THE EFFECTS OF PROCESS PARAMETERS ON CONCENTRATION OF PINEAPPLE FRUIT JUICE VIA FREEZE CONCENTRATION TECHNIQUE

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ABSTRACT

Freeze concentration of fruit juices is a method of removing water from juices without heating and changing juice flavor. Freeze concentration is effective because a solute in solution has a lower melting point than pure ice and can be separated from the water component (ice) as the temperature approaches the melting point of pure ice. In addition, the advantage of the freeze concentration technique is based on the quality of the product obtained due to the low temperatures used in the process, which makes it a very suitable technology for the processing of fruit juices. The objective of this research is to study the effects of process parameters on concentration of pineapple fruit juice via freeze concentration technique. By using crystallizer unit, different parameters were studied to find the optimum concentration: temperatures and stirring rate. The first part of this experiment will be conducted to determine the best concentration of pineapple juice stirring rate and at temperature of -16 °C. The stirring rate will be varied at 200 rpm, 600 rpm, 1000 rpm, 1400 rpm and 1800 rpm. For every 1 hour, the concentration of juice will be checked. The experiment will be conducted for 12 hours. Then, the second part will be conducted to determine the effect of temperature at constant stirring rate. The temperature will be verified at 0 °C, -4 °C, -8 °C, -12 °C and -16 °C. The stirring rate used for this part is -16 °C based on the highest concentration results obtained in part one. The concentrated juice will be determined vitamin C content by using HPLC and the concentration using refractometer in °Brix. It was found that the processing condition with -18 °C cooling medium and 1800 rpm stirring rate was the best among all studied conditions.

ABSTRAK

Kepekatan pembekuan jus buah-buahan adalah satu kaedah mengeluarkan air dari jus tanpa menggunakan pemanasan dan kesan terhdap rasa jus. Kepekatan pembekuan sangat berkesan kerana bahan larut dalam larutan mempunyai takat lebur yang lebih rendah berbanding ais tulen dan ianya boleh dipisahkan daripada komponen air (ais) pada suhu takat lebur bagi ais tulen. Walau bagaimanapun, kelebihan teknik kepekatan pembekuan adalah berdasarkan kualiti produk diperolehi disebabkan oleh suhu rendah yang digunakan dalam proses, yang menjadikannya satu teknologi yang sangat sesuai untuk pemprosesan jus buah-buahan. Objektif eksperimen ini adalah untuk mengkaji kesan proses parameter kepada kepekatan jus buah nanas melalui teknik kepekatan pembekuan. Dengan menggunakan "crystallizer unit", jus buah nanas akan dihasilkan dengan memanipulasikan suhu dan kadar kacau selain mengekalkan kandungan vitamin semula jadi. Bahagian pertama ekperimen ini dijalankan untuk menentukan kadar kacau yang terbaik untuk menghasilkan jus nanas berkepekatan tinggi pada suhu -16 °C. Kelajuan kadar kacau bagi eksperiment ini ditetapkan pada 200 rpm, 600 rpm, 1000 rpm, 1400 rpm dan 1800 rpm, Semasa proses dilakukan, kepekatan jus akan diperiksa setiap 1 jam selama 12 jam. Eksperimen pertama ini dijalankan sehingga mendapat kepekatan yang tertinggi iaitu pada 1800 rpm. Selepas itu, eksperimen kedua dijalankan untuk menentukan kesan suhu pada kadar kacau dimalarkan. Suhu akan ditetapkan pada 0 °C, -4 °C, -8 °C, -12 °C dan -16 °C. Kadar kacau yang digunakan untuk bahagian ini adalah diambil berdasarkan keputusan kepekatan jus yang tinggi dalam eksperiment pertama iaitu pada 1800 rpm. Jus pekat akan ditentukan kandungan vitamin C dengan menggunakan HPLC dan kadar kepekatan jus nenas akan diuji menggunakan refractometer didalam unit Brix. Hasil dari keputusan eksperimen mendapati bahawa kepekatan jus nenas terhasil pada suhu -16 °C dan kadar kacau pada 1800 rpm adalah yang terbaik di kalangan semua parameter yang dikaji.

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cm	centimeter
g	gram
g/ml	gram per millimeter
ml	milliliter
mm	millimeter
ng / µl	nanogram per microliter
ppm	part per million
rpm	revolutions per minute
µl	micro liter
°bx `	Brix
°C	Celsius

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Pineapple or *ananas* season lasts from March till June when fresh fruits available in the markets at their best. Pineapples have exceptional juiciness and a vibrant tropical flavor that balances the tastes of sweet and tart. In terms of worldwide production, pineapple is currently the third most important tropical fruit after bananas and mangoes (Moyle R. *et al* 2004).

For economic reasons (reduced transport and storage costs), fruit juices are routinely concentrated. This is especially true in the case of tropical fruit juices for which centres of production and consumption are normally far apart geographically. In addition, fresh pineapple is often somewhat expensive as the tropical fruit is delicate and difficult to ship. Besides, cold storage at a temperature of 4.44 °C and lower causes chilling injury and breakdown in this fruit. The existence of adequate air circulation and relative humidity of 80-90% at 7-8 °C, leads to ripening progresses during and after storage. At best, pineapples may be stored for no more than 4-6 weeks. Due to this entire storage problem, pineapple cannot be exported to that kind of countries without being juice first. The pineapple usually eaten fresh, as dessert or canned or utilize it in curries and various dishes by Malayans. But, this fresh fruit is difficult to ship and the high content of ascorbic acid in this fruit cannot last longer. Therefore, concentrated of juiced is other alternative to consume this fruit in fresh condition.

This scenario has increased the global market demand towards the fresh fruits. In order to meet the market demand throughout the year in all areas, the fresh fruits is preserved using different techniques. Nowadays, a lot more fruit juice techniques such as thermal concentration, reverse osmosis, osmotic evaporation and membrane have invented to increase the productivity and achieve better control of process to increase the product quality.

1.2 PROBLEM STATEMENT

Fruit price is an important factor for the competitiveness of products and the conquest of new markets as it reduces costs related to operation logistics such as packing, storage and transport. Meanwhile, a demand for fruit juices with better conserved nutritional and sensory qualities is increasing in industrial countries.

The concentration of juices is traditionally accomplished by the use of thermal evaporation. Thermal processes can greatly affect the sensorial and nutritional quality of fruit juices, as these attributes are mainly conferred by heat-sensitive compounds (Hongvaleerat C. *et al*. 2008). There is, indeed, a rising demand for fruit juices with the original characteristics of the fresh fruits. Such a demand leads to the search for new technologies that are able to improve the quality of the fruit juices.

Concentration of liquid foods by freezing is a selective process that avoids the problem of loss of volatile components that occurs in evaporation and the need for frequent replacements in membrane technology (Sanchez J. *et al* 2010). Considering this advantages, freeze concentration technology has been used for concentration of liquids foods (Hernández E. *et al*. 2009). Freeze concentration technique has been applied for processing fruit juices mainly due to the possibility of operating at low temperatures. Pineapple has best nutritional properties and freeze concentrated operations will maintain these nutritional properties.

Several researches must be done before the best quality of pineapple juice can be obtained by using freeze technique. In this research, the parameters for freeze technique must be study to get the best quality of fruit juice.

1.3 OBJECTIVE OF STUDY

The objective of this research project is to study the effects of processing conditions, i.e. temperature and stirring rate on concentration of pineapple fruit juice via freeze concentration technique.

1.4 SCOPE OF STUDY

The scopes of the study are listed as follows:

i. To study the effect of temperature on concentration pineapple juice.
ii. To investigate effect of stirring rate on concentration pineapple juice.
iii. To analyzed the vitamin C in pineapple juice by HPLC.

1.5 RESEARCH OUTLINE

In this research, there is a lot of work to be done to make this research complete. The first chapter contains the introduction, objective of the research, scope to complete, and problem statement. In second chapter, they include all the literature review of the research such as history of pineapple, technique of concentration fruit juice, freeze concentration technique, factor influence freeze concentration and also the analysis research. All the information about the method to run in this research contains in chapter three. They are such as how to prepare raw material, how to run sample by using crystallizer, how to make standard curve of ascorbic acid and also how to analyze the sample. Then, chapter four is result and discussion. It contains all result that had been obtained from the analysis done. This chapter also explain about the graph obtain and also the problem occurs during handling this research. Lastly, in chapter five are the conclusion and recommendation about this research for better study next time.

CHAPTER 2

LITERATURE REVIEW

2.1 PINEAPPLE

2.1.1 The History of Pineapple

Ananas comosus is a botanical name for pineapple. Native to South America, it was named from the similarity of the fruit to a pine cone. The word was first recorded in 1938. The term pineapple or pinappel in Middle English did not appear in print until nearly three centuries later in 1664. Christopher Columbus is credited with discovering the pineapple on the island of Guadeloupe in 1493, although the fruit had long been grown in South America. He called it piña de Indes meaning pine of the Indians. South American Guarani Indians cultivated pineapples for food. They called it naná, meaning excellent fruit. Another explorer, Magellan, is credited with finding pineapples in Brazil in 1519, and by 1555, the luscious fruit was being exported with gusto to England. It soon spread to India, Asia, and the West Indies. When George Washington tasted pineapple in 1751 in Barbados, he declared it his favorite tropical fruit. Although the pineapple thrived in Florida, it was still a rarity for most Americans. Captain James Cook later introduced the pineapple to Hawaii circa 1770. However, commercial cultivation did not begin until the 1880s when steamships made transporting the perishable fruit viable. In 1903, James Drummond Dole began canning pineapple, making it easily accessible worldwide. Production stepped up dramatically when a new machine automated the skinning and coring of the fruit. The Dole Hawaiian Pineapple Company was a booming business by 1921, making pineapple Hawaii's largest crop and industry. Today, Hawaii produces only ten percent of the world's pineapple crops (Okihiro G. Y. 2009).

Figure 2.1: Pineapple

Figure 2.1 shows picture of the pineapple. Pineapple was introduced in Malaya in the 16th century by the Portuguese. With rubber crop development, in the year 1921 pineapple began to be planted in Singapore, Johor and Selangor as cash crop. Pineapple plantation continued to expand in peat soil area especially in Johor. Malaysia is one of the world major producers other than Thailand, Philippines, Indonesia, Hawaii, Ivory Coast, Kenya, Brazil, Taiwan, Australia, India and South Africa. Canned pineapple fruit have high market demand in countries like Japan, United States, Europe Economics Union Countries, West Asia and Singapore (Malaysian Pineapple Industry Board, 2011).

2.1.2 Facts of Pineapple

The pineapple is technically not a single fruit, but a *sorosis*. The fruits of a hundred or more separate flowers grow on the plant spike. As they grow, they swell with juice and pulp, expanding to become the "fruit." In the natural form, every variety of pineapple has rough, diamond pattern skin. Their tasted vary slightly; through they all basically have the same juicy, tart taste.

Pineapples do not grow on trees, as many erroneously think. They are the fruit of a bromeliad, rising from the center on a single spike surrounded by sword-like leaves. The pineapple plant is the only bromeliad to produce edible fruit. Pineapple is grown all year long in the warmer climates. The pineapple plant is an herbaceous perennial that grows to be two to five feet high, and three to four feet across. Pineapples are usually grown by propagation. That is, they are grown by replanting a part of themselves. The four common parts are; the slips which is located on the stem below the fruits, the suckers that start at the leaves, the crowns the leafy growth on top of the pineapple, and the rations that are located on the roots.

Commercial pineapple plants are only harvested two to three years, because the fruit begins to get smaller with each year of plant life. Pineapples weigh between four and nine pounds on average but can reach weights up to twenty pounds. The waste parts left from canning plants, including the skin, core and ends, are used to make alcohol, vinegar and food for livestock. Pineapple also known as the fruit of kings, for many years, pineapples were available only to natives of the tropics and to wealthy Europeans. Despite the fact that the pineapple has become a familiar item in U.S. markets, it's still a true exotic. For one thing, it is a member of the bromeliad family, in which edible fruits are rare. (Sources: Malaysian Pineapple Industry Board, 2011)

2.1.3 Health Benefits of Pineapple Fruit

Fresh pineapple is storehouse of many health promoting compounds, minerals and vitamins that are essential for optimum health. Pineapple is one of the fruits which are like heaven to eat because of its lush, sweet and exotic flavor, but it may be one of the most healthful foods available today.

Pineapple contains a proteolytic enzyme bromelain that digests food by breaking down protein. Bromelain also has anti-inflammatory. Regular ingestion of at least one half cup of fresh pineapple daily is purported to relieve painful joints common to osteoarthritis (Walters S. 2009).

Fresh pineapple is an excellent source of antioxidant vitamin; vitamin C (Walters S. 2009). It is required for the collagen synthesis in the body. Collagen is a protein in the body required for maintaining the integrity of blood vessels, skin, organs, and bones. Regular consumption of foods rich in vitamin C helps body protect from scurvy; develop resistance against infectious agents (boosts immunity) and scavenge harmful, pro-inflammatory free radicals from the body.

Manganese is a vitamin that our body can’t produce on its own. Pineapple is high mineral manganese (Beattie J. K. *et al* 1999, Walters S. 2009), which is an essential cofactor in a number of enzymes important in energy production and antioxidant defenses. Manganese is responsible for bone formation, healing wounds and keeping skin healthy. It regulates blood sugar levels and helps with the immune system to fight off disease. Regularly eating pineapple will ensure you’re consuming enough manganese in your diet.

2.1.4 Composition in Pineapple

Every fruits have their own compositions and their nutrient such as vitamin C, zink, calcium and many more. Pineapples also have their own nutrients. There are listed below in table 2.1.

Table 2.1: Nutrient value per 100 g of pineapple

Composition of pineapple per 100g (3.5 oz)	
Energy	202kJ (48 kcal)
Carbohydrates	12.63 g
Sugars	9.26 g
Dietary fiber	1.4 g
Fat	0.12 g
Protein	0.54 g
Thiamine (vitamin B1)	0.079 mg (6%)
Riboflavin (vitamin B2)	0.031 mg (2%)
Niacin (vitamin B3)	0.489 mg (3%)
Pantothenic acid (B5)	0.205 mg (4%)
Vitamin B6	0.110 mg (8%)
Folate (vitamin B9)	15 μg (4%)
Vitamin C	36.2 mg (60%)
Calcium	13 mg (1%)
Iron	0.28 mg (2%)
Magnesium	12mg (3%)
Manganese	0.9 mg (45%)
Phosphorus	8 mg (1%)
Patassium	115 mg (2%)
Zinc	0.10 mg (1%)

Source: USDA Nutrient database

2.1.5 Sources of Ascorbic Acid

Ascorbic acid is familiar known as Vitamin C is a water-soluble vitamin that has a number of biological functions. Ascorbic acid is the common name for Synthetic Vitamin C which is used by most vitamin companies. Ascorbic acid is found in berries, citrus fruits like strawberry, orange, pineapple and green vegetables. The ascorbic acid contents of some representative foods are listed below in table 2.2.

Table 2.2: The comparison of Ascorbic Acid in selected fruit

Fruit	**Ascorbic Acid (mg/100g)**
Acerola	1300
Guava	300
Black currant	150-230
Lemons	50-80
Strawberries	40-90
Oranges	40-60
Grapefruits	35-45
Melons	13-33
Apples	10-30
Peaches	7-14
Bananas	5-10

Sources: The Natural Food Hub

2.2 TECHNIQUE OF CONCENTRATED FRUIT JUICE

Pineapple juice concentrate is made from fresh pineapple juice that has been processed to remove water content. This part will be observing the various techniques that available to produce fruit juice.

2.2.1 Thermal Process

The concentration of juices is traditionally accomplished by the use of thermal evaporation. Freshly fruit juice is pumped into an evaporator where most of the water is removed through vacuum-assisted heating. Commercial evaporators typically have several stages that sequentially heat the juice to ever-higher temperatures and then rapidly cool it. Based on the previous study done by Farnsworth. E. R. *et al* (2000), classical thermal concentration techniques lead to subsequent losses of aromatic compounds and vitamins. Especially for tropical fruits, which are usually valued for their distinctive aromas, these losses are a serious marketing problem.

2.2.2 Reverse Osmosis

The other methods for concentrate juice are by using reverse osmosis that would more satisfactorily conserve the original qualities of thermo sensitive aromatic fruit juices. Reverse osmosis is a pressure driven membrane process that can be an alternative for juice concentration, as it does not involve phase change or the use of high temperatures. For reverse osmosis it is necessary to use high operating pressures in order to overcome the osmotic pressure of the juice ranging from 10 to 200 bars (Jesus D.F. *et al.* 2007). However, fruit juice concentrated by reverse osmosis had a better-preserved characteristic aroma when compared to the juice concentrated by thermal evaporation.

2.2.3 Osmotic Evaporation

Osmotic evaporation (OE), a membrane process is a relatively new technology based on the use of a hydrophobic microporous membrane to separate two liquid phases that differer greatly in terms of solute concentration (Vaillant F. *et al.* 2001). Osmotic evaporation suited for the processing of heat-sensitive aqueous solutions such as fruit juices and pharmaceutical products. As osmotic evaporation can be carried out at moderate temperatures and pressures, this process has great potential for concentrating fruit juices. With this process, fruit juices can be concentrated to 60 g 100 g_1 TSS with good nutritional and sensory qualities (Hongvaleerat C. *et al.* 2008). Furthermore, this method could more highly cost because membrane used in OE most expensive compare with membranes in membrane process. Furthermore, OE processes have high energy consumption and, for must rectification, they require an additional operation of ion-exchange, which leads to severe ecological problems due to resin regeneration and disposal (Santos *et al.* 2008).

2.2.4 Membrane Technology

"Cold process" membrane technologies represent an alternative to high-temperature treatments. Cross flow microfiltration (CMF) has been applied successfully to some highly thermo sensitive juices, resulting in microbiologically stabilized clarified juice that preserves the major part of the fruit's original aroma (Vaillant F., *et al.* 2004). Fruit juice is separated from a receiving phase by a hydrophobic microporous membrane to prevent penetration of aqueous solution, creating air gaps within the membrane. The driving force of the process is given by a water vapor pressure gradient across the membrane, causing water vapor transfer across the pores from high-vapor pressure side to the low one (Pelin Onsekizoglu *et al.* 2010). As well, an innovative concentration technology such as osmotic evaporation (OE) may allow concentrating fruit juice and thus add value to the product. Both these technologies appear appropriate for concentrating the thermosensitive juice such as melon juice that is very high sugar and pleasant aroma (Vaillant F., *et al.* 2004).

Table 2.3: Summarize comparison of method for concentrated fruit juice

Method	Process description	Disadvantages
Thermal process	Traditionally method accomplished by the use of thermal evaporation.	Losses of aromatic compounds and vitamins. (Hongvaleerat C. *et al*. 2008).
Reverse osmosis	Solution of fruit juice will through out to membrane. Water (solvent) will be removing.	Use high operating pressures in order to overcome the osmotic pressure of the juice ranging from 10 to 200 bars (Jesus D.F. *et al*. 2007).
Osmotic evaporation	Use of a hydrophobic microporous membrane to separate two liquid phase that differer greatly in terms of solute concentration (Vaillant F. et al. 2001).	OE processes have high energy consumption and, for must rectification, they require an additional operation of ion-exchange, which leads to severe ecological problems due to resin regeneration and disposal (Santos *et al*. 2008).
Membrane technology	Cross flow microfiltration (CMF) has been applied successfully to some highly thermo sensitive juices, resulting in microbiologically stabilized clarified juice that preserves the major part of the fruit's original aroma (Vaillant F., *et al*. 2004).	Same as osmotic evaporation because it use of a hydrophobic microporous membrane as their filtrate.

2.3 CRYSTALLIZATION

Crystallization is a process where solid particles are formed from a homogeneus phase (Geankoplis C. H. 2003). Crystallization may be defined as a phase change in which a crystalline product is obtained from a solution. A solution is a mixture of two or more species that form a homogenous single phase. Solutions are normally thought of in terms of liquids; however, solutions may include solids suspension. Typically, the term solution has come to mean a liquid solution consist a solvent, which is a liquid, and a solute, which is a solid, at the conditions of interest. The solution to be ready for crystallization must be supersaturated. A solution in which the solute concentration exceeds the equilibrium (saturated) solute concentration at a given temperature is known as a supersaturated solution. According to Geankoplis C. H. (2003), crystallizing equipment can be classified based on methods used to bring about supersaturation as follow:

1. Supersaturation produced by cooling the solution.
2. Supersaturation produced by evaporation of the solvent.
3. Supersaturation by combined cooling and evaporation.

2.3.1 Freeze Concentration

Freeze concentration is based on the separation of soluble solids from a liquid phase by means of freezing the water content of the liquid (Hernandez *et al*. 2009. Freeze concentration of liquid foods is a technology that minimizes losses of volatiles and thermolabile components. This renders a final product with a quality that cannot be obtained by conventional concentration processes used in the food industry, such as evaporation and membrane concentration (Sánchez J. *et al.* 2010).

The process involves lowering the temperature of the product to be concentrated to below its freezing point in a controlled manner in order to avoid reaching the eutectic temperature at which all the components of the product solidify at once. If it reaches the eutectic point of the juice, separation is very difficult. The aim is to obtain a very pure ice, i.e. only water, without retaining any of the solids in the product. The purpose of removing this ice is to obtain a concentrated liquid product.

Concentration by freezing is the system that comes closest to the ideal objective of separating water from the food product without affecting the other components. The greatest advantages offered by the use of cryoconcentration rather than other technologies are the low temperatures reached in the process and the non-existence of a liquid–vapour interface. There is no loss of volatiles, making this technique very suitable for the concentration of thermo sensitive fluids (Sánchez J. *et al.* 2010).

According to various researchers (Miyawaki *et al.* 2005), there are two basic methods for freeze concentration of liquid foods as shown in Figure 2.2. In the conventional method of suspension crystallization (Figure 2.2a), individual ice crystals are formed that are enlarged in size by Ostwald ripening. Separation between ice crystals and concentrate is quite complicated in a pressurized wash column. The second method of progressive freeze concentration, as shown in Figure 2.2b, is the crystallization of water forming an ice layer present in the solution in the form of an ice layer on a cold surface. Large ice mass is formed and grown on the cooling surface and the separation from concentrate mother liquor is relatively easy.

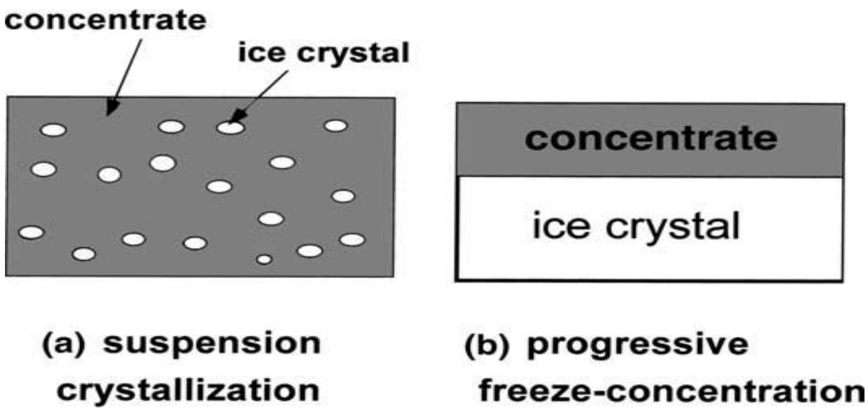

Figure 2.2: Two method for concentration by freezing (Miyawaki *et al.* 2005)

Freeze concentration is a dewatering operation that has long been recognized as one of the best concentration method to avoid quality loss of liquid food, dairy product, pharmaceutics, etc. When a crystallized ice appears and grows from aqueous solution, the ice crystal expels impurities to build up pure crystal during freezing process. Thus the impurities are piled on the solid–liquid interface to increase concentration of the solution.

The use of freezing enables to retain aroma compound in products and to minimize thermal degradation of products. The low energy consumption of freeze concentration is also a big benefit of the freeze concentration; it is approximately seven times lower than that of evaporation method due to the difference of latent heat of solidification and vaporization (Miyawaki O. *et al* 2004)