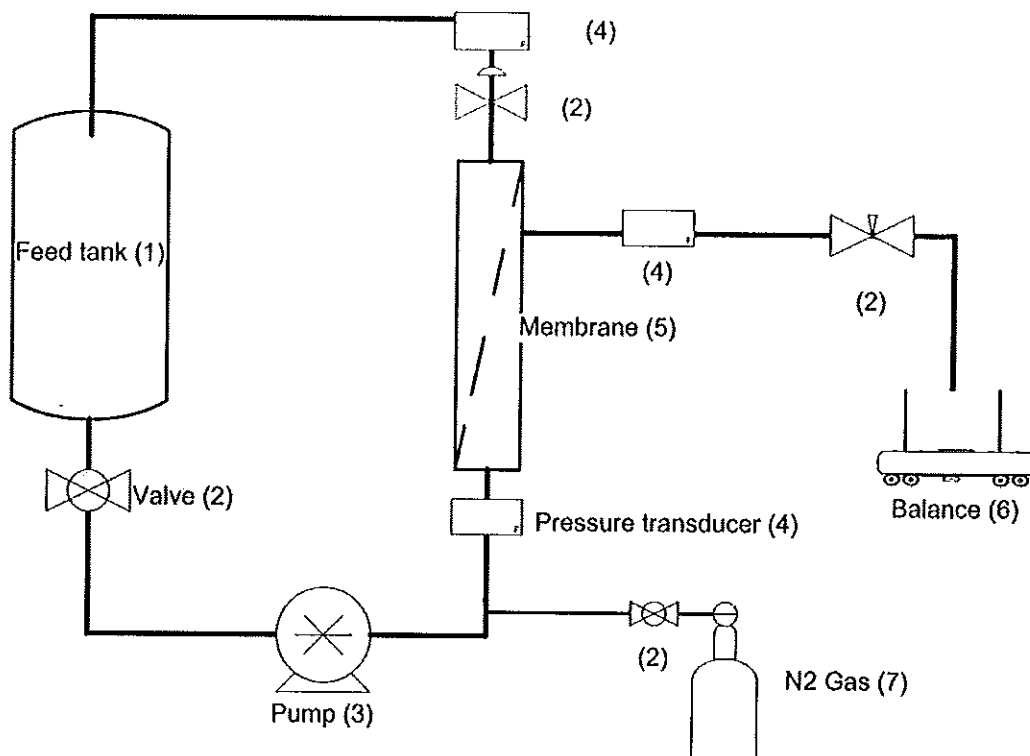
Figure 26. Schematic of the experimental set-up with gas sparging system

4.3.5 Membrane fouling and resistances analysis

The membrane filtration process can generally be described by Darcy's law as follow:

$$J = \frac{TMP}{\mu R_t} \qquad (4\text{-}1)$$

where J (m/s) is the permeation flux, TMP is the transmembrane pressure (Pa), μ (Pa s) is the viscosity of the permeate and R_t (1/m) is the total resistance to the permeate. R_t is classified by equation (4-2) as follow:

$$R_t = R_m + R_{rf} + R_{if} \qquad (4\text{-}2)$$

$$R_{if} = R_{if\text{-}in} + R_{if\text{-}ex} \qquad (4\text{-}3)$$

where, R_t is the sum of R_m (membrane resistance), R_{rf} (the resistance caused by reversible fouling) and R_{if} (the resistance caused by irreversible fouling). Furthermore, R_{if} is divided into two types, $R_{if\text{-}in}$ (the resistance caused by internal irreversible fouling) and $R_{if\text{-}ex}$ (the resistance caused by external irreversible fouling). In this study, R_{rf} was defined as the fouling which could be removed by water flushing. The residual fouling after water flushing was R_{if} and it was further cleaned by chemical cleaning. The resistance defined by equation (4-2) and (4-3) could be evaluated by measurement of water flux during cleaning process. R_m was determined by measurement of water flux of clean membrane. After filtration of pineapple juice, the water was flushed through the membrane surface to removed R_{rf} while permeate valve was closed. Water flushing was operated using clean water at CFV of 1.4 m/s and TMP of 0.3 bar for 15 min. After the first water flushing, the permeate valve was opened and water flux was measured to determined residual fouling resistance (i.e., R_m+R_{if}). Then permeate valve was closed again. A chemical cleaning was applied by circulating 0.5 N NaOH solution at 50 °C, TMP 0.3 bar and CFV of 1.4 ms^{-1} for 40 min to remove external irreversible fouling. After that the chemical cleaning solution was removed by water flushing. Then the water flux was measured to evaluate

residual resistance (i.e. $R_m + R_{if-in}$). After that the R_{if-in} was removed by circulating 50 ppm. of NaOCl at 50 °C, TMP of 0.3 bar and CFV of 1.4 m/s for at least 40 min. With R_t obtained after filtration of pineapple juice, use of equation (4-1) and the results from cleaning procedure combining with equation (4-2) and (4-3) all types of resistances could be worked out.

After each run, the system was cleaned by flushing with cleaned water follow with 0.5 N NaOH at 50 °C for 1 h. The rig was then rinsed with cleaned water until the pH return to 7. The permeate water flux was measured after every cleaning operations.

4.3.6 Pineapple juice analyses

Total soluble solid was measured by hand-refractometor (Atago, JAPAN). The pH was measured by a pH meter (PB-20, Sartorius, Germany) and the colour was measured by a colorimeter (Colour Quest XT, Hunter lab, USA). The particle size distribution was detected by a Laser Particle Size Analyzer (LS230, Beckman Coulter, USA).

L-ascorbic and dehydroascorbic acid was determined by high performance liquid chromatography (HPLC). The method was based on that of Zapata and Dupour (1992) with some modifications.

Free radical scavenging activity on 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay was determined according to the method of Singh el al., (2002). The results were expressed as milligrams of L-ascorbic acid equivalent per 100 ml pineapple juice (mg AAE/100ml). L-ascorbic acid was used as antioxidant standard reference compound.

Total phenolic content was determined by spectrophotometric determination using Folin-Ciocalteu's phenol reagent (Kim et al., 2002). Total phenol content was expressed as milligram gallic acid equivalents per100 ml pineapple juice (mg GAE/100ml).

The oxygen radical absorbance capacity (ORAC) was carried out on a FLUO star Galaxy plate reader (Fluostar optima software user manual, BMG Labtech, Germany) by using modified method of Wu et al., (2004) The oxygen radical

absorbance capacity (ORAC) was expressed as micromole Trolox equivalent (μmol TE/100 ml).

Obtained data were subjected to analysis of variance (ANOVA) and mean comparison were carried out using Duncan's Multiple Range Test (DMRT).

4.4 Results and discussion

The particle size distribution of enzymatic pineapple juice is shown in Figure 27. The particle size diameter was in the range of 0.04 to 1000 μm. The mean particle size diameter of pineapple juice was about 58 μm. Since the microfiltration with pore size of 0.2 μm was employed, most of the particle size lager than 0.2 μm was expected to be removed.
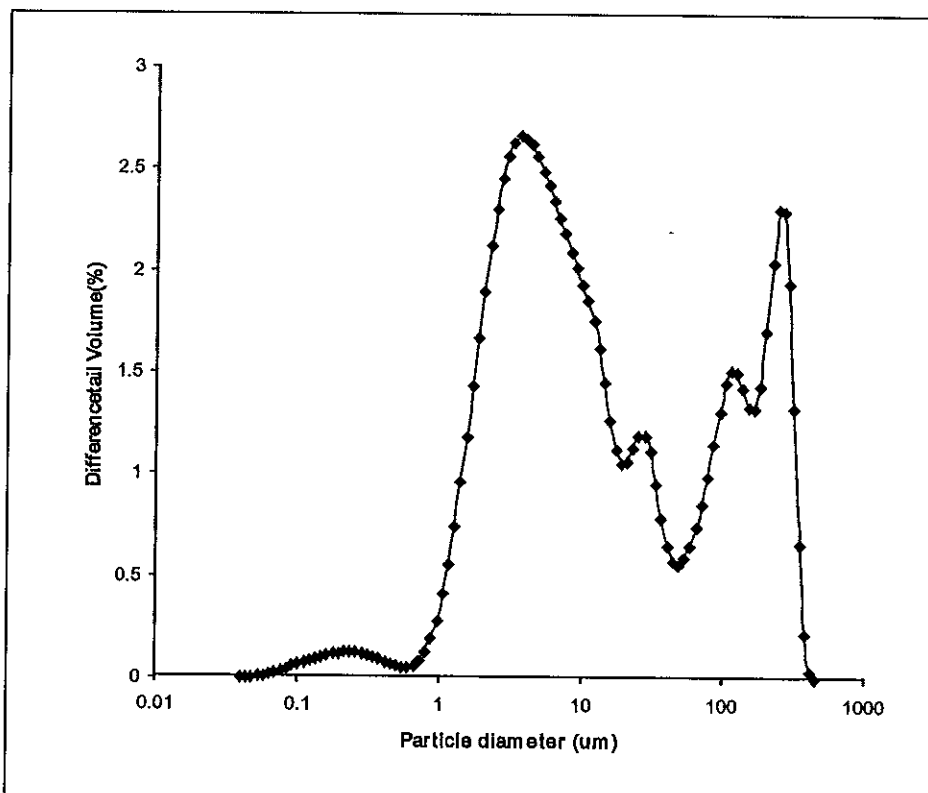
Figure 27.   Particle size distribution in enzyme treated pineapple juice

4.4.1 Effect of CFV on critical flux and limiting flux

Figure 28. shows the critical flux and limiting flux at various CFV (1.5 to 3.4 m/s) without gas sparging ($\varepsilon = 0$). The result showed that the critical flux and limiting flux presented linear relation to CFV. The critical flux and limiting flux increased from 25.4 to 40.2 l/m^2h and 36.4 to 56.5 l/m^2h while the CFV increased from 1.5 to 3.4 m/s. A similar trend is reported by the others studies (Li *et al.*, 2008; Cui *et al.*, 2003; Cheng *et al.*, 1998). The reason was due to the fact that an increase in CFV would enhance the wall shear stress on the membrane surface. Higher wall shear stress was helpful to reduce concentration polarization and increase the rate of particle removal on the membrane surface, leading to an improvement of both critical flux and limiting flux.
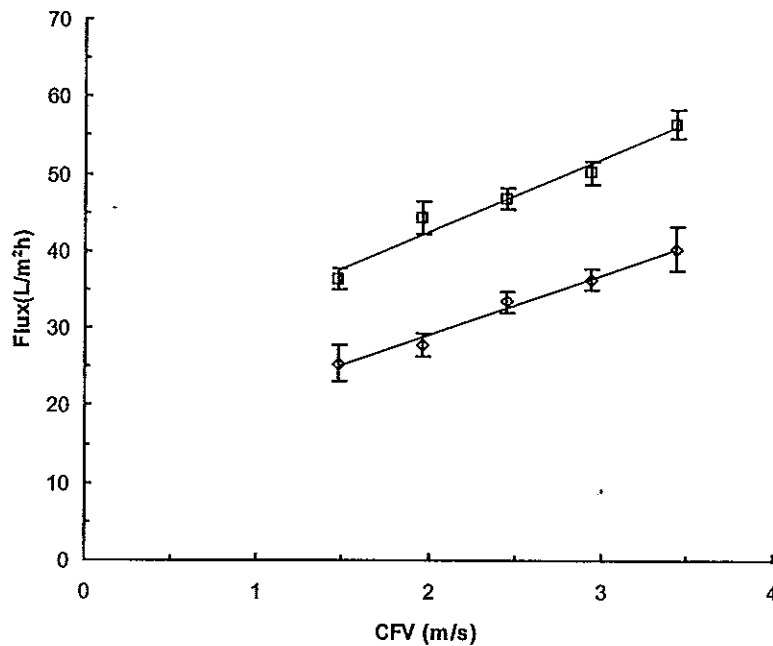
Figure 28. Effect of CFV on critical flux (◇) and limiting flux (□) during microfiltration of pineapple juice without gas sparging.

4.4.2 Effect of gas sparging and CFV on critical flux and limiting flux

The CFV of 1.5, 2.0 and 2.5 m/s were selected for studying the effect of gas sparging during microfiltration of pineapple juice with total recycle mode. The ε of 0.15, 0.25 and 0.35, indicating that the gas–liquid two phase flow patterns varied from bubble flow to slug flow were applied. Table17. shows the results of critical flux, limiting flux and flux enhancement (%) as varying CFV and ε. In general, the critical flux and limiting flux increased with an increasing of ε. The reason could be due to the present of bubble-induced secondary flows, playing an important role in promoting local mixing in the bubble wake that minimize the accumulation of the solutes and molecules on the membrane surface leading to a delay in particle deposition and a higher critical flux (Cui and Wright, 1996). Therefore, gas sparging could reduce fouling during membrane filtration process. The results were in accordance with previous studies (Li *et al.*, 2008; Chui and James, 2006; Cheng *et al.*, 1998; Cui and Wright, 1996). The permeate flux improvement (%) of critical flux and limiting flux during clarified pineapple juice at constant CFV of 1.5 m/s were 55.6, 75.5, 128.2 and 65.8, 69.7 and 95.1 with the ε of 0.15, 0.25 and 0.35 respectively. The improvement (%) at CFV of 2.0 and 2.5 m/s were in the range of 43.4-86.5% and 36.0- 86.3% for critical flux and limiting flux respectively, lower than those at CFV of 1.5 m/s (with the same level of ε). This result was probably due to at low liquid flows the bubbling is more random and increased liquid flow favors enhancement by improving the distribution of the bubble over the membrane surface. The result was in agreement with the study of Glosh, (2006) and Cui and Wright, (1996). They were observed that bubbling was most effective at low liquid flow. This indicates that gas sparged microfiltration could be a cost-effective operation from the energy consumption.

Table 17. Critical flux, limiting flux and % improvement during microfiltration with and without gas sparging

CFV (m/s)	ε	Critical flux (l/m^2h)	Limiting flux (l/m^2h)	% improvement $((J_{gas}-J_{nogas})/J_{nogas})*100$ Critical flux	Limiting flux
1.5	0	25.4±1.2	35.7±2.0		
	0.15	39.5±1.5	59.2±1.4	55.6	65.8
	0.25	44.5±1.9	60.6±2.1	75.5	69.7
	0.35	57.9±2.3	69.7±1.8	128.2	95.1
2.0	0	28.9±0.9	44.3±1.6		
	0.15	41.3±2.6	61.3±1.5	43.4	43.3
	0.25	52.7±1.7	66.1±2.4	82.9	82.7
	0.35	53.7±2.3	68.1±1.4	86.5	86.3
2.5	0	33.4±1.2	46.8±2.3		
	0.15	46.5±2.0	63.6±2.3	39.2	36.0
	0.25	45.8±1.5	65.4±3.0	37.0	39.7
	0.35	46.4±1.4	66.4±2.8	38.8	41.8

The result also showed that the higher of ε led to obtain the higher flux improvement (Table17). The slug flow pattern (ε=0.25 and 0.35) gave higher flux improvement (%) than the bubble flow pattern (ε=0.15). The mechanisms for the flux enhancement due to bubble flow and slug flow were explained as followed: (i) the bubble flow where the small gas bubble are dispersed in the liquid phase, increase the mean fluid velocity leading to higher Reynolds number hence discourage fouling; (ii) the slug flow is characterized by the presence gas slugs. These gas slugs may increase in the wall shear stress, promoting mass transfer (Chiu and James, 2006)

At the CFV of 1.5 m/s, the critical and limiting flux was effectively increased as the ε increased. However, at CFV of 2.5 m/s, the permeate flux improvement (%) did not remarkable increased when the ε was applied. It was

possible that the at high CFV and ε, the effective membrane area seem to be decreased due to the replacment liquid mass by bubble contacting to membrane surface (Mi-Jung *et al.*, 2001)

4.4.3 Effect of gas sparging on the quality of clarified pineapple juice

The physical, chemical and phytochemical properties of clarified pineapple juice samples, taken at the limiting flux operating condition, were analyzed. The effects of CFV as varying ε on the pH, total soluble solid and colour are shown in Table 18. The total soluble solid and pH ranged from13.5 to13.7 °Brix, and 3.5 to 3.7, respectively. The colour of the clarified juice as indicated by the value of L* ,b* and a* was not much varied. Therefore, it was cleared that the CFV and gas sparging did not significantly affect the total soluble solid, pH and colour of clarified pineapple juice. The result was in agreement with Rai *et al.*, (2007) that the operating pressure and stirring speed did not affected pH, citric acid and total soluble solid of clarified mosambi juice. However, they did not investigate the effect of gas sparging on product quality.

Table 18. Total soluble solid, pH and colour of clarified pineapple juice during microfiltration

CFV (m/s)	ε	Total soluble solid(°Brix)*	pH*	Color*		
				L*	a*	b*
1.5	0	13.7±0.12	3.67±0.04	99.71±0.13	-1.48±0.08	6.22±0.38
	0.15	13.62±0.15	3.63±0.03	99.63±0.07	-1.52±0.06	6.49±0.34
	0.25	13.6±0.10	3.56±0.03	99.58±0.06	-1.51±0.06	6.45±0.07
	0.35	13.5±0.10	3.56±0.03	99.55±0.11	-1.51±0.03	6.33±0.01
2.0	0	13.6±0.20	3.55±0.05	99.62±0.16	-1.53±0.08	6.42±0.07
	0.15	13.63±0.15	3.58±0.07	99.65±0.10	-1.49±0.05	6.11±0.58
	0.25	13.6±0.10	3.59±0.05	99.68±0.06	-1.48±0.04	6.06±0.52
	0.35	13.53±0.05	3.59±0.11	99.55±0.40	-1.49±0.05	6.12±0.49
2.5	0	13.50±0.15	3.62±0.05	99.67±0.06	-1.48±0.05	6.23±0.69
	0.15	13.63±0.15	3.56±0.04	99.44±0.11	-1.59±0.17	6.22±0.50
	0.25	13.63±0.03	3.56±0.05	99.54±0.03	-1.55±0.16	6.05±0.59
	0.35	13.50±0.01	3.55±0.03	99.58±0.22	-1.43±0.14	6.23±0.22

* Presents no statistical difference according to Duncan's multiple range test at $P<0.05$

The effect of CFV and gas sparging on the vitamin C content including the L-ascorbic acid and dehydroascorbic acid are shown in Table 19. In general, increasing of CFV and ε at higher level led to the higher loss of L-ascorbic acid while the dehydroascorbic acid content was fluctuated. The clarified juice obtained from the operating condition with CFV of 1.5 m/s without gas sparging (ε=0) had the highest value of total vitamin C. These results indicated that the CFV had a significant effect on L-ascorbic acid reduction. However, it did not affect the dehydroascorbic acid content. The reason was probably due to that the injection of gas promoted the stir and vortex in the flow, thus enhanced the reduction of L-ascorbic acid. It is important to note that the vitamin C is a sensitive substance and easy to loss in many conditions such as light expose, high temperature and oxygen access etc (Kabasakalis *et al.*, 2000).

Table 19. L-ascorbic acid (L-AA), dehydroascorbic acid (D-HA) and total vitamin C in MF-clarified pineapple juice with various operating conditions

CFV (m/s)	ε	Vitamin C (mg/100ml Fruit juice)		
		L-AA	D-HA	Total vitamin C
1.5	0	11.23 ± 0.39^a	10.72 ± 0.27^{ab}	22.00 ± 0.54^a
	0.15	10.50 ± 0.14^b	10.64 ± 0.07^{abc}	21.15 ± 0.20^a
	0.25	9.71 ± 0.17^c	9.92 ± 0.61^{cd}	19.63 ± 0.78^b
	0.35	9.60 ± 0.23^c	9.65 ± 0.61^d	19.25 ± 0.42^b
2.0	0	10.63 ± 0.23^b	10.51 ± 0.08^{abc}	21.15 ± 0.23^a
	0.15	10.99 ± 0.50^{ab}	10.45 ± 0.20^{abc}	21.45 ± 0.40^a
	0.25	14.48 ± 0.06^b	10.84 ± 0.34^a	21.32 ± 0.36^a
	0.35	9.12 ± 0.57^{cd}	10.72 ± 0.28^{ab}	19.85 ± 0.7^b
2.5	0	10.62 ± 0.24^b	10.65 ± 0.30^{abc}	21.27 ± 0.27^a
	0.15	9.36 ± 0.08^{cd}	10.69 ± 0.52^{ab}	20.09 ± 0.45^b
	0.25	9.26 ± 0.15^{cd}	10.08 ± 0.54^{abc}	19.34 ± 0.41^b
	0.35	8.99 ± 0.47^d	10.63 ± 0.14^{abc}	19.62 ± 0.48^b

- Same letters in the same column present no statistical differences according to Duncan's multiple range test at $P<0.05$

Total phenolic content and the antioxidant capacity (DPPH free radical scavenging and ORAC assay) of clarified pineapple juice obtained from the microfiltration with various operating conditions are shown in Table 20. The results shown that the CFV and ε did not significantly affect the total phenolic content and antioxidant capacity. These results suggesting that the phenolic compounds in clarified juice could stand to the stir and vertex flow leading to maintain polyphenolic acid and antioxidant capacity. In addition, the gas used in this study was nitrogen gas which did not react with any substance.

Table 20. Total phenol and antioxidant capacity of MF-clarified pineapple with various operating conditions

CFV (m/s)	ε	Total phenol (mg/100ml as gallic acid)*	Antioxidant capacity	
			ORAC (umolTE/100fruit juice)*	DPPH (mg/100ml as ascorbic acid)*
1.5	0	66.33±2.89	323.02±6.50	25.39±0.69
	0.15	65.04±2.95	322.94±9.63	24.80±1.11
	0.25	67.04±2.55	320.86±6.59	24.60±1.12
	0.35	67.22±2.21	320.14±6.98	25.26±1.26
2.0	0	65.85±2.54	318.57±9.70	24.63±1.56
	0.15	66.62±2.25	320.56±11.21	25.38±1.30
	0.25	67.27±2.51	317.91±11.10	25.06±0.87
	0.35	66.22±3.04	319.71±9.34	25.10±1.58
2.5	0	67.10±2.70	321.19±8.37	24.51±1.00
	0.15	66.56±1.52	317.18±6.02	24.65±1.05
	0.25	66.81±2.50	319.12±7.53	24.66±1.05
	0.35	65.93±3.30	317.73±6.37	24.66±1.15

* Presents no statistical difference according to Duncan's multiple range test at $P<0.05$

4.4.4 Flux profile, fouling analysis and quality of clarified juice in batch concentration mode

Regarding the permeate flux improvement, CFV of 1.5 m/s and TMP of 0.7 were selected for further study in batch concentration mode. Figure 29 shows the flux profile in batch concentration mode performed with different ε. It was found that the permeate flux profiles declined rapidly at the beginning of the filtration followed by a gradual decrease in the later state. The reason could probably that at the initial of filtration process the fouling was occurred rapidly. The permeate flux obtained with gas sparging was always higher than under unsparged conditions. In comparison to the effect of ε, the results showed that the higher of ε led to the higher of permeate flux. At the end of the process (85% of recovery) the steady permeate

flux was improve by 38.3%, 51.9%, 74.7 % when the ε of 0.15, 0.25 and 0.35 were applied respectively. The ε of 0.35 was the most moderate condition for applied in the CFV of 1.5 m/s. It could be improved the flux higher than the other ε.
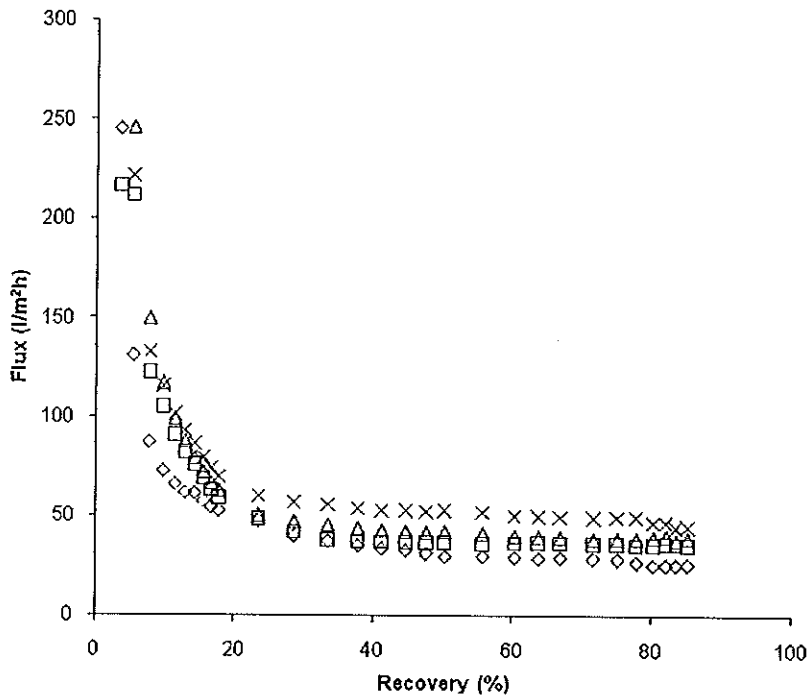
Figure 29. Effect of ε on the permeate flux under batch concentration mode with CFV of 1.5 m/s and TMP of 0.7 bar ($\diamond$, ε = 0; $\square$,ε = 0.15; $\triangle$, ε = 0.25;× ε = 0.35)

Table 21. Membrane fouling during microfiltration with batch concentration mode at various ε

ε	$R_m(\times 10^{12})$ (1/m)	$R_t(\times 10^{12})$ (1/m)	$R_{rf}(\times 10^{12})$ (1/m)	$R_{if}(\times 10^{12})$ (1/m)	$R_{if\text{-}ex}(\times 10^{12})$ (1/m)	$R_{if\text{-}in}(\times 10^{12})$ (1/m)
0	0.24 ± 0.00^{ns}	7.35 ± 0.12^a	5.04 ± 0.69^a	2.06 ± 0.26^a	1.93 ± 0.26^a	0.13 ± 0.01^{ns}
0.15	0.24 ± 0.00^{ns}	5.40 ± 0.15^b	3.64 ± 0.15^b	1.52 ± 0.01^b	1.39 ± 0.05^b	0.12 ± 0.01^{ns}
0.25	0.24 ± 0.00^{ns}	4.94 ± 0.10^c	3.42 ± 0.10^{bc}	1.28 ± 0.01^c	1.16 ± 0.05^c	0.12 ± 0.01^{ns}
0.35	0.24 ± 0.00^{ns}	4.39 ± 0.10^d	3.11 ± 0.18^c	1.00 ± 0.10^d	0.90 ± 0.10^d	0.10 ± 0.00^{ns}

Same letters in the same column present no statistical differences according to Duncan's multiple range test at P<0.05
Ns = no significant difference

The effect of gas sparging on membrane fouling during microfiltration of pineapple juice in batch concentration mode at CFV of 1.5 m/s are shown in Table 21. Generally, it can be seen that the R_t, R_{rf} and R_{if-ex} of membrane process could significantly be decreased as gas sparging increased. However, gas parging did not significantly reduce the R_{if-in}. It was likely that gas bubbling only reduced the external fouling (concentration polarization and fouling layer on the membrane surface) but internal fouling. Thus, the gas sparging was effective technique to reduced the R_{if-ex} but the R_{if-in}.

The quality of clarified pineapple juice during batch concentration mode with different ε is shown in Table 22. It was found that gas sparging did not significantly affected total phenolic content and antioxidant capacity. However the L-ascorbic acid was slightly decreased when ε of 0.35 was applied.

Table 22. L-ascorbic acid, dehydroascorbic acid, total vitamin C, total phenolic content and antioxidant capacity of MF-clarified pineapple with various ε, at CFV of 1.5 m/s

ε	Vitamin C (mg/100mlFruit juice)			Total phenol (mg/100ml as gallic acid)	Antioxidant capacity	
					DPPH (umolTE/100ml fruit juice)	ORAC (mg/100ml as ascorbic acid)
	L-AA	D-HA	Total			
0	11.11 ± 0.36^a	10.48 ± 0.10^{ns}	21.59 ± 0.47^a	66.20 ± 2.60^{ns}	25.46 ± 1.20^{ns}	320.68 ± 4.84^{ns}
0.15	10.23 ± 0.05^b	10.46 ± 0.15^{ns}	20.70 ± 0.17^{ab}	64.68 ± 3.02^{ns}	24.80 ± 1.11^{ns}	326.27 ± 7.69^{ns}
0.25	9.81 ± 0.32^{bc}	10.00 ± 0.60^{ns}	19.81 ± 0.92^{bc}	64.70 ± 2.15^{ns}	24.64 ± 0.65^{ns}	324.24 ± 6.46^{ns}
0.35	9.47 ± 0.07^c	9.73 ± 0.45^{ns}	19.20 ± 0.51^c	64.76 ± 2.54^{ns}	24.26 ± 1.63^{ns}	321.80 ± 4.68^{ns}

Same letters in the same column present no statistical differences according to Duncan's multiple range test at P<0.05
Ns = no significant difference

4.5 Conclusion

The effects of CFV and gas sparging on critical flux, limiting flux and quality of clarified pineapple juice were studied. Increasing of CFV could enhance the critical and limiting flux. The addition of gas into the membrane module led to effectively increase both critical flux and limiting flux. However, the improvement (%) of the critical flux due to gas sparging was remarkable when the lower CFV (1.5 m/s) was used. The result also indicated that the slug flow pattern appeared to give the higher improvement of both critical and limiting flux than bubble pattern. The use of gas sparging reduced the reversible fouling and external irreversible fouling but internal reversible fouling. In addition, the CFV and gas sparging did not affect the pH, total soluble solid, colour and antioxidant capacity (total phenol and DPPH) of MF-clarified juice. However, L-ascorbic acid, and total vitamin C were significantly decreased when high CFV and ε were applied. The use of gas sparging at low CFV therefore, is an effective technique for flux enhancement, fouling reduction during microfiltration of pineapple juice while most of the quality the juice was preserved.

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CHAPTER 5

COLD STERILIZATION OF COCONUT WATER USING MEMBRANE FILTRATION: EFFECT OF MEMBRANE PROPERTY AND OPERATING CONDITION

5.1 Abstract

Coconut water has been considered as a nutritional, refreshing and highly isotonic beverage with delicate aroma and flavor. In food sterilization technique, thermal processing, however tends to reduce these beneficial properties especially estrogen hormone and flavor. To overcome this limitation, this study therefore aimed to clarified and sterilized coconut water using non-thermal processing, membrane filtration. Hollow fiber microfiltration (MF) membrane with pore size of 0.1 and 0.2 µm and ultrafiltration (UF) membrane with molecular weight cut-off (MWCO) of 100 and 30 kDa were used. The effect of membrane pore size and MWCO on quality of clarified juice, permeate flux and fouling were studied. It was found that fresh coconut water and clarified coconut water obtained from MF and UF did not show difference in pH, total soluble solid, reducing sugar, estrogen hormone and minerals including calcium, magnesium, phosphorus, potassium and sodium. The results from microbiological analysis of the clarified coconut water showed that sterilized of coconut water was obtained using either MF or UF membranes. This microbiological quality of clarified coconut water was met the Thai legislation for juice and drinks. The permeate flux of MF was much higher than those of UF while the fouling resistance of UF membrane was much higher than those of MF membrane. The permeate flux of membrane with pore size of 0.1 µm was slightly lower than that of membrane with pore size of 0.2 µm. The results also indicated that the major fouling of both MF and UF membranes was reversible. The irreversible fouling resistance of 0.1 µm membrane was the lowest and most of this irreversible fouling was external irreversible fouling, formed on the membrane surface. According to these results, it could be concluded that 0.1 µm membrane was the most suitable

membrane for clarification and sterilization of coconut water. In addition, the effects of TMP, cross flow velocity (CFV) and the % recovery on permeate flux in batch concentration mode were also studied. It was found that the permeate flux of 0.1 μm membrane was significantly increased with increasing CFV and decreased as % recovery increased. These results suggested that permeate flux during MF of coconut water was dependent on reversible fouling and could be improved by using hydrodynamic modification techniques.

5.2 Introduction

Thailand is one of the biggest producers of both fresh and processed coconut water in the world. Nowadays, coconut water is becoming more widely consumed because of its beneficial health properties, naturally fat-free and low in food energy (FAO, 2007). Coconut water contains many active compounds which have different therapeutic properties. It is non-allergenic and readily accepted by the body. Coconut water contains a complex of vitamins and minerals. It is high in potassium, chloride, calcium and magnesium. It is also highly recommended as a means for oral rehydration. Athletes and sports enthusiasts use coconut water to replenish electrolytes lost in perspiration. It works ever better than some popular commercial sports drinks (Coconut Research Center, 2007). Moreover, coconut water has been successfully used as liquid in intravenous therapy in emergency situations. Furthermore, coconut water has got many medicinal properties such as estrogen hormone especially estradiol (17β-estradiol) that improves synapse formation on dendritic spines in the hippocampus of oophorectomized rats. Estrogen also may improve cerebral blood flow and glucose metabolism and it may in some way acts as an antioxidant (Monk and Brodaty, 2000). Estrogen like hormone in coconut water also has an antagonistic effect with endogenous estradiol by competing for estrogen receptor (Radenahmad et al., 2006)

The conventional process for fruit juice production involves the used of heat treatment to improve microbiological quality and extend the shelf life. However, nutritional and sensorial of the products are significantly affected. Since most of antioxidant, some nutritional components and flavor in fruit juice are not heat

tolerant therefore it is reduced significantly after heat treatment (Girard and Fukumoto, 2000). To overcome this problem the new or suitable technologies with gentle heat treatment should be employed to preserve such properties. Membrane filtration is probably an alternative method to increase the shelf life and to reserve the peculiarity of fresh fruit such as color, aroma and nutritional quality. The aim of this study was to employ membrane filtration process to sterilized and clarified coconut water. To select the best membrane pore size or MWCO, the effect of membrane pore size and MWCO on permeate flux, fouling and quality of clarified coconut water including chemical, physical and microbiological properties, minerals and estrogen hormone content were studied. In addition, the effect of CFV, TMP in total recycle mode and % recovery in batch concentration mode on permeate fluxes were also investigated.

5.3 Materials and Methods

5.3.1 Preparation of coconut water

Young coconuts of 4-5 month old fruit from local farm in Songkhla province, Thailand were used through out this study. The coconut water obtained from the open nut fruit was collected in a clean container. After that it was filtrated though a cloth sheet to remove large solid particles which may block the inlet lumen of the hollow fiber membrane before introduced to the membrane system. The total soluble solid in the coconut water obtained was in the range of 5-7 °Brix.

5.3.2 Microfiltration and ultrafiltration unit and experiment

The membrane system used was a hollow fiber module (Amersham Biosciences,UK) with a fiber diameter and length of 1 mm. and 30 cm. respectively. The membrane pore size and MWCO of the membranes were 0.1 and 0.2 μm for MF and 30 and 100 kDa for UF. The membrane system consisted of a 8 liter stainless steel jacket-feed tank, variable-fee d pump (Leeson, USA) and transducers (MBS 3000, Danfoss, Denmark) for pressure of the feed, retentate and permeate

measurement. The temperature of the feed was controlled by circulating cooling water through a jacket-feed tank. The CFV and TMP were controlled using needle permeate valve and variable speed-feed pump. The digital balance (GF-3000, A&D, Japan), connecting the computer was used to measure the permeate flux. The schematic membrane system set up is shown in Figure12.

In studying of the effect of membrane pore size and MWCO on quality of clarified juice, permeate flux and fouling, the experiments were carried out under total recycle mode (both retentate and permeate were returned to the feed tank) at constant CFV of 1.18 m/s, temperature of 20±2 °C and TMP of 0.5 (for MF) and 2.0 bar (for UF). The effect of TMP (0.05-1.0 bar) and CFV (1.6-2.5 m/s) on permeate flux in total recycle mode were studied using the best membrane pore size or MWCO obtained from the previous experiment. The optimum condition obtained was then employed for clarification and sterilization of coconut water under batch concentration (retentate was returned to the feed tank). Note that % recovery was defined as the percentage of permeate volume to initial feed volume.

5.3.3 Fouling resistance analysis

The membrane filtration process can generally be described by Darcy's law as follow:

$$J = \frac{TMP}{\mu R_t}$$

(5-1)

where J (m/s) is the permeation flux, TMP is the transmembrane pressure (kPa), μ (Pa.s) is the viscosity of the permeate and R_t (1/m) is the total resistance to the permeate. R_t could be classified by equation (5-2) as follow:

$$R_t = R_m + R_{rf} + R_{if}$$

(5-2)

$$R_{if} = R_{if-in} + R_{if-ex}$$

(5-3)

In equation (5-2), R_t is the sum of R_m (membrane resistance), R_{rf} (the resistance caused by reversible fouling) and R_{if} (the resistance caused by irreversible fouling). Furthermore, R_{if} could be divided into two types, resistance caused by internal irreversible fouling (R_{if-in}) and external irreversible fouling (R_{if-ex}) (equation (5-3)). In this study, reversible fouling was defined as the fouling which could be removed by only water flushing. The residual fouling after water flushing was irreversible fouling and it was further cleaned by chemical cleaning. The resistance defined by equation (5-2) and (5-3) could be evaluated by measurement of water flux during cleaning process which is a cleaning in place method (CIP). R_m was determined by measurement of water flux of clean membrane. After filtration of coconut water, the water was flushed through the membrane surface to removed reversible fouling while permeate valve was closed. Water flushing was operated using clean water at CFV of 1.35 m/s and TMP of 0.3 bar for 15 min. After the first water flushing, the permeate valve was opened and water flux was measured to determined residual fouling resistance (i.e., R_m+R_{if}). Then permeate valve was closed again. A chemical cleaning was applied by circulating 0.5 N NaOH solution at 50 °C, TMP 0.3 bar and CFV 1.35 m/s for 40 min to remove external irreversible fouling. After that the chemical cleaning solution was removed by water flushing. Then the water flux was measured to evaluated residual resistance (i.e. R_m+R_{if-in}). After that the internal irreversible fouling was removed by circulating 50 ppm. of NaOCl at 50 °C, TMP 0.3 bar and CFV 1.35 m/s for at least 40 min while the permeate valve open. With R_t obtained after filtration of coconut water and using from equation (5-1) and the results from cleaning procedure combining with equation (5-2) and (5-3), all types of resistances could be worked out.

5.3.4 Fresh and clarified coconut water analysis

Samples of fresh coconut water (feed) and clarified coconut water from both MF and UF operation were collected for further analysis. The pH and total soluble solid were analyzed by using pH meter (PP15, Sartorius, Germany) and hand refractometer (2311, Atago, Japan) respectively. The acidity (expressed as citric acid equivalent) was analyzed by titration method (titration of 10 ml of sample with 0.1 N

NaOH to an endpoint at pH 8.1). The total sugar and reducing sugar were determined by the method of AOAC, (2000). The color was measured by colorimeter (Color Quest XT, Hunter lab, USA). The viscosity was measured at 20 °C with u-tube capillary viscometer (Kapillarviskosimeter 50904, Schott, Germany). Protein content was determined by Lowry method (Lowry *et al.*, 1951). Microbiological analysis, the sample was performed by the methodology described in Bacteriological Analytical Manual (2002). The content of estradiol (estrogen hormone) was analyzed using CELIA method (electro generated chemiluminescence immuno assay). The minerals content including sodium, calcium, magnesium, phosphorus and potassium were determined by using the inductively coupled plasma - optical emission spectrometer (ICP-OES).

5.4 Results and discussion

5.4.1 Chemical and physical properties of fresh and clarified coconut water

Properties of fresh coconut water and clarified coconut water using various membranes are shown in Table 23. The chemical and physical properties of clarified coconut water did not show difference in pH, total soluble solid, reducing sugar and density comparing to fresh coconut water. The viscosity of clarified coconut water was lower than that of fresh coconut water. However, the total solid and total sugars were slightly decreased as membrane pore size and MWCO decreased. It was also found that the highest of luminosity (L*- value) of fresh coconut water was observed followed by MF-clarified coconut water and UF-clarified coconut water, indicating that clearer and brighter coconut water was obtained after membrane filtration. Protein content in fresh coconut water was 1.069±0.032 mg /100 ml. The protein content in clarified coconut water using 0.2 μm membrane showed no significant difference compared to that in fresh coconut water. The membrane having a larger pore size or MWCO tend to give the higher protein content or lower protein rejection. It is also important to note that this protein rejection characteristic probably involved in fouling behavior.

Table 23. Chemical and physical properties of coconut water before and after membrane filtration with various membranes pore size and MWCO

Properties	Fresh Coconut water	Clarified from 0.2μm	Clarified from 0.1 μm	Clarified from100 kDa	Clarified from 30 kDa
Total solid (%)	9.32 ± 0.06^a	7.17 ± 0.07^b	7.20 ± 0.07^b	6.50 ± 0.20^c	6.87 ± 0.14^d
Total sugar (%)	6.03 ± 0.15^a	5.48 ± 0.22^b	5.29 ± 0.21^{bc}	4.17 ± 0.22^c	5.09 ± 0.13^d
Reducing sugar (%)	4.37 ± 0.48^{ns}	4.39 ± 0.39^{ns}	4.17 ± 0.22^{ns}	4.04 ± 0.14^{ns}	4.12 ± 0.09^{ns}
Total soluble solid (°Brix)	6.83 ± 0.15^{ns}	6.80 ± 0.1^{ns}	6.9 ± 0.1^{ns}	6.9 ± 0.1^{ns}	6.83 ± 0.05^{ns}
pH	5.30 ± 0.15^{ns}	5.35 ± 0.13^{ns}	5.41 ± 0.16^{ns}	5.29 ± 0.01^{ns}	5.19 ± 0.04^{ns}
Acidity (% as citric acid)	0.053 ± 0.005^a	0.051 ± 0.001^{ab}	0.047 ± 0.002^b	0.049 ± 0.0002^{ab}	0.049 ± 0.001^{ab}
Viscosity (mPa.S)	1.19 ± 0.001^a	1.14 ± 0.000^b	1.14 ± 0.000^b	1.14 ± 0.000^b	1.13 ± 0.000^b
Density (Kg/m^3)	993.1 ± 8.6^{ns}	1001.3 ± 5.13^{ns}	999.2 ± 9.6^{ns}	994.3 ± 7.85^{ns}	1003.5 ± 4.44^{ns}
Color					
L*	99.90 ± 0.09^b	99.94 ± 0.21^a	99.92 ± 0.08^a	99.96 ± 0.13^a	99.97 ± 0.05^a
a*	-0.19 ± 0.06^{ns}	-0.18 ± 0.04^{ns}	-0.06 ± 0.24^{ns}	-0.06 ± 0.24^{ns}	0.203 ± 0.10^{ns}
b*	0.74 ± 0.06^a	0.11 ± 0.07^b	0.096 ± 0.005^b	-0.15 ± 0.08^d	-0.02 ± 0.05^c
Protein (mg/100 ml)	1.069 ± 0.032^a	0.707 ± 0.269^a	0.544 ± 0.013^b	0.386 ± 0.052^{bc}	0.149 ± 0.019^c

Same letters in the same row present no statistical differences according to Duncan's multiple range test at P<0.05

5.4.2 Mineral and estrogen hormone content in fresh and clarified coconut water

One of the primary aims of this study was to investigate the effect of membrane pore size an MWCO on clarified coconut water quality. Estrogen hormone and minerals are important components in coconut water. Table 24 shows the estradiol (estrogen hormone) and minerals content including calcium, magnesium, phosphorus, potassium and sodium in coconut water before and after membrane

filtration. The results show that there were no significant difference in the content of mineral and estrogen hormone between fresh and clarified coconut water. The result indicated that minerals and estrogen hormone could be preserved or recovered with membrane filtration process. The reason is probably due to the fact that estrogen hormone and minerals have low molecular weight (MW= 272.39 for estrogen (Zhu *et al.*, 2009)). Therefore, it was freely passed through membranes.

Table 24. Estrogen hormone (estradiol) and minerals content in fresh and clarified coconut water with various membranes

Properties	Fresh Coconut water	Clarified from 0.2 μm	Clarified from 0.1 μm	Clarified from 100 kDa	Clarified from 30 kDa
Estradiol (pg/ml)	30.55 ± 1.88^{ns}	27.46 ± 1.27^{ns}	29.15 ± 2.49^{ns}	28.78 ± 2.66^{ns}	27.90 ± 0.87^{ns}
Minerals					
Phosphorus (mg/l)	66.20 ± 7.88^{ab}	57.62 ± 1.50^{a}	57.77 ± 5.68^{a}	67.50 ± 2.19^{b}	68.38 ± 4.30^{ab}
Potassium (g/l)	1.15 ± 0.01^{ns}	0.98 ± 0.17^{ns}	1.03 ± 0.05^{ns}	1.15 ± 0.01^{ns}	1.13 ± 0.02^{ns}
Calcium (g/l)	0.143 ± 0.020^{ns}	0.123 ± 0.03^{ns}	0.123 ± 0.02^{ns}	0.143 ± 0.02^{ns}	0.140 ± 0.02^{ns}
Magnesium(g/l)	64.86 ± 4.93^{ns}	57.93 ± 12.0^{ns}	57.26 ± 3.55^{ns}	64.46 ± 7.34^{ns}	63.40 ± 6.77^{ns}
Sodium (g/l)	38.66 ± 4.50^{ns}	37.60 ± 2.95^{ns}	38.26 ± 4.27^{ns}	36.86 ± 7.00^{ns}	46.73 ± 6.01^{ns}

Same letters in the same row present no statistical differences according to Duncan's multiple range test at $P<0.05$

5.4.3 Microbiological quality of fresh and clarified coconut water.

The microbiological quality of coconut water before and after membrane filtration is presented in Table 25. It was found that no yeast, mould and *E. Coli* found in fresh coconut water. Total variable count of fresh coconut water was relatively low (77 CFU/ml) and it was completely removed by MF and UF. The microbiological quality was met to the Thai legislation for juice and drinks. These results indicated that membrane filtration could be employed for sterilization of coconut water.

Table 25. Microbiological quality of fresh and clarified coconut water obtained from various membrane pore size and MWCO

Microbiology	Fresh coconut water	Clarified from 0.2μm	Clarified from 0.1 μm	Clarified from 100 kDa	Clarified from 30 kDa
Total plate count (CFU/ml)	77±27	<25	<25	<25	<25
Yeast and mould (CFU/ml)	<15	<15	<15	<15	<15
E.Coli(MPN/ml)	<3	<3	<3	<3	<3

Same letters in the same row present no statistical differences according to Duncan's multiple range test at P<0.05

5.4.4 Permeate flux and membrane fouling

Effect of membrane pore size and MWCO

The permeate flux during MF and UF of coconut water in total recycle mode was shown in Figure 30. The permeate flux of four membranes rapidly declined in the initial state of filtration. The higher initial permeate flux was observed from the larger pore size (for MF) or higher MWCO (for UF) membranes. For MF process, although the initial permeate flux of 0.2 μm membrane was higher than that of 0.1 μm membrane (at TMP 0.5 bar) but it was more rapidly declined compared to that of 0.1 μm membrane. The steady permeate fluxes of 0.2 and 0.1 μm membranes were reached after filtration time of 1 hour at about 199 and 190 l/m²h respectively. In UF process, the initial permeate flux of 100 kDa was higher than that of 30 kDa (at TMP 2.0 bar). The permeate flux of 100 kDa membrane declined to the steady state after the filtration time about 1 hour (at 45 l/m²h) while steady state flux of 30 kDa membrane was reached after filtration time about 30 minutes (at 32 l/m²h). The declined of permeate flux could be due to fouling and concentration polarization. The major fouling materials during MF and UF of coconut water would be the suspended solid, fat, protein and other small molecules. Membrane fouling during MF and UF

could be formed on the top of membrane surface and /or inside the membrane pore (Youravong *et al.*, 2005). The difference in the rate of flux decline and filtration time to reach steady flux suggested the effect of membrane pore size or MWCO on membrane fouling and possibly fouling mechanism.
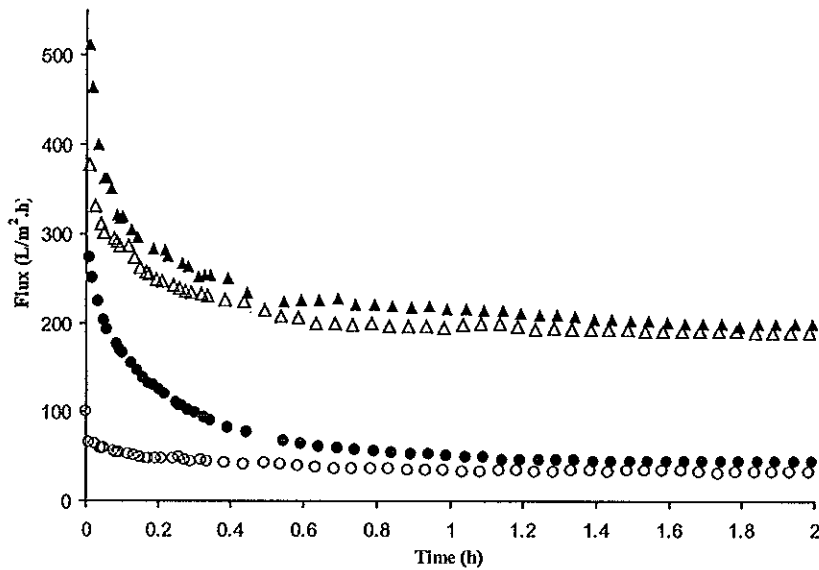
Figure 30. Permeate flux during membrane filtration of coconut water (▲, 0.2 μm, △ 0.1 μm, ●100 kDa, ○ 30 kDa) at CFV = 1.18 m/s, temperature = 20±2 °C, TMP = 0.5 bar for MF and TMP = 2.0 bar for UF

Table 26 shows the R_m, R_t, R_{rf} and R_{if} that was divided to two types i.e. $R_{if\text{-}in}$ and $R_{if\text{-}ex}$. R_t of 0.2 μm, 0.1 μm, 100 kDa and 30 kDa membrane were 7.89×10^{11}, 8.36×10^{11}, 142.43×10^{11} and 191.59×10^{11} 1/m respectively. It could be observed that the R_t of MF membrane were lower than those of UF membrane and about 40-60% of R_t of both MF and UF membranes was contributed by R_{rf}. The reason could be due to the different in R_m and operating TMP during membrane filtration process (0.5 bar for MF and 2 bar for UF) which induced the R_{rf} and compression of gel layer on the membrane surface (Youn *et al.*, 2004). For irreversible fouling, the R_{if} of MF membrane was much lower than that of UF membrane and most of R_{if} of both MF and UF membranes was contributed by $R_{if\text{-}ex}$. In addition, the $R_{if\text{-}ex}$ of 0.2 μm membrane

was much higher than that of 0.1 µm membrane while the R_{if-ex} of 100 kDa membrane was much lower than that of 30 kDa membrane. The R_{if-in} of UF membrane was higher than those of MF membrane. The R_{if-in} of 0.1 and 0.2 µm membranes did not significantly different. For UF, the R_{if-in} of 30 kDa membrane was about 4 times higher than that of 100 kDa membrane. These results suggested that both suspended solid and protein was possibly responsible for internal fouling of the MF membrane while protein and other small molecules played an important role in internal fouling of UF membrane.

Table 26. Permeate resistances during membrane filtration of coconut water

Membrane	$R_m(\times10^{11})$ 1/m	$R_t(\times10^{11})$ 1/m	$R_{rf}(\times10^{11})$ 1/m	$R_{if}(\times10^{11})$ 1/m	$R_{if-ex}(\times10^{11})$ 1/m	$R_{if-in}(\times10^{11})$ 1/m
0.2 µm	0.69	7.98	4.82	2.25	2.35	0.11
0.1 µm	2.38	8.36	4.9	1.08	0.83	0.15
100 kDa	13.0	142.32	122.77	6.05	5.65	0.4
30 kDa	48.0	191.59	95.8	44.84	43.14	1.70

From these results, 0.2 µm membrane gave the highest permeate flux followed by 0.1 µm, 100 kDa and 30 kDa membranes respectively. However, the irreversible fouling resistance of 0.1 µm membrane was the lowest. In addition, the quality of clarified coconut water obtained from both MF and UF membrane did not significantly different. According to these results, 0.1 µm membrane was considered to be the most suitable membrane for sterilization of coconut water.

5.4.5 Effect of TMP and CFV on permeate flux

MF with 0.1 µm membrane was used for studying on the effect of TMP and CFV during membrane filtration in total recycle mode. Figure 31. shows the effect of TMP on steady flux at constant CFV of 2.5 m/s. It was found that the pressure dependent region was obtained at TMP below 0.65 bar, giving the limiting

flux of about 178 l/m²h. Further increase in TMP higher than 0.65 bar didn't result in continuously increased in permeate flux and sever fouling at this pressure independent region was expected (Youn *et al.*, 2004). To avoid the sever fouling in this case, operating at TMP below 0.65 bar (at CFV 2.5 m/s) was suggested. Figure 32 shows the steady permeate flux at difference CFV using TMP at 0.65 bar. The result showed that the permeate flux significantly increased as CFV increased. Similar explanation for this phenomenon has been given. At high CFV, the rate of removal of retained material by high shear force is high and would reduce reversible fouling and enhance the mass transfer rate that benefits permeate flux (Wu *et al.*, 1999; Jiraratananon and Chanachai, 1996).
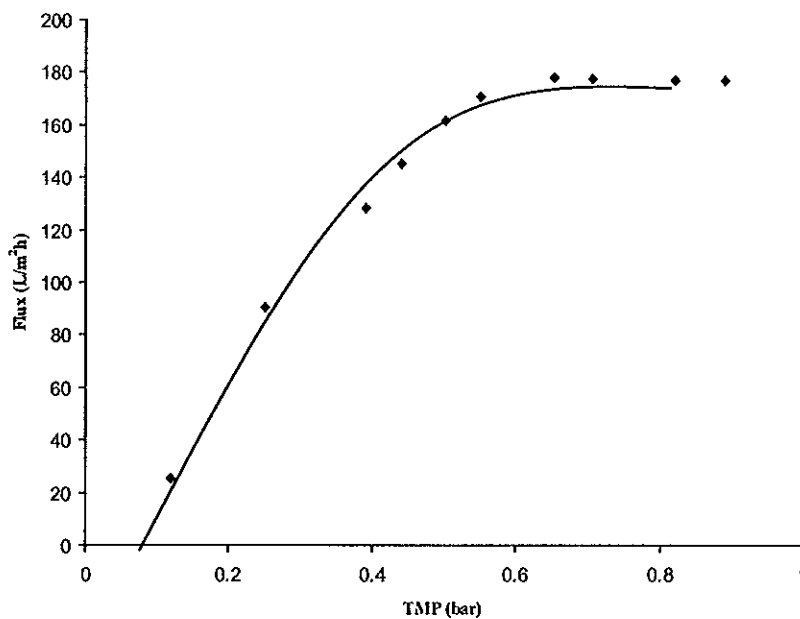
Figure 31. Effect of TMP on the permeate flux (membrane pore size 0.1 μm, CFV = 2.5 m/s, temperature = 20±2°C)
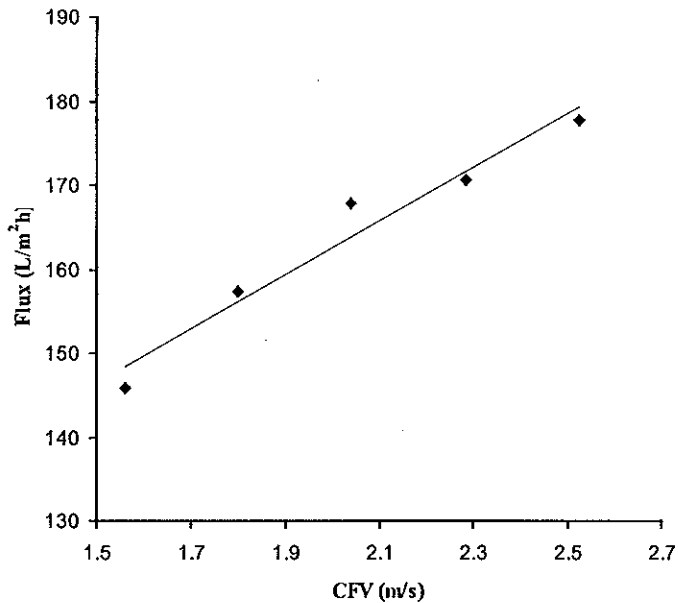
Figure 32. Effect of feed CFV on the steady state permeate flux 0.65 bar (membrane pore size 0.1 μm TMP = 0.65 bar, temperature = 20±°C)

Permeate flux in batch concentration mode

Figure 33. shows the permeate flux versus filtration time during MF using 0.1 μm membrane pore size in batch concentration mode. The permeate flux was sharply decreased in initial five minutes of the filtration time. After that the flux gradually deceased until the end of process (at 25 min). The permeate flux at the end of the process was about 148 l/m^2h which is lower than that obtained from 0.1μm membrane with total recycle mode in the section 3.4.1 at the same operation time. The reason could be due to membrane fouling and an increasing in feed viscosity and concentration of rejected suspended solid particles during batch concentration mode. The permeate flux behavior versus % recovery using the data from the same experiment was shown in Figure 32. About 88 % recovery was obtained at filtration of 25 min. The average of permeate flux was about 200 l/m^2h.
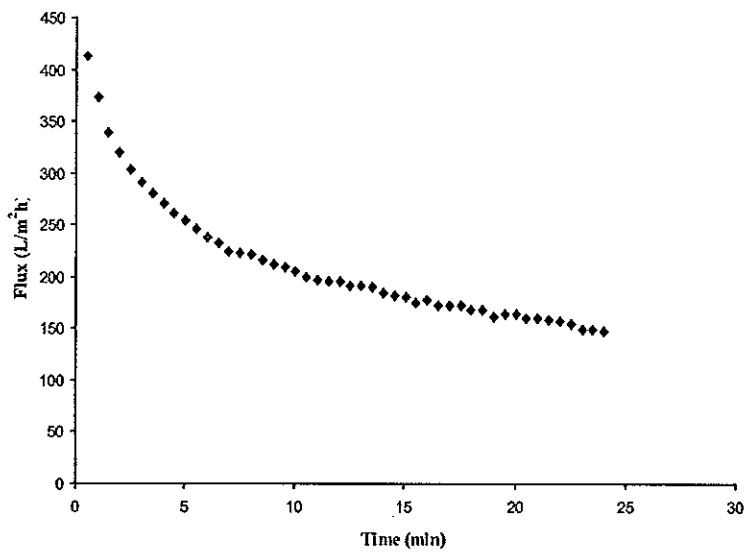
Figure 33. Permeate flux profile during MF of coconut water with batch concentration mode (membrane pore size 0.1 μm, cross flow velocity = 2.5 m/s, TMP = 0.65 bar, temperature = 20±2°C)
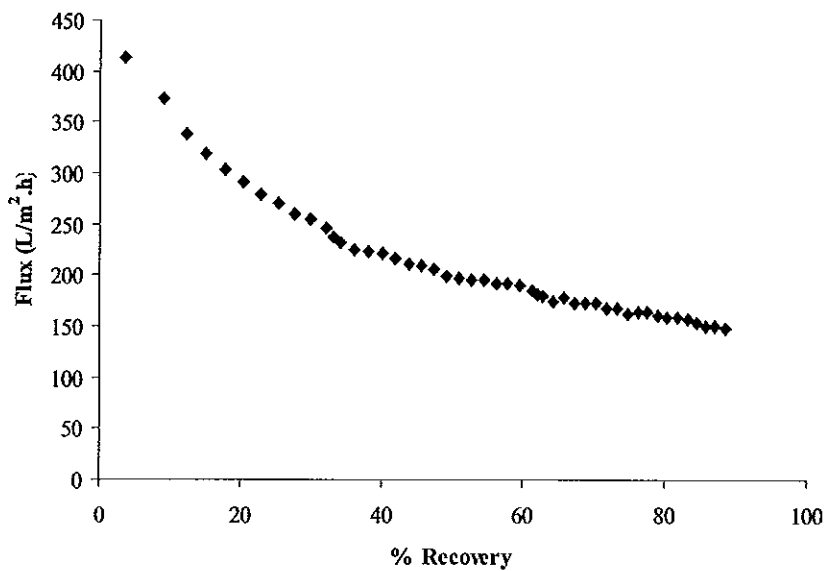
Figure 34. % Recovery versus permeate flux with batch concentration mode (membrane pore size 0.1 μm, CFV = 2.5 m/s, TMP = 0.65 bar, temperature = 20±2°C)

5.5 Conclusion

The fresh coconut water was successfully clarified and sterilized by either MF or UF membrane. The membrane pore size and MWCO did not affect the quality of clarified coconut water and the contents of minerals and estrogen hormone in clarified coconut water were closed to those found in fresh coconut water. The result from microbiological analysis indicated that clarified coconut water of MF and UF were microorganism-free (sterilized). The major fouling of both MF and UF were reversible. Both reversible and irreversible fouling resistances of UF membrane were much higher than those of MF membrane. The permeate flux of 0.1 µm was slightly lower than that of 0.2 µm membrane while the irreversible fouling resistance of 0.1 µm membrane was much lower than that of 0.2 µm membrane. According to these results, membrane with 0.1 µm pore size was considered to be the most suitable membrane for clarification and sterilization of coconut water. The permeate flux was increased dramatically with increasing CFV and decreased as feed concentration or % recovery increased. The result suggested that the permeate flux during of coconut water could be improved using hydrodynamic modification technique.

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CHAPTER 6

COLD STERILIZATION OF COCONUT WATER BY USING MEMBRANE FILTRATION: EFFECT OF GAS SPARGING ON FLUX ENHANCEMENT AND JUICE QUALITY

6.1 Abstract

In this study, the quality of MF and UF-clarified coconut water during storage were investigated. The storage time and temperature did not affect the total soluble solid, pH and estrogen hormone. The MF membrane ($0.1\mu m$) was selected to study the enhancement of process performance. The effects of cross flow velocity (CFV) and gas sparging with various gas injection factor (ε) on the critical and limiting flux during cross flow microfiltration of coconut water were studied. It was observed that the critical and limiting flux increased as the CFV increased. The critical flux varied from 97.3 to 145.3 l/m^2h and limiting flux varied from 145.5 to 176.5 l/m^2h while the CFV increased from 1.6 to 3.5 m/s without gas sparging. The use of gas sparging with various ε led to an increase in both critical and limiting flux during microfiltration of coconut water. The improvement (%) of 20.6 %, 51.4% and 63.0% were achieved for critical flux while 10.2%, 17.4 % and 22.6% were achieved for limiting flux with the ε of 0.15, 0.25 and 0.35, respectively. In addition, the CFV and gas sparging did not affect the pH, total soluble solid, colour and estrogen hormone during microfiltration process.

6.2 Introduction

Membrane filtration is wildly applied in fruit juice processing for clarification, stabilization and sterilization. The major advantage of this process was the ability of preservation of the nutritional, flavor and odor because it does not use the high heat treatment. The conventional thermal process including pasteurization

149

and sterilization is used to improve microbiological quality and extend the shelf life of the product. However, nutritional and sensorial properties of the products are significantly affected by these processes. Thailand is one of the biggest producers of both fresh and processed coconut water in the world. Coconut water is becoming more widely consumed because of its beneficial health properties, naturally fat-free and low in food energy (FAO, 2007). Coconut water contains a complex of vitamins and minerals i.e. potassium, chloride, calcium and magnesium. It is highly recommended as a means for oral rehydration. Coconut water has been successfully used as liquid in intravenous therapy in emergency situations. Furthermore, it has got many medicinal properties such as estrogen hormone especially estradiol (17β-estradiol) that improves synapse formation on dendritic spines in the hippocampus of oophorectomized rats. Estrogen also may improve cerebral blood flow and glucose metabolism and it may in some way acts as an antioxidant (Monk and Brodaty, 2000). Estrogen like hormone in coconut water also has an antagonistic effect with endogenous estradiol by competing for estrogen receptor (Radenahmad *et al.*, 2006)

It is well known that one of the major drawbacks of membrane process is the reduction of permeate flux with time, which resulted from concentration polarization and fouling. The concentration polarization is a natural consequence of the selectivity of a membrane. This leads to an accumulation of particles and solutes in a mass transfer boundary layer, adjacent to the membrane surface that can affect the flux. While the fouling build-up of the material i.e. adsorbed macromolecules, gel or deposited particle on the membrane surface. Generally, induced- surfaced shear is the main strategy to control these phenomena. There are several techniques to improve the process performance of membrane filtration such as critical flux concept, gas sparging, back pulsing etc.

One of technique to solve the problem of flux decline is operation flux below that known as "critical flux". The critical flux is first introduced by Field *et al.* (1995) defining the critical flux as the flux below with a declined of flux of time does not occur above the fouling is observed. The critical flux may be a desirable operational target for a lowering fouling during operation. If non fouling operation can be sustained and low energy promoted then the costs of cleaning are reduced and the energy is saved.

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The aim of this study was to investigate the effect of CFV and ε on the critical flux, limiting flux, membrane fouling and quality of coconut water during microfiltration. In addition, the changes of the quality of the MF and UF clarified juice during storage at various temperatures were also studied.

6.3 Materials and Methods

6.3.1 Preparation of coconut water

Young coconuts of 4-5 month old from local farm in Songkhla province, Thailand were used through out this study. The coconut water obtained from the open nut fruit was collected in a clean container. After that it was filtrated though a cloth sheet to remove large solid particles which may block the inlet lumen of the hollow fiber membrane before introducing to the membrane system. The total soluble solid in the coconut water obtained was in the range of 5-7 °Brix.

6.3.2 Membrane system

The membrane used was a polysulfone membrane with the pore size of 0.1 µm (MF) and MWCO of 100 kDa (UF) (Amersham Biosciences,UK) with a fiber diameter and length of 1 mm. and 30 cm. respectively. The membrane system consisted of a 8 liter stainless steel jacket-feed tank, variable-feed pump (Leeson, USA) and transducers (MBS 3000, Danfoss, Denmark) for pressure of the feed, retentate and permeate measurement. The temperature of the feed was controlled by circulating cooling water through a jacket-feed tank. The CFV and TMP were

controlled using needle permeate valve and variable speed-feed pump. The digital balance (GF-3000, A&D, Japan), connecting the computer was used to measure the permeate flux. The experiments were carried out under batch concentration mode (retentate was returned to the feed tank and permeate collected separately) at constant cross-flow velocity of 1.2 m/s, temperature of 20±2 °C and TMP of 1.0 (for MF) and 2.0 bar (for UF).

6.3.3 Batch concentration, packaging and the quality changes during storage

The permeate sample was filled into the sterilized glass bottles directly under aseptic conditions inside a laminar flow cabinet. The bottles were sterilized by hot air oven at 180°C for 3 hours before use. The laminar flow cabinet was sprayed with alcohol and exposal to germicidal uv light, uv-c 254 nm. with the intensity at 76 μm/cm^2 for overnight. A HEPA air filter system with 0.3 μm pore size and a 0.1375 m^2 filtration area was installed to provide positive pressure of bacteria free air in the laminar flow cabinet. The clarified juice obtained from the membrane pore size of 0.1 μm and MWCO 100 kDa were filled in sterilized glass bottles and stored at 4, 27 and 37 °C. Samples were analyzed in triplicate at 0, 1, 2, 3, 4, 5 and 6 months of storage time.

6.3.4 Process improvement experiments

The membrane pore size was selected according to the previous results. In studying of the effect of CFV and ε on the critical flux limiting flux, the experiments were carried out under total recycle mode (both retentate and permeate were returned to the feed tank).

The critical flux and limiting flux were investigated by a "step by step" technique (Chui and Jame, 2006). The initial TMP was 0.1 bar and TMP was increased at fixed interval of 0.05 bar in time step of 30 min prior to the onset of non-linearity in the increase of permeate flux, which was the indication of critical flux. There after time steps of 20 min were used. Figure 35 shows an example of

critical flux detection. The critical flux is the flux that the point where the deviation from the straight line starts and the limiting flux is the flux that it was independent on the pressure. The critical flux was investigated at cross flow CFV of 1.6-3.5 m/s.
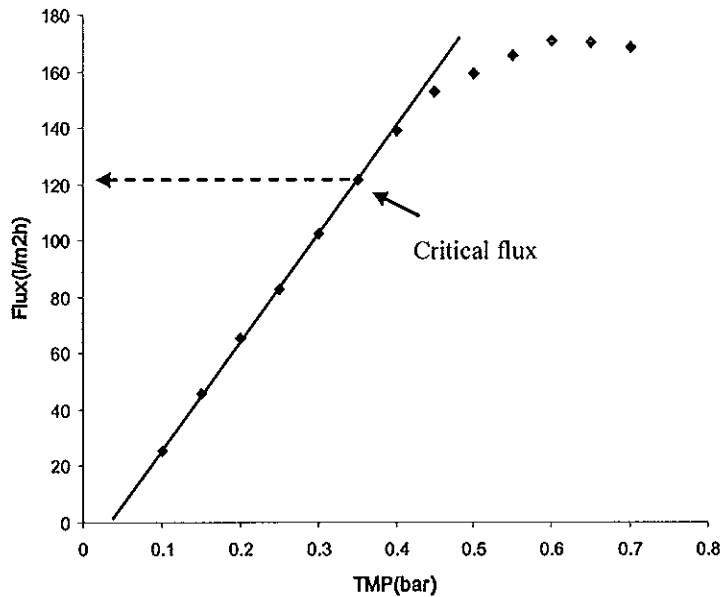
Figure 35. Detection of critical flux by a 'step by step' method in total recycle mode at CFV of 2.0 m/s

6.3.4.1 Gas sparging during microfiltration

The compressed nitrogen gas was injected into the inlet of feed pipe through a Y tube tubular piece. The CFV was varied from 1.6-2.3 m/s, gas flow rate was controlled and measure by a gas flow meter (RMB- 50D –SSV, Dwyer, USA) combined with pressure gauge (2419-2C-P, CKD, Japan). The gas-liquid two-phase flows systems, the mixture can adopt various dynamic structure know as flow patterns, corresponds to the ε. The ε which equals the superficial gas flow velocity (U_g) divided by the sum of superficial gas (U_g) and superficial liquid flow velocity (U_l). The superficial velocity is defined as the velocity if only gas or liquid is in the pipe. The dual flow pattern changes from bubble flow (0<ε<0.2) over slug flow (0.2<ε<0.9) to annular flow (0.9<ε<1.0)(Psoch and Schiewer, 2006). In this study the gas ε applied were 0, 0.15, 0.25 and 0.35 that varied from bubble flow to slug

flow. The experimental set-up during microfiltration with gas sparging is showed in Figure 26.

The membrane filtration process can generally be described by Darcy's law as follow:

$$J = \frac{TMP}{\mu R_t} \tag{6-1}$$

where J (m/s) is the permeation flux, TMP is the transmembrane pressure (kPa), μ (Pa.s) is the viscosity of the permeate and R_t (1/m) is the total resistance to the permeate. R_t could be classified by equation (6-2) as follow:

$$R_t = R_m + R_{rf} + R_{if} \tag{6-2}$$

$$R_{if} = R_{if-in} + R_{if-ex} \tag{6-3}$$

In equation (6-2), R_t is the sum of R_m (membrane resistance), R_{rf} (the resistance caused by reversible fouling) and R_{if} (the resistance caused by irreversible fouling). Furthermore, R_{if} could be divided into two types, resistance caused by internal irreversible fouling (R_{if-in}) and external irreversible fouling (R_{if-ex}) (equation (6-3)). In this study, reversible fouling was defined as the fouling which could be removed by only water flushing. The residual fouling after water flushing was irreversible fouling and it was further cleaned by chemical cleaning. The resistance defined by equation (6-2) and (6-3) could be evaluated by measurement of water flux during cleaning process which is a cleaning in place method (CIP). R_m was determined by measurement of water flux of clean membrane. After filtration of coconut water, the water was flushed through the membrane surface to removed reversible fouling while permeate valve was closed. Water flushing was operated using clean water at CFV of 1.4 m/s and TMP of 0.3 bar for 15 min After the first water flushing, the permeate valve was opened and water flux was measured to determined residual fouling resistance (i.e., $R_m + R_{if}$). Then permeate valve was closed

again. A chemical cleaning was applied by circulating 0.5 N NaOH solution at 50 °C, TMP 0.3 bar and CFV 1.4 m/s for 40 minutes to remove external irreversible fouling. After that the chemical cleaning solution was removed by water flushing. Then the water flux was measured to evaluated residual resistance (i.e. $R_m + R_{if-in}$). After that the internal irreversible fouling was removed by circulating 50 ppm. of NaOCl at 50 °C, TMP 0.3 bar and CFV 1.4 m/s for at least 40 min while the permeate valve open. With R_t obtained after filtration of coconut water and using from equation (6-1) and the results from cleaning procedure combining with equation (6-2) and (6-3) all types of resistances could be worked out.

6.3.5 Coconut water analysis

Samples of fresh coconut water (feed) and clarified coconut water were collected for further analysis. The pH and total soluble solid were analyzed by using pH meter (PP15, Sartorius, Germany) and hand refractometer (2311, Atago, Japan) respectively. The color was measured by colorimeter (Color Quest XT, Hunter lab, USA). The content of estradiol (estrogen hormone) was analyzed using CELIA method (electro generated chemiluminescence immuno assay). The Microbiological analyses of clarified juices were performed by the method described in Bacteriological Analytical Manual (BAM, 2002).

6.4 Results and discussion

6.4.1 Quality change of clarified coconut water during storage

The quality of clarified coconut water during storage at various temperatures is shown in Table 27. The total soluble solid in MF and UF-clarified coconut water ranged from 6.1 to 6.3 °Brix , the pH range from 5.18 to 5.35 and the estrogen hormone range from 32.45 to 37.42 pg /ml. It was observed that the storage time and temperature did not affect the total soluble solid and pH. The same results were observed by other authors (Cortés, *et al*, 2008; Esteve, *et al*, 2005; Martin, *et al*,

1995). The estrogen hormone values in clarified coconut water were monitored at the 0, 1, 3 and 6 months storage. It is important to note that most of estrogen hormone could be preserved by MF and UF. There were no significant differences in estrogen hormone of MF and UF coconut water during 6 months storage at various temperatures.

Table 27. Total soluble solid a, pH and estrogen hormone of MF and UF coconut water during 6 months storage at 4, 27 and 37 °C

Storage conditions		Total soluble solid (Brix)		pH		Estrogen hormone (pg/ml)	
T (°C)	Time (month)	MF	UF	MF	UF	MF	UF
4	0	6.3(0.1)*	6.2(0.1)	5.24(0.08)	5.24(0.08)	34.60(2.54)	32.70(2.96)
	1	6.2(0.1)	6.3(0.1)	5.24(0.06)	5.24(0.06)	32.97(3.57)	32.80(2.82)
	2	6.2(0.1)	6.1(0.1)	5.34(0.08)	5.32(0.03)		
	3	6.3(0.1)	6.2(0.1)	5.24(0.05)	5.22(0.01)	32.50(2.90)	32.99(3.88)
	4	6.3(0.1)	6.3(0.1)	5.25(0.02)	5.19(0.06)		
	5	6.3(0.1)	6.2(0.1)	5.29(0.08)	5.33(0.03)		
	6	6.3(0.1)	6.3(0.1)	5.27(0.04)	5.32(0.03)	35.20(2.96)	33.70(4.29)
27	0	6.3(0.1)	6.2(0.1)	5.24(0.08)	5.24(0.08)	34.60(2.54)	32.70(2.96)
	1	6.3(0.1)	6.2(0.1)	5.35(0.01)	5.25(0.02)	33.08(2.18)	33.35(1.76)
	2	6.3(0.1)	6.3(0.1)	5.31(0.06)	5.25(0.11)		
	3	6.2(0.1)	6.2(0.1)	5.23(0.04)	5.31(0.06)	37.42(1.52)	35.60(1.41)
	4	6.1(0.1)	6.2(0.1)·	5.23(0.11)	5.31(0.06)		
	5	6.2(0.1))	6.3(0.1)	5.31(0.06)	5.32(0.03)		
	6	6.2(0.1)	6.3(0.1)	5.29(0.08)	5.31(0.03)	32.45(2.47)	36.36(1.76)
37	0	6.3(0.1)	6.2(0.1)	5.24(0.08)	5.24(0.08)	34.60(2.54)	32.70(2.96)
	1	6.1(0.1)	6.1(0.1)	5.25(0.02)	5.31(0.06)	33.18(3.55)	35.01(1.56)
	2	6.3(0.1)	6.2(0.1)	5.24(0.03)	5.19(0.06)		
	3	6.1(0.1)	6.3(0.1)	5.33(0.04)	5.23(0.11)	33.76(5.14)	34.60(4.38)
	4	6.2(0.1)	6.3(0.1))	5.32(0.03)	5.32(0.03)		
	5	6.3(0.1)	6.3(0.1)	5.22(0.01)	5.19(0.06)		
	6	6.2(0.1)	6.2(0.1)	5.33(0.03)	5.18(0.06)	33.10(2.26)	35.06(3.74)

*standard deviation

Table 28. shows the microbiological analysis of MF and UF-clarified coconut water during 6 months of storage at 4, 27 and 37 °C. No microbial growth was detected during storage of either MF or UF clarified coconut water until the 6 months storage. Commonly, all yeast & molds and most bacteria are retained by MF with pore size of 0.4 µm or less (Girard & Fukomoto, 2000).

Table 28. Microbiological quality of MF and UF-clarified coconut water during 6 months storage at 4, 27 and 37 °C

Time (month)	Temp (°C)	MF			UF		
		Total plate count (CFU/ml)	Yeast& Mould (CFU/ml)	Colifroms (MPN/ml)	Total plate count (CFU/ml)	Yeast&Mould (CFU/ml)	Colifroms (MPN/ml)
0		<25	<15	<3	<25	<15	<3
1	4	<25	<15	<3	<25	<15	<3
	27	<25	<15	<3	<25	<15	<3
	37	<25	<15	<3	<25	<15	<3
2	4	<25	<15	<3	<25	<15	<3
	27	<25	<15	<3	<25	<15	<3
	37	<25	<15	<3	<25	<15	<3
3	4	<25	<15	<3	<25	<15	<3
	27	<25	<15	<3	<25	<15	<3
	37	<25	<15	<3	<25	<15	<3
4	4	<25	<15	<3	<25	<15	<3
	27	<25	<15	<3	<25	<15	<3
	37	<25	<15	<3	<25	<15	<3
5	4	<25	<15	<3	<25	<15	<3
	27	<25	<15	<3	<25	<15	<3
	37	<25	<15	<3	<25	<15	<3
6	4	<25	<15	<3	<25	<15	<3
	27	<25	<15	<3	<25	<15	<3
	37	<25	<15	<3	<25	<15	<3

The change in color of clarified coconut water stored at 4, 27 and 37 °C were also monitored during 6 months of storage. For the initial colour of clarified juice, no significant difference between MF and UF was observed. The L* value of clarified juice, indicating the lightness, the a* value indicating the redness and b* value, indicating the yellowness of clarified juice are shown in Table 29. The changes in color of coconut water across the duration of the shelf- life study was observed. The colour of MF and UF clarified coconut water before storage were clear. The MF and UF coconut water sample (stored at 4, 27 and 37 °C) changed to the pink colour at the first 3 days. After one week of storage, the MF and UF coconut water stored at the temperature of 27 and 37 °C changed to the clear colour again (the a* or/and b* value was less than 1) while the clarified juice stored at 4 °C still present pink colour (the a* and b* value was more higher than 1 that indicating of the redness and yellowness colour of MF and UF coconut water) throughout 6 months of storage. The reason for this change is not exactly known. However, the reason of the change of the colour was probably due to the enzymatic browning reaction. The polyphenol oxidase

in coconut water causes enzymatic browning by catalyzing natural phenolic compounds to quinones. Subsequent nonenzymatic oxidative polymerization reactions form red pigments (melanins) (Lopez-Nicoles *et al.*, 2007). As mentioned above, the quality of MF and UF could be preserved for more than 6 months storage base on the total soluble solid, pH, estrogen hormone and microbiological results. However, the change in the colour of the MF and UF coconut water should be further studied. In addition, the odor and flavour of the MF and UF coconut water should be also investigated.

Table 29. Colour of MF and UF -coconut water during 6 months storage at 4, 27 and 37 °C

Time (month)	Temp (°C)	MF			UF		
		L*	a*	b*	L*	a*	b*
0		99.93±0.02	-0.10±0.06	0.11±0.17	99.93±0.02	0.01±0.14	0.11±0.17
1	4	96.23±2.59	3.73±0.84	2.86±0.61	96.23±2.59	5.07±0.71	3.2±0.95
	27	99.34±0.69	-0.6±0.28	1.6±0.49	99±0.69	-0.6±0.28	1.6±0.49
	37	99.01±0.60	-2.40±0.42	1.65±0.29	99.01±0.60	-2.40±0.42	1.5±0.10
2	4	96.38±0.63	2.92±0.18	5.14±0.18	96.38±0.63	2.92±0.98	3.47±0.98
	27	99.34±0.76	-1.78±0.57	1.27±0.27	99.34±0.76	-1.51±0.50	1.19±0.32
	37	99.34±0.10	-2.65±1.42	1.48±0.43	99.34±0.10	-2.67±1.03	1.66±0.74
3	4	97.64±1.06	3.78±0.19	4.30±0.22	97.64±1.06	4.78±1.19	3.63±0.44
	27	98.58±0.46	-0.29±2.18	1.88±0.01	98.58±0.46	1.08±1.04	1.43±0.32
	37	99.31±0.69	-3.08±1.64	0.92±0.59	99.31±0.69	-1.75±0.66	1.25±1.03
4	4	97.05±1.51	6.7±0.72	2.44±1.03	97.05±1.51	3.55±1.15	2.44±1.03
	27	98.08±0.54	-0.73±0.46	1.33±0.22	98.08±0.54	-1.3±1.03	1.33±0.22
	37	99.54±0.31	-0.51±2.10	30.47±1.42	99.54±0.31	0.69±1.48	1.58±0.61
5	4	97.56±0.48	3.22±0.16	3.78±0.44	97.56±0.48	6.7±0.72	3.78±0.44
	27	98.19±0.89	-1.62±0.94	0.92±0.59	98.19±0.89	-1.62±0.94	1.47±1.03
	37	99.48±0.06	-1.02±0.75	1.53±0.03	99.48±0.06	-1.02±0.75	1.43±0.66
6	4	94.58±2.06	7.85±0.51	1.68±0.95	94.58±2.06	7.85±0.92	1.68±0.95
	27	98.53±1.83	-0.41±1.01	0.98±0.80	98.55±1.83	-0.34±1.64	0.98±0.80
	37	99.26±0.53	-0.70±0.33	1.48±0.31	99.26±0.53	0.70±0.32	1.48±0.31

Since the quality of clarified coconut water from MF and UF process during storage were similar, the membrane pore size of 0.1 μm was selected to study the performance improvement because it obtained the high permeate flux and low fouling.

The particle size distribution of coconut water is shown in Figure 36. The particle size diameter was in the ranged of 0.04 to 200 μm. The mean particle size diameter of coconut water was about 25 μm. Since the microfiltration with 0.1

μm was employed, most of the particle size lager than 0.1 μm was expected to be removed.
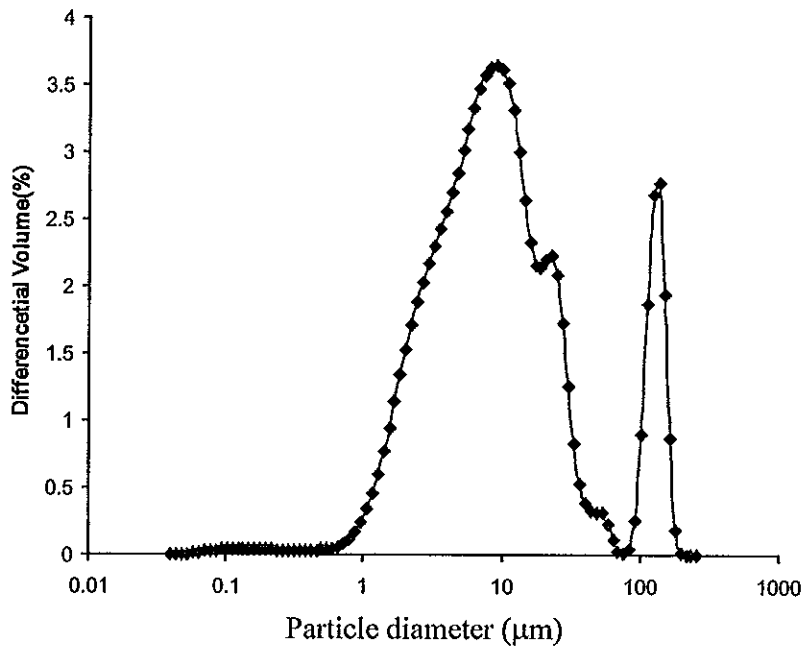
Figure 36. Particle size distribution in coconut water

6.4.2 Effect of cross- flow velocity on critical flux and limiting flux

In order to improve process performance for cold sterilization of coconut water, the combination of critical flux and gas sparging were employed. The results of critical flux and limiting flux during microfiltration with different CFV without gas sparging are shown in Figure 37. It was observed that increasing of cross-flow velocity leading to an increase in critical and limiting flux. The critical flux varied from 97.3 to 145.3 l/m^2h and the limiting flux varied from 145.5 to 176.5 l/m^2h, respectively while the CFV varied from 1.6 to 3.5 m/s. It was expected that the increase of CFV resulted in an increase in turbulence leading to an increase in the particle removing rate and produce the most significant enhancement of mass transfer, thus improving both critical and limiting flux.
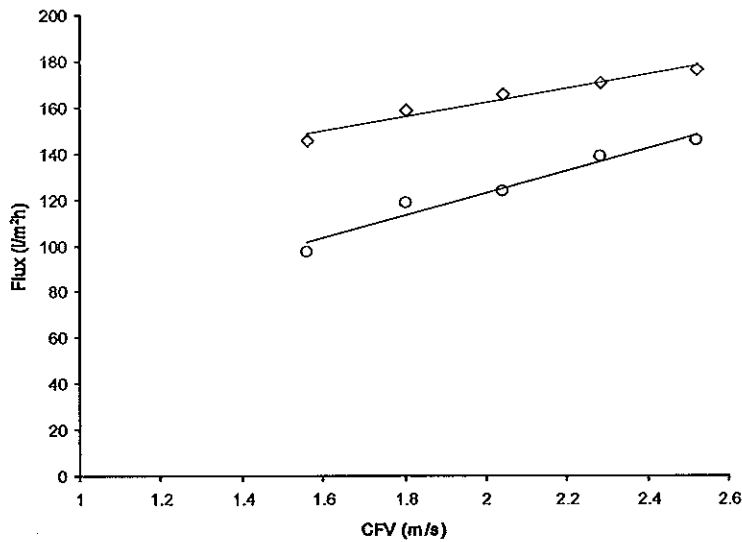
Figure 37. Effect of CFV on critical flux (o) and limiting flux (◇) during microfiltration of coconut water without gas sparging

6.4.3 Effect of gas sparging and cross-flow velocity on critical flux and limiting flux

The CFV of 1.6, 1.8 and 2.3 m/s were selected for study the effect of gas sparging during microfiltration of coconut water with total recycle mode. The ε of 0, 0.15, 0.25 and 0.35, indicating gas–liquid two phase flow patterns varying from bubble flow to slug flow were applied. Table 30 shows the results of critical flux, limiting flux, and flux improvement (%) (critical and limiting flux) during microfiltration of coconut water at different cross- flow velocities and ε . Generally, the result showed that after injecting the gas into the membrane module, the critical flux and limiting flux at selected cross flow-velocities increased. The reason could be due to the injection of nitrogen gas into the feed stream promotes turbulence in the microfiltration process of coconut water. Therefore, gas sparging could be disrupting the fouling during membrane filtration process. The result was in accordance with the studied of Li *et al.,* (2008). The CFV of 1.6 m/s gave the highest improvement (%) both critical flux and limiting flux gas sparging was applied. The improvement (%) during MF of coconut water at constant CFV of 1.6 m/s was 20.6, 51.3, 63.0 for

critical flux and 10.2, 17.4, 22.6 for limiting flux with the ε of 0.15, 0.25 and 0.35, respectively. The improvement (%) at those CFV of 1.8 and 2.3 m/s were much lower than that at CVF of 1.6 m/s. The result was in agreement with the study of Glosh (2006) and Cui and Wright (1996). They were observed that bubbling was most effective at low liquid flow. This indicates that gas sparged microfiltration could be a cost-effective operation from the energy consumption.

Table 30. Critical flux, limiting flux and flux improvement (%) during MF at various ε

CFV (m/s)	ε	Critical flux ($l/m^2 h$)	Limiting flux ($l/m^2 h$)	Flux improvement (%) Critical flux	Limiting flux
1.6	0	97.47±2.64	145.2±4.53		
	0.15	117.51±4.32	160.07±3.21	20.56	10.24
	0.25	147.55±4.46	170.48±2.94	51.37	17.41
	0.35	158.89±2.14	178.09±3.24	63.01	22.65
1.8	0	118.49±2.57	160.43±2.79		
	0.15	161.47±4.33	190.66±2.38	36.28	18.85
	0.25	170.13±3.29	188.46±2.69	43.59	17.50
	0.35	170.84±2.91	185.84±2.91	44.19	15.85
2.3	0	139.2±3.54	170.45±2.98		
	0.15	156.56±3.17	180.45±2.83	12.47	6.13
	0.25	166.62±4.64	188.45±2.67	19.70	10.82
	0.35	170.27±2.57	186.29±2.28	22.32	9.55

At CFV of 1.6 m/s, the ε of 0.35 had higher flux improvement than that of the lower ε, indicating that ε of 0.35 could effectively reduced the deposition of foulants deposited onto the membrane surface. Two major effects have been described why slug flows pattern is the most effective pattern: an increased share

stress in the liquid film surrounding the gas slugs and the wake fields behind the gas slug promotion local mixture in the region. At the CFV of 1.6 m/s, the increasing of ε was effectively increase both critical and limiting flux while higher cross-flow velocity (1.8 and 2.3 m/s) the improvement (%) did not remarkable increased when applied the higher ε. Especially, the improvement (%) of limiting flux did not improve when the higher ε was applied. This reason was probably that the condition of higher CFV and the higher of ε seem to decrease effective membrane area because of replacing liquid mass by bubble contacting to membrane surface (Mi-Jung *et al.*, 2001)

6.4.4 Effect of gas sparging on the quality of clarified coconut water

The MF coconut water sample was taken at the limiting flux operation condition to investigate the quality. The pH, total soluble solid, colour and estrogen hormone of coconut water performed under different ε and CFV are shown in Table 31. It was observed that there were no significant different in mentioned quality among samples obtained from various operating conditions. Therefore, it was cleared that CFV and gas sparging did not affect the total soluble solid, pH, colour and estrogen hormone of MF-coconut water.

Table 31. Total soluble solid, pH and colour of MF coconut water during microfiltration at various ε

CFV (m/s)	ε	Total soluble solid (°Brix)	pH	Estrogen hormone (pg/ml)	Colour L*	a*	b*
1.5	0	6.26±0.12	5.32±0.12	32.50±1.49	99.96±0.02	-0.03±0.0	0.26±0.03
	0.15	6.16±0.15	5.30±0.09	32.04±2.04	99.97±0.01	-0.02±0.0	0.22±0.02
	0.25	6.13±0.11	5.23±0.10	33.69±1.28	99.95±0.01	-0.03±0.0	0.21±0.01
	0.35	6.1±0.10	5.17±0.04	33.82±1.94	99.95±0.01	-0.02±0.0	0.21±0.02
2.0	0	6.16±0.15	5.20±0.09	32.09±2.39	99.92±0.01	-0.03±0.0	0.23±0.02
	0.15	6.26±0.15	5.20±0.07	32.45±1.20	99.96±0.01	-0.04±0.0	0.22±0.01
	0.25	6.17±0.10	5.23±0.06	33.95±2.75	99.96±0.01	-0.03±0.0	0.17±0.05
	0.35	6.20±0.10	5.17±0.05	31.32±1.27	99.96±0.01	-0.03±0.0	0.22±0.01
2.5	0	6.15±0.05	5.21±0.07	32.09±2.39	99.97±0.01	-0.03±0.0	0.22±0.01
	0.15	6.27±0.06	5.18±0.08	31.95±1.90	99.97±0.03	-0.03±0.0	0.23±0.01
	0.25	6.23±0.03	5.19±0.06	34.95±1.34	99.88±0.04	-0.05±0.0	0.22±0.01
	0.35	6.13±0.12	5.26±0.06	32.82±3.35	99.96±0.06	-0.03±0.0	0.22±0.01

6.4.5 Flux profile, fouling analysis and quality of clarified coconut water in batch concentration mode

According to the highest of permeate flux, CFV of 1.6 m/s and TMP of 0.6 bar were selected for studying the effect of ε during batch concentration mode. The result showed that the gas sparging could remarkably enhance permeate flux (Figure 38). The permeate flux profile could be divided into two stages, i.e. flux declined stage and steady state flux state. After microfiltration process at the VCF of 1.6 m/s and TMP of 6.0 bar should be recovery 85 %. It was observed that the permeate flux obtained with gas sparging was always higher than that under unsparged conditions. Varying of ε from 0 to 0.35 the flux improved the permeate flux from 18.9% to 45.9% respectively. The ε of 0.35 was the most effective for application in the CFV of 1.6 m/s.
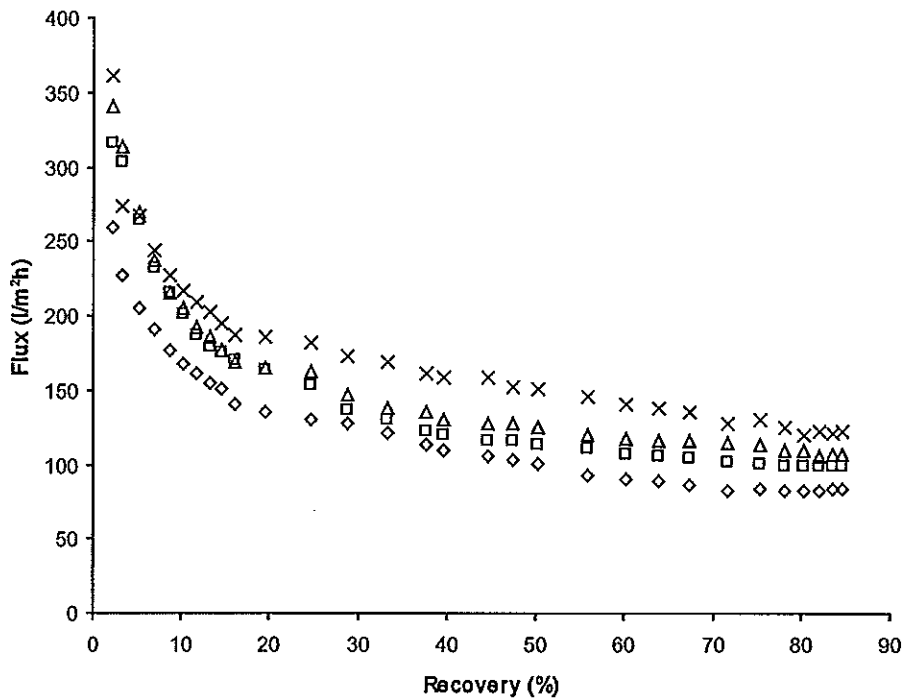
Figure 38 Effect of ε on the permeate flux under batch concentration mode with CFV of 1.6 m/s and TMP= 0.6 bar (Δ, ε =0; □, ε = 0.15;O, ε = 0.25;× ε =0.35)

The effect of gas sparging on membrane fouling during microfiltration of coconut water in batch concentration mode at CFV of 1.6 m/s are shown in Table 32. Generally, it can be seen that the R_t, R_{rf} and $R_{if\text{-}ex}$ could significantly be reduced by increasing of ε. The reversible fouling is sensitive to the hydrodynamic conditions and could be eliminated by hydrodynamic techniques. Thus the reversible could be significantly reduced by gas sparging. Application of higher ε resulted in higher reduction of all types of fouling but irreversible internal fouling as indicated by the $R_{if\text{-}in}$. The reason was clearly that the gas bubbling reduced concentration polarization and formation of fouling layer on the membrane surface. In the case of the quality of MF coconut water during batch concentration mode using various ε, there were no significant differences in pH, colour and estrogen hormone as various ε were applied (data not shown).

Table 32. Membrane fouling during microfiltration of coconut water with total recycle mode at CFV 1.6 m/s, TMP 0.6 bar at various ε

Injection factor	$R_m(\times 10^{11})$ (1/m)	$R_t(\times 10^{11})$ (1/m)	$R_{rf}(\times 10^{11})$ (1/m)	R_{if} $(\times 10^{11})$ (1/m)	$R_{if\text{-}ex}$ $(\times 10^{11})$ (1/m)	$R_{if\text{-}in}$ $(\times 10^{11})$ (1/m)
0	4.25±0.00	21.36±1.69	12.83±2.03	4.27±0.56	3.50±0.34	0.77±0.21
0.15	4.25±0.00	18.49±0.80	10.08±0.77	4.15±0.47	3.33±0.37	0.82±0.09
0.25	4.25±0.00	17.57±0.83	9.26±0.49	4.04±1.11	3.17±0.98	0.86±0.13
0.35	4.25±0.00	15.32±0.78	7.12±0.86	3.95±0.34	3.07±0.21	0.88±0.12

6.5 Conclusion

The quality of MF and UF-clarified coconut water during 6 months of storage were investigated. The storage time and temperature did not affect the total soluble solid, pH, estrogen hormone and microbiological quality. The MF membrane (0.1 μm) was selected to study the process performance due to obtaining high value of permeate flux. Both CFV and gas sparging could enhance critical flux, limiting flux and did not affect the quality of MF coconut water. The increasing of CFV from 1.6 to 2.3 m/s without gas sparging significantly increased the critical flux and limiting flux. The addition of gas on the membrane module led to effectively increase the critical flux and limiting flux. However, improvement (%) of the critical flux was high when the CFV of 1.6 m/s was applied. Higher CFV did not give remarkable improvemenofin both critical flux and limiting flux. The CFV gas sparging did not affect the pH, total soluble solid, colour and estrogen hormone of MF coconut water. The R_t, R_{rf} and $R_{if\text{-}ex}$ could significantly reduced by increasing of ε. The use of gas sparging was beneficial for flux improvement and reduction of fouling while the quality of MF- coconut water was preserved.

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CHAPTER 7

FOULING AND FOULING MECHANISM DURING MICROFILTRATION OF PINEAPPLE JUICE AND COCONUT WATER

7.1 Abstract

Flux reduction due to fouling is the major problem during microfiltration. This study aimed to investigate the role of gas sparging, an effective technique for flux enhancement, on fouling and fouling mechanism during microfiltration of pineapple juice and coconut water. A hollow fiber membrane was used and the experiments were performed at the cross flow velocity (CFV) of 1.5 m/s, transmembrane pressure (TMP) of 0.7 bar for pineapple juice and CFV of 1.6 m/s, TMP of 0.6 bar for coconut water using various gas injection factors (ϵ). It was found that the fouling mechanism during the microfiltration of both pineapple juice and coconut water began with complete blocking, followed by an intermediate blocking and then cake filtration. Gas sparging affected both intensity and duration of these fouling mechanisms. The duration of complete blocking stage was about 5-6 min at the beginning of the microfiltration for both feed. The initial points of defined cake filtration stages reduced from 1.3 to 0.9 h for pineapple juice and 1.0 to 0.67 h for coconut water as the ϵ varied from 0 to 0.35. In the case of fouling resistance, increase in gas injection factor could significantly reduce the reversible fouling, external irreversible fouling but the $R_{if\text{-}in}$.

7.2. Introduction

One of the major limitations of the use of microfiltration in many applications, is membrane fouling. The membrane fouling typically manifests itself as decay in permeate flux and alteration in membrane selectivity. These changes

continue through out the membrane process and eventually require extensive cleaning or replacement of the membrane (Zeman and Zydney, 1996).

The fouling in cross-flow microfiltration is a key factor affecting the economic and commercial viability of a membrane system which essentially depended on the permeate fluxes obtained and their stability with time. To prevent or reduce membrane fouling, several research studies have focused on hydrodynamic improvement method. The effective methods have been recently developed to reduce fouling and/or to enhance permeate flux during the process such as critical flux operation (Youravong et al., 2003; Li et al., 2008), backplusing (Ma et al., 2001) and gas sparging (Li et al., 2008). The gas sparging is one of the techniques that not only successfully enhance the permeate flux during microfiltration and ultrafiltration but also pose less risk to the membrane. In addition, the created- gas bubbles are easily to be separated from the process stream (Cui and Fane, 2003). In order to enhance its economy and efficiency, understanding the membrane fouling mechanism is necessary for the further development.

There are several factors that affecting the fouling and fouling mechanism during microfiltration process such as the CFV, transmembrane pressure (TMP), membrane properties, feed properties etc. Vela et al. (2008) investigated the effect of CFV and TMP on the fouling mechanisms during ultrafiltration of polyethylene glycol (PEG). The result showed that the best fitted model of experimental data corresponded to the cake layer formation model followed by the intermediate blocking model. Moreover, they found that the fouling mechanism depended on the operating conditions. For example, cake layer formation was only observed at the highest TMP and the lowest CFV. de Barros et al. (2003) studied the fouling mechanism of pineapple juice and found that complete pore blocking predominated in the ceramic membrane while cake formation predominated in hollow fiber membranes. Cassano et al. (2007) studied the fouling mechanism of kiwifruit juice. They found that only the regression coefficient (R^2) of cake filtration model was close to unity (0.98). Keskinler et al. (2004) studied fouling mechanism of low-concentration-non leaving yeast suspension. It was found that flux declined profile fit to intermediate blocking model at the beginning of the filtration before the classical cake filtration became dominant filtration mechanism. Nataraj et al. (2008) analyzed

fouling mechanism during cross flow microfiltration of polysaccharide. They found that the feed concentration play a role in fouling mechanism. The cake filtration model appear to fit at a low concentration of polysaccharide solution (20 mg/l) while with higher concentration, identification of the predominant fouling mechanism was difficult.

As mention above, the difference of feed solution and operating parameters presented the different fouling and fouling mechanism. Therefore, in order to control the fouling, it is importance to understand its key characters and behavior of fouling during microfiltration process.

This study aimed to understand the role of gas sparging on fouling and fouling mechanism during microfiltration of pineapple juice and coconut water. The effect of gas injection factor (ε) on fouling mechanism and membrane resistance were also investigated.

7.3 Materials and methods

7.3.1 Preparation fruit juice

Fresh pineapples (*Ananus Comosus L. Merr.*) were cleaned by tap water. After the shells were peeled by a stainless steel knife, the fresh pineapples were chopped into pieces of 1 cm^3 and the juice was extracted by a hydraulic press. The total soluble solid and pH values of the juice were in the range of 12.2-14.2 °Brix and 3.5-4.0 respectively. The fresh pineapple juice was stored at 4 °C before use. Before using the membrane filtration process, the pineapple juice was treated with 0.03 % (V/V) of commercial pectinese (Pectinex® ultra SP-L),(PA(EN)) at room temperature (25±3°C) for 60 min (Carneiro *et al.*, 2002).

Young coconut of 4-5 month old from local farm in Songkhla province, Thailand was used through out this study. The coconut water obtained from the open nut fruit was collected in a clean container. After that it was filtrated though a cloth sheet to remove large solid particles which may block the inlet lumen of the

hollow fiber membrane before introducing to the membrane system. The total soluble solid in the coconut water obtained was in the range of 5-7 °Brix.

Particle size distribution in pineapple juice and coconut water was detected by a Laser Particle Size Analyzer (LS230, Beckman Coulter, USA). The mean particle size was about 58.92 μm in pineapple juice and 25 μm in coconut water (Figure 39). It is important to note that the concentration of suspended particle in pineapple juice was much higher than that of coconut water.

a   b
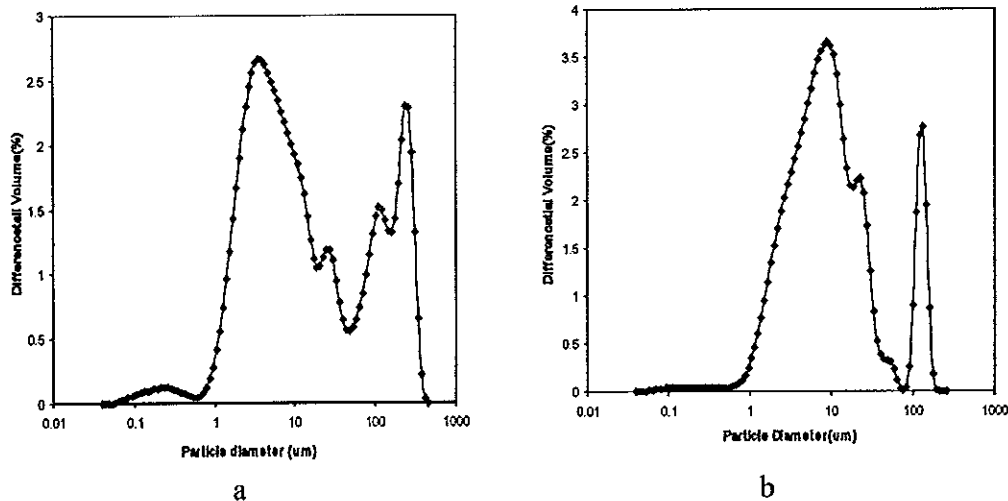
Figure 39. Particle size distribution of pre-treated enzymatic pineapple juice (a) and coconut water (b)

7.3.2 Microflitration

The membrane system used was a polysulfone hollow fiber module (Amersham Biosciences, UK) with a fiber diameter and length of 1 mm. and 30 cm. respectively. The membrane pore size was 0.2 μm for pineapple juice and 0.1 μm for coconut water. The effective membrane area was 0.011 m². The membrane system consisted of a 8 liter stainless steel jacket-feed tank, variable-feed pump (Leeson, USA) and transducers (MBS 3000, Danfoss, Denmark) for pressure measurement of the feed, retentate and permeate measurement. The temperature of the feed was controlled by circulating cooling water through a jacket-feed tank. The CFV and TMP were controlled using needle permeate valve and variable speed-feed pump. The

digital balance (GF-3000, A&D, Japan), connecting the computer was used to measure the permeate flux.

The compressed nitrogen gas was injected into the inlet of feed pipe through a Y tube tubular piece. The gas flow rate was controlled and measured by a gas flow meter (RMB- 50D–SSV, Dwyer, USA) combined with pressure gauge (2419-2C-P, CKD, Japan), The gas-liquid dual flow pattern depends on the gas injection factor (ε) which equals to U_g / (U_g + U_l). U_g and U_l are the superficial gas and liquid flow rate or flow velocity, respectively. The dual flow pattern changes from bubble flow (0 < ε < 0.2) over slug flow (0.2 < ε < 0.9) to annular flow (0.9 < ε < 1.0) (Psoch and Schiewer, 2005). In this study, the ε applied were 0, 0.15, 0.25 and 0.35 that varied from bubble flow to slug flow. The schematic membrane system set up is shown in Figure 26.

7.3.3 Models of membrane fouling

Generally, a microfiltration process can be described by Darcy's Law as follow:

$$J = \frac{TMP}{\mu R_t} \tag{7-1}$$

where J is the volumetric flux of permeate across the membrane (m/s), TMP is the transmembrane pressure (Pa), μ is the permeate viscosity (Pa.s) and R_t is the total hydraulic resistance (1/m).

Four constant pressure blocking filtration laws including standard blocking (each particle arriving to the membrane deposits onto the internal pore walls leading to a decease of pore volume), intermediate blocking (each particle can settle on other particle previously arrived and already blocking some pores or it can also directly block some membrane area), complete blocking (each particle reaching the membrane blocks a pore) and cake filtration (particles deposit onto the membrane surface and a filter cake forms), proposed by Hermia (1982) are directly applicable for description of flux decline during dead-end membrane filtration. By modification of the relevant mass balance, the equivalent equations as follows have also been

obtained for description of flux decline during cross flow membrane filtration (Koltuniewicz *et al.*, 1995; Arnot *et al.*, 2000)

Standard blocking model:	$J^{-1/2} = J_0^{-1/2} + k_s t$	(7-2)
Intermediate blocking model:	$J^{-1} = J_0^{-1} + k_i t$	(7-3)
Complete blocking model:	$\ln(J^{-1}) = \ln(J_0^{-1}) + k_b t$	(7-4)
Cake filtration model:	$J^{-2} = J_0^{-2} + k_c t$	(7-5)

In these models, k_s, k_i, k_b, k_c are constant relating to each model respectively. t is the filtration time and J_0 is the initial permeate flux. The fouling mechanism can be analyzed by fitting experimental data to Equations (7-2), (7-3), (7-4) and (7-5). The linear stages in the figures based on these equations indicate the type and duration of the fouling.

The experiments were performed at the CFV of 1.5 m/s and the TMP of 0.7 bar. All experiments were carried out at a temperature of 20 °C. Both permeate and retentate were recycled back to the feed tank. Therefore, the concentration in the feed remained constant.

7.3.4 Membrane fouling and resistances analysis

The resistance to the permeate flow during microfiltration was defined by Darcy's law (Equation1). The total resistance is divided as follows,

$$R_t = R_m + R_{rf} + R_{if}$$

(7-6)

$$R_{if} = R_{if-in} + R_{if-ex}$$

(7-7)

where R_t is the sum of R_m (membrane resistance), R_{rf} (the resistance caused by reversible fouling) and R_{if} (the resistance caused by irreversible fouling). Furthermore, R_{if} is divided into two types, R_{if-in} (the resistance caused by internal irreversible fouling) and R_{if-ex} (the resistance caused by external irreversible fouling). In this study, R_{rf} was defined as the fouling which could be removed by water flushing. The residual fouling after water flushing was R_{if} and it was further cleaned

by chemical cleaning. The resistance defined by equation (7-6) and (7-7) could be evaluated by measurement of water flux during cleaning process. R_m was determined by measurement of water flux of clean membrane. After filtration of the juices, the water was flushed through the membrane surface to removed R_{rf} while permeate valve was closed. Water flushing was operated using clean water at CFV of 1.35 m/s and TMP of 0.3 bar for 15 min. After the first water flushing, the permeate valve was opened and water flux was measured to determined residual fouling resistance (i.e., R_m+R_{if}). Then permeate valve was closed again. A chemical cleaning was applied by circulating 0.5 N NaOH solution at 50 °C, TMP 0.3 bar and cross-flow velocity of 1.4 m/s for 40 min to remove external irreversible fouling. After that the chemical cleaning solution was removed by water flushing. Then the water flux was measured to evaluated residual resistance (i.e. R_m+R_{if-in}). After that the R_{if-in} was removed by circulating 50 ppm. of NaOCl at 50 °C, TMP of 0.3 bar and CFV of 1.4 m/s for at least 40 min. With R_t obtained after filtration of juice, use of equation (1) and the results from cleaning procedure combining with equation (7-6) and (7-7) all types of resistances could be worked out.

After each run, the system was cleaned by flushing with cleaned water follow with 0.5 N NaOH at 50 °C for 1 h. The rig was then rinsed with cleaned water until the pH return to 7. The permeate water flux of clean membrane was measured after cleaning operation.

7.4 Results and discussion

7.4.1 Effect of gas sparging on flux behavior

Figure 40. shows the permeate flux profile during microfiltration of pineapple juice (a) and coconut water (b) with various ε. The result showed that the gas sparging could significantly enhance permeate flux during running time of 2 hours under total recycle mode. It was observed that a steady flux was improved as ε increase. The whole microfiltration process could be divided into two stages, i.e. flux decline stage and steady flux stage. Varying ε from 0.15 to 0.35 could improve steady

flux from 23.7 to 58.2 % for pineapple juice while the improvement of coconut water flux varied from 11.5 to 42.1%. The higher of ε resulted in the higher of permeate flux. The permeate flux improvement (%) of pineapple was higher than that of coconut water. Since the pineapple juice contained larger particle size and higher concentration of suspended solid than coconut water, thus more severe concentration polarization was expected. The mechanism of flux enhancement is related to the disruption of the concentration polarization layer and improved mass transfer (Cui and Fane,2003).
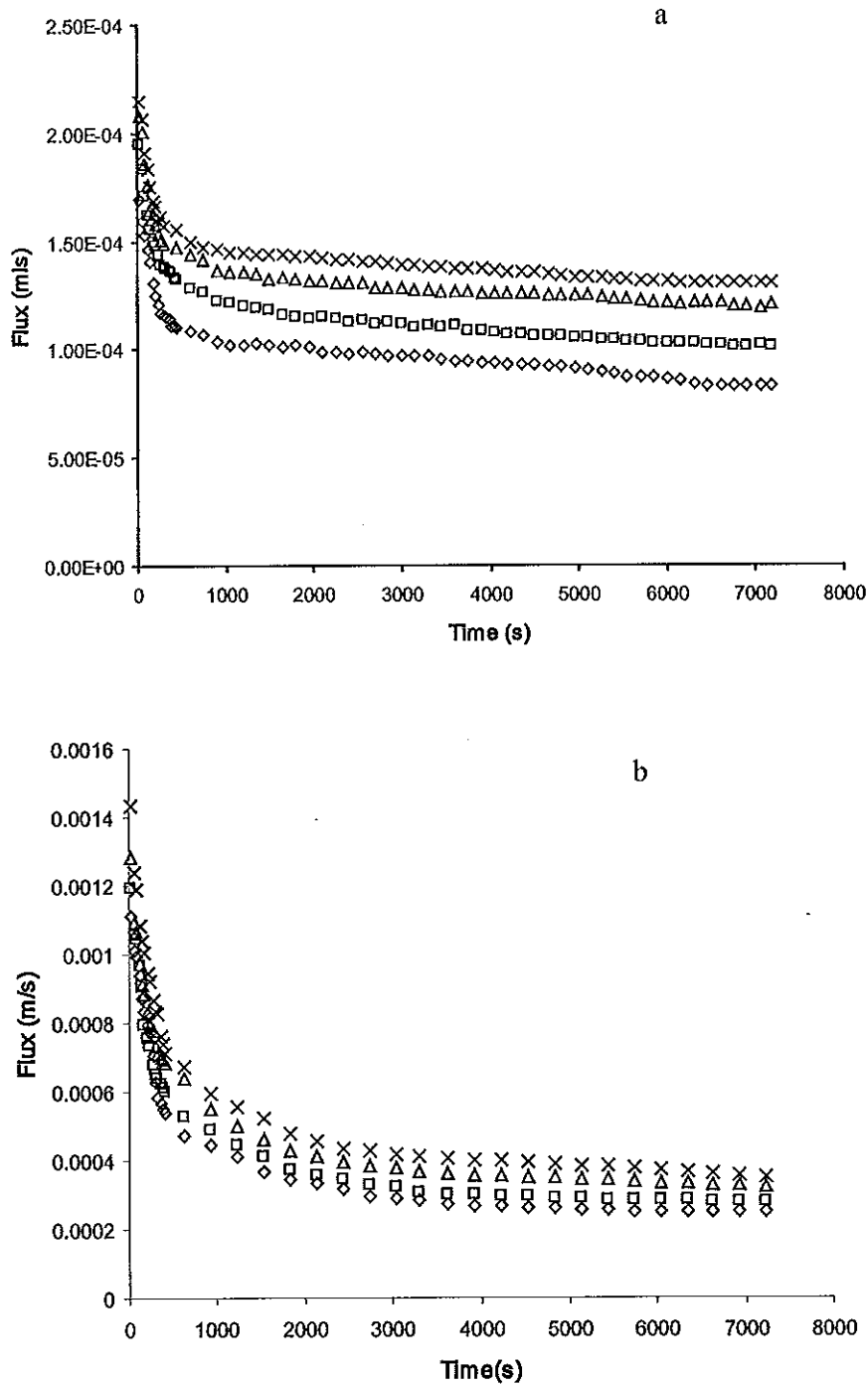
Figure 40. Effect of gas sparging on permeate flux during the microfiltration of pineapple juice at CFV =1.5m/s, TMP = 0.7 bar (a) and coconut water CFV=1.6 m/s, TMP= 0.6 bar (b) with various ε (◇, ε = 0; □, ε = 0.15; Δ, ε = 0.25; ×, ε = 0.35)

a

b
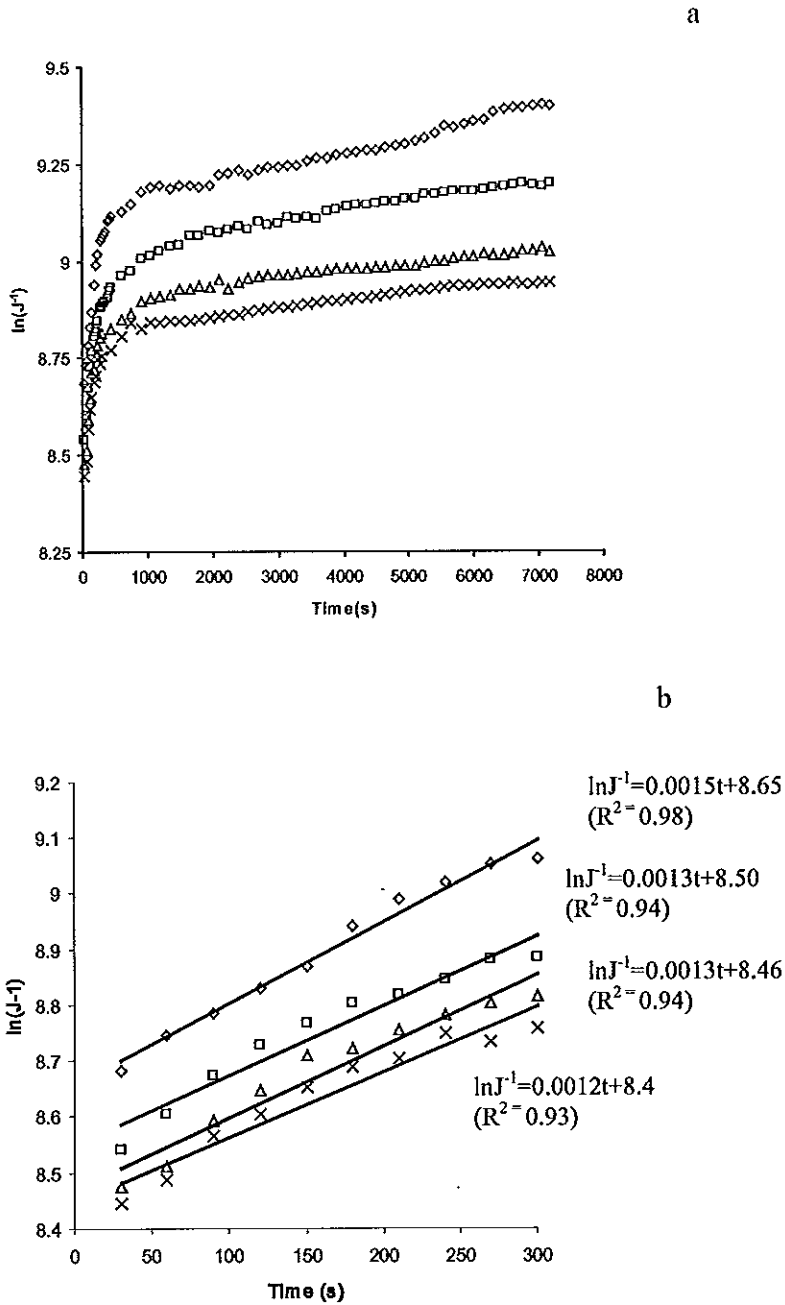
Figure 41. Effect of gas sparging on the fouling due to complete blocking during the microfiltration of pineapple juice with various ε at CFV = 1.5 m/s and TMP = 0.7 bar ($\Diamond$, $\varepsilon = 0$; $\Box$, $\varepsilon = 0.15$; Δ, $\varepsilon = 0.25$; ×, $\varepsilon = 0.35$) a, complete blocking model fitted to the flux data; b, selected linear phase of complete blocking model.
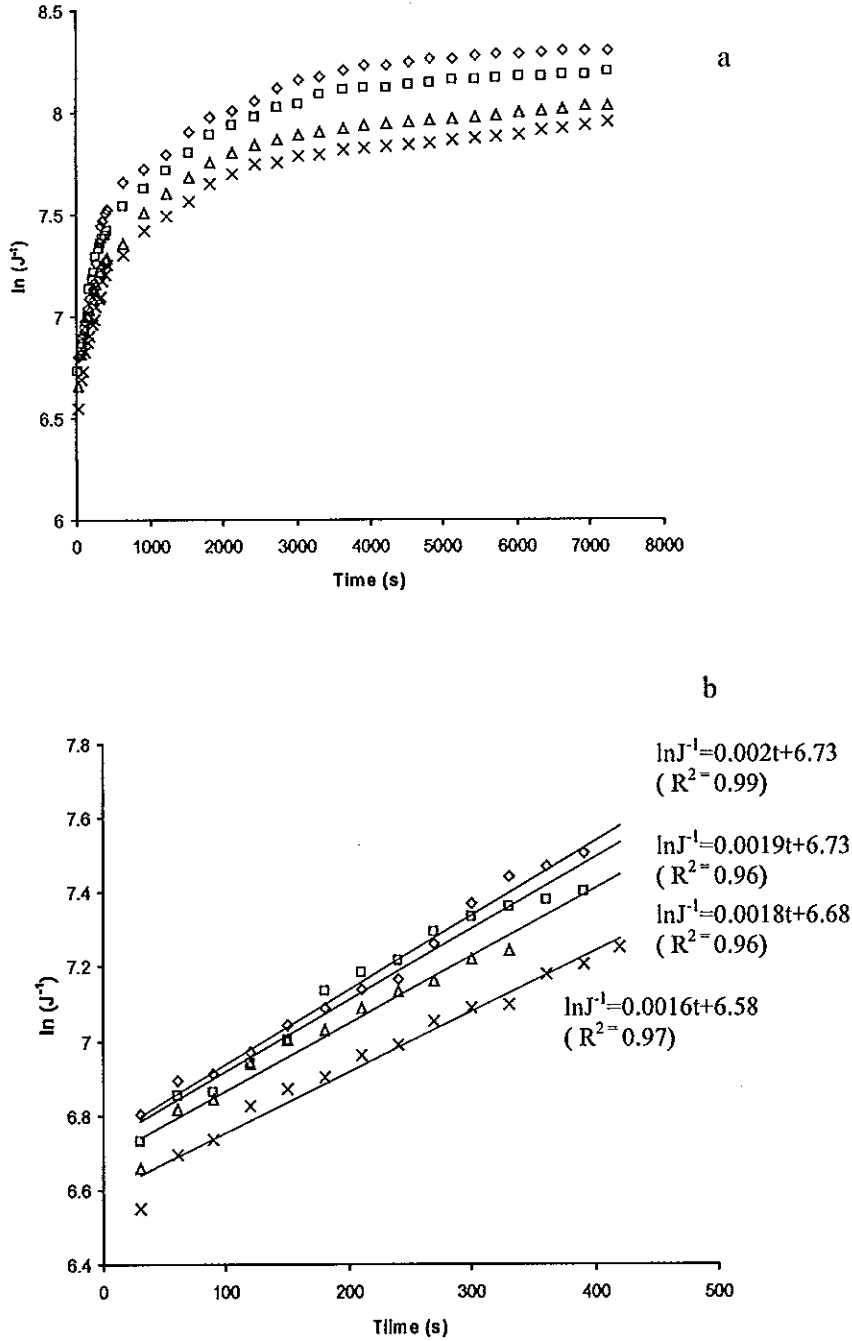
Figure 42. Effect of gas sparging on the fouling due to complete blocking during the microfiltration of coconut water with various ε at CFV= 1.6 m/s and TMP = 0.6 bar (◇, ε = 0; □, ε = 0.15; △, ε = 0.25; ×, ε = 0.35) a, complete blocking model fitted to the flux data; b, selected linear phase of complete blocking mode

a

b

$J^{-2}=12694t+6E+07$
$(R^2=0.96)$

$J^{-2}=3599t+7E+06$
$(R^2=0.96)$

$J^{-2}=2346t+6E+06$
$(R^2=0.99)$

$J^{-2}=1788t+4E+06$
$(R^2=0.98)$
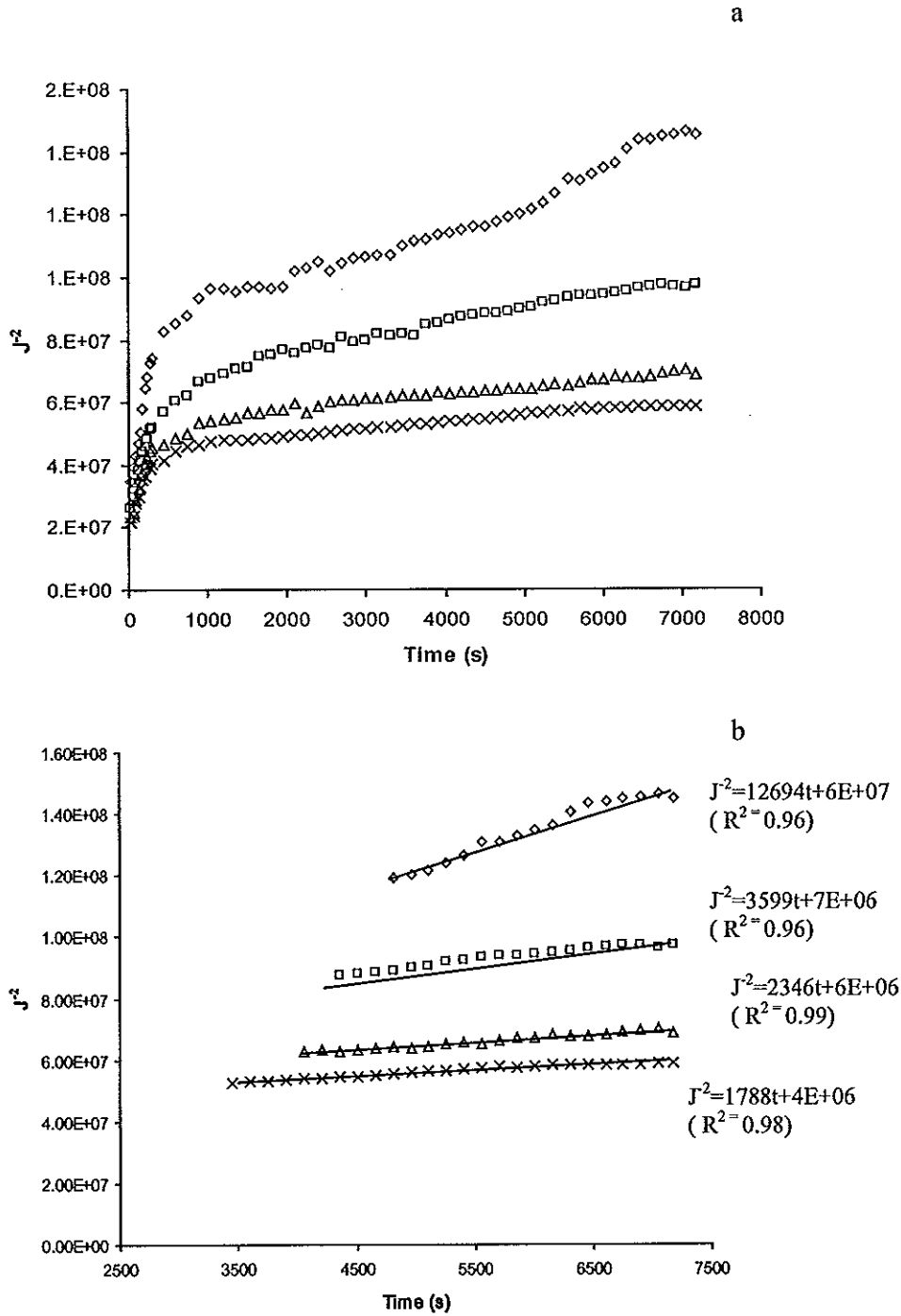
Figure 43. Effect of gas sparging on the fouling due to cake filtration during the microfiltration of pineapple juice with various ε at CFV= 1.5 m/s and TMP = 0.7 bar ($\lozenge$, ε = 0; $\square$, ε = 0.15; Δ, ε = 0.25; ×, ε = 0.35) a, cake filtration model fitted to the flux data; b, selected linear phase of cake filtration model.
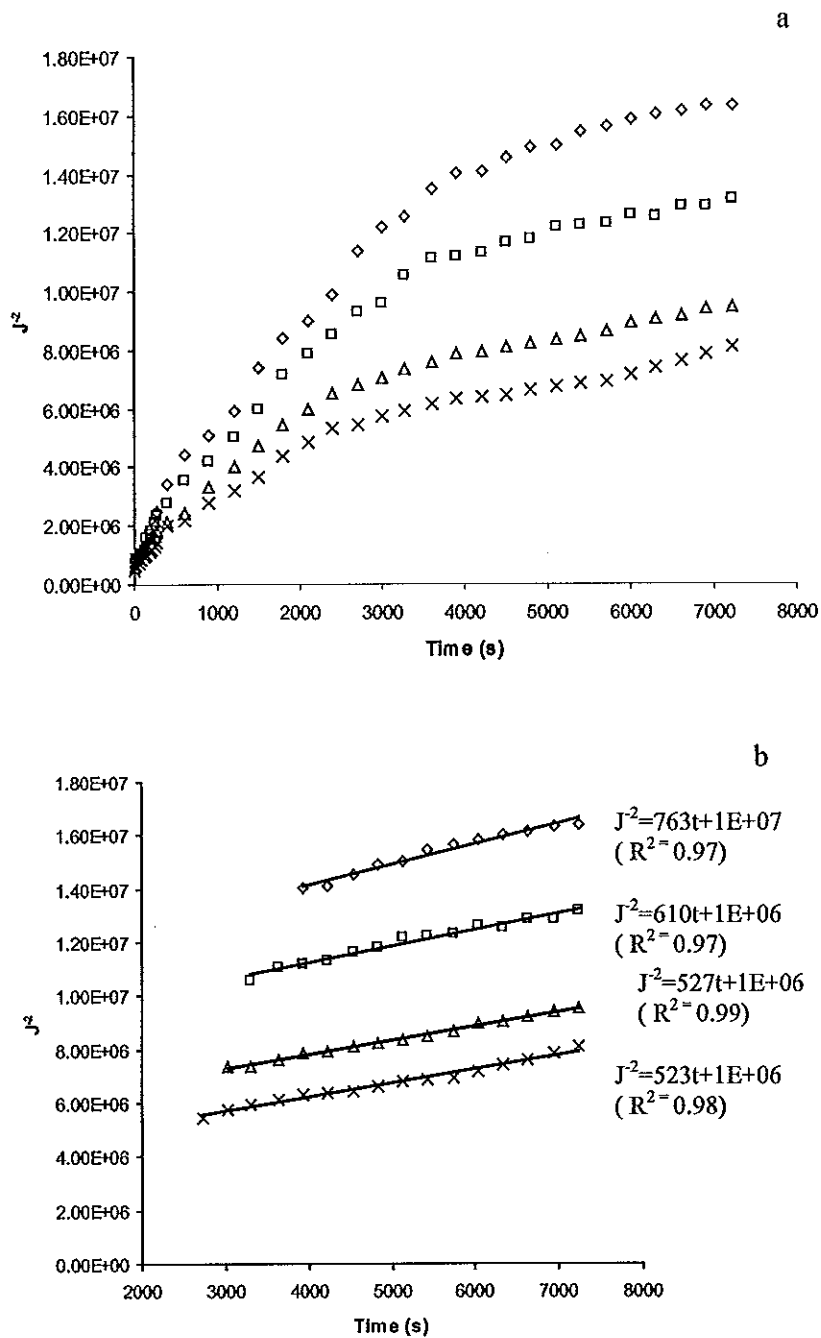
Figure 44. Effect of gas sparging on the fouling due to cake filtration during the microfiltration of coconut water with various ε at CFV= 1.6 m/s and TMP = 0.6 bar ($\diamond$, ε = 0; $\square$, ε = 0.15; $\triangle$, ε = 0.25; ×, ε = 0.35) a, cake filtration model fitted to the flux data; b, selected linear phase of cake filtration model.

The equations shown in plot b:

$$J^{-2}=763t+1E+07 \quad (R^2=0.97)$$
$$J^{-2}=610t+1E+06 \quad (R^2=0.97)$$
$$J^{-2}=527t+1E+06 \quad (R^2=0.99)$$
$$J^{-2}=523t+1E+06 \quad (R^2=0.98)$$
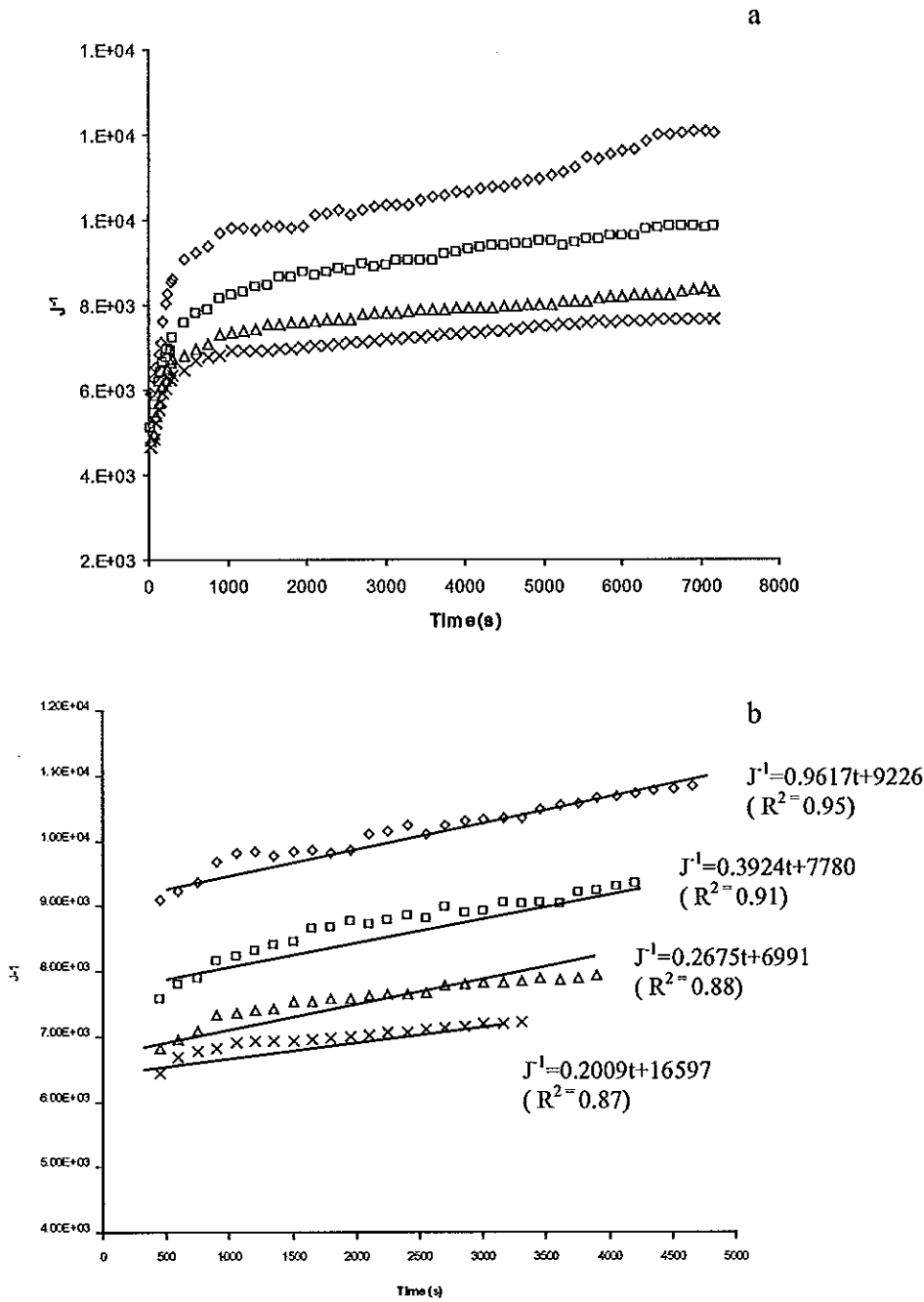
Figure 45. Effect of gas sparging on the fouling due to intermediate blocking during the microfiltration of pineapple juice with various ε at CFV= 1.5 m/s and TMP = 0.7 bar ($\Diamond$, ε = 0; $\Box$, ε = 0.15; Δ, ε = 0.25; ×, ε = 0.35).; a, intermediate blocking model fitted to the flux data; b, selected linear phase of intermediate blocking model).

a

b
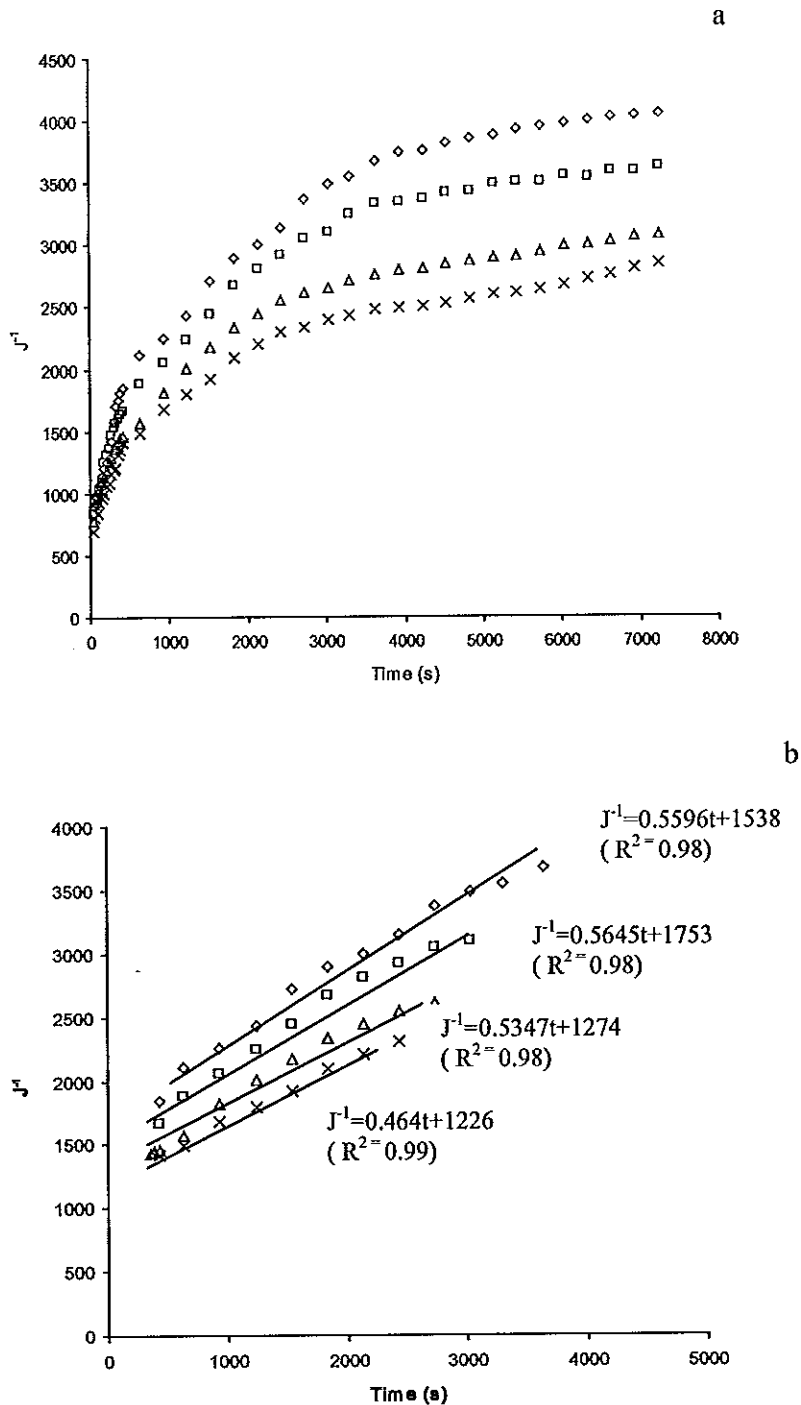
Figure 46. Effect of gas sparging on the fouling due to intermediate blocking during the microfiltration of coconut water with various ε at CFV= 1.6 m/s and TMP = 0.6 bar ($\Diamond$, ε = 0; $\Box$, ε = 0.15; Δ, ε = 0.25; ×, ε = 0.35).; a, intermediate blocking model fitted to the flux data; b, selected linear phase of intermediate blocking model.

7.4.2 Effect of gas sparging on fouling mechanism

In practice, all fouling phenomena, e.g. adsorption, pore blocking and cake layer formation might occur simultaneously because of the complexity of the feed composition, operating conditions and membrane properties. However it is possible to detect one or more dominant fouling mechanisms at different state of membrane filtration process. Experimental data was tested with fouling models, expressed by Equation (7-2) to (7-5). The selected linear phase of the curves indicates the intensity and duration of fouling.

The fitting of experimental data to these models permit to distinguish if the permeate flux decline is controlled by cake layer formation or pore blocking. When pore blocking occurs, it can take place inside the pores (standard blocking) or outside them (intermediate and complete blocking). It has been proved that the fouling should start with a complete blocking followed by an intermediate blocking and a cake filtration process if the molecule is much greater than the pore (Bowen *et al.*, 1995). Most particle size of pineapple juice and coconut water ranged from 0.9 to -100 μm and 0.9 to 80 μm respectively (the smaller and larger particles were negligible). Comparing to the mean membrane pore size used (0.1 and 0.2 μm), the sizes of suspended particles and their possible aggregates were much larger than the membrane pore size. Figure 39 and 40 show the fitting of the experimental results to the complete blocking model of pineapple juice (Figure 39a) and coconut water (Figure 40a) according equation (7-4). It could be seen that only the data at the initial short period could be fitted to the complete blocking model. The linear phase was defined with coefficient of linear regression (R^2), shown in Table 33. The duration of complete blocking stage of pineapple juice was about 5 min from the beginning of the microfiltration. The k_b (Equation 7-4) were 0.15×10^{-2}, 0.13×10^{-2}, 0.13×10^{-2} and 0.12×10^{-2} for ε of 0, 0.15, 0.25 and 0.35 respectively (Figure 39b). The similar reduction in k_b of coconut water was observed. The k_b were 0.20×10^{-2}, 0.19×10^{-2}, 0.18×10^{-2} and 0.16×10^{-2} for ε of 0, 0.15, 0.25 and 0.35 respectively (Figure 40b). The result showed that the higher ε led to a decrease in k_b. The reason was probably

due to the higher ε present more bubble near the membrane surface, led to reduce some particles that attached the membrane pore. According to the mechanism of complete blocking, a clean membrane surface is required to allow the blocking of the membrane pore by particles arriving membrane surface (Hermia, 1982; Koltuniewicz et al., 1995). Therefore, the complete blocking only occurred in the initial stage of microfiltration and for a short period of time.

The cake layer fouling mechanism occurs when solute molecules are much greater than the membrane pore. Consequently, they are unable to enter the membrane pores. Some of the main factors that have the main influence on the cake layer resistance are: molecular deformation, cake compression and cake layer thickness (Vela et al., 2008). Generally, the dominant fouling mechanism would be cake filtration at the end of filtration if a steady permeate flux is achieved. In this study, the steady fluxes were observed. The data of flux were fitted to the cake filtration model from the end of the runs (Figure 43,44). All data could be fitted to cake filtration model with defined coefficient of linear regression at the end of microfiltration processes. It was observed that the stages dominated by cake filtration could occur earlier when gas sparging was applied (Figure 43b, 44b). The initial points of defined cake filtration stages dominated at the filtration time of 1.3, 1.2, 1.1 and 0.9 h (pineapple juice, Figure 43b) and 1.0, 0.84, 0.75 and 0.67 h (coconut water, Figure 44b) for ε of 0, 0.15, 0.25 and 0.35 respectively. In addition to the duration of stages dominated by cake filtration, gas sparging had influence on k_c (Equation 5) as well. The k_c of pineapple juice were 12694, 3599, 2346 and 1788 while the k_c of coconut water were 763, 610, 527 and 523 when the ε of 0, 0.15, 0.25 and 0.35 were applied respectively. The lower k_c indicated a lower intensive cake layer. The higher of ε produced the higher the vertex of the particle near the membrane surface leading to less compact of the cake. Therefore, the higher steady flux was observed when ε was increased. The result suggested that the higher ε significantly reduced the cake formation on the membrane surface (Hwang and Wu., 2008). This reason could be explained by both solvent mass transportation and solute mass transportation. Gas induced bubbles in the flow channel could increase turbulence leading to flux enhancement. The reduction of k_c was in accordance with the studied of Li, et al.,

(2010). They found that the k_c decreased when the higher CFV during microfiltration of pineapple wine was applied. Comparing to k_c between the two juices, the k_c of pineapple juice was higher than the k_c of coconut water. The reason was due to the pineapple juice had more severe particles and foulants than that the coconut water, therefore it was more cake, formed on the membrane surface.

Apart from the complete blocking dominated stage and cake filtration dominated stages, the dominant fouling should be intermediate blocking in the middle of microfiltration process (Bowen et al., 1995). Figure 45a and 46a show the fitting of the experiment permeate flux of pineapple juice (Figure 45a) and coconut water (Figure 46a) to the intermediate blocking model for all condition tests according to equation (7-3). The intermediate blocking fouling mechanism occurs when the membrane pore size is similar to the size of solute molecules. Membrane pores are blocked on near theirs the entrance in the feed side. However, not all of them are completely blocked. The duration of intermediate blocking stage of pineapple juice was defined as the period from the end of complete blocking stage evaluated from Figure 41b to the beginning of cake filtration dominated stages evaluated from Figure 43b while the duration of intermediate blocking stage of coconut water was defined as the period from the end of complete blocking stage evaluated from Figure 42b to the beginning of cake filtration dominated stages evaluated from Figure 44b. Gas sparging reduced the time of intermediate blocking. The shortest duration of intermediate blocking was obtained by ε of 0.35 for both juices (Figure 45b, 46b). As mentioned above, the presence and movement of bubbles in flow could remove larger particles away from the membrane and draw smaller particles to the membrane surface. Hence gas sparging could accelerate the formation of fouling layer on the membrane, consequently reduce the period of intermediate blocking. However, it should be noted that the R^2 for linear phase evaluated by intermediate blocking of pineapple juice was not as high as those evaluated by complete blocking and cake filtration model (Table 33). The dominant fouling mechanism changes with time. It could be supposed that the fouling mechanism is relatively simple at the beginning of the process with a cleaned membrane and at the end of the process with a stable fouling layer on the membrane surface. The transition of fouling mechanisms occurred in the middle of the process, therefore, the coefficient of linear regression

appeared a lower value by fitting experimental data to the dominant fouling mechanism, i.e. intermediate blocking model. In this study, the complete blocking mechanism appeared to be the major part of microfiltration process for permeate flux decline while cake filtration dominated the steady flux. On the other hand, the R^2 for linear phase intermediate blocking model of coconut water was high. It indicated that fouling mechanism during microfiltration of coconut water, which can occur by complete blocking mechanism, appeared to be the major part of microfiltration process at the beginning of filtration and follow with the intermediate blocking while cake filtration dominated the steady flux. However, the fouling mechanism of different feed solution and operating condition could show the different of fouling mechanism. The summary of kinetic constant and duration of fouling models are shown in Table 33 and 34.

Table 33. Constant of fouling mechanism model during microfiltration of pineapple juice and coconut water with various ε

ε	Pineapple juice			Coconut water		
	k_b*10^{-2}	k_i	k_c	k_b*10^{-2}	k_i	k_c
0	0.15(0.98)	0.36(0.95)	12694(0.97)	0.20(0.99)	0.56(0.98)	763(0.97)
0.15	0.13(0.94)	0.39(0.91)	3599(0.96)	0.19(0.96)	0.56(0.98)	610(0.97)
0.25	0.13(0.94)	0.27(0.88)	2346(0.96)	0.18(0.96)	0.53(0.98)	527(0.99)
0.35	0.12(0.93)	0.20(0.87)	1788(0.95)	0.16(0.97)	0.46(0.99)	523(0.98)

* R^2

Table 34. Duration time of fouling mechanism during microfiltration of pineapple juice with various ε

Juice	ε	Duration time (s)		
		Complete blocking	Intermediate blocking	Cake filtration
Pineapple	0	0-300	300-4650	4650-7230
juice	0.15	0-300	300-4200	4200-7230
	0.25	0-300	300-3900	3900-7230
	0.35	0-300	300-3300	3300-7230
Coconut	0	0-390	390-3630	3630-7230
water	0.15	0-390	390-3030	3030-7230
	0.25	0-360	360-2730	2730-7230
	0.35	0-390	390-2430	2430-7230

7.4.3 Effect of gas sparging on filtration resistance

According to the above analysis, an increasing in ε seems to be an effective way for enhancing the permeate flux. The effect of gas sparging on membrane resistance of pineapple juice and coconut water are shown in Table 35 and 36. It could be seen that R_t, R_{rf} and $R_{if\text{-}ex}$ decreased with increasing of ε. The results indicated that the gas bubbling reduced concentration polarization and formation of fouling layer on the membrane surface leading to a decrease in fouling resistant (Table 35 and 36). Generally the reversible fouling (e.g. loss layer caused by accumulation of solutes on the membrane surface) is sensitive to the hydrodynamic conditions and could be eliminated by hydrodynamic techniques. All fouling resistance of pineapple juice was higher than the fouling of coconut water it was due to the higher foulants and larger particles and molecules. However $R_{if\text{-}in}$ did not change when the different ε were applied. The small values of $R_{if\text{-}in}$ was due to the most particle diameter of pineapple juice were larger than the membrane pore. For this reason the standard blocking model was not fitted to this study.

Table 35. Membrane fouling during microfiltration of pineapple juice with total recycle mode at various ε at CFV of 1.5 m/s TMP 0.7 bar

ε	R_m $(\times 10^{12})$ (1/m)	$R_t (\times 10^{12})$ (1/m)	$R_{rf} (\times 10^{12})$ (1/m)	$R_{if} (\times 10^{12})$ (1/m)	$R_{if\text{-}ex}$ $(\times 10^{12})$ (1/m)	$R_{if\text{-}in} (\times 10^{12})$ (1/m)
0	0.24	6.52 ± 0.27^a	4.58 ± 0.27^a	1.65 ± 0.26^a	1.54 ± 0.10^a	0.11 ± 0.0^{ns}
0.15	0.24	5.30 ± 0.22^b	3.54 ± 0.22^b	1.50 ± 0.01^b	1.39 ± 0.01^b	0.11 ± 0.0^{ns}
0.25	0.24	4.46 ± 0.10^c	2.92 ± 0.10^c	1.28 ± 0.01^c	1.18 ± 0.01^c	0.11 ± 0.0^{ns}
0.35	0.24	3.95 ± 0.10^d	2.69 ± 0.05^d	1.02 ± 0.10^d	0.92 ± 0.10^d	0.10 ± 0.0^{ns}

Same letters in the same column present no statistical differences according to Duncan's multiple range test at P<0.05
Ns = no significant difference

Table 36. Membrane fouling during microfiltration of coconut water with total recycle mode at various ε at CFV of 1.6 m/s TMP 0.6 bar

ε	$R_{m}(\times 10^{11})$ (1/m)	$R_{t}(\times 10^{11})$ (1/m)	$R_{rf}(\times 10^{11})$ (1/m)	$R_{if}(\times 10^{11})$ (1/m)	$R_{if\text{-}ex}$ $(\times 10^{11})$ (1/m)	$R_{if\text{-}in}$ $(\times 10^{11})$ (1/m)
0	4.25^{ns}	20.71 ± 0.78^{a}	4.58 ± 0.27^{a}	4.92 ± 0.63^{a}	3.92 ± 0.66^{a}	0.99 ± 0.1^{ns}
0.15	4.25^{ns}	19.24 ± 0.91^{b}	3.54 ± 0.22^{b}	4.24 ± 0.27^{b}	3.23 ± 0.24^{b}	1.00 ± 0.1^{ns}
0.25	4.25^{ns}	16.71 ± 0.31	2.92 ± 0.10^{c}	3.92 ± 0.61^{c}	2.95 ± 0.63^{c}	0.97 ± 0.0^{ns}
0.35	4.25^{ns}	14.43 ± 0.39^{d}	2.69 ± 0.05^{d}	3.69 ± 0.39^{d}	2.64 ± 0.04^{d}	1.04 ± 0.1^{ns}

Same letters in the same column present no statistical differences according to Duncan's multiple range test at $P<0.05$
Ns = no significant difference

7.5 Conclusion

The dominant fouling mechanism of pineapple juice and coconut water were complete pore blocking followed by an intermediate blocking and then a cake filtration process. The complete blocking was the major reason for the flux decline period while the cake filtration dominated during the steady flux period. Gas sparging affected both intensive and duration of different fouling mechanism. For pineapple juices, increase in ε led to a decrease in fouling intensity or kinetic constant. It was probably due to the higher of ε produced the higher the vertex of the particle near the membrane surface leading to less compact of the cake.... The use of ε at 0.35 could remarkable reduce fouling resistant. It was important to note that gas sparging plaied an important role in reduction of the R_{t}, R_{rf} and $R_{if\text{-}ex}$ but the $R_{if\text{-}in}$. Regarding this result, the other techniques need to be developed to reduce the internal fouling.

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CHAPTER 8

ECONOMIC ASSESSMENT: COLD STERILIZATION OF PINEAPPLE JUICE AND COCONUT WATER

8.1 Abstract

This study aims to assess the technical and economical feasibility for production of sterilized/clarified pineapple juice and coconut water using cross flow microfiltration (MF). The data for MF- plant design is based on the experimental result from the previous study. The capacity of processing plant for the juice production is assumed to be 20,000 liter/day for each juice. The 0.2 μm and 0.1 μm hollow fiber membranes are used for producing clarified/sterilized pineapple juice and coconut water respectively. The outline of the calculation of investment cost and the operating cost under various operating conditions is summarized. The operating conditions have a major influence on capital cost as well as operation cost. The economic assessment of pineapple juice by microfiltration are accomplished for production of 5000 ton/year, yielding an interest rate of return of 38.3-53.6 % and payback period of 1.9-2.6 years for pineapple juice while the yielding an interest rate of return of 19.2-23.2 % and payback period of 3.9-4.4 years for coconut water, depending on the operating conditions.

8.2 Introduction

The conventional process widely used for tropical fruit juice production is thermal process, significantly affecting the characteristic of fruit juice such as nutritional and flavour. Membrane technology, microfiltration/ultrafiltration can be an alternative process for fruit juice preservation and conservation. The advantages of membrane technology in relation to the thermal processes are the use of mild temperature and pressure conditions. The process and techniques developed

therefore can be used for production of cold-stabilized fruit juice, which potentially maintain the nutritional quality and sensorial attributes of the products, so call fresh-like products. However, with the exception of cold sterilization, membrane have not been wildly used within fruit juice industry, the main reason for this are: (i) high capital and operating cost;(ii) current regulatory standards can be achieved by conventional thermal processes; (iii) difficulties in disposing of chemical waste from cleaning;(iv) limited experience of use of membranes in these application areas (Owen *et al.*, 1995). The performance of membrane process largely depends on membrane fouling and concentration polarization. The techniques for improvement membrane process performance by reducing fouling and concentration effects have been developed and evaluated. The previous study showed that the permeate flux of pineapple juice and coconut water were varied, depending on operating conditions such as cross flow velocity (CFV) and an additional flux enhancement technique, gas sparing. This may has a major influence on MF- plant design, investment cost as well as operating cost.

Before making a decision on investments of clarified/sterilized processing plant using microfiltration plant, the feasibility of the project has to be studied. Therefore, this study aim to analyze the capital cost and operating cost for production of clarified/sterilized pineapple juice and coconut water by microfiltration. In addition, the influence of MF-operating conditions (i.e. low cross flux velocity, high cross flow velocity and with gas sparging) on the capital cost, operation cost, interest rate of return and payback period are studied.

8.3 Microfiltration plant and cost determination

8.3.1 Microfiltration plant system

A Schematic diagram of the microfiltration process is shown in Figure 47. Multi-stage systems with more than one array are used for higher system recovery without exceeding the single element recovery limits. The design of the membrane system was divided in to two stages. Stage one, the system was designed with two or more modules, arranged in parallel. The concept of connecting the module was feed and bleed system. The design has the advantage of maintaining the cross flow velocity

irrespective of other system parameters which can vary with time or feed composition (Mannapperuma, 1997). The retentate of the juice from stage one was fed continuously to the membrane stage 2 which design by two or more module have to be connected in series. In order to compensate for the permeate that is removed and to maintain a uniform feed flow to each array, the number of pressure vessels per array decrease in the direction for feed flow (Filmtec membrane, 2010).

The system consists of membrane unit (hollow fiber membrane), storage feed tank, pressure transducer, valves, magnetic flow meter, feed and circulation pump and aseptic tank. The circulation pump was used 1 pump per 4 membrane module. The quantity of pumps for each condition was depended on amount of membrane used.
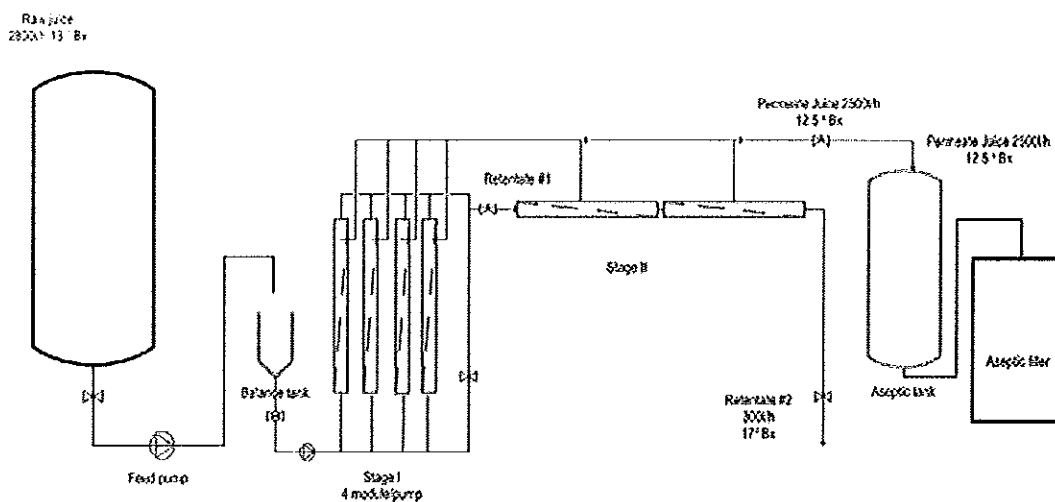
Figure 47. A Schematic of a multi-stage system (feed and bleed)

The membrane used in this plant is a hollow fiber membrane. The membrane specification and characteristic are shown in Table 37.

Table 37. Characteristic and specification of membranes

Membrane	Pineapple juice	Coconut water
Pore size	0.2μm	0.1μm
Model	CFP2E9A	CFP1E9A
Length	63.5 cm	63.5 cm
Fiber count/cartridge	520 fibers	520 fibers
Fiber lumen ID	1mm	1mm
Membrane area/cartridge	3.36 m^2	3.36 m^2
Steam sterilization	Yes	Yes

This study assumed that the membrane system is a new plant in the conventional juice production factory; therefore this plant is separated from fruit juice process. The finished product is the clarified juice and the estimated cost was in accordant to raw feed juice to the sterilized product in aseptic tank.

The clarified pineapple juice system is a new processing line, in the pineapple juice processing plant. The desired production of clarified juice is about 20,000 liter /day, corresponding to 70,000 kg fresh pineapple/day production. The production time is 8 h /day. The recovery of the juice is 90%, so that the feed juice flow is 2800 liter/h. obtaining the permeate juice of 2500 l/h and the retentate juice of 300 l/h. The operation temperature is assumed constant at 20°C. In this system, the pre-filter was neglected. The concentrated juice (final retantate) can be pasteurized and mix with the permeate juice as fresh-like product or processed as a concentrate product.

The raw coconut water fruit is transferred from the farm. The average juice of coconut is about 350 ml /fruit. The desired production of clarified coconut water is about 20,000 liter/day. The production time and recovery rate of the juice is 8 h /day and 90 % respectively.

After clarification and cold sterilization process, the sterilized-clarified juice is stored in aseptic tank to further process as the conventional product such as aseptic filling machine.

8.3.2 Cost determination

The main components of the cost of membrane filtration of fruit juice processing line are capital cost, membrane replacement, power supply, labor, maintenance and cleaning chemical agents. The total cost has been determined as the sum of this factors expressed as cost per liter of MF-clarified juice.

A. Capital cost

The capital cost has been considered as the some of two components: cost of membrane unit and "non membrane" plant. The non- membrane cost includes all mechanical items, electrical items, control equipment and associated civil engineering cost. No account has been taken for land cost.

Membrane installation cost, the membrane lifetime is estimated at 5 years, The membrane cost, depending on the membrane area, is 45,000 Bht/m^2.

The depreciation period of mechanical engineering costs (pumps, filters, piping, etc.), is 15 years.

The depreciation period of electrochemical investments cost (energy supply, cabling, transformations, control engineering, and all electronic components. is 15 years.

The working capital cost (for preparation of the installation and support) are estimated at 10% of the fixed cost.

B. Operating cost

Generally, operation cost is a cost that is required to run the processing line. Six main components of operating costs, to be considered are:

- Depreciation costs: 10% of investment on the construction of the installation. The investments are linearly depreciated and interests are neglected.

- Consumption cost – energy costs: The electricity cost is approximately 2.7 Bht/kwh (The Metropolitan Electricity Authority, 2006). The cost is calculated from the power supply per membrane area, estimating the information from the our previous work (for high CFV membrane area of 0.11m^2 consumed electric cost = 0.59 Bht/h while low CFV and gas sparging consumed electric cost = 0.44 Bht/h). In this work, the electricity cost at high and low cross flow velocity (CFV) were

assumed at 5.4 Bht/m^2/h and 4 Bht/ m^2/h respectively. The calculation example of pineapple juice with high CFV for was equal to (5.4* (10h/day)*250 (day/year)* membrane area). The cost for each condition was showed in Table 41 and 42.

- Cleaning chemicals: costs of chemical agent, calculated from the cleaning method in the previous experiment are used. The chemical agent and cost are 0.5N NaOH (50 % NaOH, 33.33 Baht/liter) and 50 ppm NaOHCl (10% NaOHCl, 27 Bht/liter). The chemical agent is assumed to be 0.02% of 2500 liter of water used for cleaning. The cost of cleaning of fouled membrane, operated at high CFV while at the low CFV and gas sparging were 50 were 45 Bht/ m^2. The cleaning cost/ membrane area of high CFV and gas sparging was higher than the cost of low CFV it was leading to the higher fouled membrane consequently higher chemical used.

- Maintenance cost is assumed to be 5 % of the total investment cost.

- The quality control is assumed to be 2% of the total investment cost.

- Labour, the number of man hours per day required to operate the plant
  - is assumed to be proportional to the size of the plant since a significant part of operating time is likely to be associated with membrane cleaning and maintenance. The costs would be expected to fall as experience of operating membrane plants increases, since there is much greater potential for automation compared with conventional processes. Labour cost is taken as 32 Bht per man hour for plant operator.

C. Capital investment decision (Hansen and Mowen, 2007).

Capital investment decisions are concerned with the process planning, setting goals and priorities, arranging financing and using certain criteria to select long-term assets. Because capital investment decisions place large amounts of resources at risk for long periods of time and simultaneously affect the future development of the firm, they are among the most important decisions managers make. Every organization has limited resources, which should be used to maintain or enhance its long-run profitability. Poor capital investment decisions can be disastrous.

The parameters that used for investment decision for this study were pay back period time, net present value (NPV) and internal rate of return (IRR), the equation for calculation for each parameter are shown in equation as follow.

Type of capital investment decisions

-Payback Period

One type of non-discounting model is the payback period. The payback period is the time required for a firm to recover its original investment. When the cash flows of a project are assumed to be even, the following formula can be used to compute its payback period:

$$\text{Payback period} = \text{Original investment} / \text{Annual cash flows} \qquad (8\text{-}1)$$

If, however, the cash flows are uneven, the payback period is computed by adding the annual cash flows until such time as the original investment is recovered. If a fraction of a year is needed, it is assumed that cash flows occur evenly within each year.

One way to use the payback period is to set a maximum payback period for all projects and to reject any project that exceeds this level.

-The Net Present Value Method

Discounting models explicitly consider the time value of money and therefore incorporate the concept of discounting cash inflows and outflows. Two discounting models will be considered: net present value (NPV) and internal rate of return (IRR). The net present value method will be discussed first; the internal rate of return method is discussed in the following section.

Net present value (NPV) is the difference between the present value of the cash inflows and outflows associated with a project:

$$NPV = [\sum CF_t / (1+i)^t - I]$$
$$= [CF_t \, df_t] - I$$
$$= P - I \qquad (8\text{-}2)$$

Where

I   = The present value of the project's cost (usually the initial outlay)

CF_t = The cash inflow to be received in period t, with t = 1.....n

n   = The useful life of the project

i   = The required rate of return

t   = The time period

P   = The present valve of the project's future cash inflows

df_t = $1/(1 + i)^t$, the discount factor

Net present value measures the profitability of an investment. If the NPV is positive, it measures the increase in wealth. For a firm, this means that the size of a positive NPV measures the increase in the value of the firm resulting from an investment. To use the NPV method, a required rate of return must be defined. The required rate of return is the minimum acceptable rate of return. It is also referred to as the discount rate, the hurdle rate, and the cost of capital.

If the net present value is positive, it signals that (1) the initial investment has been recovered, (2) the required rate of return has been recovered, and (3) a return in excess of (1) and (2) has been received. Thus, if NPV is greater than zero, the investment is profitable and, therefore, is acceptable. If NPV equals zero, the decision maker will find acceptance or rejection of the investment equal because the investment will earn exactly the required rate of return. Finally, if NPV is less than zero, the investment should be rejected. In this case, it is earning less than the required rate of return.

-Internal rate of return

Another discounting model is the internal rate of return (IRR) method. The internal rate of return is defined as the interest rate that sets the present value of project's cash inflows equal to the present value of the project's cost. In other words, it is the interest rate that sets the project's NPV at zero. The following equation can be used to determine a project's IRR.

$$I = \sum CF_t / (1+I)^t \qquad\qquad (8\text{-}3)$$

where t = 1.......n

The right-hand side of Equation is the present value of future cash flows, and the left-hand side is the investment. I, CF_t and t are known. Thus, the IRR (the interest rate, I, in the equation) can be found using trial and error. Once the IRR for a project is computed, it is compared with the firm's required rate of return. If the IRR is greater than the required rate, the project is deemed acceptable; it the IRR is equal to the required rate of return, acceptance or rejection of the investment is equal; if the IRR is less than the required rate of return, the project is rejected.

8.4. Results and discussion

8.4.1 Membrane system and operating condition

The cost of membranes, membrane replacement and power are be calculated, based on the basis of the relationships established from the lab scale trials for flux, TMP, CFV and pressure drop (ΔP). It is important to note that since the membrane module length of industrial scale is about double of the lab scale and the CFV is designed to be same value. This leads to the higher the pressure drop and TMP gradient along the module for the industrial scale, potentially affected the permeate flux and fouling. However, in this study, the effect TMP gradient along the membrane module is assumed to be negligible. These results can be used in combination with other factors to obtain a total cost under a range of operating conditions and hence to select optimum conditions. They are three operating conditions including low CFV (1.5 m/s), high CFV (3.4 m/s) and with gas sparging ($\varepsilon=0.35$) are used as parameter to calculate the cost for clarified pineapple juice and coconut water and the calculated results are compared. The details of operating conditions from our previous experiments are given in Table 38.

Table 38. Constant of fouling mechanism model during microfiltration of pineapple juice and coconut water with various ε

Fruit juice	Pore size	Without gas sparging			With gas sparging			
	(μm)	Flux (l/m²h)	TMP (bar)	CFV (m/s)	Flux (l/m²h)	TMP (bar)	CFV (m/s)	ε
Pineapple	0.2	37	0.7	3.4				
juice	0.2	33	0.7	1.5	50	0.7	1.5	0.35
Coconut	0.1	100	0.65	2.5				
water	0.1	80	0.65	1.5	122	0.6	1.6	0.35

As can be seen from table 38, the highest average permeate flux was achieved when the gas sparging was applied. The lowest permeate flux was achieved when operating at low CFV, thus larger membrane area MF- plant are required (see Table 39).

For the pineapple juice, the 0.2 μm membrane gives the best recovery of phytochemical properties i.e. vitamin C, total phenolic content, and antioxidant capacity. Therefore, this membrane is selected to be the optimal membrane pore size for clarification of pineapple juice. In the case of coconut water, the 0.1 μm membrane is selected, based on the high permeate flux, low fouling and could completely reserved the juice quality. The optimal operation condition of clarified pineapple juice was CFV of 1.5 m/s and TMP of 0.7 bar with gas injection of 0.35 while optimal operating condition of coconut water was CFV 1.5 m/s, TMP of 0.65 bar and the gas the gas injection of 0.35.

The capacity of MF processing plant is assumed be 2800 liter/h of feed juice. The plant will be operated 250 days per year (2 months off due to low season for raw fruit). The process plant specifications are summarized in Table 39.

Table 39. Treatment plant specification

	Pineapple juice			Coconut water		
	Low CFV	High CFV	Gas sparpging	Low CFV	High CFV	Gas sparging
Feed	2800l/h	2800l/h	2800l/h	2800l/h	2800l/h	2800l/h
permeate	2500/h	2500/h	2500/h	2500/h	2500/h	2500/h
Operating time	8h/day	8h/day	8h/day	8h/day	8h/day	8h/day
MF membrane area	76 m^2	68 m^2	46 m^2	35 m^2	28 m^2	23 m^2
membrane life time	5 year	5 year	5 year	5 year	5 year	5 year
Juice tank capacity	5000 l	5000 l	5000 l	5000 l	5000 l	5000 l
Material of construction	316 stainless steel	316 stainless steel	316 stainless steel	316 stainless steel	316 stainless steel	316 stainless steel

8.4.2 Cost estimation

The building/ room area of cold sterilization of fruit juice is a hygienic design. The building cost is estimated at 4,000,000 Bht for each plant. All equipment used is easy to be clean. The construction materials of equipment (fitting, piping, valve, pump etc.) are made of 316L stainless steel. The CIP (cleaning in place) system design is taken into consideration with the spray or distribution system.

In calculation of required membrane area, flux values from the previous experiment of pineapple juice and coconut water (shown in Table 39) are used. The required membrane area for MF-plant could be calculated as $A_m = Q_p/J_p$, A_m is the required membrane area, Q_p is the permeate flow rate and J_p is the permeate flux .The membrane price is provided by Ge Healthcare Bioscience company; 45,000 Bht/m^2. The price of membrane for each plant is shown in Table 41 and 42. It is clearly that when the gas sparging is applied the membrane area is reduced, resulting in the lower capital fixed cost. The costs of feed pump with the flow rate of 5000 l/h and the recirculation with the flow rate of 300 l/h are showed in Table 40.

Table 40. Quantity and estimated price of pumps for each condition

Fruit condition	Feed pump Quantity(set*price(Bht))	Circulation pump (Quantity(set*price(Bht))	Total cost (Bht)
Pineapple juice			
Low CFV	1*100,000	6*50,000	400,000
High CFV	1*100,000	5*80,000	500,000
Gas sparging	1*100,000	4*50,000	300,000
Coconut water			
Low CFV	1*100,000	4*50,000	300,000
High CFV	1*100,000	3*80,000	340,000
Gas sparging	1*100,000	2*50,000	200,000

The quantity of pumps in each system is calculated from the membrane area used. The higher of membrane area need the higher amount of circulation pumps. The low CFV and the gas sparging are used the same type pump for the circulating the system, therefore, the high CFV used the larger pump than the low CFV and gas sparging condition. The electricity cost are calculated and showed in Table 41 and 42.

The manufactures of the pressure vessels (MF modules) and the purchased of valve piping, flow meter, pressure transducer and accessories is 50 % of membrane cost (membrane cost *0.50). This cost is estimated according to Afonso *et al.*, (2004). The cost of stainless steel feed tank, capacity of 5000 l is estimated 200,000 Bht. The technical electricity cost is assumed to be 500,000 Bht. Working capital cost is 10% of total fixed capital cost.

The operating costs are membrane replacement, chemical agent, labour, maintenance and depreciation. The membrane is assumed to be replaced every 5 years, therefore the depreciation will be 9,000 Bht/ m^2/year. The membrane replacement for each condition is shown in Table 41. The cost of chemical cleaning agent (50%NaOH, 10%NaOCl) is calculated, depending on the membrane area and severity of membrane fouling. The chemical agents and concentration of solution are used, based on the previous study (0.5N NaOH and 50 ppm NaOCl). The cost of

chemical agent for cleaning of fouled membrane operated at low CFV is lower than those at high CFV. The cost of membrane chemical cleaning agent used for each condition is shown in Table 41 (The example for calculation of low CFV condition of pineapple juice was 45 (Baht/day)*250(day/year) *76 (membrane area) =855,000 Bht). The condition of gas sparging and low CFV consumed the lower cleaning cost than the condition of high CFV. It was due to the gas sparging and low CFV gave the less fouling on the membrane surface during process. The energy associated cost was calculated from the data of the pump and membrane area used. The labor cost, four skill worker for the plant operation and quality control would be (4*8*32*250) 256,000 Bht/year. The maintenance cost is 5% of investment cost while the quality control cost is 2 % of investment cost (Mohammad *et al.,* 2004) (Table 41 and 42). The steam energy for sterilization before juice process is estimated from the steam, consumed for pre-sterilization of the membrane system at 121 °C and for heating up of the CIP solution system. It estimated cost is 800,000 baht/year. The cost of nitrogen gas consumption estimated, based on our previous study is 500,000 Bht/year.

The raw material of pineapple juice will be purchased from the pineapple juice plant and the estimated price is 16.5 Bht/liter (data from the Thai pineapple juice factory, 2010). The average price of coconut water is about 5 Baht/ fruit, thus the price of raw coconut water is estimated at 15 Bht/liter. The costs of clarified pineapple juice and coconut water are showed in Table 41 and 42. The expected price of clarified pineapple juice is 18.5 Bht/liter and the expected price of coconut water is 17.5 Bht/liter. The estimated clarified pineapple juice price is assumed, based on the present pineapple juice price (personal communicate with the pineapple juice exporter, 2010). The revenues per year of clarified pineapple juice and coconut water for each condition are also shown in Table 41 and Table 42 respectively.

Table 41. Treatment plant cost of pineapple juice

Cost (Bht.)	Condition		
	Low CFV	High CFV	Gas sparging
Fixed capital costs			
Building	4,000,000	4,000,000	4,000,000
MF membrane	3,420,000	4,040,540	2,070,000
MF modules, valve, piping and accessories	1,710,000	1,520,270	1,035,000
Pump	400,000	500,000	300,000
Tank	200,000	200,000	200,000
Electro technical cost	500,000	500,000	500,000
Working capital 10% of fixed capital cost	1,023,000	976,081	810,500
Capital investment	11,253,000	10,738,892	8,815,500
Expense per year			
Electricity cost	855,000	912,162	529,000
Cleaning	852,000	850,000	522,675
Quality control	225,060	214,737	178,310
Membrane replacement	684,000	608,108	414,000
Maintenance	560,650	536,844	445,775
Operating labour	256,000	256,000	256,000
Depreciation	1,125,300	1,073,689	885,300
Steam energy (lump sum)	800,000	800,000	800,000
Nitrogen gas	-	-	500,000
Feed juice	82,500,000	82,500,000	82,500,000
Revenue (Bht/year)	92,500,000	92,500,000	92,500,000
2500 l/h of clarified juice			

Table 42. Treatment plant cost of coconut water

Cost (Bht.)	Condition		
	Low CFV	High CFV	Gas sparging
Fixed capital costs			
Building	4,000,000	4,000,000	4,000,000
MF membrane	1,575,000	1,260,000	1,032,786
MF modules, valve, piping and accessories	787500	630,000	516,393
Pump	280,000	230,000	180,000
Tank	200,000	200,000	200,000
Electro technical cost	500,000	500,000	500,000
Working capital 10% of fixed capital cost	734,250	682,000	642,918
Capital investment	12,250,432	10,637,000	8,376,500
Expense per year			
Electricity cost	350,000	378,000	309,836
Cleaning	393,750	350,000	287,500
Quality control	161,535	150,040	141,441
Membrane replacement	315,000	252,000	206,557
Maintenance	612,522	531,850	418,825
Operating labour	256,000	256,000	256,000
Depreciation	807,675	750,200	707,209
Steam energy (lump sum)	800,000	800,000	800,000
Nitrogen gas	-	-	500,000
Feed juice	75,000,000	75,000,000	75,000,000
Revenue (Bht/year)	87,500,000	87,500,000	87,500,000
2500 l/h of clarified juice			

The estimation cost from Table 41 and 42 show that, the main cost of the capital cost is membrane and membrane system. The capital cost of pineapple juice plant is higher than the cost of coconut water plant due to the lower of permeate flux, thus more membrane area are required. The use of gas sparging for flux enhancement could reduces the cost of membrane and membrane replacement and other related cost. However, the cost due to gas consumption needs to be added in the production cost. The production cost of clarified juice/liter is shown in Table 43. The cost of clarified pineapple juice and coconut water were calculated from the operating cost in Table 41 and 42 divided by the total clarified juice produced in 1 year (5000 ton). For pineapple juice, the cost of the condition of gas sparging was lowest while the cost of low CFV and high CFV were no different. The main reason for the lowest cost using gas sparging condition it was due to the less used of membrane area. In the case of coconut water cost, the results show that there were no significantly differences in the cost for all conditions.

The retentate from the process (300 l/h) could be mixed with the concentrated juice or other use therefore it can reduce the operating cost for each condition.

Table 43. The product cost of clarified pineapple juice and coconut water (Baht/liter of product)

Cost (Baht/liter)	Pineapple juice			Coconut water		
	Low CVF	High CVF	gas	Low CVF	High CVF	Gas sparging
Raw juice	16.5	16.5	16.5	15	15	15
Electricity	0.15	0.18	0.12	0.06	0.08	0.06
Cleaning	0.17	0.17	0.11	0.08	0.07	0.06
Quality control	0.04	0.04	0.04	0.03	0.03	0.03
Membrane replacement	0.14	0.12	0.08	0.06	0.05	0.04
Maintenance	0.11	0.11	0.09	0.12	0.11	0.08
Operating labour	0.05	0.05	0.05	0.05	0.05	0.05
Depreciation	0.22	0.21	0.18	0.16	0.15	0.14
Steam energy	0.16	0.16	0.16	0.16	0.16	0.16
Gas	-	-	0.10	-	-	0.10
Total cost	17.54	17.54	17.43	15.73	15.70	15.72

Table 44. Cash flow analysis of pineapple juice and coconut water processing plant

Cash flow analysis	Condition		
	Low CFV	High CFV	Gas
Pineapple juice			
Net present value(NPV)	12,211,578	12,860,190	16,045,445
Interest rate of return(IRR)	38.7	40.7	53.6
Payback period	2.6	2.4	1.9
Coconut water			
Net present value (NPV)	2,193,445	3,245,4455	2,583,518
Interest rate of return(IRR)	19.2	23.2	21.6
Payback period	4.4	3.9	4.1
Discounting interest rate	12	12	12
Tax rate	30	30	30

Table 44 shows the net present value, interest rate of return and payback time of the project for clarified pineapple juice and coconut water, operating with various conditions. The economic assessment reveals that the project for cold sterilization of pineapple juice and coconut water is economically feasible. The payback time for clarified pineapple juice plant with the assisted gas sparging is less than those without assisted gas sparging. It is also evident that the value of IRR and NPV are relatively high. From economic point of view and quality aspects, therefore, microfiltration is an alternative process for cold sterilization of pineapple juice and coconut water.

8.5 Conclusion

The result of this study shows that the pineapple juice and coconut water is technically and economically feasible for cold sterilization by using membrane filtration. The MF-plant, designed base on three different operating conditions has influence on both fix capital cost and production cost. The assisted gas

sparging technique is remarkable benefit for MF-pineapple juice plant and less benefit for MF- coconut water plant. The major investment cost of the MF- plant is building cost, followed by membrane cost. The raw juice cost is about 85 % of production cost. The payback period for the pineapple juice plant and coconut water are 1.9-2.6 year and 3.9-.4.4 years respectively, depending on operating conditions. The assisted gas sparging technique in MF-clarified pineapple juice production could reduce the payback period at 1.9 years compared to those with assisted gas sparging technique while the assisted gas sparging technique does not reduce payback period time in MF-coconut water production. From these results, it is proved that microfiltration is an alternative method for production cold-sterilized pineapple juice and coconut water.

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CHAPTER 9

SUMMARY AND FUTURE WORKS

9.1 Summary

Tropical fruit juice is considered as good appreciated of aroma, flavour and also rich in nutritional properties. In food sterilization technique, thermal processing, however tends to reduce these beneficial properties especially phytochemical and flavor. To overcome this limitation, membrane technology may be an alternative for fruit juice preservation and conservation because of its operational advantages such as mild temperature, the ease of scaling up and simplicity of operation. The present work was aimed to develop a membrane filtration process to sterilized and clarified pineapple juice and coconut water in order to preserved all nutritional quality and flavour. In addition, the membrane process performance during microfiltration process could be improved by using gas sparging technique.

The effect of the membrane pore size and MWCO may possibly influence the permeate flux and quality of the clarified fruit juice. Moreover, the process performance of membrane filtration is limited by membrane fouling which results in flux decline and a possible change in product characteristics. Cold sterilization of pineapple juice was performed by MF and UF membranes. The MF membrane with a pore size of 0.2 μm gave the highest recovery of phytochemical compounds including vitamin C (94.3%), total phenolic content (93.4%) and DPPH free radical scavenging capacity (99.6%). The membrane pore size and MWCO did not affect the oxygen radical absorbance capacity. Total variable count, yeast & mold and coliforms were removed completely by all membranes employed. The results indicate that membrane filtration with a pore size of 0.2 μm could serve as a cold sterilization process which could achieve the preservation of phytochemical compounds. This gives perfect clarification and sterilization in one step. The highest permeate flux was obtained from a 0.2 μm membrane while the highest irreversible fouling (9.79×10^{12} 1/m) was obtained from this membrane as well. However there was no difference in permeate flux between 0.2 and 0.1 μm membranes. The lowest

irreversible fouling (1.58×10^{12} 1/m) was observed from a 0.1 μm membrane. According to the highest permeate flux, total phenolic content and antioxidant capacity, a membrane with a pore size of 0.2 μm was considered to be the most suitable membrane in this study. The CFV and TMP did not have significant effect on the phytochemical properties of clarified pineapple juice. The optimal operating condition of the 0.2 μm membrane was CFV of 3.4 m/s and TMP of 0.7 bar.

In order to determine and validate the quality of the product; the shelf life of clarified pineapple juice was studied. The quality change during storage for 6 months at various temperatures of MF and UF-clarified pineapple juice were studied. It was found that no microbial growth was detected during storage and the storage time and temperature did not affect the pH and total soluble solid of MF and UF-clarified pineapple juice. There were no significant different in L* a* and b* between the MF and UF clarified pineapple juice, however the clarified pineapple juice stored at 4°C gave the less values of total colour difference (ΔE) and browning index than those of the juice stored at 27 and 37 °C. For the total vitamin C, total phenol and antioxidant capacity study, there were no statically different between clarified juice form MF and UF. During 6 months of storage at 4, 27 and 37 °C the loss of total phenol content were 11.2, 14.9 and 15.3% for MF-clarified juice and 10.9, 12.8, 14.3 %, for UF-clarified juice stored, respectively. The vitamin C contents (L-ascorbic acid) were the most affected by storage time and temperature whereas the antioxidant capacity (DPPH and ORAC) were slightly decreased during 6 months of storage. The rate of kinetic constant (k) of vitamin C, total phenol antioxidant capacity and colour in the juice stored at 4°C was less than the juice stored at 27 and 37 °C. The shelf-life of MF and UF-clarified juice based on 50 % vitamin C reduction were 0.8 month at 37 °C, 2.0 months at 27 °C and 3.5 months at 4 °C. However, the shelf life, stored at 4, 27 and 37 °C and based on total phenol and antioxidant capacity reduction by 50% was longer than 6 months. The storage temperature at 4°C was the best condition to retain appreciates quality in chemical, physical and phytochemical properties.

In order to improve the process performance during microfiltration of tropical fruit juice, the gas sparging technique was applied to reduce the concentration polarization and fouling. The effects of CFV and gas sparging on critical flux,

limiting flux and quality of clarified pineapple juice were studied. The CFV had significantly affected the critical and limiting flux. The addition of gas into the membrane module led to effectively increase both critical flux and limiting flux. However, the improvement (%) of the critical flux due to gas sparging assisted was remarkable increased when the lower CFV (1.5 m/s) was used. The higher CFV (2, 2.5 m/s) did not give remarkable improvement (%) of critical flux and limiting flux. The slug flow pattern appeared to give the higher improvement of both critical and limiting flux than bubble pattern. The use of gas sparging reduced the reversible fouling and external irreversible fouling and effect on internal reversible fouling was negligible. In addition, the CFV and gas sparging did not affect the pH, total soluble solid, colour and antioxidant capacity (total phenol and DPPH) of clarified juice. However, L-ascorbic acid, and total vitamin C were significantly decreased after the use of higher CFV and higher of gas injection factor. The use of gas sparging therefore, is an effective technique for flux enhancement, fouling reduction during microfiltration of pineapple juice while the quality the juice was preserved.

In the case of coconut water, the fresh coconut water was successfully clarified and sterilized by either MF or UF membrane. The membrane pore size and MWCO did not affect the quality of clarified coconut water and the contents of minerals and estrogen hormone in clarified coconut water were closed to those found in fresh coconut water. There were no microbiological detected in MF and UF clarified coconut water. The major fouling of both MF and UF were reversible. Both reversible and irreversible fouling resistances of UF membrane were much higher than those of MF membrane. The permeate flux of 0.1 μm was slightly lower than that of 0.2 μm membrane while the irreversible fouling resistance of 0.1 μm membrane was much lower than that of 0.2 μm membrane. According to these results, membrane with 0.1 μm pore size was considered to be the most suitable membrane for clarification and sterilization of coconut water. The permeate flux increased dramatically with increasing CFV and decreased as the feed concentration or % recovery increased. The result suggested that the permeate flux during of coconut water could be improved using hydrodynamic modification technique. The quality of MF and UF-clarified coconut water during 6 months of storage were investigated. The storage time and temperature did not affect the total soluble solid,

pH, estrogen hormone and microbiological quality. The $0.1\mu m$ membrane was selected to study the process performance due to obtaining high value of permeate flux. Both CFV and gas sparging could enhance critical flux, limiting flux and did not affect the quality of MF coconut water. The increasing of CFV from 1.6 to 2.3 m/s without gas sparging significantly increased the critical flux and limiting flux. The addition of gas into the membrane module led to effectively increase the critical flux and limiting flux. However, improvement (%) of the critical flux was high when the CFV of 1.6 m/s was applied. Higher CFV did not give remarkable improvement of both critical flux and limiting flux. The CFV and gas sparging did not affect the pH, total soluble solid, colour and estrogen hormone of MF coconut water. The R_t, R_{rf} and R_{if-ex} could significantly reduced by increasing of gas injection factor. The use of gas sparging was beneficial for flux improvement and reduction of fouling while the quality of MF- coconut water was preserved. Regarding of the gas sparging of pineapple juice and coconut water, it could be concluded that the flux improvement of pineapple juice was higher than the flux improvement of coconut water. The reason was due to the the pineapple juice contained larger particle size and higher concentration of suspended solid than coconut water, thus more severe concentration polarization was expected. The mechanism of flux enhancement is related to the disruption of the concentration polarization layer and improved mass transfer.

The fouling in cross-flow microfiltration is a key factor affecting the economic and commercial viability of a membrane system which essentially depended on the permeate fluxes obtained and their stability with time. To prevent or reduce membrane fouling, several research studies have focusing on hydrodynamic improvement method. As mentioned above, the gas sparging could reduce concentration polarization and fouling during microfiltration of pineapple juice and coconut water. However, to understand the fouling and fouling mechanism during the process was important.

The dominant fouling mechanism of pineapple juice and coconut water were complete pore blocking followed by an intermediate blocking and then a cake filtration process. The complete blocking was the major reason for the flux decline period while cake filtration dominated during the steady flux period. Gas sparging affected both intensive and duration of different fouling mechanism. For coconut

water, increase in gas injection factor led to a decrease in fouling intensity or kinetic constant. In contrast, increase in gas injection factor during microfiltration of pineapple led to an increase in k_c value. This could be due to the difference in particle size and suspended solid concentration between pineapple juice and coconut water. Gas injection factor of 0.35 could reduce remarkable fouling resistant. It is important to note that gas sparging was an effective method to reduce the R_t, R_{rf} and R_{if-ex} but the R_{if-in}. Regarding this result, the other technique much be employed or developed to reduce the internal fouling.

All of these results it could be indicated that the process and techniques developed, therefore can be used for production of cold-stabilized tropical fruit juice, which potentially maintain the nutritional quality and sensorial attributes of the products, so call fresh-like products. Since the exception of cold sterilization by membrane filtration have not been wildly used within fruit juice industry. Therefore, the economic assessment of microfiltration of pineapple juice and coconut water by using cross flow microfiltration process was study. It was proved that the pineapple juice and coconut water is technically and economically feasible for cold sterilization by using membrane filtration. The major cost investment of the plant is the membrane cost. The payback period time for the pineapple juice plant and coconut water is 1.9-2.6 year and 3.9-.4.4 years respectively, depending on operating conditions.

9.2 Future works

1. Effect of membrane pore size and operating condition on the flavour, odor and volatile acid of clarified pineapple juice and coconut water should be studied.

2. The sensory evaluation of clarified pineapple juice and coconut water during storage should be investigated.

3. The relation of membrane materials and fouling during microfiltration of pineapple juice and coconut water should be studied.

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